ORGANOTRANSITION METAL CHEMISTRY OF
ISELENOCYANATES AND ALKYNYL CHALCOETHERS

Lorraine Margaret Caldwell

A thesis submitted for the degree of Doctor of Philosophy
of
The Australian National University

December 2006

THE AUSTRALIAN NATIONAL UNIVERSITY
DECLARATION

The research described in this thesis is the author's own original work with the exception of that to which reference is made in the text.

Lorraine Margaret Caldwell
ACKNOWLEDGEMENTS

First and foremost thanks are offered to Professor Anthony Hill, who has successfully balanced the delicate role of intellectual supervisor with friend. His boundless enthusiasm for the field is inspiring and I am honoured to have had the opportunity to work under his guidance.

Thanks must also go to past and present members of the Hill group: Horst, Nevah, Liz, Rian, Madeleine, Robyn, Mike, Matt, Ian, Gavin, Spike and Jörg, each of whom have helped to shape my time in Canberra for the better. Particular thanks must be offered to Ian for his proof-reading efforts and to Gavin for his willingness to help with the least exciting aspects of thesis preparation. Thanks also to the (past and present) members of the Wild group, Bruce, Heather, Michelle, Nathan, Paul and Rebecca, who I feel privileged to be able to name amongst my friends.

I am at a loss of words that would serve to adequately express my gratitude to Tony Willis for his phenomenal efforts in the collection of X-ray crystallographic data for this body of work.

Finally, a special thank you is offered to my beautiful sisters, Roslynne, Karen and Tracey, for their support, tolerance, love and friendship and to my wonderful friends Danielle, Ashley, Karen, Evan and Alice. All of these people have particularly supported me during this all-consuming undertaking. I will be seeing you all in Dublin soon!

As it turns out, blind faith may get you somewhere after all.
ABSTRACT

The organometallic chemistry of unsaturated organoselenium ligands is far less mature than that of the sulfur or oxygen based analogues, a situation that may be traced to the higher reactivity of multiple bonds between selenium and carbon. The work to be described addresses this issue by investigating the coordination and organometallic chemistry of two organoselenium heterocumulenic functional groups that have been little-studied in an organometallic context. Organic isoselenocyanates (R-NCSe) and alkynylselenolates (R-CCSe\(^-\) and their derived alkynyl selenoethers) may be considered isoelectronic and it is these classes of compound with which this thesis is concerned. In particular, a major focus is provided by the interaction of these compounds with Group 6 alkylidyne complexes co-ligated by hydrotris(pyrazolyl)borates. Accordingly, Chapter 1 presents a review of this class of complex, which attempts to be comprehensive to the close of 2005. This review has been accepted for publication in its entirety in the monograph series *Advances in Organometallic Chemistry*.

Chapter 2 concerns the synthesis, and complete spectroscopic and crystallographic characterisation of SeCNMes (Mes = C\(_6\)H\(_3\)Me\(_2\)-2,4,6) and subsequent investigations into the organometallic chemistry of isoselenocyanates with this lead substrate. Although the reaction of SeCNMes with [Pt(\(\eta^2\)-C\(_2\)H\(_4\))(PPh\(_3\))\(_2\)] afforded the first structurally characterised complex of an isoselenocyanate, [Pt(\(\eta^2\)-SeCNMes)(PPh\(_3\))\(_2\)], a more commonly encountered mode of reactivity for SeCNMes involved transition metal-mediated selenium extrusion accompanied by the formation of the corresponding isonitrile complex. Thus the complexes [RuHCl(CO)(PPh\(_3\))\(_3\)], [Ru(CO)\(_2\)(PPh\(_3\))\(_3\)], [Ru(CO)(CNMes)(PPh\(_3\))\(_3\)] and [Ru(CH=CH-i-Pr)Cl(CO)(PPh\(_3\))\(_2\)] when treated with SeCNMes afforded the new isonitrile complexes [RuHCl(CO)(CNMes)(PPh\(_3\))\(_2\)], [Ru(CO)\(_2\)(CNMes)(PPh\(_3\))\(_2\)], [Ru(CO)(CNMes)\(_2\)(PPh\(_3\))\(_2\)] and [Ru(CH=CH-i-Pr)Cl(CO)(CNMes)(PPh\(_3\))\(_2\)], respectively. The failure of SeCNMes to either thermally or photochemically eliminate selenium in the absence of transition metal substrates was demonstrated, thereby confirming that the above selenium extrusion reactions were indeed metal-mediated.

The metal-induced fragility of SeCNMes that was established in Chapter 2 could be exploited in a productive manner by identifying situations where the development of an organic soluble single selenium atom transfer agent was desirable. Chapter 3 describes the use of SeCNMes to afford the first mononuclear selenoacetyl complexes of Group 6 metals, amongst which were the first structurally authenticated selenoacetyl complexes. Thus, expedient access to selenoacetyl...
complexes of molybdenum was afforded via the reactions of alkylidyne complexes \([\text{Mo(=CR)(CO)}_2\text{Tp}^*]\) \((R = \text{C}_4\text{H}_3\text{S}-2, \text{Ph}, \text{C}_6\text{H}_4\text{Me}-4, \text{Tp}^* = \text{Tp}, \text{Tp}^*\) with \text{SeCNMes}. In general, this protocol provided three types of derivative: the selenoacyl complexes \([\text{Mo(=CR)(CO)}_2\text{Tp}^*]\) and \([\text{Mo}^2\text{SeCR}(\text{CO})(\text{CNMes})\text{Tp}]\) and the diselenocarboxylato complexes \([\text{Mo}(\kappa^2\text{=SeCR})(\text{CO})_2\text{Tp}^*]\). The relative proportions of the three products were shown to be dependent, in part, upon the steric bulk of the alkylidyne substituent ‘R’ and the borate co-ligand ‘Tp*’ as well as temperature and reaction duration. The first structurally characterised dihapto selenolatocarbene complexes \([\text{Mo}(\eta^2\text{-RSeCC}_4\text{H}_3\text{S}-2)(\text{CO})(\text{L})\text{Tp}]\) \((\text{L} = \text{CO}, \text{CNMes})\) were readily obtained by electrophilic alkylation \(\left(\text{[Me}_3\text{O}]\text{BF}_4\right)\) of the selenoacyl complexes \([\text{Mo}(\eta^2\text{-SeCC}_4\text{H}_3\text{S}-2)(\text{CO})(\text{L})\text{Tp}^*]\) \((R = \text{CH}_3)\) or electrophilic arylselenenation of the alkylidyne complex \([\text{Mo(=CC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) by a combination of PhSeCl and AgPF₆ \((R = \text{Ph})\). In contrast to the chemistry of related thiolatocarbene complexes, the reactions of the selenolatocarbene complexes with various nucleophiles, as a rule, resulted in loss of the selenolate group and reformation of the alkylidyne precursor. Whilst the reaction of \([\text{Mo}(\eta^2\text{-SeCR})(\text{CO})_2\text{Tp}]\) with \([\text{Fe}_2(\text{CO})_3]\) failed to produce any identifiable binuclear derivatives, the sequential treatment of \([\text{Mo(=CC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) \(\text{with} [\text{Fe}_2(\text{CO})_3]\) and elemental selenium provided the first structurally characterised dinuclear selenoacyl complex \([\text{MoFe(µ-SeCR})(\text{CO})_2\text{Tp}]\).

Chapter 4 introduces alkynyl chalcoethers, commencing with calculated energies of the frontier orbitals of the lead substrates \(i\text{-PrEC}-\text{CPh} (E = \text{O, S, Se, Te})\). The first complete set of analogous alkynyl chalcoether complexes is described, isolated as the structurally characterised salts \([\text{W(}=\text{i-PrEC}-\text{CPh})(\text{CO})_2\text{Tp}^*]\text{BF}_4\). These result from the reactions of the free alkynes \(i\text{-PrEC}-\text{CPh} [\text{WI(=CO)}_2\text{Tp}^*]\) in the presence of AgBF₄. The spectroscopic and structural data are rationalised in terms of the changes in the energies of the alkynyl frontier orbitals upon varying the chalcogen, E. The neutral complex \([\text{W(}=\text{i-PrSeC}-\text{CPh})(\text{Cl})(\text{CO})_2\text{Tp}^*]\) was obtained from the reaction of \([\text{W(}=\text{i-PrSeC}-\text{CPh})(\text{CO})_2\text{Tp}^*]\text{BF}_4\) \(\text{with} [\text{Bu}_4\text{N}]\text{Cl}\) and exists in two forms in solution as a result of rotational isomerism of the alkyne. Depending on the choice of solvent, either pure rotamer could be crystallised from solution and each was structurally characterised.

Chapter 5 reports the first study of the reactions of hetero-atom substituted alkynes (specifically, \(i\text{-PrEC}-\text{CPh} \ E = \text{S, Se, Te}\)) with dinuclear alkylidyne complexes of molybdenum and iron and accordingly begins with a brief overview of the chemistry of such substrates and their reactions with simple hydrocarbon alkynes. For alkynyl chalcoethers, a more complex manifold of processes was established than previously observed for simple
alkynes, which could be related to the migratory aptitude of the chalcogenolate groups. Three products dominated the mixture obtained from the reaction of \([\text{MoFe}(\mu-CR)(\text{CO})_5\text{Tp}]\) \((R = \text{C}_2\text{H}_5\text{S}-2)\) with \(i-\text{PrSeC}=\text{CPh}\). The first, \([\text{MoFe}(\mu-CR(\text{Sei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\), involved the formation of a 3-carbon bridge in which the selenolato group was bound to the carbon opposite the molybdenum centre. However, with time these derivatives evolved via selenolate migration into a pair of isomeric \(\mu\)-allenyl complexes \([\text{MoFe}(\mu-CR(\text{Sei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\) and \([\text{MoFe}(\mu-CR(\text{Sei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\) that differed according to which \(\text{Mo}-\alpha\) atom \((\text{CR} \text{ or CO})\) of the former molybdacycle the selenolato group migrated to. The third major component corresponded to the complex \([\text{MoFe}(\mu-CR(\text{Sei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\) in which the \(\text{Mo}-\text{Fe}\) vector is bridged by a 4-carbon chain comprising a carbonyl ligand coupled with the alkylidyne and alkyne. In the reaction of \([\text{MoFe}(\mu-CR(\text{Sei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\) with \(i-\text{PrSC}=\text{CPh}\), an early \(\pi\)-adduct \([\text{MoFe}(\mu-CR(i-\text{PrSeC}=\text{CPh})(\text{CO})_4\text{Tp}]\), which converted over time to a mixture of alkynyl/alkylidyne coupled products. Similar results were obtained for \(i-\text{PrSC}=\text{CPh}\) to those obtained for \(i-\text{PrSeC}=\text{CPh}\). However, for \(i-\text{PrTeC}=\text{CPh}\), the only tractable product obtained was one isomer of the final teurololate migration product, \([\text{MoFe}(\mu-CR(\text{Tei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\) or \([\text{MoFe}(\mu-CR(\text{Tei-Pr})\text{CPh})(\text{CO})_4\text{Tp}]\), attesting perhaps to the greater migratory aptitude of the Tei-Pr group.

Chapter 6 describes the synthesis of the first examples of alkynylchalcogenolatocarbony complexes, i.e., selenoethers that bear both \(\text{C}=\text{C}\) and \(\text{C}=:\text{Mo}\) substituents, allowing for an internal comparison of the reactivity of the two triple bonds. Thus the reactions of \(\text{LiSeC}=\text{CR}\) \((R = t-\text{Bu}, \text{SiMe}_3, \text{C}_6\text{H}_4\text{Me}-4)\) with \([\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*]\) provide the complexes \([\text{Mo}(=\text{CSeC}=\text{CR})(\text{CO})_2\text{Tp}^*]\), one of which \((R = \text{SiMe}_3)\) was structurally characterised. The reaction of \([\text{Mo}(=\text{CSeC}=\text{Ct-Bu})(\text{CO})_2\text{Tp}^*]\) with \([\text{Co}_2(\text{CO})_8]\) results in the addition of the alkenyl group across the \(\text{Co}-\text{Co}\) bond to provide the simple dicobaltatetrahedrane \([\text{Co}_2(\mu-t-\text{BuC}_2\text{SeC}=\text{Mo}(\text{CO})_2\text{Tp}^*)(\text{CO})_8]\), which was converted with \text{dppe} to the derivative \([\text{Co}_2(\mu-t-\text{BuC}_2\text{SeC}=\text{Mo}(\text{CO})_2\text{Tp}^*)(\mu-\text{dppe})(\text{CO})_4]\), in both cases with retention of the integrity of the \(\text{MoCSeC}_2\) spine. In contrast, the reaction of \([\text{Mo}(=\text{CSeC}=\text{Ct-Bu})(\text{CO})_2\text{Tp}^*]\) with \([\text{Pt}(\eta^2-\text{C}_2\text{H}_4)(\text{PPh}_3)_2]\) proceeds through a sequence of three complexes. The initially formed \(\pi\)-adduct \([\text{Pt}(\mu-t-\text{BuC}_2\text{SeC}=\text{Mo}(\text{CO})_2\text{Tp}^*)(\text{PPh}_3)_2]\) could be characterised spectroscopically, but evolves into the structurally characterised complex \(\text{cis-}[\text{Pt}(\text{SeC}=\text{Mo}(\text{CO})_2\text{Tp}^*)(\text{C}=\text{Ct-Bu})(\text{PPh}_3)_2]\). This in turn converts very slowly to \(\text{trans-}[\text{Pt}(\text{SeC}=\text{Mo}(\text{CO})_2\text{Tp}^*)(\text{C}=\text{Ct-Bu})(\text{PPh}_3)_2]\), which was also structurally characterised. The final and penultimate compounds in this sequence may from one perspective be described as
elaborate selenolatocarbyne complexes, or alternatively as isoselenocarbonyl complexes, given that they represent the first examples of carbon monoselenide serving a bridging role between two metals.
ABBREVIATIONS

δ  chemical shift, expressed in ppm
Ar  generalised aryl group
bipy  2,2'-dipyridyl
cod  1,5-cyclooctadiene
Cp  η⁵-cyclopentadienyl
Cp*  η⁵-pentamethylcyclopentadienyl
dppe  1,2-bis(diphenylphosphino)ethane
dppm  bis(diphenylphosphino)methane
E  generalised electrophile
ESI-MS  electrospray mass spectroscopy
HMBC  heteronuclear multiple-bond correlation
HOMO  highest occupied molecular orbital
IR  infrared
i-R  iso-R
Lₙ,M  generalised metal fragment (M) with n ligands (L)
LUMO  lowest unoccupied molecular orbital
m/z  mass-to-charge ratio
Me, Et, Pr, Bu, Ph, Cy methyl, ethyl, propyl, butyl, phenyl, cyclohexyl
Mes  mesityl (2,4,6-trimethylphenyl)
n.a., n.r., n.d.  not applicable, not reported, not determined
n J_AB  n-bond coupling between nuclei A and B, expressed in Hz
NMR  nuclear magnetic resonance
n-R  normal-R
Nu  generalised nucleophile
OTf, O₂SCF₃  triflate (trifluoromethanesulfonate)
ppm  parts per million
py  pyridine
pz  pyrazolyl
pz*  3,5-dimethylpyrazolyl
R  generalised organic group
r.t.  room temperature
s, d, t, vt, br, sh  singlet, doublet, triplet, virtual triplet, broad, shoulder
THF  tetrahydrofuran
TLC  thin layer chromatography
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>tmeda</td>
<td>$N,N',N''$-tetramethylethylene-1,2-diamine</td>
</tr>
<tr>
<td>Tp</td>
<td>hydrotris(pyrazolyl)borate</td>
</tr>
<tr>
<td>Tp*</td>
<td>hydrotris(3,5-dimethylpyrazolyl)borate</td>
</tr>
<tr>
<td>$\tau$-R</td>
<td>tertiary-$R$</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS

Chapter 1. Alkylidyne Complexes Ligated by Poly(pyrazolyl)borates – A Review 1
1.1 Introduction 2
1.2 Synthesis 4
   1.2.1 Alkyl, aryl, alkenyl and alkylnyl substituents 4
   1.2.2 Heteroatom substituents 13
   1.2.3 Metals other than Cr, Mo, and W 23
   1.2.4 Alkylidyne complexes ligated by poly(pyrazolyl)methanes 25
1.3 Structure and spectroscopy 28
   1.3.1 $^{13}$C{$^1$H} NMR 28
   1.3.2 Crystallography 29
   1.3.3 Other spectroscopic methods 31
1.4 Reactivity 35
   1.4.1 The metal centre 35
   1.4.2 The metal–carbon multiple bond 37
   1.4.3 The carbon substituent 48
   1.4.4 The heteroatom substituent 60
   1.4.5 The poly(pyrazolyl)borate ligand 62
   1.4.6 Bi- and polymetallic compounds 63
1.5 Concluding remarks 81
A.1 $^{13}$C{$^1$H} NMR data for the alkylidyne carbon and co-ligand carbonyl(s) 82
A.2 Compilation of structural data for crystallographically characterised
   alkylidyne metal complexes 91
A.3 Characteristic infrared absorptions for known alkylidyne metal complexes 93
References 98

Chapter 2. Chemistry of Organyl Isoselenocyanates with Platinum Group Metals 104
2.1 Introduction 105
   2.1.1 The isoselenocyanate ligand 105
   2.1.2 Metal substrates for SeCNMes coordination 109
2.2 Ligand synthesis and characterisation 111
2.3 Coordination chemistry of mesityl isoselenocyanate: Platinum(0) 115
2.4 Attempted coordination of mesityl isoselenocyanate:
   Ru(0) and Ru(II) complexes 118
   2.4.1 Reaction of SeCNMes with [Ru(CO)(L)(PPh$_3$)$_3$] (L = CO, CNMes) 118
   2.4.2 Reaction of SeCNMes with [Ru(CO)$_2$(PPh$_3$)$_2$(C$_2$H$_4$)] 121
2.4.3 Towards ruthenium(0) complexes that are devoid of a labile phosphine ligand

2.4.4 Reaction of SeCNMes with [RuHCl(CO)(PPh₃)₃]: a reactive metal–hydride bond

2.4.5 Reaction of SeCNMes with [Ru(CH=CH₂-Pr)Cl(CO)(PPh₃)₃]: a reactive metal–σ-organyl bond

2.5 Summary and conclusions

References

Chapter 3. Selenoaroyl Complexes of Molybdenum

3.1 Introduction

3.1.1 Chalcoacyl complexes

3.1.2 Synthesis of chalcoacyl complexes

3.1.3 Structural properties of η²-chalcoacys

3.1.4 Spectroscopic properties of chalcoacyl complexes

3.1.5 The addition of selenium to unsaturated M–C bonds

3.2 Crystallographic study of [Mo(η²CC₄H₃S-2)(CO)₂Tp⁺] (Tp⁺ = Tp, Tp⁺)

3.3 Synthesis of mononuclear selenoaroyl complexes

3.4 Proposed mechanism for selenium delivery from SeCNMes

3.4.1 Isolation of the novel η²-vinyl [Mo{CNR'C(=NR')SeC(=NR')-C(C₄H₃S-2)}(CO)₂Tp] (R' = Mes)

3.4.2 Catalytic activation of elemental selenium by CNMes

3.5 Preparation of η²-selenolatocarbenes [Mo(η²-RSeCC₄H₃S-2)(CO)(L)Tp][X]

3.5.1 Treatment of η²-selenolatocarbenes with nucleophiles

3.6 Attempted preparation of [Mo(η²-TeCC₄H₃S-2)(CO)₂Tp] from Et₃P/Te

3.7 Binuclear selenoaroyl complexes

3.7.1 Preparation and characterisation of [MoFe(µ-CC₄H₃S-2)(CO)₅Tp]

3.7.2 Preparation and characterisation of [MoFe(µ-SeCC₄H₃S-2)(CO)₅Tp]

3.8 Summary and conclusions

References

Chapter 4. Tungsten–Alkyne Complexes

4.1 Introduction

4.1.1 Four-electron donor alkyne complexes co-ligated by hydrotris(pyrazolyl)borates
4.1.2 Heteroalkyne complexes of Group 6 metals
4.1.3 Metal–alkyne bonding

4.2 Influence of heteroatom substituents on alkyne bonding

4.3 Synthesis

4.4 Structural characterisation

4.4.1 Molecular structures of the salts
\[ W(\eta^2-i-PrEC\equivCPh)(CO)_2Tp^*][BF_4] \]
\( (E = O, S, Se, Te) \)

4.4.2 Molecular structure of the chiral molecule
\[ W(\eta^2-i-PrSeC\equivCPh)Cl(CO)Tp^*] \]

4.5 Spectroscopic properties

4.6 Electronic spectra

4.7 Summary and conclusions

References

Chapter 5. Alkylidyne–Alkynyl Chalcogen Ether Coupling Reactions

5.1 Introduction

5.1.1 Chemistry of polynuclear metal complexes with bridging carbyne ligands

5.1.2 Alkylidyne–alkyne coupling reactions

5.1.3 Cluster chemistry of alkynyl chalcogen ethers

5.2 Reaction between \([\text{MoFe}(\mu-C\equivC\equivC\equivC)(CO)_5Tp]\) and \(i-\text{PrEC\equivCPh}\ (E = S, Se, Te)\)

5.2.1 Carbon–carbon bond formation and chalcogenolate migration

5.3 Mechanism of C–C bond formation and chalcogenolate migration

5.4 Reactions between \([\text{MoFe}(\mu-C\equivC\equivC\equivC\equivC)(CO)_5Tp]\) and alkynyl chalcogen ethers

5.4.1 Preparation and characterisation of \([\text{MoFe}(\mu-C\equivC\equivC\equivC\equivC)(CO)_5Tp]\)

5.4.2 Reaction between \([\text{MoFe}(\mu-C\equivC\equivC\equivC\equivC)(CO)_5Tp]\) and \(i-\text{PrSeC\equivCPh}\)

5.5 Summary and conclusions

References

Chapter 6. Tp* Ligated Alkynylselenomethylidyne Complexes of Molybdenum

6.1 Introduction

6.1.1 Heteroatom-substituted methylidyenes

6.1.2 Alkynylmethylidyne complexes
6.2 Synthesis and characterisation of alkynylselenomethylidyne complexes

6.3 Reaction of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] with [Co₂(CO)₈]

6.4 Reaction of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] with [Mo(CO)₃Cp]₂

6.5 Reaction of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] with [Pt(PPh₃)₂(C₂H₄)]

6.5.1 Mechanism of Pt-insertion into the C–Se bond of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*]

6.6 Summary and conclusions

References

Chapter 7. Experimental

7.1 General methods

7.2 Chemistry of organyl isoselenocyanates

7.3 Molybdenum selenoaroyl complexes

7.4 Tungsten–alkyne complexes

7.5 Alkylidyne–alkyne chalcoether coupling reactions

7.6 Tp* ligated alkynylselenomethylidyne complexes of molybdenum

References
CHAPTER ONE

ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES – A REVIEW
CHAPTER 1. ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

This Thesis describes the coordination chemistry of several compounds containing carbon–selenium bonds. Much of this work is concerned with the elaboration of Group 6 poly(pyrazolyl)borate alkylidyne complexes and, accordingly, an appraisal of the chemistry of this class of compounds is first appropriate. The following Chapter forms a comprehensive review of the chemistry of alkylidyne complexes co-ligated by poly(pyrazolyl)borates and has been accepted for publication in Advances in Organometallic Chemistry in its entirety.

1.1 Introduction

The first alkylidyne metal complexes were prepared by Fischer et al. more than 30 years ago.\(^1\) Since this pioneering event, the chemistry of the transition metal–carbon triple bond present in such complexes has developed into a major field of research and though the poly(pyrazolyl)borate ligands were discovered seven years prior to the synthesis of the first alkylidyne complexes\(^2\) their importance and significance in this field has only more recently been truly appreciated.

There are a number of reviews that detail the various facets of alkylidyne chemistry\(^3\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) but the majority of these pre-date the enormous growth in the field that has been possible with the appreciation of the kinetic and thermodynamic stability conferred upon alkylidyne complexes by the inclusion of the bulky pyrazolylborate ligands. Furthermore, while a general overview of the chemistry of pyrazolylborate derivatives has recently been published,\(^13\) there currently exists no comprehensive source of information specific to the chemistry of alkylidyne complexes co-ligated by poly(pyrazolyl)borates, which this review attempts to remedy. Very few examples of such complexes have been isolated outside of Group 6 but the (rare) Group 7 and 8 alkylidyne complexes have been included. Alkylidyne complexes co-ligated by the closely related pyrazolylmethane ligands, where relevant, have also been discussed. An effort has been made to comprehensively cover the literature up to the end of 2005.

The terms carbyne and alkylidyne are used interchangeably in the literature and in this review. For the scorpionate ligand derivatives, the abbreviated nomenclature adopted by Curtis\(^14\)\(^15\) will be utilised (see Chart 1.1). As such, for the hydrotris(pyrazolyl)borate ligand, \([\text{HB}(pz)_3]^–\) (\(pz = \text{pyrazolyl}\)), the abbreviation ‘Tp’ will be employed. For the commonly employed 3,5-dimethylpyrazolyl substituted derivative, \([\text{HB}(pz^*)_3]^–\), Tp* will be used. The abbreviation \(pzTp\) represents the homoscorpionate tetrakis(pyrazolyl)borate ligand, \([\text{B}(pz)_4]^–\), and Bp refers to the heteroscorpionate dihydrobis(pyrazolyl)borate anion, \([\text{H}_2\text{B}(pz)_2]^–\). Expansion of this system of nomenclature according to the rules of creating these abbreviations suggested by Trofimenko\(^13\) allows encompassment of all of the variously substituted pyrazolyl derivatives, but very few examples of alkylidyne complexes exist that are not based on these preceding ligands. For a general poly(pyrazolyl) borate ligand the abbreviation Tp* will be used.
CHAPTER 1. ALKYLIDyne COMPLEXES Ligated BY POLy(PYRAZOLYl)BORATES

The incorporation of facially capping tripodal ligands such as the cyclopentadienyl anion ($\eta$-C$_5$H$_5^-$, Cp) and its substituted derivatives (Cp$^x$, $x$ = H, alkyl or aryl, Chart 1.1) into the molecular architecture of alkylidyne complexes is well-established. In their coordination chemistry, the tridentate Tp$^x$ ligand systems display similarity to the two cyclopentadienyl ligands, Cp and Cp$^*$ ($\eta$-C$_5$Me$_3$); both ligands are uninegative and each provides six electrons (in the charged formalism), being considered to occupy three coordination sites. Accordingly, a particular effort has been made to contrast the chemistry of the poly(pyrazolyl)borate complexes with their cyclopentadienyl analogues. The topology of both the Tp$^x$ and Cp$^x$ ligands predisposes their complexes towards pseudo-octahedral geometry, however, the Tp$^x$ ligands present a significantly greater steric profile than the cyclopentadienyl systems (cone angles of 239° and 183° for Tp$^*$ and Tp, respectively, cf. 100° and 146° for Cp and Cp$^*$). Furthermore, in contrast to the cyclopentadienyl ligand where the bonds to Cp$^x$ substituents ($x$ = H, Me, other alkyl or aryl groups) point away from the coordinated metal, the bonds in a 3,5-substituted Tp$^x$ ligand emanate at an angle which makes the pyrazolyl substituents protrude in space past the metal, forming a protective pocket. Thus, in many cases the tris(pyrazolyl)borate metal cages exhibit thermal and chemical properties notably different from their Cp analogues.

Chemistry involving the first generation pyrazolylborate ligands, Tp and Tp$^*$, forms the foundation of the initial 20 years of scorpionate research and, unsurprisingly, these ligands have been particularly popular in the chemistry of alkylidyne complexes whereas the related bis- and tetrakis- analogues have received much less attention. The merits and special features of the poly(pyrazolyl)borate co-ligands have traditionally been exploited to provide robust molecular platforms that support ligand transformations under very demanding conditions. Moreover, the enhanced kinetic stability of the alkylidyne complexes that is imparted by the limited access to the metal centre makes the poly(pyrazolyl)borate anions ideal capping ligands in metal-alkylidyne cluster chemistry, steric factors notwithstanding.

![Chart 1.1](chart.png)
1.2 Synthesis

The first reported examples of hydrotris(pyrazolyl)borate alkylidyne complexes were the mercaptoalkylidyne complexes prepared by Angelici and co-workers in 1981.\textsuperscript{23} Alkylation of the nucleophilic sulfur atom in the anionic thiocarbonyl complex \([W(\text{CO})_2(\text{CS})\text{Tp}]^-\) resulted in formal reduction of the C–S multiple bond to a C–S single bond, furnishing the thiomethylidyne derivatives \([W(\equiv\text{CSR})(\text{CO})_2\text{Tp}]\) (\(R = C_6H_4(NO_2)_2\)–2,4, Me, Et) (Scheme 1.1). The mercaptocarbonyl complex \([W(\equiv\text{CSMe})(\text{CO})_2\text{Tp}]\) could similarly be generated by treatment of \([W(\text{CO})_2(\text{CS})\text{Tp}]\) with the nucleophile LiMe, though the intimate mechanism is different and probably involves single electron transfer processes.\textsuperscript{23} Analogous reactions for the Cp-ligated complexes were also described.

![Scheme 1.1. Preparation of \([W(\equiv\text{CSR})(\text{CO})_2\text{Tp}]\) (\(R = C_6H_4(NO_2)_2\)–2,4, Me, Et; \(X = \text{Cl} \text{ or I}\).)](image)

The most commonly employed synthetic strategy for inclusion of the bulky poly(pyrazolyl)borate ligand into the coordination sphere of alkylidyne complexes involves late incorporation of the \(\text{Tp}^+\) anion into a more highly functionalised organometallic substrate in much the same way that Cp\(^\text{X}\) derivatives are utilised to generate cyclopentadienyl-containing alkylidyne complexes.\textsuperscript{24} Frequently, this involves modification of the metal-ligand framework of a pre-existing alkylidyne complex, which can be achieved by one of three ways: altering the alkylidyne ligand (e.g., replacement of \(R\) in MCR with \(R'\)), ligand substitution, or oxidation/reduction of the metal centre. Thus, the common preparative routes to both Fischer-\textsuperscript{1,25-30} and Schrock-type\textsuperscript{31-35} alkylidyne complexes are generally employed en route to \(\text{Tp}^+\) alkylidyne complexes. It should be noted, however, that the strategy for constructing the metal–carbon triple bond in Lalor’s haloalkylidyne complexes \([M(\equiv\text{CCl})(\text{CO})_2\text{Tp}^\text{X}]\) (\(M = \text{Mo, W}\))\textsuperscript{36,37} (vide infra) is unique to the pyrazolylborate systems.

1.2.1 Alkyl, aryl, alkenyl and alkynyl substituents

Synthesis by ligand substitution

A typical synthesis of poly(pyrazolyl)borate alkylidyne complexes involves displacement of labile ligands from pre-existing alkylidyne complexes prepared according to the classic oxide–abstraction Fischer preparation (Scheme 1.2), which has been developed by Mayr\textsuperscript{30,38} into an efficient approach to Group 6 alkylidyynes.
Treatment of the thermolabile bromoalkylidyne complex trans-[M(\equiv CR)Br(CO)₄] with the tris(pyrazolyl)borate salts K[Tp⁺] leads to displacement of not only the anionic ligand but also the additional elimination of two carbonyl ligands, affording the cis-dicarbonyl complexes [M(\equiv CR)(CO)₂Tp⁺] (M = Cr, Mo, W; Tp⁺ = Tp, pzTp, Tp*; TpP⁺, R = Me or aryl) (Scheme 1.3). Depending on the Lewis acid utilised in the transformation of the acyl or carbene ligands into the alkylidyne, different anions may be present, i.e., X = Cl with oxalyl chloride or the better leaving group CF₃CO₂⁻ with trifluoroacetic anhydride. This protocol has been similarly applied by Stone and co-workers in the preparation of a series of cyclopentadienyl complexes [M(\equiv CAr)(CO)₂Cp] (Ar = substituted phenyl; M = Cr, Mo, W). The bidentate Bp anion is sterically less demanding than the tridentate congeners and alkylidyne complexes ligated by Bp thus require an additional ancillary ligand in order to obtain a complete coordination sphere. Consequently, treatment of the tetracarbonyl precursors with salts of the bidentate Bp ligand result in displacement of a single carbonyl ligand along with the anionic leaving group to afford the tricarbonyl alkylidyne complexes [M(\equiv CR)₁(CO)₃Bp] (M = W, R = Me, C₆H₄Me⁻4) (Scheme 1.4).

Due to the trans-disposition of the four π-acidic carbonyls in the precursor complex [M(\equiv CR)X(CO)₄], thermal decomposition may compete with the ligand substitution process and, accordingly, the synthesis of Tp-alkylidyne complexes is often achieved indirectly via the
intermediacy of more stable carbonyl-substitution products. Bis-substituted metal-alkylidyne complexes of the form trans,cis,cis-[M(=CR)X(CO)2(L')2] (X = anionic ligand) are obtained upon the treatment of the tetracarbonyl compounds with donor ligands, L' (L' = py, ½ 2,2'-bipyridine (bipy), γ-picoline (pic), ½ tmeda (N,N,N',N'-tetramethylethlenediamine), isocyanide (CNR) ). The coordinative lability of the N-donors renders these complexes highly susceptible to ligand displacement reactions, however the greater electron density at the metal centre confers an enhanced thermal stability when compared with the [M(=CR)X(CO)4] derivatives. Displacement of L' in trans,cis,cis-[M(=CR)X(CO)2(L')2] with the stronger N-donor poly(pyrazolyl)borate ligands readily affords the desired cis-dicarbonyl complexes [M(=CR)(CO)2Tp'] (L' = py, Tp' = Tp*, M = Cr, R = C6H4Me-4,47 L' = pic, Tp' = Tp, M = Mo, R = C6H4OMe-4) (Scheme 1.5).48

![Scheme 1.5. Ligand substitution from carbonyl-substitution products (M = Cr, Mo, W; X = anionic ligand; M' = Na, K; Tp' = Tp, Tp*, pzTp; R = alkyl, aryl; L' = py, pic, CNR, ½ bipy, ½ tmeda).](image)

As mentioned above, in the case of the bidentate Bp ligand only the anionic ligand and one additional ligand are displaced in subsequent substitution reactions. Thus, for the Bp analogues, complexes of the type [M(=CR)(CO)2(L')Bp] (M = W, R = xylyl or mesityl; L' = pic, CNR') are generated, which retain an N-donor ligand.49 Moreover, the bidentate nature of the Bp ligands allows for the formation of two possible geometric isomers of theses alkylidyne complexes, i.e., the alkylidyne fragment may be oriented meridionally or facially with respect to the chelated pyrazolyl arms and the favoured geometry depends upon the relative π Basicity of the remaining ligands. The trans disposition of π-donor ligands appears to strengthen M=C bonds and, accordingly, the alkylidyne fragment is typically oriented trans to the strongest π-base (Scheme 1.6).49 For L' = pic, both geometric isomers were formed in unequal proportions, with interconversion between the two evident in solution. Nevertheless, 13C{1H} NMR spectral data suggested that the dominant isomeric form featured the more symmetric geometry in which the picoline ligand was trans to the alkylidyne substituent (i.e., facial Bp/alkylidyne coordination).49 This orientation was also found in the solid state structure. Spectroscopic data for the complexes [W(=CR)(CO)2(CNR')Bp], containing a π-acidic isonitrile ligand, are consistent with the alternate geometry in which the alkylidyne ligand is trans to a pyrazolyl arm.49
CHAPTER 1. ALKYLIDYNE COMPLEXES Ligated By Poly(pyrazolyl)borates

Scheme 1.6. Meridional vs facial coordination of Bp/alkylidyne fragments (M = Mo, W; M' = Na, K; R = alkyl, aryl; L' = py, pic, CNR, \(1/2\) bipy, \(1/2\) tmeda).

Enhanced thermal stability for the precursor complexes \([M(\equiv CR)(CO)\_2(L')_2]\) (X = anionic ligand) employed in ligand substitution reactions is likewise achieved when \(L'\) is a phosphorus donor. Direct reaction of the dicarbonyl complex \(\text{trans,cis,cis-}[W(\equiv CR)Br(CO)\_2(PPh\_3)\_2]\) (R = C\(_6\)H\(_4\)Me-4) with K[Tp] provides \([W(\equiv CR)(CO)\_2Tp]\). However, initial photolysis of this same substrate leads to a \(\text{trans}-\)disposition of the PR\(_3\) ligands and subsequent reaction with K[Tp] initially provides the thermally unstable alkylidyne–carbonyl coupling product \([W(n^2-C\equiv CCCR)(CO)(PPh\_3)Tp]\), which in solution undergoes slow CO extrusion to afford \([W(\equiv CR)(CO)(PPh\_3)Tp]\).

The tris(phosphine) alkylidyne derivatives similarly serve as precursors for ligand displacement reactions. The alkylidyne complexes \(\text{mer-[M(\equiv CR)Cl(CO)(PR\_3)\_3]}\) react with K[Bp] leading to \(\text{mer-[M(\equiv CR)(CO)(L')_2(Bp)]}\) (M = Mo, R = C\(_6\)H\(_4\)OMe-2, L' = P(O\(_2\)Me)\(_3\)) (Scheme 1.7). The dimethylphenyl phosphine analogue (M = W, L' = PMe\(_2\)Ph) can be prepared similarly via the intermediacy of a bis(picoline) complex that reacts with three equivalents of phosphine.

Scheme 1.7. Bp-alkylidyne synthesis from a tris(phosphine) alkylidyne precursor \([M(\equiv CR')X(CO)-(PR\_3)\_3]\) (M = Mo; \(X = Cl; PR\_3 = P(O\(_2\)Me)\(_3\); R' = C\(_6\)H\(_4\)OMe-2).

A variety of alkyl-, aryl- and alkynyl-substituted alkylidynes are accessible via the ligand substitution pathway. An illustrative example involves the complex \([M(\equiv CC=Cr-Bu)(O\(_2\)CCF\(_3\))(CO)\_2(L')_2]\) (L' = tmeda, M = Mo or W; L' = 2 \times py, M = W), which reacts with Tp\(^x\) salts (but not with Cp sources) to produce \([M(\equiv CC=Cr-Bu)(CO)\_2Tp]\) (M = Mo, Tp\(^x\) = Tp, Tp*) via displacement of the chelating tmeda ligand and the excellent leaving group.
O₂CCF₃⁻. Due to stronger binding of tmeda to tungsten than molybdenum, the Tp tungsten complex must instead be prepared from the bis(pyridine) precursor. More exotic examples may be obtained in which the alkylidyne substituent is itself a coordinated arene. Treatment of the alkylidyne-metal complex [CrMo(µ-η⁵-σ-CC₆H₄OMe-2)(O₂CCF₃)(CO)₅(tmeda)] with K[Tp] in dichloromethane affords [CrMo(µ-η⁵-σ-CC₆H₄OMe-2)(CO)₅Tp], in which the alkylidyne ligand is η⁶-coordinated to a Cr(CO)₃ group. The cymantrenylmethyldiyne complex [MoMn(µ-σ⁵-CC₅H₄)(CO)₅Tp] and the ferrocene-substituted bis(alkylidynemolybdenum) complex [Mo₂Fe(µ-σ₆-σ⁵-CC₅H₄)₂-(CO)₄Tp₂] can be similarly prepared in good yields (Chart 1.2). Not surprisingly, the coordination of metal fragments to the arene ring results in a significant shielding of the alkylidyne carbon resonance.

The preparation of high-valent, Schrock-type alkylidyne complexes containing poly(pyrazolyl)borate ligands may also be achieved by ligand substitution reactions. For example, the air-stable tungsten complexes [W(≡CR)X₂Tp*] (R = t-Bu, X = Cl; R = Ph, X = Br) were synthesised from [W(Cr-Bu)Cl₃(DME)] (DME = dimethoxyethane) or [W(CPh)Br₃(DME)] with K[Tp*] in yields of 50 and 10%, respectively. Similarly, the complex [W(Cr-Bu)Cl(NHPh)Tp*] was prepared by reaction of Me₃SiN(H)Ph with [W(Cr-Bu)Cl₃(DME)], to displace a halide, followed by the addition of K[Tp*] to displace the bidentate DME and a second chloride ligand (Scheme 1.8).

![Chart 1.2.](image)

**Chart 1.2.**

The preparation of high-valent, Schrock-type alkylidyne complexes containing poly(pyrazolyl)borate ligands may also be achieved by ligand substitution reactions. For example, the air-stable tungsten complexes [W(≡CR)X₂Tp*] (R = t-Bu, X = Cl; R = Ph, X = Br) were synthesised from [W(Cr-Bu)Cl₃(DME)] (DME = dimethoxyethane) or [W(CPh)Br₃(DME)] with K[Tp*] in yields of 50 and 10%, respectively. Similarly, the complex [W(Cr-Bu)Cl(NHPh)Tp*] was prepared by reaction of Me₃SiN(H)Ph with [W(Cr-Bu)Cl₃(DME)], to displace a halide, followed by the addition of K[Tp*] to displace the bidentate DME and a second chloride ligand (Scheme 1.8).

![Scheme 1.8.](image)

**Scheme 1.8.** High-valent Tp₅-alkylidyne synthesis from ligand substitution.
For the complexes [W(≡Ct-Bu)Cl(NHR)Tp\(^x\)], the sterically demanding Tp\(^x\) ligand and strong N–W bond disfavour rotational isomerism.\(^5\) In contrast, the related Mo complex, [Mo(≡CCMe\(_2\)Ph)(OMe){NHC\(_6\)H\(_2\)(i-Pr)\(_2\)-2,6}Tp] exists as a mixture of two rotamers due to \(\pi\)-donation from the methoxy group, which competes with the amido N–Mo \(\pi\) interaction and lowers the barrier to rotation about the N–Mo bond enough to allow the formation of \textit{syn} and \textit{anti} isomers.\(^6\)

More recently, a modification of the Mayr procedure in which the weakly coordinated trifluoroacetato ligand is directly replaced by the poly(pyrazolyl)borate anion (with concomitant CO ligand displacement) has allowed development of a ‘one-pot’ synthetic procedure. An early example of this involved stepwise preparation of the (alkynylmethylidyne)tungsten complexes [W(≡CC\(_4\)I-hS-2)(CO)\(_2\)Tp] (Tp\(^x\) = Tp*, Tp; R = SiMe\(_3\), Ph) from [W(CO)\(_6\)], Li[≡C], (CF\(_3\)CO)\(_2\)O and M[TP\(^x\)] (M = Na, K) directly, as shown in Scheme 1.9.\(^6\) The complex [Mo(≡CC\(_6\)H\(_5\)S-2)(CO)\(_2\)Tp] was similarly obtained directly from [Mo(CO)\(_6\)], 2-thienyllithium, (CF\(_3\)CO)\(_2\)O, and K[TP].\(^4\)

\[\text{Scheme 1.9. One-pot carbyne synthesis (M = Mo, W; M' = Na, K).}\]

\textit{Elaborated synthesis from alkylidynes}

Synthesis from pre-existing alkylidyne complexes [L\(_2\)M(≡CR)] can also occur via the modification of the alkylidyne ligand, involving the elaboration of R or the replacement of R by R'. These modifications typically involve alkylidyne complexes that already incorporate the poly(pyrazolyl)borate ligand and consequently there is overlap between this section and Section 1.5, and such syntheses will be expanded upon therein.
Synthesis from acyl complexes

Under strongly basic conditions in alcohol solvent, the molybdenum η²-acyl complexes [Mo(η²-OCR)(CO)_2Tp*] (R = Me, Et) were converted to molybdenum alkylidyne complexes [Mo(=CR)(CO)_2Tp*] in 20% yield (Scheme 1.10). In the infrared spectrum, the average CO stretching frequency of the carbyne thus produced is ca. 30 cm⁻¹ higher than that of the corresponding η²-acyl complex, consistent with the strong π-acidity of the alkylidyne ligand.

\[
\begin{align*}
\text{Scheme 1.10. Alkylidyne preparation from [Mo(\eta^2-OCR)(CO)_2Tp*] (R = Et, Me).}
\end{align*}
\]

Synthesis from alkylidenes

Base-catalysed proton transfer results upon the addition of excess potassium methoxide to the complex [Mo(=CHCMe_2Ph)(O_3SCF_3)]{NHC_6H_3(i-Pr)_{2,6}}Tp, affording the corresponding alkylidyne compound [Mo(=CCMe_2Ph)(OMe){NHC_6H_3(i-Pr)_{2,6}}Tp] (Scheme 1.11). The reverse reaction is negligible due to the extreme stability of the metal–carbon triple bond and restricted rotation around the molybdenum–amide bond resulting in the presence of two rotamers, as evident in the \(^1\)H and \(^{13}\)C{\(^1\)H} NMR spectra.

\[
\begin{align*}
\text{Scheme 1.11. Alkylidene/imido–amido/alkylidyne conversion involving [Mo(=CHR)(X)(NHAr)Tp] (R = CMe_2Ph; Ar = C_6H_5(i-Pr)_{2,6}; X = O_3SCF_3, OMe).}
\end{align*}
\]

Similarly, photolysis of the complex [W(=CH-t-Bu)Cl(NPh)Tp] induces rotational isomerism of the alkylidene ligand and proton transfer to generate [W(=C-t-Bu)Cl(NHPH)Tp]. The \(\text{syn}\) orientation of the alkylidyne complexes positions the amide proton away from the alkylidyne ligand, rendering the reverse tautomerisation reaction impossible without prior amide rotation or catalysis.

Synthesis via alkyne insertion

In a reaction that parallels that described by Geoffroy et al. for the formation of \([W\{\eta^3-(=CPhCPh=CHR)](CO)_2Cp][BF_4]\), protonation of (aryloxy)carbynes generates an agostic carbene complex which undergoes insertion of PhC=CH to afford the cationic vinyl
carbene complexes \([W\{\eta^3-\text{CPh}CH=CH(OAr)\}(\text{CO})_2\text{Tp}^*\}]^+ (\text{Ar} = \text{Ph}, C_6\text{H}_5\text{Me}-4)\). Subsequent treatment with base affords the corresponding vinyl carbynes \([W\{\text{CCPh}CH(OAr)\}(\text{CO})_2\text{Tp}^*\}]\) in low yield. The thermodynamically favoured product of this synthesis is, however, the metallafuran complex \([W\{\kappa^2-O-\text{CPh}CH-\text{CHO}\}(\text{CO})_2\text{Tp}^*\}]\) (Scheme 1.12).  

\[\begin{align*}
\text{Tp}^* &\quad \text{H}^+ \quad \text{PhCH} \\
\text{W} &\quad \eta^3\text{C} &\quad \text{OAr} \\
\end{align*}\]

Scheme 1.12. Vinylcarbyne synthesis from (aryloxy)carbyne complexes \([W(\equiv\text{COAr})(\text{CO})_2\text{Tp}^*]\) (\text{Ar} = \text{Ph}, C_6\text{H}_5\text{Me}-4, C_6\text{H}_4\text{OMe}-4).

Cis insertion of alkynes into a photogenerated \([\text{WH}(\text{CO})_2\text{Tp}^*]\) species may produce alkylidyne complexes, \(\eta^2\)-vinyl, \(\eta^2\)-acyl or metallafuran complexes, depending on the alkyne employed. Initial \(cis\)-2,1-insertion is favoured by terminal alkynes, leading to the \(\eta^2\)-vinyl and \(\eta^2\)-allyl products. In contrast, alkynes with large substituents such as \(t\)-butyl acetylene instead favour \(cis\)-1,2-insertion. However, in this case, the \(\eta^2\)-vinyl complex is destabilised by steric interactions between the \(C_\beta\)-substituent and the \(\text{Tp}^*\) methyls and further reactions occur, with a 1,2-H-migration from \(C_\alpha\) affording the alkylidyne complexes or the addition of CO providing \(\eta^2\)-acyls. In the absence of \(trans\) substituents, 1,2-migration to afford the carbyne is faster than CO trapping (Scheme 1.13).
Departing from these generalisations is the reaction with ethynyltrimethylsilane, which yields an η²-vinyl complex \([W\eta^2-C(SiMe_3)=CH_2](CO)_2Tp^*\) in addition to the alkylidyne complex \([W(=CCH_2SiMe_3)(CO)_2Tp^*]\) in a 45:37 ratio, consistent with competing 1,2- and 2,1-insertion pathways. The vinyl ligand slowly undergoes 1,2-silyl migration (> 5 days) to generate the alkylidyne complex.\(^{66}\)

With \(t\)-butyl acetylene, the η²-acyl \([W\{trans-\eta^2-C(O)CH=CHt-Bu\}](CO)_2Tp^*\) forms as the major product along with small amounts of the η²-vinyl and alkylidyne complexes, \([W\eta^2-C(t-Bu)=CH_2](CO)_2Tp^*\) and \([W(=CCH_2-t-Bu)(CO)_2Tp^*]\), respectively. With \(Me_3SiC=CCH_3\), the allyl complex \([W(\eta^3-syn-CH_2CHCHSiMe_3)(CO)_2Tp^*]\) is produced in addition to a significant amount of the alkylidyne complex \([W(=CEt)(CO)_2Tp^*]\), which is perhaps produced by hydrolysis of an intermediate η²-vinyl intermediate. Thermal isomerisation of the η³-allyl complex to the η²-vinyl species followed by a 1,2-H-shift produces the alkylidyne complex \([W(=CCHMeSiMe_3)(CO)_2Tp^*]\).

The equivalent alkyne insertion reaction with PhC≡CR (R = H or Ph) gives only η²-vinyl products whereas RCH_2C≡CH (R = H or \(n\)-Pr) gives η²-vinyl and metallafuran products while the same substrate with HC≡CH yields exclusively the ethylidyne complex \([W(=CMe)(CO)_2Tp^*]\).\(^{66}\) For the latter, an identical reaction course resulted from stoichiometric addition of Li[HBEt_3] to a tetrahydrofuran solution of \([W(HC≡CH)(CO)_2Tp^*][O_2SCF_3]\)\(^{66}\) and this complex may also be prepared by an alternative route involving elaboration of an alkylidyne ligand (vide infra).\(^{67}\)
1.2.2 Heteroatom substituents

**Haloalkylidyynes**

The halomethylidyne complexes [M(=CX)(CO)\textsubscript{2}Tp*] (M = Mo, W; X = Cl, Br, and I) are prepared from the displacement of three mutually cis (fac) terminal carboxyls from metal hexacarboxyls and subsequent oxidation of the poly(pyrazolyl)borate complexes [M(CO)\textsubscript{3}Tp*] (M = Mo, W) as their [Et\textsubscript{4}N]+ salts with either [ArN\textsubscript{2}]\textsuperscript{+} (Ar = aryl) or [Pb\textsubscript{2}]\textsuperscript{+} in the presence of haloalkanes (dichloromethane, bromoform or iodoform) (Scheme 1.14). The iodomethylidyne complex is unstable and formed in very low yield,\textsuperscript{36,37} though an alternative route to this species was later demonstrated by Templeton.\textsuperscript{68}

In acetonitrile solvent, the \(\eta^2\)-aryloyl complexes [M(\(\eta^2\)-OCAr)(CO)\textsubscript{2}Tp\textsuperscript{*}] (Ar = C\textsubscript{6}H\textsubscript{4}X-4, X = NO\textsubscript{2}, CN, COMe, CF\textsubscript{3}, H, Me, OMe or NMe\textsubscript{2}; C\textsubscript{6}H\textsubscript{4}X-3, X = NO\textsubscript{2} or OMe) are instead produced.\textsuperscript{36}

![Scheme 1.14. Synthesis of haloalkylidyne complexes [M(=CX)(CO)\textsubscript{2}Tp*] (M = Mo, W; Tp* = Tp*; n = 2, 3; X = Cl, Br, I).](image)

The relief of steric crowding and propensity for pseudo-octahedral geometries for the Tp*M fragment are believed to provide the driving force behind formation of the chloromethylidyne complexes and the proposed synthetic mechanism is depicted in Scheme 1.15. A seven-coordinate dichloromethyl compound is suggested as an intermediate, with rearrangement to the \(\eta^2\)-dichloroacetyl complex being disfavoured in view of the less crowded coordination sphere which can be obtained via simultaneous loss of a proton from the dichloromethyl group and expulsion of CO with formation of anionic [Mo(=CCl\textsubscript{2})(CO)\textsubscript{2}Tp*]. Loss of chloride anion would then lead directly to the more compact \(\eta^1\)-chloromethylidyne ligand.\textsuperscript{36}

![Scheme 1.15. Proposed mechanism for haloalkylidyne synthesis.](image)

Through comparative studies for a range of [M(CO)\textsubscript{3}Tp\textsuperscript{*}] analogues with different substituents in the pyrazolyl ring, Lalor demonstrated that the oxidation by arenediazonium cations occurred
in response to the steric rather than the electronic effect of the 3-methyl substituents. However, further steric crowding in either the hydrotris(pyrazolyl)borate ligand or the diazonium cation promoted a reversion to the carbonyl-substitution pathway, producing aryldiazenido complexes \([\text{M}(\text{N}_2\text{Ar})(\text{CO})_2\text{Tp}^\ast]\), which are also the products observed for the parallel reaction with the more sterically modest Cp and Tp analogues (Scheme 1.16).

\[
\begin{align*}
\text{M}^2\text{CO}_2\text{CO}^- & \quad [\text{ArN}_2]^+ \\
\text{CH}_4\text{e}X_n & \quad \text{OC} \quad \text{OC} \quad \text{OC} \\
\end{align*}
\]

Scheme 1.16. Carbonyl-substitution pathway favoured by increased steric crowding of \(\text{N}_2\text{Ar}\) or \(\text{Tp}^\ast\) (\(\text{Ar} = \text{aryl}\)).

A general and powerful approach to heteroatom-substituted molybdenum and tungsten alkylidyne complexes is based upon chloride displacement in these haloalkylidyne complexes by a variety of anionic as well as neutral nucleophiles. While some nucleophilic attack at the metal centre in \([\text{L}_n\text{M}(\equiv\text{Cl})]\) might be expected, the bulky \(\text{Tp}^\ast\) ligand sphere seems to inhibit approach of the incoming nucleophile to the coordinatively saturated metal, resulting in clean reactions at \(\text{Co}\).

**Organothio-, seleno- and telluroalkylidyne**

Nucleophilic displacement at the carbon atom of the terminal methylidyne halide \([\text{M}(\equiv\text{Cl})(\text{CO})_2\text{Tp}^\ast]\) (\(\text{M} = \text{Mo}, \text{W}\)) with alkyl and aryl thiolates\(^{73}\) and phenylselenolate\(^{73}\) produces organothiomethylidyne and organoselenomethylidyne complexes (Scheme 1.17).

\[
\begin{align*}
\text{Tp}^\ast & \quad \text{M} = \text{Mo}, \text{W} \\
\text{OC} & \quad \text{CO} \\
\text{X} & \quad \text{E} \\
\end{align*}
\]

Scheme 1.17. Reagents: (i) \(\text{ER}^-\) (\(\text{E} = \text{S}, \text{Se}; \text{R} = \text{alkyl}, \text{aryl}\)); (ii) \(\text{Li}_2\text{E}\) (\(\text{E} = \text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-}\)); (iii) \(\text{MeI}\) (\(\text{M} = \text{Mo}, \text{W}\)).

Methylthiocarbyne, methylselenocarbyne, and methyltellurocarbyne complexes are also available by reacting the chlorocarbyne with \(\text{Li}_2\text{S}, \text{Li}_2\text{Se}, \text{or Na}_2\text{Te}\) and subsequent methylation of the anionic carbon monochalcogenide complexes.\(^{73}\) As mentioned earlier, the related tungsten complexes have also been prepared in much lower overall yields from the reaction of
the anionic thiocarbonyl complex $[W(CO)_2(CS)Tp]^- \text{ with reactive organic halides and the treatment of trans-}[WI(CO)_2(CS)Tp]$ with organolithium compounds (Scheme 1.1).$^{23}$ The requisite $[W(CO)_3(CE)]$ (E = Se or Te) have yet to be reported, making this route unavailable for the heavier chalcogenolatoalkylidynes.

Angelici has reported a variety of novel synthetic routes to the thiocarbyne $[W(=CSMe)(CO)_2Tp]$. The Bronstead bases NaH, NaBH₄, NaOMe, NaOPh, PPN[SH], NaSCH₂Ph, NaSePh, LiMe, NEt₃, K₂CO₃, NH₂NH₂, NHMeNH₂, and NHMeNHMe react with the thiocarbene complex $[W(\eta^2\text{-MeSCH})(CO)_2Tp]$ to give the thiocarbyne (in 10–20% yields) and $[W(\eta^2\text{-MeSCH(SMe)})_2(CO)_2Tp]$ (ca. 5–40%) as a side product.$^{74,75}$ The ylide complex $[W(\eta^2\text{-MeSCH(PPh})_3(CO)_2Tp]$ can also be deprotonated at the methyne hydrogen with NaH, accompanied by phosphine dissociation to give the thiocarbyne compound in good yield (90%).$^{76}$ Although these transformations do not represent useful routes to $[W(=CSMe)(CO)_2Tp]$, being as it is the precursor to $[W(\eta^2\text{-MeSCH})(CO)_2Tp]^+$, they do illustrate fundamental transformations that might be extendable to other systems.

Similarly, the dithiocarbene cation $[W(\eta^2\text{-MeSC(SMe)}_2)(CO)_2Tp]^+$, which is produced from SMe₂ addition to $[W(=CSMe)(CO)_2Tp]$, reacts with the reducing agent sodium naphthalenide or the bases LiPh, LiPPh₂ and NaSePh to produce a 1:1 mixture of the MeS⁻ alkylidene adduct $[W(\eta^2\text{-MeSC(SMe)}_2)(CO)_2Tp]$ and the regenerated thiocarbyne complex.$^{77}$ In reactions with SR⁻ nucleophiles, release of the thiocarbyne occurs in addition to adduct formation, suggesting perhaps a competing electron transfer pathway, the operation of which increases with the increasing size of RS⁻.$^{77}$ The dithiocarbene can also be used to regenerate Angelici’s thiomethylidyne complex (along with $[Mo(SMe)(CO)Cp]$ or $[Mn(SMe)(CO)Cp]$) via sulfenium ion transfer reactions with $[Mo(CO)_3Cp]^-$ or $[Mn(CO)_3]^-$, respectively (Scheme 1.18).$^{77}$

![Scheme 1.18](image)

**Scheme 1.18. Reagents:** (i) RS⁻ (R = Me, Et); (ii) NaNp, LiPPh₂, LiPh, NaSePh; (iii) $[M]^-$, ([M] = $[Mo(CO)_3Cp]^-$ or $[Mn(CO)_3]^-$).
Angelici’s synthesis of \([W(=CS\text{Me})(\text{SMe})_2\text{Tp}]\) via the thermally induced double \(\alpha\)-tungsten-thiolate elimination reaction of the complex \([W\{\eta^2-\text{MeSC}(-\text{SMe})_2\}\{\text{CO}\}_2\text{Tp}]\) was the first example of the general class of alkylidyne complex \([W\{\equiv\text{CR}\}_2\text{Tp}^*}\) (\(X = \text{anionic ligand, } \text{Tp}^* = \text{Tp, } \text{Tp}^*\)).\(^{19}\) \(\alpha\)-Thiolate migration and concomitant CO loss from dithiocarbene complexes of the type \([W\{\eta^2-\text{MeSC}(\text{SR})(\text{SMe})\}\{\text{CO}\}_2\text{Tp}]\) (\(R = \text{Me, Et, Ph, } C_6\text{H}_4\text{Me-4}\)) may be thermally (\(R = \text{alkyl}\)) or photolytically (\(R = \text{aryl}\)) induced (Scheme 1.19). Photolysis may also be used to induce the alkylthiolato reactions at the expense of the yield. The resulting alkylidyne complexes \([W(=CS\text{Me})(\text{SMe})(\text{SR})\text{Tp}]\) are spectroscopically and crystallographically similar to the related dicarbonyl complex \([W(=CS\text{Me})(\text{CO})_2\text{Tp}]\), despite the difference in oxidation state and formal electron count of the metal centre.\(^{19}\) Crystallographic evidence suggests a \(\pi\)-donor stabilising role for the SR ligands in the formally 16-electron complexes, with \(W-S\) bonds that are shorter than expected for simple organylthiolato ligands. Under thermal conditions, the less nucleophilic and less basic arylthiolato derivatives eliminate disulfide and produce the known thiocarbyne complex \([W(=CS\text{Me})(\text{CO})_2\text{Tp}]\), proposed to proceed via concerted \(\alpha\)-elimination of the disulfide.\(^{19}\)

\[
\begin{align*}
\text{Scheme 1.19. Double } \alpha\text{-thiolate elimination to generate } [W(=CS\text{Me})(\text{SMe})(\text{SR})\text{Tp}] (R = \text{alkyl, aryl}).
\end{align*}
\]

Photolysis of \([W\{\eta^2-\text{MeSC}(\text{Me})(\text{SMe})\}\{\text{CO}\}_2\text{Tp}]\) similarly yields \([W(=\text{CMe})(\text{SMe})_2\text{Tp}]\), however this reaction does not proceed under thermal conditions.\(^{19}\) The proposed mechanism for the photolytic reactions involves UV-promoted CO loss followed by C–SR bond cleavage and complete transfer of the SR group to tungsten centre.\(^{19}\)

**Phosphonioalkylidyne**

The SMe substituent is likewise a good leaving group and addition of excess \(\text{PR}_3\) (\(R = \text{Et, Me}\)) to \([W(=CS\text{Me})(\text{CO})_2\text{Tp}^*]\) in dichloromethane yields the cationic phosphonium alkylidyne and bis(phosphonio)carbene complexes, \([W(=\text{CPMe}_3)(\text{CO})_2\text{Tp}^*]\) and \([W\{\equiv\text{C(\text{PMe})}_3\}(\text{CO})_2\text{Tp}^*]\), respectively, which are isolated as their \(\text{PF}_6\) salts by metathesis with \(\text{NH}_4\text{PF}_6\).\(^{72}\) The bis(trimethylphosphonio)carbene complex is in equilibrium with the monophosphonioalkylidyne complex in solution and the addition of \(\text{MeI}\) allows the isolation of the monophosphine analogue \([W(=\text{CPMe}_3)(\text{CO})_2\text{Tp}^*]\) by trapping liberated \(\text{Me}_3\text{P}\) as [\(\text{Me}_4\text{P}\)].\(^{72}\) This differs from the work of Angelici and Kim involving the Tp-substituted carbynes, which
participated in nucleophile-induced carbonyl–carbyne coupling and ketenyl formation. The increased steric congestion of the Tp* system means the reactions more closely resemble the nucleophilic substitution reactions described by Lalor involving [Mo(=CCl)(CO)₂Tp*] wherein Cl⁻ is the nucleofuge.

Accordingly, tertiary phosphines (PMe₂Ph, PPh₃, PCy₃) displace chloride in [M(=CCl)(CO)₂Tp*] (M = Mo, W) to give the cationic phosphonio-carbynes [W(=CPMe₂Ph)(CO)₂Tp*][PF₆] in the presence of K[PF₆] and in a polar solvent (acetonitrile) (Scheme 1.20). The structure of [W(=CPMe₂Ph)(CO)₂Tp*][PF₆] has been crystallographically determined. High energy CO stretching frequencies (ca. 2022 and 1934 cm⁻¹) reflect the cationic nature of the dicarbonyl products, from which it may be inferred that the phosphonioalkylidyne ligand is a particularly potent π-acid.

\[
\text{Scheme 1.20. General synthesis of phosphonioalkylidynes } [\text{M}(=\text{CPMe}_2\text{Ph})(\text{CO})_2\text{Tp}^*] \quad (\text{M} = \text{Mo, W}; \text{PR}_3 = \text{PMe}_2\text{Ph, PPh}_3, \text{PCy}_3; \text{X} = \text{leaving group: SMe, Cl}).
\]

**Aryloxyalkylidynes**

Aryloxides similarly displace chloride in [M(=CCl)(CO)₂Tp*] (M = Mo, W) with the formation of (aryloxy)carbyne complexes [M(=COAr)(CO)₂Tp*] (Ar = Ph, C₆H₄Me-4, C₆H₄OMe-4), which are of interest in that they provide models for the elusive hydroxycarbyne ligand that is implicated in the Fischer–Tropsch processes.

The neutral PR₃ substituent in the cationic phosphonio-carbyne complexes [W(=PR₂Ph)(CO)₂Tp*][PF₆] (R = Me, Ph) has proven to be an excellent leaving group, with electron-rich aryloxides (ArO⁻) replacing the phosphine to afford (aryloxy)alkylidyne products [W(=COAr)(CO)₂Tp*]. With electron-poor aryloxy nucleophiles, η²-ketenyl complexes are also formed (Scheme 1.21).
CHAPTER 1. ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

The product ratio of substitution at the carbyne carbon vs carbonyl–carbyne coupling can be tuned by variation of the aryloxide para-substituent, which augments the nucleophilic strength. A larger proportion of the alkylidyne product is formed with the dimethylphenylphosphonio-cationic reagents than with the triphenylphosphonio-reagents, perhaps due to the greater steric bulk of the ‘LuW(-CPPh3') fragment, which inhibits nucleophilic attack at the alkylidyne carbon atom.

Addition of methoxide to the cationic phosphonioalkylidyne complexes [W≡CPh3(CO)2Tp*]⁺ likewise allows the isolation of the thermally- and light-sensitive methoxycarbyne complex [W≡COMe(CO)2Tp*] in 48% yield. It is necessary to quench the reaction with excess Mel to prevent subsequent conversion to the tricarbonyl anion [W(CO)3Tp*]. The electron-rich methoxy group results in νCO frequencies at 1558 and 1862 cm⁻¹, which are towards the low end of the range observed for neutral Tp* dicarbonyl tungsten complexes.

Aminoalkylidyynes

Group 6 aminocarbyne complexes [M≡CN(i-Pr)2](CO)2Tp*] can be synthesised from trans-[M≡CN(i-Pr)2](O2CCF3)(CO)2(PPh3)] (M = Cr, Mo, W)⁸⁰ or trans-[Cr≡CN(i-Pr)2]-X(CO)4 (X = Cl, Br)⁸¹,⁸² in a manner analogous to the formation of aryl and alkyl alkylidyynes. The thermally labile tetracarbonyl complexes are obtained from [M(CO)6] using the nucleophile Li[N(i-Pr)2] in a Mayr carbyne synthesis. Filippou and co-workers reported that thermal decarbonylation of the tetracarbonyl complex with γ-picoline resulted in the quantitative formation of [Cr≡CN(i-Pr)2]X(CO)2(pic)2] (X = Cl; X = Br) in 60–75% overall isolated yield. Treating the bromo complex with Na[Cp'] or K[Tp*] affords [Cr≡CN(i-Pr)2](CO)2L] (L = Cp, Cp*, Tp*). The displacement reaction with Tp* occurs at a higher temperature but is lower yielding than that of the analogous cyclopentadienyl aminocarbyne syntheses.⁸¹,⁸² The trans

Scheme 1.21. Available reaction pathways for the treatment of [W≡CPR2Ph](CO)2Tp*]⁺ (R = Me, Ph) with aryloxide nucleophiles (ArO⁻).
complexes \([M\{\equiv CN(i-Pr)_2\}(O_2CCF_3)(CO)_3(PPh_3)] \) \((M = Cr, Mo, W)\) reported by Hill equally provide convenient precursors for the synthesis of \([M\{\equiv CN(i-Pr)_2\}(CO)_2Tp]\) through a ligand exchange reaction with \(K[Tp]\).\(^8^0\)

The isocyanide substituted complexes can be correspondingly obtained following thermal decarboxylation of the bromotetracarbonyl species with \(t\)-butyl isonitrile to produce the cationic aminocarbyne complex \([Cr\{\equiv CN(i-Pr)_2\}(CO)(CNt-Bu)]^+\). Subsequent treatment with \(Na[Cp]\) or \(K[Tp^*]\) in tetrahydrofuran at 50 °C results in formation of \([Cr\{\equiv CN(i-Pr)_2\}(CO)(CNt-Bu)L]\) \((L = Cp or Tp^* in 61% and 58% yield, respectively). In both reactions the minor product \([Cr\{\equiv CN(i-Pr)_2\}(CNt-Bu)]^+\) is formed by a competitive carbonyl substitution reaction of the tetra(isonitrile) complex with liberated \(CNt-Bu\).\(^8^1,^8^2\)

Electrophilic addition to anionic molybdenum isocyanide derivatives \(Na[Mo(CNR)(CO)_2Tp^*]\) is dominated by direct attack at nitrogen to form alkylidyne products, however alkylation at the metal followed by insertion can lead to \(\eta^2\)-iminoacyl complexes in some cases. The aminocarbyne products \([Mo(\equiv CN(R)Me)(CO)_2Tp^*]\) are formed in high yield for methyl and phenyl isocyanide reagents. However, formation of the \(t\)-butyl aminoalkylidyne complex is accompanied by formation of \(\eta^2\)-acyl and \(\eta^2\)-iminoacyl complexes (Scheme 1.22).\(^8^3\)

![Scheme 1.22. Synthesis of aminoalkylidyne complexes \([\text{Mo}(\equiv \text{CN(R)Me})(\text{CO})_2\text{Tp}^*)\] from electrophilic addition to coordinated isonitriles \((R = t\text{-Bu, Ph, Me; } E = O, E' = NR, E = NR, E' = O)\).](image)

Increased nucleophilicity at nitrogen and steric hindrance at the metal centre promote formation of the aminoalkylidyne complexes. It is suggested that the bulky \(t\)-butyl substituent serves to shield the nitrogen atom.\(^8^3\)

In a similar fashion, addition of HCl to the anionic \([\text{Mo}(\text{CNR})(\text{CO})_2\text{Tp}^*]\) generates the neutral alkylidyne complex \([\text{Mo}(\equiv \text{CN}(t\text{-Bu})H)(\text{CO})_2\text{Tp}^*)]\).\(^8^3\)

A large scale, high-yield, stepwise synthesis of the aminoalkylidyne complexes \([\text{W}(\equiv \text{CN(R)Et})(\text{CO})_2\text{Tp}^*)\] \((R = \text{Me, Et})\) from \([\text{W}(\text{CO})_3\text{Tp}^*)]\) has been reported. Thermal
decarbonylation of \([\text{WI(CO)}_3\text{Tp}^*]\) in the presence of \(\text{CNEt}\) gives \(\text{cis-}[\text{WI(CNEt)}(\text{CO})_2\text{Tp}^*]\). Subsequent reduction with \(\text{Na/Hg}\) provides the metalate \(\text{Na}[\text{W(CNEt)}(\text{CO})_2\text{Tp}^*]\), which can be alkylation with \(\text{RI} (R = \text{Me, Et})\) exclusively at the isocyanide nitrogen to give the aminoalkyldyne complexes.\(^{84}\) In contrast, the metalates \(\text{Na}[\text{W(CNEt)}(\text{CO})_2\text{Cp}^*]\) (\(\text{Cp}^* = \text{Cp, Cp}^*\)) undergo alkylation with \(\text{RI}\) at the metal centre to afford the \(\text{W(II)}\) alkyl complexes \(\text{cis/trans-}[\text{WR(CNEt)}(\text{CO})_2\text{Cp}^*]\). The difference in reactivity is ascribed to the steric demands of the \(\text{Tp}^*\) ligand, which shields the metal centre from the incoming electrophile.\(^{84}\)

By following a related stepwise procedure, aminocarbyne complexes can be used to prepare rare examples of mononuclear bis(aminocarbyne) complexes.\(^{85}\) Oxidative decarbonylation of \([\text{W} (=\text{CNREt})(\text{CO})_2\text{Tp}^*]\) (\(R = \text{Me, Et}\)) with \(\text{Br}_2\) or \(\text{I}_2\) affords the six-coordinate dihalidominoaminocarbyne complexes \([\text{W} (=\text{CNREt})\text{X}_2\text{Tp}^*]\) (\(X = \text{Br, I}\)) in high yield. Subsequent reductive dehalogenation by \(\text{Na/Hg}\) in the presence of \(\text{CNEt}\) gives the electron-rich mono-aminocarbyne complexes \([\text{W} (=\text{CNREt})(\text{CNEt})_2\text{Tp}^*]\). An unusually low-field chemical shift for the metal-bonded isonitrile carbons as well as low-frequency \(\nu_{\text{CN}}\) absorptions confirms the presence of a very electron-rich metal centre. Chemoselective alkylation with \([\text{Et}_3\text{O}][\text{BF}_4]\) at one isocyanide nitrogen yields the bis(aminocarbyne) salts \([\text{W} (=\text{CNREt})(=\text{CNEt})_2(\text{CNEt})\text{Tp}^*][\text{BF}_4]\) (Scheme 1.23).\(^{85}\)

![Scheme 1.23. Stepwise preparation of mono- and bis(aminocarbyne) complexes of tungsten (\(R, R' = \text{Me or Et; } X = \text{I or Br}\)).](attachment:image.png)

The introduction of amino substituents on both carbyne carbons stabilises the bis(carbyne) form relative to the carbyne–carbyne coupled alkyne isomer due to strong interaction of the \(\pi\)-type lone pair at the amino nitrogen with the two vacant \(\pi\)-orbitals at the carbyne carbon atom.\(^{85}\) Calculations reproduce the preference for the bis(alkyldyne) formulation.
The thiocarbene \([W(\eta^2-SMe(CO)_{2}Tp)]^+\) reacts with the primary amines \(NH_2R\) to produce the related aminoalkylidyne compounds \([W(\equiv CNHR)(CO)_{2}Tp]\) in 25–35% yield, which are in equilibrium with their hydride–isocyanide tautomers \([WH(CNR)(CO)_{2}Tp]\) \((R = Me, Et, CH_2CH_2OH-i-Pr, t-Bu)\) (Scheme 1.24). The related Cp complex \([MoH(CNMe)(CO)_{2}Cp]\) shows no evidence for the alkylidyne tautomer, which suggests that it may be the preference of the Tp complexes for six- rather than seven-coordination or the greater electron donor ability of Tp that favours the aminoalkylidyne structure in contrast to the Cp system. If there exists a similar equilibrium for tautomerisation in the Tp\(^*\) aminoalkylidyne complexes it greatly favours the alkylidyne version, presumably due to steric congestion at the metal centre.

Reaction of the thiocarbene \([W(\eta^2-SMeCH)(CO)_{2}Tp]^+\) with \(N,N\)-dimethylhydrazine produces the dimethylaminocarbonyne complex \([W(\equiv CNMe)(CO)_{2}Tp]\) (28% yield) along with \([W(\eta^2-SMeCH(SMe))_{2}CO)]^+\) (28% yield) and a third product not sufficiently stable to be isolated. With secondary amines (HNMe\(_2\), HNEt\(_2\)) the carbene \([W(\eta^2-SMeCH)(CO)_{2}Tp]^+\) reacts to form air-stable aminocarbonyne complexes \([W(\equiv CNR_{2})(CO)_{2}Tp]\) in approximately 30% yield.

**Phospha- and arsaalkenyl alkylidyne**

Condensation of Lalor’s chlorocarbyne with P-silylated phosphaalkenes \(Me_3SiP=C(NR_{2})\_2\) \((R = Me, Et)\) produces phosphaalkenyl-functionalised carbyne complexes via nucleophilic displacement of the chloride atom. In an analogous reaction requiring the exclusion of light, the complexes \([M(\equiv CAs=C(NMe_{2})_{2})(CO)_{2}Tp^*]\) \((M = Mo, W)\) are prepared by condensation with the corresponding arsa-alkene \(Me_3SiAs=C(NMe_{2})_{2}\). Three mesomeric structures are considered to contribute to a full description of the bonding in these alkylidyne complexes (Scheme 1.25).
CHAPTER 1. ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

Scheme 1.25. Preparation and resonance forms of phospha- and arsaalkene-functionalised carbynes \([M(=C(E(NR_2)_2})(CO)_2Tp^\ast)\) (\(E = \text{As, } R = \text{Me, } M = \text{Mo, W; } E = \text{P, } R = \text{Me, Et; } M = \text{Mo, W}\)).

(i) \(\text{Me}_3\text{SiE} = \text{C}(\text{NR}_2)_2\).

The \(\pi\)-basicity of the organophosphorus and organoarsenic ligands are reflected in their highly deshielded \(\text{C}_\alpha\) signals (\(\delta_{\text{C}} 318-334\) for the phosphaalkenyls; \(\delta_{\text{C}} 330-350\) for the arsaalkenyls) compared to those of the starting chloromethylidyne complexes (\(\delta_{\text{C}} 206-209\)). This property is also reflected in the infrared \(\nu_{\text{CO}}\) stretches at ca. 1950 and 1850 cm\(^{-1}\), which are at much lower wavenumbers than for the precursor alkylidyne complexes at ca. 2005 and 1921 cm\(^{-1}\). 87,88

**Silyl alkylidyynes**

By employing the dimethylphenylsilyl anion as nucleophile to initiate Mayr's multistep Fischer-carbyne synthesis, 30,38 and later using the \(\text{Tp}^\ast\) anion as a capping tridentate ligand, new alkylidyne complexes in which a silyl group is directly attached to the methylidyne carbon can be obtained, i.e., \([M(=\text{CSiMe}_2\text{Ph})(\text{CO})_2\text{Tp}^\ast]\) \((M = \text{Mo, W})\). 89

Deprotonation of the methylidyne complex \([W(=\text{CH})(\text{CO})_2\text{Tp}^\ast]\) and subsequent addition of \(\text{SiMe}_3^+\) electrophile also generates a silyl alkylidyne complex of the type \([W(=\text{CSiMe}_3)(\text{CO})_2\text{Tp}^\ast]\). 68

\(\text{Tp}^\ast\) co-ligated germyl, stannyl and plumbyl substituted alkylidyynes appear unknown at present.

**Metal-substituted alkylidyynes (\(\mu\)-carbido)**

Good yields of \([\text{Mo}(=\text{CFe}(\text{CO})_2\text{Cp})(\text{CO})_2\text{Tp}^\ast]\) result from the reaction of Lalor's chlorocarbyne with K[Fe(CO)_2Cp] (Scheme 1.26). The \(^{13}\text{C}^{\{1\}}\text{H}\)NMR spectrum shows the bridging carbon at \(\delta 381\), which is near the range expected for \(\text{C}_\alpha\) vinylidene shifts and below those typical of alkylidyne complexes, suggesting that a vinylidene resonance form in which both metals are in the same d-configuration may contribute to the bonding. The X-ray structure revealed a near linear bridge with a Fe–C–Mo angle of 172.2(5)° and a short Mo–C separation that is consistent with a normal M=C triple bond. 71
1.2.3 Metals other than Cr, Mo, and W

The vast majority of poly(pyrazolyl)borate alkylidyne chemistry is concerned with the Group 6 metal triad Cr, Mo and W, however, rare examples of Group 7 and 8 complexes have also been isolated.

*Group 7 alkylidyne*

Schrock and co-workers have described the synthesis of a rhenium neopentylidyne complex containing the tris(pyrazolyl)borate ligand from \([\text{Re}==(\text{C}_t\text{-Bu})(\text{CH}_2\text{-t-Bu})_3\text{O}_3\text{SCF}_3])\). Treatment of this complex with excess pyridine afforded the colourless, six-coordinate rhenium neopentylidene/neopentylidyne complex \([\text{Re}==(\text{C}_t\text{-Bu})(\text{CH}_2\text{-t-Bu})(=\text{CHt-Bu})\text{(py)}_2])\), which was subsequently subject to ligand substitution by \(\text{Na}[\text{Tp}]\), producing the thermally stable, 18-electron complex \([\text{Re}==(\text{C}_t\text{-Bu})(\text{CH}_2\text{-t-Bu})(=\text{CHt-Bu})\text{Tp}])\) (Scheme 1.27). Rhenium is one of three metals (along with molybdenum and tungsten) that are active in classic olefin metathesis systems; however, this alkylidyne complex showed no metathesis activity, due in part to a LUMO that is not metal-based and the low lability of the multidentate Tp ligand, which does not allow for a vacant coordination site for initial olefin binding prior to metallacyclobutane formation.

The synthetic route to the rhenium(V) complex \([\text{Re}==(\text{C}_6\text{H}_5\text{Me}_{2}\text{-2,4,6})(\text{CO})_2\text{Tp}^*])\)](O$_3$SCF$_3$), like the Group 6 benzylidyne analogues, involves ligand substitution from the labile tetracarbonyl species \([\text{Re}==(\text{C}_6\text{H}_5\text{Me}_{2}\text{-2,4,6})\text{Cl}(\text{CO})_4])\)](O$_3$SCF$_3$) with \(\text{K}[\text{Tp}^*]\). However, in contrast to the related Group 6 systems in which the calculated energy and composition of the near frontier orbitals assigns the HOMO to a metal d orbital that is non-bonding with respect to the benzylidyne ligand, the \(\pi\)-system of the aromatic system of
[Re(≡CC₂H₂Me₃-2,4,6)(CO)₂Tp*][O₃SCF₃] is in conjugation with the metal–carbon triple bond.⁹⁵,⁹⁶

In dichloromethane solution, low-temperature, acid-promoted addition of methanol to the furan complex [Re(η²-C₆H₄O)(CO)(PMe₃)Tp] generates two diastereomers of the complex [Re(4,5-η²-2β-methoxy-2,3-dihydrofuran)(CO)(PMe₃)Tp].⁹⁷ However, if the reaction is performed at ambient temperature in tetrahydrofuran solution, rather than formation of the 2-methoxy-2,3-dihydrofuran ligand, oxidation of the metal by triflic acid yields the ring-opened rhenium(V) alkylidyne complexes [Re(≡CH₂CH₂R)(CO)(PMe₃)Tp] (R = CHO, CH(OMe)₂) (Scheme 1.28).⁹⁷

(i) (i) (ii) (iii)

Scheme 1.28. Reagents: (i) H₂O₂SCF₃, MeOH; (ii) CH₂Cl₂ –40 °C; (iii) THF, 25 °C (R = CHO, CH(OMe)₂).

Group 8 alkylidyines

Prior to the synthesis of the rhenium(V) neopentylidyne complexes discussed above, osmium(VI) analogues were prepared using a similar synthetic strategy.⁹² Treatment of the complex [(PPh₄)₂(OsO₂Cl₄)] with excess dineopentylzinc afforded the dioxo complex [OsO₂(CH₂t-Bu)₂], which underwent an alkylidyne/oxo exchange reaction when treated with two equivalents of the tantalum neopentylidene complex [Ta(-CH₂t-Bu)(CH₂t-Bu)₃]. α-Hydrogen abstraction from the resulting bis(alkylidene) complex [Os(-CH₂t-Bu)₂(CH₂t-Bu)₃] with pyridinium triflate (in the presence of excess pyridine) provided neopentane and the alkylidyne complex [Os(-Ct-Bu)(CH₂t-Bu)₂(O₃SCF₃)(py)₂]. Subsequent treatment with Na[Tp] affords the crystallographically characterised complex [Os(-Ct-Bu)(CH₂t-Bu)₂Tp] (Scheme 1.29).⁹²,⁹³ The proposed intermediate [Os(-CH₂t-Bu)(CH₂t-Bu)₃(O₃SCF₃)] appears similar to the stable d⁹ rhenium complex [Re(-Ct-Bu)(CH₂t-Bu)₂(O₃SCF₃)], however in the latter only a single α-proton is available for abstraction and two metal-ligand π-bonds are available to stabilise the metal in the high oxidation state.⁹¹ As for the rhenium neopentylidyne complex [Re(-Ct-Bu)(CH₂t-Bu)(≡Ct-Bu)Tp], the metal–carbon multiple bond is remarkably unreactive towards olefin metathesis.
The in situ formation of tris(pyrazolyl)borate-ruthenium carbyne complexes resulting from electrophilic addition at C₆ of ruthenium vinylidene or allenylidene precursors has recently been reported. Kirchner and co-workers described the reversible formation of the novel ruthenium vinylcarbyne complexes [Ru(≡C=CHR)Cl(PR₃)Tp]⁺ (PR₃= PPh₃(i-Pr), R' = Ph, Fe; PR₃ = PPh₃, R' = Ph) in dichloromethane solution via protonation of the neutral ruthenium allenylidene precursor [Ru(≡C=CHR)Cl(PR₃)Tp] with triflic acid. Similarly, formation of the ruthenium alkylidyne salts [Ru(≡CH₂R)Cl(PPh₃)Tp][BF₄] (R = t-Bu, n-Bu, Ph) has been observed from the low-temperature treatment of the vinylidene complexes [Ru(≡C=CHR)Cl(PPh₃)Tp] with excess HBF₄•Et₂O (Scheme 1.30). Pentamethylcyclopentadienyl-supported systems (R = t-Bu and n-Bu) exhibit increased stability over the corresponding tris(pyrazolyl)borate analogues, being isolable in the solid state. Furthermore, the alkyl carbyne substituents prove to be more stable than the benzyl carbyne substituents, showing stability up to -20 °C (cf. -70 °C for R = Ph).

1.2.4 Alkylidyne complexes ligated by poly(pyrazolyl)methanes

The pyrazolylmethane ligands, HC(pz)₃, MeC(pz)₃, and H₂C(pz)₂ (tris(pyrazolyl)methane, tris(pyrazolyl)ethane and bis(pyrazolyl)methane, respectively) shown in Chart 1.3 are neutral analogues of the corresponding pyrazolylborate versions and display remarkably similar ligand properties.
The preparative routes for obtaining Group 6 alkylidyne complexes co-ligated by the pyrazolylmethane ligands parallel those previously described for Tp, involving ligand substitution from the halotetracarbonyl precursor \([\text{M(=CR)Br(CO)}_4]\). However, alkylidyne complexes of the neutral pyrazolylmethane ligands differ from the complexes bearing pyrazolylborate co-ligands by being positively charged, and consequently a non-coordinating anion source (in this case \(\text{TiBF}_4\)) must also be included (Scheme 1.31). The cationic thiocarbyne complex \([\text{W(=CSMe)(CO)}_2\{\text{HC(pz)}_3\}]^+\) has also been prepared by alkylation of the nucleophilic sulfur atom in the thiocarbonyl complex \([\text{W(CO)}_2(\text{CS})\{\text{HC(pz)}_3\}]\). The spectroscopic properties and the reactivity towards low-valent metal fragments of these cationic alkylidyne salts mirror those of the pyrazolylborate analogues, with one notable
exception being that pyrazolyl methan ligands exhibit a reactivity at the bridgehead carbon, allowing for modification of the ligand within the alkylidyne complex (Section 1.4.5), a phenomenon which has not been similarly documented for \([\text{LnM}(=\text{CR})\text{Tp}]^+\) complexes.

The anionic, \(N,N,O\)-chelating ligands, bis(3,5-dimethylpyrazolyl)acetate, \([\text{HC}(\text{pz}^*)_2(\text{CO}_2)]^-\), and bis(3,5-dimethylpyrazolyl)(2-phenoxy)methane, \([\text{HC}(\text{pz}^*)_2(\text{C}_6\text{H}_4\text{O}-2)]^-\), are unusual asymmetrical analogues of the Tp ligand that have also been employed in alkylidyne complexes of the type \([\text{W}(=\text{CR})(\text{CO})_2\text{L}](\text{L} = [\text{HC}(\text{pz}^*)_2(\text{C}_6\text{H}_4\text{O}-2)]^-\), \(R = \text{Me}, \text{Ph}, \text{C}_6\text{H}_4\text{Me}-2, \text{C}_6\text{H}_3\text{Me}-2-\text{OMe}-4, \text{C}_6\text{H}_2\text{Me}-4,5-\text{OMe}-2, \text{C}_6\text{H}_3\text{OMe}-4, \text{C}_6\text{H}_2\text{Me}_3-2,4,6, \text{C}_6\text{H}_4\text{Me}-\text{C}(\text{CO})_3; \text{L} = [\text{HC}(\text{pz}^*)_2(\text{CO}_2)]^-\), \(R = \text{C}≡\text{Ph}, \text{C}≡\text{CSiMe}_3\)).
1.3  Structure and spectroscopy

1.3.1  $^{13}$C{H} NMR

$^{13}$C{H} NMR resonances of the alkylidyne carbon nucleus and (where applicable) the metal carbonyls are given in Table 1.1 (Appendix A.1). Chemical shifts for the Group 6 alkylidyne carbons, $\delta_C$, range from $\delta_C = 183.2$ in $[\text{W(Cl)(CO)}_2\text{Tp}^*]_6$ to $\delta_C = 381$ for $[\text{Mo(CFe(CO)}_2\text{Cp})(CO)_2\text{Tp}^*]_7$ and are highly dependent on the electron-donating ability of the alkylidyne substituent. For example, for $[\text{W(\text{CR})(CO)}_2\text{Tp}^*]_6$ the alkylidyne resonance moves from high to low field with changes in R in the order Cl (205.58) > OPh (219.3) > PPh$_3$ (242.1) > C=Ph (247.3) = NEtMe (249.0) > Ph (277.9) > Me (289.6) > P= C(NMe$_2$)$_2$ (318.3). The alkylidyne resonances are, however, rather insensitive to changes in the tripodal ligand. For the series $[\text{W(\text{C}_6\text{H}_4\text{Me-4})(CO)}_n\text{Tp}_x]$, the $\delta_C$ resonance moves from high to low field with $\text{Tp}_x = \text{Tp}^*$ > Bp > Tp > pzTp, which is consistent with the $^{13}$C{H} shielding trend observed for the Group 6 metal triad. The resonances are also sensitive to the oxidation state of the metal with the $[\text{M(CR)}_2\text{Tp}_x]_6$ complexes having $\delta_C$ typically 20 ppm lower field than the $[\text{M(CR)(CO)}_2\text{Tp}_x]_6$ complexes. There is, however, an exception to this rule. For $[\text{W(\text{CSMe})(SMe)}_2\text{Tp}]$, the alkylidyne carbon resonance is virtually unaffected by the increase in oxidation state of the tungsten with $\delta_C$ appearing at $\delta_C = 268.3$, which is similar to the chemical shift reported for the 18-electron complex $[\text{W(\text{CSMe})(CO)}_2\text{Tp}]$ ($\delta_C = 264.4$) and suggests that the former is an electron-rich alkylidyne by virtue of the π-basic thiolate coordination.

The tungsten complexes show $^{13}$C–$^{183}$W coupling constants in the range 160–250 Hz for $\delta_C$ that are diagnostic of the high s character of the M–C triple bond. The corresponding one bond coupling constants ($^1J_{\text{CW}}$) for the carbonyl carbons are typically smaller by 30–40 Hz, however, a notable exception is provided by the silyl alkylidyne complexes in which the measured $^1J_{\text{CW}}$ values for $\delta_C$ and CO are comparable. The alkylidyne complexes $[\text{W(\text{C}_6\text{H}_5\text{Bu})(CO)}_2\text{L}]$ ($\text{L} = \text{Cp}$, Tp) clearly demonstrate the decrease in s-orbital contribution and subsequent decrease in $^1J_{\text{CW}}$ with increasing donor strength of the tripodal ligand, i.e., for the cyclopentadienyl complex ($\text{L} = \text{Cp}$), the measured one bond coupling constants are $^1J_{\text{WC}} = 226$ Hz and 196 Hz for
ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

CHAPTER 1

C₆ and CO, respectively, vs 202 Hz and 168 Hz for the stronger donor, Tp. Table 1.1 is relatively bereft of measured 1JCW coupling constants due in general to the low intensity of the resonance for the quaternary carbon, such that spectra are not usually measured with sufficient signal-to-noise ratio to observe the tungsten satellites. Thus although this information is in principle accessible, it is not generally deemed sufficiently informative as to warrant extended acquisition times, given that for all examples the hybridisation for both the sp³d⁵–tungsten and sp–carbon are constant. With inter-ligand angles close to 90°, complexes of the form [W(=CR)(PR₃)(CO)Tp] show 2JCₚ values in the range 5–30 Hz. For [W(=CR)(PMe₂Ph)(CO)₂Bp] (R = mesityl or xylyl), a significantly larger 2JCₚ coupling constant is measured for the trans-disposed carbonyl than for that which is cis (2JCₚ trans = 53 Hz vs 2JCₚ cis = 3.6 Hz). In many cases for octahedral organometallic complexes, rotation of the poly(pyrazolyl) ligands on the NMR timescale leads to all pyrazolyl rings being chemically equivalent. However, if fluxional behaviour is not occurring (as is generally the case for [M(=CR)(CO)₂L] alkylidyne complexes), the pattern exhibited by the pyrazolyl rings in the ¹H and ¹³C{¹H} NMR spectra provides insight into the symmetry of the molecule in solution. For Cs symmetry substituted alkylidyne complexes [M(=CR)(CO)₂Tp], a symmetry plane exists which contains the alkylidyne–metal bond and one pyrazole ring and bisects the two terminal metal carbonyls, resulting in a 2:1 out-of-plane:in-plane pattern for the coordinated pyrazolyl groups. A 1:1:1 pattern indicates that the molecule is chiral (C₁ symmetry). The lack of observable fluxional processes presumably reflects a barrier originating from the disparity in trans influences of alkylidyne and carbonyl ligands. In the case of [W(=CR)(CO)₂Tm] (Tm = tris(methimazolyl)borate), fluxionality has been observed to chemically equilibrate the methimazolyl (mt) environments, however given that the coalescence temperature (Tc) is very strongly dependent on the nature of the alkylidyne substituents (C₅H₄Me-4, 90 °C vs N(i-Pr)₂, 15 °C), it has been argued that equilibration proceeds via dissociation of one mt arm to provide a stereochemically non-rigid five-coordinate species, rather than a more conventional Bailar twist. This is consistent with both the superlative trans effect of alkylidynes (especially aminomethylidyynes) and the geometric flexibility of Tm coordination.

1.3.2 Crystallography

Up to March 2006 the molecular structures of about 40 alkylidyne complexes ligated by poly(pyrazolyl)borates had been reported and structural data for the crystallographically characterised alkylidyne metal complexes are compiled in Table 1.2, Appendix A.2. Of these, Tp and Tp* ligated complexes represent more than 80%, with one third of the total known structures being bi- and polymetallic complexes. Structural features of alkylidyne complexes
have been discussed elsewhere\textsuperscript{7} and, accordingly, an attempt to restrict this discussion to features which are unique to or characteristic of the scorpionate alkylidyne complexes has been made.

Structural features of the scorpionate complexes include a short M–C bond and an M=C–R angle which departs little from linearity, as found for other alkylidyne complexes.\textsuperscript{6} The M–C alkylidyne separations are predominantly influenced by the nature of the alkylidyne substituent rather than the tridentate co-ligand. For example, for [Mo(≡CC₄H₃S-2)(CO)₂Tp\textsuperscript{3}] (Tp\textsuperscript{*} = Tp, Tp\textsuperscript{*}) in which all other factors are constant, the Mo–C\textsubscript{α} separation for Tp\textsuperscript{*} = Tp (1.809(4)\textsuperscript{106} differs little from Tp\textsuperscript{x} = Tp* (1.810(3) Å).\textsuperscript{106} Similarly, for [W(≡CC₆H₄Me-4)(CO)₂L\textsubscript{2}], the W–C\textsubscript{α} separation does not significantly differ for L = Cp, 1.82(2) Å,\textsuperscript{107} and L = pzTp, 1.82(1) Å.\textsuperscript{39,40}

The complexes display distorted octahedral geometry, with the N–M–N angles being contracted by approximately 10° from the idealised 90° expected for octahedral geometry due to the geometrical constraints of the scorpionate ligands.\textsuperscript{108} For [Mo(≡CC₄H₃S-2)(CO)₂Tp\textsuperscript{3}] (Tp\textsuperscript{*} = Tp, Tp\textsuperscript{*}) the slightly expanded sum of the N–Mo–N chelate angles for Tp* compared with those of the Tp analogue (247° vs 244°) is a modest expression of the steric bulk and relative donor ability of the pyrazolylborate ligands, with M–N and N–N bond lengths that are slightly elongated for the Tp* complex (δ M–N: 0.015 Å, δ N–N: 0.015 Å).

The occupation of three facial positions by the nitrogen atoms of the tripodal ligand forces the remaining substituents to be mutually cis. The pyrazolyl N–metal separations are highly sensitive to the π-acidity of trans-disposed ligands. Typically, the pyrazolyl-N–metal bond trans to the alkylidyne carbon is appreciably lengthened with respect to the two remaining pyrazolyl groups due to the strong trans influence of the alkylidyne. In the crystal structure of [Mo(≡CCMe₂Ph)(OMe){NH₃C₆H₃(t-Pr)₂-2,6}Tp], the N–Mo bond lengths are consistent with the decreasing trans influence of the ligands in the order alkylidyne > amido > methoxide.\textsuperscript{60}

M(pz\textsubscript{2})BH\textsubscript{3} metallacycles in Bp alkylidyne complexes typically adopt a shallow boat confirmation. Due to the bidentate nature of the scorpionate, the alkylidyne fragment can be oriented meridionally or facially with respect to the chelated pyrazolyl arms. The alkylidyne fragment is typically oriented trans to the strongest π-donor\textsuperscript{49} and as such the favoured geometry depends upon the relative π-donor abilities of the remaining ligands.

The structure determination of the chloromethylidyne complex [Mo(≡CCL)(CO)₂pzTp]\textsuperscript{37} revealed an anomalously long Mo–C bond length (average: 1.894(10) Å). In the related
complex \( [\text{Mo}(\equiv \text{CCl})(\text{CO})_2 \text{Tp}^*\text{Me}] \) this distance is normal at 1.798(5) Å,\(^{109}\) which suggests that this is an artefact of residual disordering of the carbonyl and chloromethylidyne ligands rather than the result of \( \pi \)-donation from the chloroalkylidyne substituent leading to a strongly contributing \( [\text{LnMo}^{\pi}(-)\equiv \text{C}=\text{Cl}(\pi)] \) resonance form, as was previously suggested.\(^7\)

The \( \text{M}-\text{C}-\text{R} \) angles for the complexes are within the range 179.5(2)° \( [\text{Mo}(\equiv \text{CSC}_{6}\text{H}_{4}\text{NO}_{2}-4)-(\text{CO})_2 \text{Tp}^*]\)\(^{73}\) to 160.56(11)° \( [\text{Mo}\{\text{CP(}\text{AuCl})_2\text{C(NMe}_2)_2\}\} (\text{CO})_2 \text{Tp}^*] \),\(^{110}\) showing greater deviation than what is typically expected for terminal alkylidyenes. There is, however, no discernible pattern driving this distortion. The deviation from linearity for the bond angle at \( \text{C}_\alpha \) has been suggested to arise from both steric interactions between the substituent and bulky \( \text{Tp}^* \) ligand\(^7\) and crystal packing forces.\(^{109}\) Support for the latter argument is provided by the structure of \( [\text{Mo}(\equiv \text{CSC}_{6}\text{H}_{4}\text{NO}_{2}-4)(\text{CO})_2 \text{Tp}^*] \), which shows a near linear angle across \( \text{C}_\alpha \) (179.5(2))\(^\circ\),\(^{73}\) despite the large alkylidyne substituent and bulky 3,5-dimethyl(pyrazolyl)borate ligand.

### 1.3.3 Other spectroscopic methods

In the infrared spectrum, bands due to the poly(pyrazolyl) ligands can be identified near 1560 and 2500 cm\(^{-1}\), arising from the pyrazolyl ring and B–H stretching vibrations, respectively. The B–H stretching vibrations are remarkably insensitive to the nature of the alkylidyne complex, appearing over a relatively narrow range \( \nu_{\text{BH}} 2462 \text{ cm}^{-1} \) in \( [\text{W}(\equiv \text{C} \text{C}_{6}\text{H}_{2}\text{Me}-2,4,6)(\text{CO})_2 \text{Tp}] \)\(^{108}\) to 2560 cm\(^{-1}\) in \( [\text{W}\{\text{CP(}\text{Me})\text{C(NEt}_2)_2\}\} (\text{CO})_2 \text{Tp}^*][\text{O}_3 \text{SCF}_3] \),\(^{111}\) as might be expected given that the B–H bond is protected (especially in \( \text{Tp}^* \) complexes) from external influences (solid state effects) and remote from variations in the nature of the alkylidyne substituent.

The characteristic infrared absorptions for known alkylidyne metal complexes are collected in Table 1.3, Appendix A.3. Complexes of the type \( \text{cis-L}_4\text{M} (\text{CO})_2 \) display two \( \nu_{\text{CO}} \) absorptions of similar intensity,\(^6\) with the higher frequency absorption assigned to the symmetric \( \text{A}_1 \) mode and the lower frequency absorption to the antisymmetric \( \text{B}_1 \) mode. Values of \( \nu_{\text{CO}} \) and \( k_{\text{CO}} \) for the tungsten analogues are lower than those for the related molybdenum examples, as is generally observed for isostructural pairs of carbonyl complexes of 4d and 5d metals.\(^112\) From the \( k_{\text{CO}} \) values for the series \( [\text{W}(\equiv \text{C} \text{C}_{6}\text{H}_{4}\text{Me}-4)(\text{CO})_n \text{L}] \), it can be seen that the donor properties of the tripodal ligands increase in the order \( \text{L} = \text{Cp} < \text{Cp}^* = \text{pzTp} = \text{Tp} < \text{Tp}^\text{Ph} < \text{Tp}^* \). When the pyrazole-containing ligands are replaced by \( \text{Cp} \) there is a significant shift towards higher energy for the carbonyl absorptions due to decreased electron density at the metal centre and subsequent reduction in \( \pi \)-back-bonding with the metal carbonyls.
Table 1.4. IR absorptions for alkylidyne metal complexes with a range of tripodal ligands \([\text{W}(=\text{CR})(\text{CO})_2\text{Tp*})\]^a

<table>
<thead>
<tr>
<th>L</th>
<th>R</th>
<th>X</th>
<th>(\nu_{\text{CO}}, \text{cm}^{-1})</th>
<th>(k_{\text{CO}}, \text{N m}^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\kappa^2\text{-CpCo(P}_{3}\text{Me}_2\text{)})</td>
<td>Me</td>
<td>0</td>
<td>1961, 1859</td>
<td>14.74</td>
<td>113</td>
</tr>
<tr>
<td>(\eta^1\text{-C}<em>{2}\text{B}</em>{3}\text{H}_{5}\text{Me}_2)</td>
<td>Me</td>
<td>1-</td>
<td>1956, 1874</td>
<td>14.82</td>
<td>114</td>
</tr>
<tr>
<td>(\kappa^2\text{-HB(mt)})</td>
<td>Me</td>
<td>0</td>
<td>1967, 1875</td>
<td>14.91</td>
<td>105</td>
</tr>
<tr>
<td>(\kappa^2\text{-C}<em>{2}\text{B}</em>{3}\text{H}_{11})</td>
<td>Me</td>
<td>1-</td>
<td>1965, 1880</td>
<td>14.93</td>
<td>114</td>
</tr>
<tr>
<td>(\kappa^2\text{-HC(pz*),}(\text{C}<em>{2}\text{H}</em>{4}\text{O}-2))</td>
<td>H</td>
<td>0</td>
<td>1890, 1958</td>
<td>14.95</td>
<td>102</td>
</tr>
<tr>
<td>(\kappa^2\text{-Me}(9\text{laneN}_3)</td>
<td>H</td>
<td>1+</td>
<td>1975, 1879</td>
<td>15.00</td>
<td>115</td>
</tr>
<tr>
<td>(\kappa^2\text{-HB(pz*)})</td>
<td>Me</td>
<td>0</td>
<td>1974, 1888</td>
<td>15.06</td>
<td>43</td>
</tr>
<tr>
<td>(\kappa^3\text{-HB(pzPh)})</td>
<td>Me</td>
<td>0</td>
<td>1982, 1897</td>
<td>15.20</td>
<td>43</td>
</tr>
<tr>
<td>(\kappa^3\text{-HC(py)})</td>
<td>H</td>
<td>1+</td>
<td>1988, 1894</td>
<td>15.22</td>
<td>116</td>
</tr>
<tr>
<td>(\kappa^2\text{-P(py)})</td>
<td>H</td>
<td>1+</td>
<td>1984, 1899</td>
<td>15.23</td>
<td>116</td>
</tr>
<tr>
<td>(\eta^1\text{-C}<em>{2}\text{H}</em>{5})</td>
<td>Me</td>
<td>0</td>
<td>1982, 1902</td>
<td>15.24</td>
<td>103</td>
</tr>
<tr>
<td>(\kappa^2\text{-}(\text{C}<em>{6}\text{F}</em>{3}\text{)}\text{AuC(pz)})</td>
<td>Me</td>
<td>0</td>
<td>1985, 1899</td>
<td>15.24</td>
<td>117</td>
</tr>
<tr>
<td>(\kappa^2\text{-B(pz)})</td>
<td>Me</td>
<td>0</td>
<td>1986, 1903</td>
<td>15.28</td>
<td>39,40</td>
</tr>
<tr>
<td>(\kappa^2\text{-HB(pz)})</td>
<td>Me</td>
<td>0</td>
<td>1986, 1903</td>
<td>15.28</td>
<td>39,40</td>
</tr>
<tr>
<td>(\kappa^2\text{-}(\text{F}_{3}\text{B})\text{C(pz)})</td>
<td>Me</td>
<td>0</td>
<td>1988, 1902</td>
<td>15.28</td>
<td>118</td>
</tr>
<tr>
<td>(\eta^1\text{-C}<em>{2}\text{Me}</em>{5})</td>
<td>Me</td>
<td>0</td>
<td>1981, 1910</td>
<td>15.29</td>
<td>104</td>
</tr>
<tr>
<td>(\kappa^1\text{-HC(pz)})</td>
<td>Me</td>
<td>1+</td>
<td>1995, 1912</td>
<td>15.42</td>
<td>100</td>
</tr>
<tr>
<td>(\eta^1\text{-C}<em>{2}\text{B}</em>{10}\text{H}<em>{10}\text{Me}</em>{2})</td>
<td>Me</td>
<td>1-</td>
<td>1990, 1930</td>
<td>15.52</td>
<td>119</td>
</tr>
<tr>
<td>(\kappa^2\text{-}[9\text{laneS}_3)</td>
<td>H</td>
<td>1+</td>
<td>2007, 1925</td>
<td>15.62</td>
<td>116</td>
</tr>
<tr>
<td>(\kappa^2\text{-Me}(\text{C}<em>{2}\text{H}</em>{2}\text{Ph}))</td>
<td>H</td>
<td>1+</td>
<td>1999, 1934</td>
<td>15.62</td>
<td>116</td>
</tr>
<tr>
<td>(\kappa^1\text{-Ph}(\text{C}<em>{3}\text{H}</em>{2}\text{Ph}))</td>
<td>Me</td>
<td>1+</td>
<td>2005, 1941</td>
<td>15.72</td>
<td>120</td>
</tr>
</tbody>
</table>

^a Unless otherwise indicated, measurements in CH$_2$Cl$_2$ solution. ^b CHCl$_3$. ^c KBr. ^d Hexane. Alternate abbreviations: \(\eta^1\text{-C}_{2}\text{H}_{5} = \text{Cp}; \quad \eta^1\text{-C}_{2}\text{Me}_{5} = \text{Cp*}; \quad \kappa^2\text{-HB(pz)} = \text{Tp}; \quad \kappa^3\text{-B(pz)} = \text{pzTp}; \quad \kappa^3\text{-HB(pzPh)} = \text{Tp*}; \quad \kappa^3\text{-HB(mt)} = \text{Tm}.

Table 1.5. Infrared absorptions for alkylidyne metal complexes \([\text{W}(=\text{CR})(\text{CO})_2\text{Tp*})\]^a

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{CO}}, \text{cm}^{-1})</th>
<th>(k_{\text{CO}}, \text{N m}^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="=%5Ctext%7BCPMe%7D_2%5Ctext%7BPh%7D">\text{W}</a>)</td>
<td>2022, 1934</td>
<td>15.81</td>
<td>70</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCC%7D(%5Ctext%7BO%7D)%5Ctext%7BPh%7D">\text{W}</a>)</td>
<td>1999, 1918</td>
<td>15.50</td>
<td>68</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCH%7D">\text{W}</a>)</td>
<td>1902, 1903</td>
<td>15.32</td>
<td>121</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCCI%7D">\text{W}</a>)</td>
<td>1991, 1902</td>
<td>15.31</td>
<td>36</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCC%7D=%5Ctext%7BCPh%7D">\text{W}</a>)</td>
<td>1979, 1893</td>
<td>15.14</td>
<td>61</td>
</tr>
<tr>
<td>([\text{W}](=\text{CSiMe}_3)</td>
<td>1976, 1884</td>
<td>15.05</td>
<td>68</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCPh%7D">\text{W}</a>)</td>
<td>1969, 1876</td>
<td>14.93</td>
<td>78</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCOPh%7D">\text{W}</a>)</td>
<td>1967, 1870</td>
<td>14.87</td>
<td>70</td>
</tr>
<tr>
<td>(<a href="=%5Ctext%7BCMe%7D">\text{W}</a>)</td>
<td>1968, 1867</td>
<td>14.86</td>
<td>67</td>
</tr>
<tr>
<td>([\text{W}]=\text{CC}=\text{CCHCH}_3)</td>
<td>1965, 1862</td>
<td>14.80</td>
<td>122</td>
</tr>
<tr>
<td>([\text{W}]=\text{CAs}=\text{C(NMe}_2\text{)})</td>
<td>1936, 1848</td>
<td>14.46</td>
<td>88</td>
</tr>
<tr>
<td>([\text{W}]=\text{CNEt}_2)</td>
<td>1936, 1833</td>
<td>14.35</td>
<td>84</td>
</tr>
</tbody>
</table>

^a \([\text{W}] = \text{W(CO)}_2\text{Tp*}. Unless otherwise noted, data are reported from KBr. ^b CH$_3$CN. ^c Hexane. ^d Cyclohexane. ^e Ether. ^f CH$_2$Cl$_2$.
Table 1.5 shows that the position of the cis-W(CO)$_2$ infrared stretch is highly sensitive to the π-acidity of the alkylidyne group. Conjugation of the M–C triple bond with π-donating alkylidyne substituents, as demonstrated in Scheme 1.32, leads to a decrease in the π-acidity of the M≡C bond in line with the heteroallenic form and a subsequent increase in available electron density for the π-acidic carbonyls, which leads to a decrease in the frequency of $\nu_{\text{CO}}$.

![Scheme 1.32. Delocalisation of electron density from heteroatom alkylidyne substituents (X = Cl, NR$_2$, OR, SR, SeR, TeR).](image)

In line with this phenomenon for π-donating alkylidyne substituents, in the alkylidynes with the strongly donating amino groups the $\nu_{\text{CO}}$ stretches appear at extremely low frequency. For cationic alkylidynes, $\nu_{\text{CO}}$ typically appears at high frequency. In principle, the integrated intensities of the two $\nu_{\text{CO}}$ absorptions can be used to calculate the angle between the two carbonyl ligands. However, the approximations involved limit the accuracy of this method to $\pm 5^\circ$ and this, together with the ‘octahedral enforcer’ character of the Tp and Tp* ligands, mean this exercise is not generally worthwhile. However in a qualitative sense visual inspection of the intensity profile may be useful in interpreting reactions that occur across the M≡C bond such that steric factors accompanying increased coordination at the metal can lead to a reversal of the relative intensities. Thus e.g., the sequential addition of selenium to the alkylidyne complex [Mo(≡CR)(CO)$_2$Tp] ($R = \text{C}_4\text{H}_3\text{S-2}$) provides [Mo($\eta^2$-SeCR)(CO)$_2$Tp] and then [Mo($\kappa^2$-S$_2$CR)(CO)$_2$Tp] with the relative intensity of the high frequency absorption progressively increasing.$^{123}$

The $k_{\text{CO}}$ force constants for range of Group 6 poly(pyrazolyl)borate cis-dicarbonyl complexes [M(L')$_3$(CO)$_2$Tp] with 3 valence electron ligands (L') that are isoelectronic with (CR) are tabulated (Table 1.6) and exhibit the previously observed trend of Cr > Mo > W, whilst for the same metal, $k_{\text{CO}}$ decreases in the order L = NO > NS > NNR > CR > C$_3$H$_5$, mirroring the trend in π-acidity for L'. A curious feature is that whilst CS is recognised to be a stronger net acceptor than CO, the reverse appears to be true for NO and NS in this system.
### Table 1.6. Characteristic infrared absorptions for a range of Group 6 Tp<sup>x</sup> complexes [M(L')(CO)<sub>2</sub>·p(·)]<sup>y</sup>

<table>
<thead>
<tr>
<th>L'&lt;sup&gt;y&lt;/sup&gt;</th>
<th>Tp&lt;sup&gt;x&lt;/sup&gt;</th>
<th>M</th>
<th>v&lt;sub&gt;CO&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>k&lt;sub&gt;CO&lt;/sub&gt;, N m&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp</td>
<td>Cr</td>
<td>2038, 1951</td>
<td>16.07</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>pzTp</td>
<td>Cr</td>
<td>2039, 1951</td>
<td>16.08</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp*</td>
<td>Cr</td>
<td>2029, 1941</td>
<td>15.92</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp</td>
<td>Cr</td>
<td>1997, 1913&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.44</td>
<td>41</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp*</td>
<td>Cr</td>
<td>1987, 1909</td>
<td>15.33</td>
<td>47</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp</td>
<td>Mo</td>
<td>2025, 1933&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.82</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>pzTp</td>
<td>Mo</td>
<td>2024, 1937</td>
<td>15.85</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp*</td>
<td>Mo</td>
<td>2016, 1925</td>
<td>15.69</td>
<td>125</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NS</td>
<td>Tp*</td>
<td>Mo</td>
<td>1997, 1905&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15.38</td>
<td>124,125</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NNPh</td>
<td>pzTp</td>
<td>Mo</td>
<td>1996, 1913</td>
<td>15.43</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NNPh</td>
<td>Tp</td>
<td>Mo</td>
<td>1994, 1904&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.39</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp*</td>
<td>Mo</td>
<td>1998, 1921&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.51</td>
<td>41,42</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp*</td>
<td>Mo</td>
<td>1982, 1899&lt;sup&gt;f&lt;/sup&gt;</td>
<td>15.21</td>
<td>44</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Tp</td>
<td>Mo</td>
<td>1958, 1874</td>
<td>14.83</td>
<td>126</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>pzTp</td>
<td>Mo</td>
<td>1958, 1875</td>
<td>14.84</td>
<td>126</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp</td>
<td>W</td>
<td>2010, 1910&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.52</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>pzTp</td>
<td>W</td>
<td>2010, 1917</td>
<td>15.58</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NO</td>
<td>Tp*</td>
<td>W</td>
<td>1993, 1884&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15.38</td>
<td>124,125</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NS</td>
<td>Tp*</td>
<td>W</td>
<td>2001, 1905</td>
<td>15.41</td>
<td></td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp</td>
<td>W</td>
<td>1988, 1902&lt;sup&gt;c&lt;/sup&gt;</td>
<td>15.28</td>
<td>125</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp</td>
<td>W</td>
<td>1986, 1903&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.28</td>
<td>39,40</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NNPh</td>
<td>pzTp</td>
<td>W</td>
<td>1984, 1896</td>
<td>15.20</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-NNPh</td>
<td>Tp</td>
<td>W</td>
<td>1983, 1894</td>
<td>15.18</td>
<td>124</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-CC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Me-4</td>
<td>Tp*</td>
<td>W</td>
<td>1974, 1888&lt;sup&gt;e&lt;/sup&gt;</td>
<td>15.06</td>
<td>43</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Tp</td>
<td>W</td>
<td>1949, 1862</td>
<td>14.67</td>
<td>126</td>
</tr>
<tr>
<td>η&lt;sup&gt;1&lt;/sup&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>pzTp</td>
<td>W</td>
<td>1949, 1862</td>
<td>14.67</td>
<td>126</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data were obtained in cyclohexane solution unless otherwise indicated. <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>.<br><sup>c</sup> KBr. <sup>d</sup> Light petroleum. <sup>e</sup> Pentane. <sup>f</sup> THF. <sup>g</sup> Hexane.
1.4 Reactivity

Reactivity modes of the poly(pyrazolyl)borate alkylidyne complexes follow a number of recognised routes for transition metal complexes containing metal–carbon triple bonds including ligand substitution or redox reactions at the transition metal centre, insertion of a molecule into the metal–carbon triple bond, and electrophilic or nucleophilic attack at the alkylidyne carbon, \( \text{C}_\text{a} \). Cationic alkylidyne complexes generally react with nucleophiles at the alkylidyne carbon, while neutral alkylidyne complexes can react at either the metal centre or the alkylidyne carbon. Substantive work has been devoted to neutral and cationic alkylidyne complexes bearing heteroatom substituents. Differences between the chemistry of the various \( \text{Tp}^2 \) complexes have previously been rationalised largely on the basis of steric effects.\(^{127,128}\)

1.4.1 The metal centre

Ligand substitution and metal oxidation

The complex \([\text{Mo}(=\text{CMe})(\text{CO})_2\text{Tp}^*]\) undergoes photochemical carbonyl substitution in acetonitrile or in acetone with excess \( \text{PMe}_3 \) to produce \([\text{Mo}(=\text{CMe})(L')(\text{CO})\text{Tp}^*]\) \((L' = \text{NCMe}, \text{PMe}_3)\), in which there is no evidence for any ketenyl formation.\(^6^2\)

The coordinatively labile picoline ligand in \([\text{W}(=\text{CR})(\text{pic})(\text{CO})_2\text{Bp}]\) \((\text{R} = \text{mesityl}, \text{xylyl})\) can be replaced by isonitriles (in the absence of light) and phosphines to give moderate yields of \([\text{W}(=\text{CR})(L')(\text{CO})_2\text{Bp}]\) \((L' = \text{CNR'}, \text{PMe}_2\text{Ph})\),\(^4^9\) in which the alkylidyne ligand is trans to a pyrazolyl arm and the ligand \(L'\) is trans to a carbonyl ligand (i.e., mer arrangement of \(\text{Bp/alkylidyne}\) as confirmed by structural characterisation of \(L' = \text{PMe}_2\text{Ph}, \text{R} = \text{xylyl})\).\(^5^9\)

The analogous tricarbonyl \(p\)-tolyl complex \([\text{W}(=\text{CR})(\text{CO})_3\text{Bp}]\) reacts with \(\text{PPh}_3\) and \(\text{PMe}_3\) similarly via carbonyl substitution, again with no evidence for ketenyl formation.\(^4^6\) The reaction of either \([\text{W}(=\text{CR})(\text{PMe}_2\text{Ph})(\text{CO})_2\text{Bp}]\) or \([\text{W}(=\text{CR})(\text{pic})(\text{CO})_2\text{Bp}]\) \((\text{R} = \text{mesityl})\) with excess \(\text{PMe}_3\text{Ph}\) provide the trans-bis(phosphine) complex \([\text{W}(=\text{CR})(\text{PMe}_2\text{Ph})_2(\text{CO})\text{Bp}]\).\(^4^9\) Formation from the monophosphine complex under mild conditions is suggested to proceed through ketenyl formation followed by CO extrusion, as has been demonstrated in the synthesis of \([\text{W}(=\text{CR})(\text{PMe}_3)(\text{CO})\text{Cp}]\) from \([\text{W}(=\text{CR})(\text{CO})_2\text{Cp}]\) \((\text{R} = \text{C}_6\text{H}_4\text{Me}-4, \text{SMe})\) with \(\text{PMe}_3\) or \(\text{PEt}_3\) (respectively) stop at the \(\eta^2\)-ketenyl stage providing \([\text{W}(\eta^2-\text{C,C}-\text{OCCR})(\text{PR}_3)(\text{CO})\text{Tp}]\). The lowered steric demand and denticity of the bis(pyrazolyl) ligand allows its complexes to participate in ligand substitution reactions not typically observed for the bulkier \(\text{Tp}^2\) analogues.

The coordinatively saturated dicarbonyl carbynes are generally inert to ligand substitution reactions without photochemical or thermal activation. However, oxidative carbonyl ligand substitution reactions occur upon reacting the dicarbonyl(trispyrazolyl)borate carbyne
complexes $[M(\equiv CR)(CO)_{2}Tp^\lambda]$ with $X_2$ ($X = \text{Cl, Br, I}$) at low temperature, yielding the six-coordinate dihalocarbonyl complexes, $[M(\equiv CR)X_2Tp^\lambda]$ ($Tp^\lambda = Tp$, $M = W$, $R = \text{Ph}$, $X = \text{Br}$).\textsuperscript{131} Aminocarbones behave similarly ($Tp^\lambda = Tp^*$, $M = W$, $R = \text{NR}_2$, $X = \text{Br, I}$).\textsuperscript{85} In contrast, oxidative decarbonylations of Cp aminocarbonyl complexes with PhI, Br$_2$, or I$_2$ afford the seven-coordinate, 18-electron aminocarbonyl complexes $[M(\equiv CNR_2)X_2(CO)Cp^\lambda]$ ($Cp^\lambda = Cp$ or $Cp^*$; $X = \text{Cl, Br, I}$; $M = \text{Mo, W}$).\textsuperscript{132-134} This difference in reactivity can be ascribed to the greater steric bulk of the $Tp^\lambda$ ligand, which destabilizes such seven-coordinate species.

Reaction of the complex $[W(\equiv CR)(CO)_{2}Tp]$ ($R = \text{xylyl}$) under high dilution conditions with thionyl chloride provides the dichloro alkylidyne complex $[W(\equiv CR)Cl_2Tp]$ (Scheme 1.33), which can also be obtained from the reaction of $[W(\equiv CR)(CO)_{2}Tp]$ with two equivalents of the non-electrophilic reagent $[\text{FeCp}_2]Cl$.\textsuperscript{108} Reaction with the molybdenum analogues does not proceed similarly. More sterically modest alkylidyne substituents ($R = \text{C}_6\text{H}_4\text{Me-4}$) yield only unreacted starting material and the complex $[WCl(CO)Tp]$ in which the alkylidyne ligand has been cleaved.\textsuperscript{108} The corresponding cyclopentadienyl complex $[W(\equiv CR)(CO)_{2}Cp]$ ($R = \text{xylyl}$) is much more reactive towards thionyl chloride, providing the novel metallacyclic alkylidene complex $[W\{\kappa^2-C,S=\text{CRSCRS}\}Cp]$ containing two xylyl groups and presumably requiring a bimolecular dimerisation step in the mechanism.\textsuperscript{108}

![Scheme 1.33. Reactions of tungsten alkylidyne with thionyl chloride.](image)

The dihaloaminocarbonyl complexes $[W(\equiv CNREt)X_2Tp^\lambda]$ ($R = \text{Et, Me}$) can undergo reductive dehalogenation by Na/Hg in the presence of EtNC to give the electron-rich aminocarbonyl complexes $[W(\equiv CN(R)Et)(CNEt)_{2}Tp^\lambda]$.\textsuperscript{85}

Reaction of $[W(\equiv Cz-Bu)Cl_2Tp]$ with the appropriate metal amide $M[NHR]$ ($M = \text{Li, K, Na}$) yields the amido alkylidyne complexes $[W(\equiv Cz-Bu)Cl(NHR)Tp]$ ($R = \text{Ph, C}_6\text{H}_4\text{Br-4, C}_6\text{H}_3(\text{CF}_3)_2-3,5$, and $\text{H}$) in moderate yields (Scheme 1.34). The lack of symmetry in these alkylidyne renders all the $Tp$ ring protons inequivalent.\textsuperscript{59}
In the presence of excess Li[NHPh], both chloride ligands are substituted and [W(=Ct-Bu)(NHPh)₂Tp] can be isolated in which the protons of the pyrazolyl rings appear in a 2:1 ratio, indicating the presence of a mirror plane in the molecule.\(^{59}\)

Reaction of [W(=CR)X₂Tp*] (R = t-Bu, X = Cl; R = Ph, X = Br)\(^{57}\) with neutral alumina or aniline produces the compounds [W(=CHR)(=E)XTp*] (R = t-Bu, E = O, X = Cl;\(^{56}\) R = Ph, E = O, X = Br; R = Ph, E = NHPh, X = Br) (Scheme 1.35). The corresponding dihalo complexes containing the less sterically bulky Tp ligand [W(=CPh)Br₂Tp] react with primary amines and water similarly to yield alkylidene imido and oxo complexes [W(=CPh)Br(X)Tp] (X = t-BuN, N-1-adamantyl, N-xylyl, O) in 55–98% yields.\(^{135}\) For [W(=CPh)Br₂Tp*] the oxocarbene species is not isolable.\(^{58}\) Instead, further reaction results in formation of the dioxo–benzyl species [W(CH₂Ph)(O)₂Tp*], perhaps due to a weaker halide–metal interaction.\(^{57}\) The crystallographically characterised oxocarbene complex [W(=CHR)(O)ClTp*] (R = t-Bu) can be used as a ROMP catalyst for cyclo-octene and norbornene when activated with AlCl₃.\(^{56}\)

\[\text{Scheme 1.35. Synthesis of tungsten imido or oxo alkylidene complexes (Tp}^\text{X} = \text{Tp, Tp*; X = Cl, Br;} \text{R = t-Bu, Ph;} \text{E = NR, O).}\]

### 1.4.2 The metal–carbon multiple bond

**Cycloaddition**

\[\text{Scheme 1.36. Chauvin–Herisson mechanism for alkene metathesis.}\]

The formal [2+2] cycloadditions of metal–carbon and carbon–carbon multiple bonds that are central to the accepted olefin/alkyne metathesis (Chauvin–Herisson) mechanism (Scheme 1.36) have been extended to include the reactions of metal–carbon multiply bonded compounds with
molecules containing unsaturated P=Cr linkages. Treatment of [Mo(=CC6H4OMe-2)(CO){P(OMe)3}2Bp] with a stoichiometric amount of t-BuC≡P under mild conditions gave [Mo(=Ct-Bu)(CO){P(OMe)3}2Bp] in 84% yield via an alkylidyne exchange reaction, which is consistent with the intermediacy of a 1-phospha-3-molybdcyclobutadiene (Scheme 1.37), although an alternative metallaphosphatetrahedrane cannot be excluded. The relative instability of the aryl-substituted phosphaalkyne 2-MeOC6H4C≡P is proposed to drive the equilibrium reaction to completion.51,136

\[
\text{Bp(OC)((MeO)3P)2Mo=CC≡C-R} \quad \text{R'=C6H4OMe-4; R'=t-Bu).}
\]

Scheme 1.37. Metal-alkylidyne/phosphaalkyne metathesis (R = C6H4OMe-4; R' = t-Bu).

Reactions of [Mo(=CR)(CO)(L')Tp] (R = C6H4Me-4; L' = CO, PPh3) with CS2 ultimately provide the metallacyclic thioke tene complex [Mo{η^2-C(S)=C(S)≡C(=O)S}S≡C(=O)Tp],137 incorporating the elements of CS2, one carbonyl ligand and the alkylidyne unit into the metallacycle. The first step of the suggested mechanism, as shown in Scheme 1.38, involves cycloaddition of Mo≡C and C=S bonds.

\[
\text{Scheme 1.38. Proposed metal-alkylidyne/carbon disulfide cycloaddition step (L = CO, PPh3).}
\]

A similar initial cycloaddition step is proposed in the reaction of molybdenum alkylidynes [Mo(=CC4H3S-2)(CO)3Tp] with the heterocumulenic mesityl isoselenocyanate (SeCNMes) to provide a mixture of products including the mononuclear selenoaroyl complexes, [Mo(η^2-SeCC4H3S-2)(CO)3Tp] and [Mo(η^2-SeCC4H3S-2)(CO)(CNMes)Tp], which may also be obtained directly from elemental Se in the presence of a catalytic amount of mesityl isocyanide (Scheme 1.39). Cycloaddition is proposed to produce a common metallacyclobuten-imine intermediate, from which isonitrile extrusion competes with carbonyl dissociation, followed by metallacycle collapse (See Chapter 3).123
Ketenyl formation

The chemistry of ketenyls has been reviewed, with particular emphasis on their origins from carbyne–carbonyl coupling reactions. In electron-rich carbyne complexes the carbyne ligand is not susceptible to nucleophilic attack and nucleophiles cause carboxylation of the carbyne to give $\eta^1$- or $\eta^2$-ketenyl compounds (Scheme 1.40). Nucleophile-induced alkylidyne–carbonyl coupling is typically carried out under thermal or photolytic conditions and is facilitated by increasing the electron density of the metal centre, i.e., increasing $\pi$-back-bonding to the carbonyl ligand.

The electron-rich thiocarbyne complex $[W(\equiv\text{CSMe})(CO)_2 TP]$ reacts with the strongly basic phosphine $\text{PET}_3$ at 40 °C to give the $\eta^2$-ketenyl derivative $[W(\eta^2-C,C'-\text{OCOSMe})(CO)(\text{PET}_3)TP]$, indirectly coupling a carbonyl and thiocarbonyl ligand (the latter from which the thiocarbyne ligand was derived by electrophilic addition). This coupling reaction takes place under more forcing conditions than those for analogous Cp complexes, probably due to the greater steric hindrance provided by the TP ligand at the metal centre.

Similarly, $[W(\equiv\text{CR})(CO)_2 TP]$ ($R = \text{C}_6\text{H}_4\text{Me}-4$) reacts with $\text{PMe}_3$ to give a $\eta^2$-ketenyl complex $[W(\eta^2-C,C'-\text{OCCR})(CO)(\text{PMe}_3)TP]$. Coupling reactions are sensitive to the steric and electronic properties of the system and an analogous product is not formed with the bulkier and
less nucleophilic PPh₃ under thermal reaction conditions. [W(η²-C₆H₄Me-4-CCR)(CO)(PPh₃)Tp] is instead prepared by reaction of the photochemically generated all-trans-[W≡CRBr(CO)₂(PPh₃)] with late introduction of the Tp nucleophile under thermal conditions resulting in displacement of a phosphine ligand and trapping of the resultant ketenyl product. The corresponding complex [Mo(η²-C₆H₄Me-4-CCR)(CO)(PPh₃)Tp] is not available by this route. Nucleophilicity at the oxygen atom of [W(η²-C₆H₄Me-4-CCR)(CO)(PPh₃)Tp] allows subsequent treatment of the ketenyl with Cl₂PPh₃ to provide the chloroalkyne complex [W(η²-ClC≡CR)Cl(CO)Tp]. These transformations are summarised below in Scheme 1.41.

![Scheme 1.41](image)

The thermally inaccessible ketenyl complexes [M(η²-C₆H₄Me-4-CCR)(CO)(L')Tp] (R = C₆H₄Me-4; M = Mo, W; L' = P(OMe)₃, PMe₂Ph, PPh₃) can be prepared via photochemical induction of carbonyl–alkylidyne coupling in the presence of a trapping phosphine (L'). Subsequent reaction with Woollins’ oxygen/selenium or Lawesson’s oxygen/sulfur exchange reagent provides seleno- or thioketenyl complexes [M(η²-C₆H₄Me-4-CCR)(CO)(L')Tp] (E = Se, S), respectively, one example of which (M = W, L' = PMe₂Ph, E = S) is also obtained from the reaction of [W(η²-ClC≡CR)Cl(CO)Tp] with NaSH in the presence of PMe₂Ph. In solution, the molybdenum ketenyl complexes thermally revert to either [Mo≡CR(CO)₂Tp] or [Mo≡CR(CO)(L')Tp], depending on the donor properties of the phosphine, L'.

Under mild photolytic conditions the reaction of [W≡CRBr(CO)₂(CNR')₂] (R = C₆H₄Me-4, xylyl, R' = t-butyl, xylyl) with K[Bp] or [W≡CR(CO)₂(pic)Bp] and CNR' both provide...
primarily the thermally unstable ketenyl complex \[[W(\eta^2-C,C'-OCCR)(CO)(CNR')_2Bp]\]. In contrast, the thermal reaction of \([W(\equiv CR)(CO)_2Bp]\) with \(PR'_3\) (\(R' = \text{Me, Ph}\)) proceeds via carbonyl displacement to yield \([W(\equiv CR)(CO)_2(PR'_3)Bp]\), perhaps via a transiently formed ketenyl compound.

In contrast to the ethylidyne complex \([\text{Mo}(\equiv C\text{Me})(CO)_2Tp^*]\), photoinduced carbonyl coupling occurs in acetonitrile solutions of \([\text{Mo}(\equiv CR)(CO)_2Tp^*]\) (\(R = \text{Ph}, C_6H_4\text{Me}-4\)) to generate the \(\eta^2\)-ketenyl complexes \([\text{Mo}(\eta^2-C,C'-OCCR)(CO)(NCMe)Tp^*]\). Similar reactivity is, however, not observed for the corresponding tungsten complexes \([W(\equiv CR)(CO)_2Tp^*]\) (\(R = C_6H_4\text{Me}-4; Tp^* = pzTp, Tp^*\)).

In \([\text{Mo}(\eta^2-C,C'-OCCR)(CO)(NCMe)Tp^*]\) (\(R = \text{Ph}, C_6H_4\text{Me}-4\)), the \(\eta^2\)-ketenyl ligand is acting as a three-electron donor (neutral convention) (a, Chart 1.4). In contrast, for the \(\text{Cp}^*\)-containing complex \([W\{\eta^1-C-OCC(Si\text{Ph}_3)\}(\eta^2-\text{NCMe})(CO)\text{Cp}^*]\) produced from photoinduced carbonyl–carbyne coupling in \([W(\equiv CSi\text{Ph}_3)(CO)_2\text{Cp}^*]\), the acetonitrile displays a highly unusual ‘four-electron donor’ mode of coordination whilst an \(\eta^1\)-ketenyl ligand completes the tungsten centre’s 18-electron configuration (b, Chart 1.4). This unusual behavior may be traced, in part, to the electronic nature of octahedral tungsten(II) such that the \(d^4\) centre will be most stabilised by ligand arrangements that offer a \(\pi\)-dative component for the one vacant \(t_{2g}\) type orbital.

\[\text{chart 1.4.} \quad \eta^2\text{- vs } \eta^1\text{-ketenyl coordination with associated valence electron (VE) contributions.}\]

The most favourable orientation of the formally six-coordinate \(\eta^2\)-ketenyl complexes \([M(\eta^2-C,C'-OCCR)(CO)(L')Tp^*]\) is that in which the oxygen atom of the ketenyl lies proximal to the carbonyl and the W–C–O and ketenyl C–C–O components are co-planar in order to maximise \(\pi\)-overlap with the metal centre.

The cationic carbyne complexes \([W(\equiv \text{CPMe}_2\text{R})(CO)_2Tp^*]^+\) (\(R = \text{Me, Ph}\)) react with aryloxides of low nucleophilicity to provide \(\eta^2\)-ketenyl complexes \([W(\eta^2-C,C'-OCC\text{CPMe}_2\text{R})(OC_6\text{H}_4\text{R'}-4)]^+\).
(CO)Tp*] (R' = NO₂, R = Me, Ph; R' = CN, R = Me, Ph; R' = Cl, R = Ph) along with the aryloxy carbynes [W(=COCl₂H₃R')(CO)₂Tp*]. As mentioned in Section 1.2.2. (Scheme 1.21), ketenyl complexes are formed simultaneously with aryloxy carbyne products that result from nucleophilic attack at Cₐ. The dimethylphenylphosphonio- and triphenylphosphonio-ketenyl products have similar spectroscopic characteristics. Both contain a stereogenic centre at tungsten and display 1:1:1 patterns for the Tp* arms. Characteristic absorptions attributable to νₐ₈ appear at ca. 1870 and 1710 cm⁻¹, i.e., at notably low frequencies, presumably reflecting the π-dative role of the aryloxy.

Hydroboration

Building on earlier results from Stone for Cp analogues, it was shown that hydroboration of the metal–carbon triple bond in Tp* carbyne complexes [M(=CR)(CO)₂Tp*] with HBR₂ leads to the novel borylmetal complexes [M{η²-B(R'CH₃R')₂CO}₂Tp*] (M = W, R' = Et, R = C₆H₄Me-4 or Me; M = Mo, R' = Et, R = C₆H₄Me-4; M = W, R' = Ph, R = C₆H₄Me-4 or Me) (Scheme 1.42).

These reaction products can be considered as comprising the addition of RBH₂ to the M–C triple bond, by which the carbyne carbon atom is reduced to a methylene group and the borylene BR' is inserted into the M–C bond. The X-ray crystal structure reveals β-agostic C–H–M interactions between the metal atom and boryl ligands. Despite use of the dialkylborane HBR₂, the product composition is such that it formally requires addition of dihydromoorganoborane H₂BR' to the carbyne complex. Deuterium labeling experiments showed selective transfer of deuterium to the former carbyne carbon, with only deuterium participating in the agostic interaction. This transfer of deuterium from the borane to the carbyne complex ruled out intermediates containing conventional η²-bora-alkene ligands (i.e., without agostic interactions).

In contrast, the corresponding unsubstituted Tp complexes decompose with HBEt₂ at 0 °C, whereas the cyclopentadienyl complexes [M(=CR)(CO)₂Cp*⁵] (Cp*⁵ = Cp, Cp*⁵) react with
dialkyl boranes (9-borabicyclo[3.3.1]nonane\textsuperscript{141,142} or diethylborane\textsuperscript{145}) at low temperatures to provide $\alpha$-boryl-$\eta^2$-benzyl metal complexes $[M\{CH(BR')_2(C_6H_4Me-4)\}(CO)_2Cp^\ast] \quad (M = W, \quad Cp^\ast = C_5Me_5Et; \quad M = Mo, \quad Cp^\ast = Cp^*, \quad R' = Et)$, amounting to 1,1-hydroboration of the metal–carbon triple bond at the carbyne carbon.\textsuperscript{141,142}

The $\mu$-‘bora-alkyne’ ditungsten complexes $[\{W(CO)_2Cp^\ast\}_2\{\mu-RCB(H)CH_2R'\}]$ obtained from the carbyne metal complexes $[W(CR)(CO)_2Cp^\ast] \quad (R = C_6H_4Me-4 \text{ or } Me)$ and $BH_3\cdot$THF\textsuperscript{141,142} may be considered as the products of the starting metal carbyne and a boryl metal complex, $[W\{B(H)CH_2R'\}(CO)_2Cp^\ast]$, as depicted in Scheme 1.43, which is in effect comparable to the Tp$^\ast$ boryl metal complexes described above\textsuperscript{144} and implies that Cp systems are more reactive than the related Tp$^\ast$ systems.

![Scheme 1.43. Unit composition of $\mu$-boraalkyne ditungsten Cp$^\ast$ hydroboration complex.](image)

**Protonation**

The product of protonation of carbyne complexes is dependent on the metal, the ancillary ligands, and the counter ion of the acid. It is, however, not always clear that the thermodynamic site of protonation reflects the kinetic site due to the possibility of $\alpha$-M–H elimination. In the presence of coordinating conjugate bases, carbyne protonation can induce further reaction to produce $\eta^2$-acyl complexes and compounds in which the original alkylidyne ligand has been lost via protonolysis.\textsuperscript{146} The site of protonation (metal, alkylidyne face, or alkylidyne carbon generating alkylidyne/hydride, face-protonated alkylidyne, and non-agostic alkylidene products, respectively) ultimately depends on the electron density at the metal centre, as depicted in Scheme 1.44. The Tp and Cp series of complexes display parallel protonation activity.\textsuperscript{146}

![Scheme 1.44. Sites of protonation in alkylidyne complexes.](image)

In alkylidyne complexes that bear no $\pi$-acid co-ligands, thermodynamic protonation occurs either on the alkylidyne face or at the metal,\textsuperscript{146} and steric considerations are invoked to explain
the preference. Sub-stoichiometric quantities of H₂O or HCl catalyse the tautomerisation of [W(≡Cl-Bu)Cl(NHR)Tp] (R = Ph)⁵⁹ to the corresponding imido alkylidyne complex [W(≡CHr-Bu)Cl(NR)Tp]. The first step in the tautomerisation is, however, suggested to involve protonation of the amide group (as shown in Scheme 1.45) since weaker donors (i.e., those with electron-withdrawing groups such as NH₂C₆H₃(CF₃)₂-3,4, NH₂C₆H₄F-4, and NH₃) dissociate from the metal under protonation conditions before proton transfer to the alkylidyne ligand can occur.⁵⁹

![Scheme 1.45. Acid-catalysed proton transfer (X = OH or Cl).](image)

In the presence of π-acid ligands (typically prevalent for metals with higher d configurations), thermodynamic protonation shifts from the metal toward the carbyne carbon, occurring either on the alkylidyne face or at the carbyne carbon. Electronic effects appear to be the overriding factor in determining the ultimate site of protonation. For cis-dicarbonyl [M(≡CR)(CO)₂Tp] complexes, the electron density at the metal centre is substantially decreased by π-backbonding. Protonation (HBF₄) of [Mo(≡CBu)(CO)₂Tp] at the carbyne carbon yields salts of the cationic carbene [Mo{≡C(H)Bu]}(CO)₂Tp][BF₄]. In contrast, protonation of the Cp analogue [Mo(≡CBu)(CO)₂Cp] proceeds via secondary reaction of the initially formed carbene species with starting carbyne [Mo(≡CBu)(CO)₂Cp] to generate the binuclear alkyne salt [Mo₂(μ-H)[μ-C₅(Bu)₂](CO)₄Cp₂][BF₄].⁶⁴ ¹⁴⁶ The poly(pyrazolyl) ligand is sufficiently sterically encumbered to prevent similar reaction of the alkylidyne.

Increasing electron density at the molybdenum centre by replacement of the strong π-acid carbonyl with a phosphite ligand shifts the ultimate protonation site from the carbyne carbon to the alkylidyne face and complexes of the type [Mo(≡CBu)(CO)(P(OMe)₃)L] (L = Tp, Cp) undergo protonation to yield α-agostic pentylidenes.¹⁴⁶
The greater electron density of tungsten centres and the more electron-rich Tp* ligand means protonation of the dicarbonyl \([W(=\text{CH})(\text{CO})_2\text{Tp}^\ast]\) produces the cationic \(\alpha\)-agostic methylidene salts \([W(=\text{CH}_2)(\text{CO})_2\text{Tp}^\ast][\text{BX}_4]\) \((X = \text{F}, \text{C}_6\text{H}_3(\text{CF}_3)_{2-3,5}).\)

Low temperature treatment of \([\text{Mo}\{=\text{CFe}(\text{CO})_2\text{Cp}\}(\text{CO})_2\text{Tp}^\ast]\) with \(\text{HBF}_4\) forms an agostic methyne bridge in the cationic protonation product, which serves to stabilise the unsaturated carbene.\(^{71}\)

Protonation of \([W(=\text{CR})(\text{CO})_2\text{Tp}]\) \((R = \text{C}_6\text{H}_4\text{OMe}-2)\) with \(\text{HBF}_4\cdot\text{Et}_2\text{O}\) occurs at the carbyne carbon to give the salt \([W\{=\text{C}(\text{H})\text{C}_6\text{H}_4\text{OMe}-2\}(\text{CO})_2\text{Tp}][\text{BF}_4]\).\(^{43}\) The related complexes \((\text{Tp}^x = \text{Tp}, \text{Tp}^\ast, R = \text{C}_6\text{H}_4\text{Me}-4; \text{Tp}^x = \text{Tp}, R = \text{xyllyl}; \text{Tp}^x = \text{Tp}^{\text{ph}}, R = \text{C}_6\text{H}_4\text{Me}-4)\) do not form stable species under the same conditions and it is suggested that a dative interaction from the OMe-2 group on the phenyl ring stabilises the 16-electron tungsten centre.\(^{43}\) Similar stabilisation has been demonstrated for the carbene complex \([W\{=\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{OMe}-2\}(\text{CO})_4]\)^{147} and underpins the operational efficiency of the Grubbs–Hoveyda catalyst \([\text{RuCl}_2\{=\text{CHC}_6\text{H}_4(\text{Oi-Pr})-2\}](\text{IMesH}_2)\) \((\text{IMesH}_2 = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})-4,5\text{-dihydroimidazol-2-ylidene}).\)^{148}

The heterocarbyne \([W(=\text{CSMe})(\text{CO})_2\text{Tp}]\) undergoes reversible protonation with strong acids \((\text{CF}_3\text{SO}_2\text{H}, \text{HBF}_4, \text{CF}_3\text{CO}_2\text{H})\) at low temperature giving salts of the cation \(W(\eta^2\text{-CH-SMe})(\text{CO})_2\text{Tp}^\ast\), in which the carbene ligand is bonded to the metal through both the C and S atoms (Scheme 1.46), rather than an agostic C–H–M interaction.\(^{74,76}\) Attempted protonation with HCl or HI leads to complete cleavage of the alkylidyne group, with \([WX(\text{CO})_2\text{Tp}]\) \((X = \text{Cl, I})\) being the only isolable reaction products.\(^{76}\)

\[\text{Scheme 1.46. Reversible protonation of } [W(=\text{CSMe})(\text{CO})_2\text{Tp}] \text{ (X = O}_3\text{SCF}_3, \text{BF}_4, \text{O}_2\text{CCF}_3; \text{Base} = \text{NaH, K}_2\text{CO}_3, \text{Et}_3\text{N).}\]

The methoxycarbyne complex \([W(=\text{COMe})(\text{CO})_2\text{Tp}^\ast]\) undergoes reversible protonation at the carbyne carbon in the presence of \([\text{H(\text{Et}_2\text{O})}_2][\text{Ar'}_4]\) \((\text{Ar'} = \text{C}_6\text{H}_3(\text{CF}_3)_{2-3,5})\) to provide the \(\alpha\)-agostic carbene complex \([W\{=\text{C}(\text{H})\text{OMe}\}(\text{CO})_2\text{Tp}^\ast][\text{Ar'}_4]\),\(^{79}\) rather than the \(\eta^2\text{-C,O} isomer which would be analogous to Angelici’s thiolatocarbene.
Proton addition and subsequent phenyl acetylene insertion convert (aryl oxy)carbyne complexes \([W(=\text{COAr})(\text{CO})_2\text{Tp}^*]\) (Ar = Ph, \(\text{C}_6\text{H}_4\text{Me}-4\), \(\text{C}_6\text{H}_4\text{OMe}-4\)) into \(\eta^3\)-vinylcarbene complexes \([W[\eta^3-(=\text{CPhCH}=\text{CHO}(\text{C}_6\text{H}_4\text{R}-4))]_2(\text{CO})_2\text{Tp}^*][X]\) (R = H, Me, OMe, X = BF\(_4\); R = H, X = BaR\(_4\), Ar\(_1\) = 3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\)) (Scheme 1.12).\(^{65}\) The intermediate agostic carbene complex \([W[=\text{CHO}(\text{C}_6\text{H}_4\text{OMe}-4)](\text{CO})_2\text{Tp}^*][\text{BaR}_4]\) was characterised by IR, \(^1\)H NMR, and \(^{13}\)C\({}^1\)H NMR spectroscopy.\(^{65}\)

Protonation of \([\text{Mo}\{=\text{CN(Me)}(\text{t-Bu})\}(\text{CO})_2\text{Tp}^*]\) in the presence of PhC\(=\text{CH}\) ultimately yields the crystallographically characterised cationic \(\eta^2\)-vinyliminium complex \([\text{Mo}\{\eta^2\text{-CPh}=\text{CH}=\text{N-(Me)}(\text{t-Bu})\}(\text{CO})_2\text{Tp}^*][\text{BF}_4]\) via alkyne insertion into the transient metal–carbene bond (Scheme 1.47).\(^{83}\)

![Scheme 1.47. Protonation of [Mo{=CN(Me)\text{t-Bu}]{(CO)}_2\text{Tp}^*] in the presence of PhC=CH (R = Me, R' = \text{t-Bu}).](image)

Proton addition to the anionic methylene carbene complex Na\([W(=\text{CH}_2)\text{(CO)}_2\text{Tp}^*]\)\(^{68}\) (prepared in situ from addition of Na[HBE\(_3\)] to a tetrahydrofuran solution of \([W(=\text{CH})\text{(CO)}_2\text{Tp}^*]\) at \(-78\) °C) results in the formation of a methyl ligand poised to insert CO. Trapping of the protonated carbene complex with phenyl acetylene yields an \(\eta^1\)-acyl product \([W\{\eta^1\text{-C(O)Me}\}(\eta^2\text{-PhC}=\text{CH})\text{(CO)}\text{Tp}^*]\). With a two-electron donor phosphine ligand, seven-coordinate methyl dicarbonyl complexes of the form \([W(=\text{CH}_2)(\text{CO})_2\text{(PR}_3)\text{Tp}^*]\) (PR\(_3\) = PMe\(_3\), PMe\(_2\)Ph, PMePh\(_2\)) are generated as the kinetic products. The seven-coordinate phosphine complexes are in equilibrium with their CO-insertion products \([W\{\eta^2\text{-C(O)Me}\}-(\text{CO})(\text{PR}_3)\text{Tp}^*]\).\(^{149}\)
Reaction with chalcogens

Group 6 alkylidyne poly(pyrazolyl)borate and cyclopentadienyl complexes generate dichalcocarboxylates \([\text{M}(\kappa^2-\text{A}:\text{CR})]\) with elemental chalcogens. \([\text{Mo}(=\text{CR})(\text{CO})_2\text{Tp}]\) complexes, however, fail to react with tellurium and this is attributed to a kinetic phenomenon.

The sequential treatment of \([\text{W}(=\text{CR})\text{Br}(\text{CO})_4]\) \((R = \text{C}_6\text{H}_4\text{Me}-4)\) with sulfur and K[\text{Tp}] provides \([\text{W}(\eta^2-\text{S}_2\text{CR})(\text{CO})_2\text{Tp}]\) via initial thioacyl or dithiocarboxylate formation and subsequent reaction with \text{Tp} \((\text{and, for the latter, excess sulfur}).\)

Treating \([\text{Mo}(=\text{CR})(\text{CO})_2\text{Tp}]\) \((R = \text{C}_6\text{H}_4\text{Me}-4)\) with sulfur in tetrahydrofuran at reflux temperature affords \([\text{Mo}(\eta^3-\text{S}_2\text{CR})(\text{O})\text{Tp}]\) containing an oxo ligand (presumably from adventitious oxygen) and a trihapto dithiocarboxylate ligand (Scheme 1.48). The oxo is presumed to arise during chromatographic purification.

![Scheme 1.48. Preparation of a \(\eta^3\)-dithiocarboxylato complex (\(R = \text{C}_6\text{H}_4\text{Me}-4\)).](image)

The chalcoacyl complexes have been stabilised through coordination to polymetallic ensembles. Binuclear complexes prepared from solvent-stabilised ‘\(\text{Ru}(\text{CO})_2(\eta^5-7,8-\text{C}_2\text{B}_9\text{H}_{11})\)’ and the corresponding alkylidyne ‘trap’ the Group 6 chalcoacyls, and this property will be elaborated upon in a later section devoted to such multinuclear complexes (Scheme 1.80, Section 1.4.6). Mononuclear thioacyl complexes \([\text{Mo}(\eta^2-\text{SCR})(\text{CO})_2\text{Tp}]\) \((R = \text{C}_6\text{H}_4\text{Me}-4, \text{C}_6\text{H}_4\text{OMe}-4, \text{C}_4\text{H}_3\text{S}-2)\) were successfully prepared through the use of 2-methylthiirane as a single atom sulfur source (Scheme 1.49). Only small amounts of the corresponding dithiocarboxylates \([\text{Mo}(\eta^2-\text{S}_2\text{CR})(\text{CO})_2\text{Tp}]\) were formed, which also arise from treatment of \([\text{Mo}(\eta^2-\text{SCR})(\text{CO})_2\text{Tp}])\) with further methylthiirane or elemental sulfur. This reaction fails for alkylidyne complexes of chromium, sterically congested benzylidyne complexes and aminomethylidyne complexes. The thioacyl complexes serve as precursors for complexes bearing dithiocarboxylate, thioselenocarboxylate, thiolato-carbene and \(\alpha\)-thioalkyl ligands as well as thioacyl-bridged binuclear complexes. With copper chloride, the chalcoacyl complex \([\text{Mo}(\eta^2-\text{SCC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}])\) regenerates \([\text{Mo}(=\text{CC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}])\) in 15% yield.
The acyl formation reaction is suggested to proceed via initial attack at the carbyne carbon, but
evidence is not conclusive.\textsuperscript{48} Reaction of the analogous Cp complexes with cyclohexene sulfide
provides exclusively the dithiocarboxylate derivatives. Presumably the second sulfur addition is
considerably more rapid than for the Tp complexes due to lowered steric crowding around the
molybdenum centre.\textsuperscript{48}

1.4.3 The carbon substituent
The carbon in electron-rich transition-metal carbyne complexes is known to be susceptible to
electrophilic attack. The SM\textsuperscript{+} electrophile from dimethyl(methylthio)sulfonium
tetrafluoroborate adds to the carbyne carbon atom of \([M(=CR)(CO)\textsubscript{2}Tp]\) (\(M = Mo,\)
\(R = C\textsubscript{6}H\textsubscript{4}Me-4, C\textsubscript{4}H\textsubscript{3}S-2; 48\)
\(M = W, R = C\textsubscript{6}H\textsubscript{4}Me-4, 155 R = SM\textsubscript{e}^{19,77} \)) to yield the cationic
\(\eta^2\)-thiocarbene complexes \([M(\eta^2-MeSCR)(CO)\textsubscript{2}Tp][BF\textsubscript{4}]\) (Scheme 1.50). The structure of the
related \([W\{\eta^2-C(H)SMe\}(CO)\textsubscript{2}Tp][O\textsubscript{3}SCF\textsubscript{3}]\)\textsuperscript{74} suggests that in these thiocarbenes the methyl
group on the coordinated sulfur is oriented above the MCS ring toward the pyrazolyl groups and
away from the metal carbonyls.

\begin{equation}
\text{Scheme 1.50. Addition of SM}^{+}\text{ electrophile (M = Mo, R = C}_{6}\text{H}_{4}\text{Me-4; M = W, R = SM}_{e}, C_{6}\text{H}_{4}\text{Me-4).}
\end{equation}

The direct conversion of carbyne complexes \([W(=CR)(CO)\textsubscript{2}Tp]\) (\(R = Ph, C\textsubscript{6}H\textsubscript{4}Me-4))
to cationic, \(cis\)-dicarboxyl \(\eta^2\)-phosphinocarbene (metallaphosphacyclopropene) complexes can be
achieved by the addition of chlorodiorganophosphines in the presence of sodium
tetraphenylborate\textsuperscript{156} or thallium hexafluorophosphate (Scheme 1.51).\textsuperscript{157} In the absence of these
sodium salts, nucleophile (Cl\textsuperscript{-}) induced carbonyl–carbene coupling affords neutral
\(\eta^1\)-phosphinoketene complexes.\textsuperscript{156}
Addition of excess PMe$_3$ to [W(\(\equiv\)CSMe)(CO)$_2$Tp*] in dichloromethane yields the cationic bis(phosphonio)carbene complex [W{=C(PMe$_3$)$_2$}(CO)$_2$Tp*]$^+$, isolated as the PF$_6$ salt by metathesis with NH$_4$PF$_6$. Two nonequivalent phosphorus environments are spectroscopically evident and the molecular structure of this complex has been determined. The bis(phosphonio)carbene complex is in equilibrium with the phosphoniocarbonyl complex in solution and the addition of MeI readily forms the monophosphine analogue [W(\(\equiv\)CPMe$_3$)(CO)$_2$Tp*][PF$_6$].

Nucleophiles react with carbyne complexes to promote carbyne–carbonyl coupling, attack the metal–carbon triple bond, or displace a substituent on the carbyne carbon. Complexes of the form [M(\(\equiv\)CR)(CO)$_2$L] are coordinatively saturated and in the case of L = Tp*, the metal also enjoys a degree of steric protection. Accordingly, the reaction of these complexes with nucleophiles does not, in general, involve attack at the metal but rather at a co-ligand. Attempted synthesis of [W(\(\equiv\)CCH$_3$)(CO)$_2$Tp*] via reaction of MeLi with the chlorocarbonyl complex [W(\(\equiv\)CCL)(CO)$_2$Tp*] instead proceeds via attack at a carbonyl carbon to provide an acyl anion (observed in situ by IR and $^{13}$C{H} NMR spectroscopy). Treatment of [W(\(\equiv\)CCL)(CO)$_2$Tp*] with [Me$_3$LiCu] at 0 °C results in the formation of [W(\(\eta^3\)-C(CH$_3$)=CMe$_2$)(CO)$_2$Tp*] through initial chloride displacement and ensuing reaction with a second equivalent of CH$_3^-$ and net hydride loss. Similar behaviour was seen for the molybdenum analogue. The vinyl complexes slowly rearrange to stable $\eta^3$-allyl products in non-aromatic solvents. At -22 °C, chloride displacement from [M(\(\equiv\)CCL)(CO)$_2$Tp*] (M = Mo, W) with LiMe$_2$Cu affords the ethylidyne complexes [M(\(\equiv\)CMe)(CO)$_2$Tp*] (M = Mo, W) (Scheme 1.52). Similarly, nucleophilic halide displacement of [Mo(\(\equiv\)CCL)(CO)$_2$Tp*] with phenyl lithium produces [Mo(\(\equiv\)CPh)(CO)$_2$Tp*] in modest yields, however wider success has been achieved with heteroatom nucleophiles (vide supra).
CHAPTER 1. ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

Scheme 1.52. Cuprate addition to a chlorocarbonyl complex. (i) $\sim-22^\circ C$; (ii) HCl (Et$_2$O); (iii) 0 to 25 $^\circ C$ (M = Mo or W).

Conversion of the ethylidyne ligand in [Mo(=CMe)(CO)$_2$Tp*] to a vinylidene ligand is achieved via deprotonation with Na[N(SiMe$_3$)$_2$] in tetrahydrofuran. This vinylidene is susceptible to electrophilic attack at the $\beta$-carbon by RI (R = Et or Me) to generate elaborated alkylidyne ligands (Scheme 1.53).

Scheme 1.53. Nucleophilic attack at $\beta$-carbon of vinylidene anion.

Preparation of the monomeric methylidyne complexes [M(=CH)(CO)$_2$Tp*] (M = Mo, W) from [W(=CPR$_3$)(CO)$_2$Tp*]$^+$ has been achieved via phosphine abstraction by iodomethane from the zwitterionic carbene complexes [W{=C(H)(PR$_3$)}(CO)$_2$Tp*] (PR$_3$ = PMe$_3$, PMe$_2$Ph, PMe$_2$Et) with [PR$_3$]I as byproduct (Scheme 1.54). Triphenylphosphine provides a better leaving group than PMe$_2$R and treatment of [W(=CPPPh$_3$)(CO)$_2$Tp*][PF$_6$] with Na[HBEt$_3$] in tetrahydrofuran forms the methylidyne complex [W(=CH)(CO)$_2$Tp*] via the formyl and zwitterionic carbene intermediates [W(=CPPPh$_3$){C(=O)H}(CO)Tp*] and [W{=CH(PPh$_3$)}(CO)$_2$Tp*], respectively.

Scheme 1.54. Preparation of terminal methylidyne ligand from a phosphonioalkylidyne complex.
The tungsten alkylidyne complexes \([W(\equiv CH)(CO)_2Tp^\#]\) and \([W(\equiv CPh)(CO)_2Tp^\#]\) also arise from side reactions of phosphonium alkylidyne complexes with aryloxide nucleophiles from reaction of the quarternary phosphonium salts with adventitious hydroxide to give a dissociated alkyl anion or a product resulting from a 1,2-phenyl migration. At low temperature, phenyl migration is inhibited and only the terminal dissociation product is observed. At room temperature, both phenyl and C–H alkylidyne products form in an approximate 1:1 ratio.\(^7\)

The methylidyne complex \([W(\equiv CH)(CO)_2Tp^\#]\) can be deprotonated with alkyllithium reagents to provide the anionic terminal carbide \(Li[W(\equiv C)(CO)_2Tp^\#]\); characterised by a downfield resonance for \(C_\alpha\) at \(\delta 556\) in the \(^{13}C\{^1H\}\) NMR spectrum due to substantial deshielding from the electropositive metal. The negative charge is localised primarily on the \(\alpha\)-carbon and addition of electrophiles (E\(^+\)) generates modified alkylidyynes \([W(\equiv CE)(CO)_2Tp^\#]\) (E = Me, SiMe\(_3\), I, C(OH)Ph\(_2\), CH(OH)Ph, and C(O)Ph).\(^6\)

The methylidyne and above-mentioned chloromethylidyne complexes, useful in the synthesis of elaborated alkylidyynes, are also employed in the synthesis of bimetallic complexes spanned by hydrocarbon and carbon-only bridges. These latter reactions are described in a later section dedicated to such polymetallic systems.

Lalor's chlorocarbynes can be utilised as a starting point for the in situ construction of anionic Mo- or W- complexes with C-substituted vinylidene ligands \([M(\equiv C=CRR')(CO)_2Tp^\#]\) through use of the stabilised secondary carbanions \([CRR']^-\) \((R, R' = \text{CN, CO}_2\text{Et, Scheme 1.55}).\(^6\)

Presumably, formation of the C-substituted vinylidene proceeds via the neutral carbyne complex. Reaction with a variety of electrophilic or oxidizing reagents (HCl or PhCOCl with \([\text{FeCp}_2][\text{BF}_4], [\text{Ph}_2\text{I}][\text{PF}_6]\) and NaOCl or with CoCl\(_2\)) yields neutral, seven-coordinate oxametallacyclic carbene complexes, which is noteworthy given the established tendency of Group 6 Tp complexes to avoid seven-coordination.\(^6\)

Electrophilic attack occurs at the \(\beta\)-carbon of the vinylidene ligands in \([M(\equiv C=CRR')(CO)_2Tp^\#]\) \((R, R' = \text{CN, CO}_2\text{Et})\) to provide highly functionalised carbyne complexes \([\text{Mo} \{\equiv \text{CC(CN)(CO}_2\text{Et)Z}](\text{CO}_2\text{Tp}^\#)](Z = \text{HgX, Cu, N}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-4}).\(^6\)
CHAPTER I. ALKYLIDYNE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

1. ALKYLIDYNE COMPLEXES Ligated by Poly(pyrazolyl)borates

The air-stable, anionic carbene complexes with a metal-centred negative charge $[\text{M}\{\text{C}(\text{CN})_2\}(\text{CO})_2\text{Tp}^*\}^{-}$ (M = Mo, W), $[\text{Mo}\{\text{C}(\text{CN})_2\}(\text{CO})_2\text{Tp}^*\}^{-}$], $[\text{Mo}\{\text{C}(\text{CN})_2\}(\text{CO})_2\text{Tp}^*\}^{-}$] and $[\text{Mo}\{\text{C}(\text{CN})\text{R}\}(\text{CO})_2\text{Tp}^*\}^{-}$ (R = C(CN)Me, C(CN)(Me)C$_6$H$_4$Br-4, C(CN)(Me)C$_6$H$_4$Me-4, C(CN)(Me)(1-C$_{10}$H$_7$)) can be similarly synthesised by addition of cyanide anion to the corresponding chlorocarbyne or alkylcarbyne complexes in dimethylsulfoxide and isolated as their tetra(alkyl)ammonium salts (alkyl = Bu, Et, Scheme 1.56).

The dicyanocarbene complexes are stereochemically rigid, with the plane of the carbene ligand coinciding with the molecular mirror plane. The electron-rich carbene carbons in these dicyanocarbene complexes show some of the most highly shielded values of $\delta$C so far observed, ranging from $\delta$C = 167.8–194.5. The dicyanocarbene ligands are much stronger $\pi$-acceptors than conventional carbene ligands with average carbonyl absorptions at ca.1830 cm$^{-1}$ due to the resonance anion-stabilising effects of the cyano-substituents.

When $[\text{M}\{\text{C}(\text{CN})\text{Me}(\text{Y})\}(\text{CO})_2\text{Tp}^*\}^{-}$ complexes are treated with KCN and X is a poor leaving group (R), the anionic cyano(alkyl)carbene complexes $[\text{Mo}\{\text{C}(\text{CN})\text{R}\}(\text{CO})_2\text{Tp}^*\}^{-}$ are produced (R = C(CN)Me, C(CN)(Me)C$_6$H$_4$Br-4, C(CN)(Me)C$_6$H$_4$Me-4, C(CN)(Me)(1-C$_{10}$H$_7$)).

Scheme 1.55. Synthesis and reactivity of anionic $\eta^1$-vinylidene complexes.

Scheme 1.56. Synthesis of cyanomethylidene complexes (M = Mo or W; X = Cl, R = CN; X = R = C(CN)Me(Y), Y = CN, C$_6$H$_4$Br-4, C$_6$H$_4$Me-4, 1-C$_{10}$H$_7$).
reaction is observed when R = C(CN)(Ph)₂. These ligands are poorer π-acceptors than the dicyanocarbene complexes but remain significantly stronger than more conventional carbene ligands that lack strongly electron-withdrawing groups.¹⁵⁸

Unlike the closely related anionic vinylidene complexes [M(≡C=CRR')(CO)₂Tp*]⁻ (R, R' = CN, CO₂Et), the dicyanocarbene complexes do not give stable products with electrophiles. The cyano(alkyl)carbene complexes [Mo{≡C(CN)R}(CO)₂Tp*]⁻ (R = C(CN)(Me)C₆H₄Br-4, C(CN)(Me)(C₆H₄Me-4), C(CN)(Me)(1-C₁₀H₇)), however, could be doubly alkylated at the CN nitrogen to give the cationic (dialkylamino)alkyne complexes [Mo(Me₂NC≡CR)(CO)₂Tp*]⁺ (Scheme 1.57).¹⁵⁸

![Scheme 1.57. Suggested sequence of events leading to the formation of cationic dialkylaminoalkyne complexes (R = C(CN)(Me)(C₆H₄Br-4), C(CN)(Me)(1-C₁₀H₇)).](image)

The complex [Mo{≡C(CN)C(CN)₂Me₁}(CO)₂Tp*] eliminates [CH₃C(CN)₂]⁻ in the presence of excess Mel to yield purple [M≡CCN(CO)₂Tp*] in 74% yield, the first example of a cyanocarbyne complex and a presumed intermediate in the formation of the dicyanocarbenes (Scheme 1.58).¹⁵⁸ Infrared carbonyl frequencies are higher than for the chlorocarbyne complex, reflecting the greater inductive electron-withdrawing capacity of a cyano group compared to a chlorine atom and less efficient π-donation from the filled π-orbitals of the C≡N bond to the M=C bond π*-orbitals than from the lone pair orbitals on chlorine.¹⁵⁸ The cyanocarbyne complex may be considered isoelectronic with alkynylcarbynes.⁵²

![Scheme 1.58. Suggested rationale for cyanocarbene complex formation, R = C(CN)₂Me.](image)
Templeton has reported the synthesis of a number of elaborated and bridging carbyne ligands through reactions at the carbyne substituent that ultimately leave the M–C bond intact, although its formal multiplicity may vary during reaction sequences.

The methylidyne complexes \([M(=CH)(CO)_2\text{Tp}^*] (M = \text{Mo, W})\) are formed from fluorodesilylation of silylcarbynes \([M(=CSiMe_2Ph)(CO)_2\text{Tp}^*]\) with \([\text{Bu}_4\text{NF}]\) in wet tetrahydrofuran solution at low temperature.\(^{12}\) The yield obtained for the hydridocarbyne (30%) offers improvement over that from Templeton’s previous method involving hydrido(alkylphosphonio)carbene precursors.\(^{72}\) In solution, spontaneous dimerisation to vinylidene-bridge complexes \([\text{Tp}^*(\text{CO})_2\cdot M(=\text{CCH})_2M(\text{CO})_2\text{Tp}^*]\) occurs. The molecular structure of the tungsten derivative has been determined by X-ray crystallographic analysis, revealing a non-classical bridging vinylidene ligand that is perpendicular to the metal–metal axis but has an essentially linear M–C\(_\alpha–\)M spine (Scheme 1.59).

\[\begin{align*}
\text{Tp}^* & \quad \text{SiMe}_2\text{Ph} \quad \text{Me} \quad \text{Me} \quad \text{SiMe}_2\text{Ph} \\
\text{OC} & \quad \text{OC} \quad \text{CO} \quad \text{CO} \quad \text{CO} \\
\end{align*}\]

Scheme 1.59. Terminal methylidyne and non-classical bridging vinylidene complexes via fluoride mediated desilylation of silylmethylidyines \((M = \text{Mo, W})\).

The dimeric complexes display four band CO patterns in their infrared spectrum whilst NMR spectroscopy reveals the bridging carbide carbon resonance at \(\Delta\varepsilon\) 346.7 \((M = \text{Mo})\) or 304.4 \((M = \text{W})\), consistent with a vinylidene-like carbide centre.\(^{121}\) Electrochemical studies reveal that the W and Mo vinylidene complexes are readily oxidized.\(^{89}\)

In contrast to the situation with aryloxy nucleophiles, the cationic carbyne in \([\text{W}(=\text{CPMe}_3)(\text{CO})_2\text{Tp}^*][\text{PF}_6]\) reacts with nucleophiles such as MeLi or \([\text{KHB(Oi-Pr)}_3]\) at the carbyne carbon to form neutral substituted phosphoniocarbene complexes, \([\text{W}(-\text{C(Me)(PMMe}_3)\text{(CO)}_2\text{Tp}^*])\) or \([\text{W}(-\text{CH}(\text{PMMe}_3)\text{(CO)}_2\text{Tp}^*])\), respectively.\(^{72}\) Addition of excess Na[HBEt\(_3\)] to neutral \([\text{W}(=\text{CH}(\text{PMMe}_3)\text{(CO)}_2\text{Tp}^*])\) generates the electronically similar anionic methylidyene complex Na[\([\text{W}(=\text{CH}_2)\text{(CO)}_2\text{Tp}^*])\], which whilst not isolated, is nevertheless a valuable synthetic intermediate.\(^{68}\) An ensuing reaction with PhSSPh proceeds via formal addition of SPh\(^+\) to the methylidyne to form the saturated tungsten product \([\text{W}(\eta^2-\text{CH}_2\text{SPh})(\text{CO})_2\text{Tp}^*])\), which is bound to the metal through both the carbon and the sulfur atoms.\(^{68}\) In contrast, when \([\text{W}(=\text{C}_8\text{PMe}_2\text{Ph})(\text{CO})_2\text{Tp}^*][\text{PF}_6]\) reacts with Grignard reagents \([\text{RCH}_2\text{MgCl}]) (R = \text{Ph, CH} = \text{CH}_2\), nucleophilic displacement of phosphine occurs at C\(_\alpha\) to generate the intermediate zwitterionic carbene complexes \([\text{W}(=\text{C}(\text{CH}_2R)(\text{PMe}_2\text{Ph}))\text{(CO)}_2\text{Tp}^*])\) that lose phosphine to form \([\text{W}(=\text{CCH}_2R)(\text{CO})_2\text{Tp}^*])\).\(^{122}\)
CHAPTER 1. ALKYLDYNE COMPLEXES LIGATED BY POLYPYRAZOLYL BORATES

55

Scheme 1.60. Derivatisation of carbyne complexes, \([W] = W(CO)_2Tp^*\).

Deprotonation of the alkyl carbynes \([M=\{CCH_2R\}(CO)_2Tp^*]\) with \(n\)-BuLi or KOt-Bu at \(C_\beta\) forms synthetically versatile vinylidene anions \([W=\{C=CHR\}(CO)_2Tp^*]\) (R = H, Ph, CH=CH_2, Scheme 1.60) which add electrophiles, \(E^+\), primarily at \(C_\beta\) allowing access to elaborated alkyl carbynes \([W=\{CCHRE\}(CO)_2Tp^*]\) (R = H, E = Me, CH_2Ph, R = Ph, CH=CH_2, E = Me, Scheme 1.60). Subsequent deprotonation and alkylation \((E')\) is again possible, leading to the more highly substituted carbynes \([W=\{CCMeEE'\}(CO)_2Tp^*]\).

Due to resonance stabilisation, the vinylvinylidene anions \([W=\{C=CMeCH=CH_2\}(CO)_2Tp^*]\) (R = H, Me) can react with electrophiles at either \(C_\eta\) or \(C_\delta\). Alkylation at \(C_\beta\) is favoured but a small amount of alkylation occurs at \(C_\delta\) for R = Me, perhaps due to steric crowding at \(C_\beta\), which generates \(E\) and \(Z\) isomers of the conjugated vinylcarbyne \([W=\{CCMe=CHCH_2R\}(CO)_2Tp^*]\). By quenching a tetrahydrofuran solution of the anion \([W=\{C=CMMe=CH=CH_2\}(CO)_2Tp^*]\) (R = Me, H), vinylcarbyne complexes of the type \([W=\{CC(R)=C(H)Me\}(CO)_2Tp^*}\] may be obtained selectively as a mixture of \(E\) and \(Z\) isomers. Formation of the \(E\) isomer (in which the \('C=W(CO)_2Tp^*\) unit is trans to the substituent on \(C_\delta\)) is favoured, presumably due to unfavourable steric interactions in the \(Z\) isomer.

Addition of Et_3N promotes isomerisation of the allyl carbyne complex \([W=\{CCH_2CH=CH_2\}-\text{(CO)}_2Tp^*]\) to the conjugated vinyl carbyne isomer \([W=\{CCH=CHMe\}(CO)_2Tp^*}\].
Aldehydes and ketones can also be used as electrophiles in reactions with the vinylidene anion \([M(=C=CH_2)(CO)_2Tp^*]^-\). Low temperature reaction of \([M(=C=CH_2)(CO)_2Tp^*]^-\) with \(RR'C=O\) (\(R = \text{Ph}, \text{n-Pr}, R' = \text{H}; R = \text{Ph}, R' = \text{Me}\)) followed by protonation yields \([W\{=CCH_2(OH)\cdot(R)(R')\}(CO)_2Tp^*]^-\). When \(R = \text{Ph}\) and \(R' = \text{H}\), one equivalent of base leads to deprotonation and hydroxide elimination to form the conjugated vinyl carbyne complex \([W\{=CCH=CH\text{Ph}\}(CO)_2Tp^*]\) in 53% yield; two equivalents of base produces a 1:1 mixture of the vinylcarbyne and the ethylidyne complex. With base, \([W\{=CCH_2(OH)\text{PhMe}\}(CO)_2Tp^*]\) simply regenerates the starting ethylidyne complex and ketone.

The reaction of the tungsten vinylidene anion \([W(=C=CH_2)(CO)_2Tp^*]^-\) with benzoyl chloride \((\text{PhC}(O)\text{Cl})\) and then base forms the ketone-containing carbyne \([W(=CCH\text{HC(O)Ph})(CO)_2Tp^*]\) (and ethylidyne complex in approximately 1:1 ratio) that rearranges in solution to a metallafuran complex \([W(=CH\text{HC(O)Ph})(CO)_2Tp^*]\). Spectroscopic data suggests that the dinuclear intermediate \([Tp^*\text{CO})_2W(=CCH\text{MeC(OH)CH}_2\text{C}=W(CO)_2Tp^*]\) is first formed before the addition of base produces the expected monomeric product \([W(=CCH_2\text{C(O)Ph})(CO)_2Tp^*]\).

The synthesis of the \(=C(CRR')_2\text{C}=\) bridged dimers \((R = \text{H}, R' = \text{H}, \text{Me}, \text{CH}_2\text{Ph})\) with metal–carbon triple bond anchors is accomplished via oxidative dimerisation of the anionic vinylidene compounds \([W(=C=CRR')(CO)_2Tp^*]\). Diastereomers (meso and dl pairs) arise from the methyl and benzyl derivatives. Stepwise deprotonation and oxidation of the \(=C(CRR')_2\text{C}=\) bis(carbynes) affords unsaturated bis(carbyne) complexes bridged by \(=CC(R')\text{Cl}=C(R')\text{CC}\) units (Scheme 1.61).

![Scheme 1.61. Oxidative coupling and dehydrogenation of anionic vinylidene complexes, \([M]\text{=M(CO)}_2\text{Tp^* (M = Mo or W.)}\)](image)

A crystal structure determination of \([Tp^*\text{CO})_2W=C\text{CM}e=C\text{CMe}=W(CO)_2Tp^*]\) reveals an inversion centre with a trans configuration of metal centres about the olefinic bridge.

The synthetically versatile anionic vinylvinylidene anion \([W(=C=CH\text{CH}=_2\text{C}_2\text{H}_2\text{(CO)}_2\text{Tp^*}]^-\) is capable of acting as a nucleophile towards heteroatom substituted carbynes. No reaction occurs at \(\text{C}_8\) with \([W(=\text{CCl})(CO)_2Tp^*]\), however the phosphoniocarbyne \([W(=\text{CPMe}_2\text{Ph})(CO)_2\text{Tp^*}]^-\)
add to C₈, forming a reactive zwitterionic phosphonium carbene intermediate that loses PMe₂Ph to form the dinuclear bis(carbene) C₅H₄-bridged compound \([\text{Tp}^*(\text{CO})_2\text{W}≡\text{CCH}_2\text{CH}≡\text{CH}≡\text{W}(\text{CO})_2\text{Tp}^*]\) as a 3.5:1 mixture of \(E\) and \(Z\) isomers in 56% yield (Scheme 1.62).\(^{122}\) The reaction pathway is analogous to that suggested for the synthesis of the monomeric methylidyne complex \([\text{W}(≡\text{CH})(\text{CO})_2\text{Tp}^*]\) via treatment of \([\text{W}(≡\text{CPPh}_3)(\text{CO})_2\text{Tp}^*]\)[PF₆] with Na[HBEt₃].\(^{68}\) Deprotonation at \(C_β\) of the resultant C₅H₄-bridged bimetallic complex forms the deep blue, anionic complex \([\text{Tp}^*(\text{CO})_2\text{W}≡\text{C}(\text{CH})_3\text{C}≡\text{W}(\text{CO})_2\text{Tp}^*]\), which has a conjugated \(π\)-system between the tungsten atoms. Spectroscopic data suggest that the dinuclear, anionic complex exists as a symmetrically allyl-bridged species in solution with a ‘\(\text{W}≡\text{C}(\text{CO})_2\text{Tp}^*\)’ moiety on each end.\(^{122}\)

\[
\begin{align*}
\text{W}≡\text{C} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{W}
\end{align*}
\]

\[
\begin{align*}
\text{[W]}≡\text{CPMe}_2\text{Ph}^+ & \quad \text{[W]}≡\text{CPMe}_2\text{Ph}^+ \\
\text{HCl (Et}_2\text{O)} & \quad \text{HCl (Et}_2\text{O)}
\end{align*}
\]

\[
\begin{align*}
\text{[W]}≡\text{C} & \quad \text{Z} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{E} & \quad \text{[W]} \\
\text{H}_2 & \quad \text{C} & \quad \text{=}[\text{W}] & \quad \text{[W]}
\end{align*}
\]

Scheme 1.62. Synthesis of the neutral C₅H₄-linked dinuclear carbyne complex.

The anionic vinylidene intermediate similarly acts as a nucleophile towards halocarbynes \([\text{M}≡\text{CX}(\text{CO})_2\text{Tp}^*]\) (\(X = \text{Br}, \text{Cl}\)) to produce \(≡\text{CCH}_2\text{C}≡\) bridged dimers via halide displacement.\(^{160}\) Stepwise deprotonation and alkylation of the methylene bridged biscarbonye molecules \([\text{M}]=\text{CCH}_2\text{C}≡\text{M}][\text{M}]\) yield the mono- or dimethylated products \([\text{Tp}^*(\text{CO})_2\text{W}≡\text{CCHMeC}=\text{Mo}(\text{CO})_2\text{Tp}^*]\) and \([\text{Tp}^*(\text{CO})_2\text{W}≡\text{CCMe}_2\text{C}=\text{Mo}(\text{CO})_2\text{Tp}^*].\(^{160}\) Electrochemical and aerial oxidation of the doubly deprotonated anion yields the C₅-bridged complexes \([\text{Tp}^*(\text{CO})_2\text{M}≡\text{CC}≡\text{CM(O)}_2\text{Tp}^*]\) (\(M = \text{Mo, W}\)) as well as the ketone complex \([\text{Tp}^*(\text{CO})_2\text{W}≡\text{CC}(=\text{O})\text{C}≡\text{Mo}(\text{CO})_2\text{Tp}^*].\(^{160}\)

The electrochemical behaviour of the bis(carbonye) complexes, \([\text{Tp}^*(\text{CO})_2\text{M}≡\text{(C}≡\text{H}_2)\text{M}(\text{CO})_2\text{Tp}^*]\) (\(M = \text{Mo, W}; m = 3, n = 2; m = 4, n = 0, 2, 4\)), was studied.\(^{161}\) These complexes exhibit two oxidation potentials between 0 and 0.5 V (vs ferrocene). Coupling in the three carbon saturated bridge is stronger than the saturated four carbon bridge, as expected for a decrease in the metal–metal distance, and is comparable to that observed for the \(≡\text{CCH}≡\text{CHC}≡\group\). The difference in \(E_{1/2}\) for the two oxidation waves is a function of the hydrocarbon spacer with the \(≡\text{CCH}≡\text{CC}≡\) spacers (\(m = 4, n = 0\)) exhibiting considerably larger \(ΔE_{1/2}\) values.
than the corresponding $=\text{CCH}=\text{CHC}=\text{C}$ spacers ($m = 4, n = 2$), which were in turn more strongly coupled than the saturated analogues ($m = 4, n = 4$). The tungsten complexes are easier to oxidize and show larger $\Delta E_{1/2}$ values than their molybdenum analogues. While the trend in electronic coupling was quantitatively as expected for the degree of unsaturation in the bridge, the absolute magnitude of the coupling as indicated by the comproportionation constants ($K_c = 100–104$) was much smaller than that in isologous dimers where the bridge is connected to the metal centres via single bonds ($K_c = 108–1012$). A qualitative model based on relevant orbital occupancy as a function of metal oxidation state was developed to account for the experimental results. It is suggested that the lower coupling in the bis(carbyne) systems is due primarily to a HOMO that is oriented orthogonal to the bis(carbyne) bridge.\(^{161}\)

The reaction of the anionic vinylidene $[\text{M}=(\text{C}=\text{CH})_2(\text{CO})_2\text{Tp}^*]$ with $[\text{W}(\text{PhC}=\text{CPh})\text{l}(\text{CO})\text{Tp}]$ proceeds via displacement of iodide and yields the dinuclear $[\text{Tp}^*(\text{CO})_2\text{M}=\text{CCH}_2\text{W(PhC}=\text{CPh})-(\text{CO})\text{Tp}]$ ($\text{M} = \text{Mo}, \text{W}$) containing an unsymmetrical $\text{C}_2\text{H}_2$ bridge composed of a carbyne moiety and a methylene group (Scheme 1.63).\(^{162}\)

\[
\begin{align*}
\text{Scheme 1.63. Synthesis of a CCH}_2\text{ hydrocarbon bridge between metal centres (M = Mo, W).}
\end{align*}
\]

Removal of the methylene protons and subsequent oxidation leads to net hydrogen removal and yields the $C_2$-bridged bis(carbyne) dimers $[\text{Tp}^*(\text{CO})_2\text{M}=\text{C}=\text{W(PhC}=\text{CPh})-(\text{CO})\text{Tp}]$ ($\text{M} = \text{Mo}, \text{W}$) in good yields.\(^{162}\) Conversion of the $W$–C single bond in the precursor complex to a triple bond in the product is accompanied by retraction of the alkyne from a four- to a two-electron donor role.\(^{162}\)

Dewhurst has reported the fluoride-mediated protodesilylation of silylated propargylidyynes in the presence of rhodium,\(^{163}\) ruthenium,\(^{164}\) iridium,\(^{165}\) gold\(^{166}\) and mercury\(^{167}\) complexes to provide a range of $C_3$-spanned heterobi- and trimetallic complexes.

Desilylation of the silylpropargylidyynes $[\text{W}(=\text{CC}=\text{CSiMe}_3)(\text{CO})_2\text{Tp}^*]$ ($\text{Tp}^* = \text{Tp}, \text{Tp}^*$) with $[\text{Bu}_4\text{N}]\text{F}$ produces in situ both the terminal propargylidyynes $[\text{W}(=\text{CC}=\text{CH})(\text{CO})_2\text{Tp}^*]$ and their conjugate base, due to the water present in commercial tetrabutylammonium fluoride (Scheme 1.64). The $C_3$-spanned heterobimetallics $[\text{Ru}\{\text{C}=\text{CC}=\text{W(}\text{CO})_2\text{Tp}\}_1\text{H(}\text{CO})(\text{PPh}_3)_2(\text{L})\}]^{164}$ ($\text{Tp}^* = \text{Tp}, \text{Tp}^*$; $\text{L} = \text{CO}, \text{Hpz}^*, \text{PPh}_3$) and $[\text{Rh}\{\text{C}=\text{CC}=\text{W(}\text{CO})_2\text{Tp}\}_1\text{CO}(\text{PPh}_3)_2]^{164}$ are produced in modest yields via oxidative addition of $[\text{W}(=\text{CC}=\text{CH})(\text{CO})_2\text{Tp}^*]$ to $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2]$ or
halide metathesis of the nucleophilic anion \[W(\equiv C\equiv C)(CO)\_2Tpx^+\] with \[\text{[RuHCl(CO)(L')(PPh\_3)] \ (L' = Hpz*, PPh\_3)}\] or \[\text{[RhCl(CO)(PPh\_3)]}\].\(^{163}\) The metal centres containing the \(\sigma\)-bonded \(W(\equiv C\equiv C)(CO)\_2Tpx^+\) undergo typical ligand substitution and oxidative addition reactions\(^{163}\) and the coordinatively saturated rhodium complex \[\text{[Rh\{C\equiv C=W(CO)\_2Tpx\}\_2(PPh\_3)]}\] has been crystallographically characterised.\(^{163}\)

Fluoride-mediated desilylation of \[W(\equiv C\equiv C\equiv SiMe\_3)(CO)\_2Tpx^+\] in the presence of Vaska’s complex \[\text{[IrCl(CO)(PPh\_3)]}\] or half an equivalent of mercuric chloride proceeds to provide the first bis(tricarbido) trimetallic complexes \[\text{[Ir\{C\equiv C=W(CO)\_2Tpx\}_2H(CO)(PPh\_3)]}\] and \[\text{[Hg\{C\equiv C=W(CO)\_2Tpx\}_2]}\].\(^{167}\)

![Scheme 1.64. Fluoride-mediated desilylation of \(Tpx^+\) silylpropargylidynes.](image)

In the presence of \(\text{AuCl(PPh\_3)}\), the neutral tricarbido complexes \[W(\equiv C\equiv CAuPPh\_3)(CO)\_2Tpx^+\] are obtained in addition to formation of traces of the bis(tricarbido)aurates \[\text{[Bu\_4NF][Au\{C\equiv C=W(CO)\_2Tpx^+\}_2]}\].\(^{166}\) The corresponding salt \[\text{[(PPh\_3)\_2N][Au\{C\equiv C=W(CO)\_2Tpx^+\}_2]}\] may be obtained in high yield via propargylidyne desilylation with methanolic KOH in the presence of \(\text{AuCl(SMe\_2)}\) and subsequent salt metathesis with \[\text{[N(PPh\_3)]Cl}\].\(^{166}\) Spectroscopic data for the salt show that the \(\nu_{CO}\) stretches are shifted to lower frequency than for the neutral complex. The crystal structure of \[\text{[(PPh\_3)\_2N][Au\{C\equiv C=W(CO)\_2Tpx^+\}_2]}\] confirms the essentially linear bis(carbido)aurate structure.\(^{166}\)
In the neutral complexes, the tungsten–carbonyl absorptions are lowered by replacement of the SiMe₃ substituent with the iridium(III) or Au(I) centres (ca. 40 and 15 cm⁻¹, respectively), but replacement with Hg does not give rise to a discernible shift in the νCO values, presumably reflecting the d⁹ closed shell configuration of mercury(II).¹⁶⁷¹³C{¹H} NMR chemical shifts of the bridging carbon nuclei and crystallographic characterisation of the C₃-bridged polymetallic complexes point to a localised M(C=CC=W)ₙ (n = 1 or 2) valence bond description along the near linear M(C₃=W)ₙ spines.¹⁶³⁻¹⁶⁷

Demercuration of the bis(tricarbido)mercurials [Hg{C=CC=W(CO)₂Tp*}₂] (Tp* = Tp, Tp*) occurs with one equivalent of cis-[PtCl₂(PPh₃)₂] or a catalytic amount of [RhCl(CO)(PPh₃)₃]₂, resulting in alkynyl coupling to provide the dimetallaoctatetra-1,3,5,7-ynes [Tp³(CO)₃W=CC=CC=CC=W(CO)₂Tp*] in good yields.¹⁶⁸ Demercuration with the rhodium complex is proposed to proceed via addition of a Hg–C bond followed by extrusion of elemental mercury to provide a cis-bis(alkynyl) rhodium(III) intermediate that reductively eliminates the diyne group.¹⁶⁹ The C₃ and C₇ resonances are found at much higher field (δ: C₃ 96.2, C₇ 58.6) than those of the corresponding mercurial complex (δ: C₃ 120.5, C₇ 106.4). The alkylidyne carbon nuclei, however, are comparatively insensitive to changes in substitution at C₇. A crystal structure confirmed the WC₆W connectivity.¹⁶⁸

**1.4.4 The heteroatom substituent**

Neutral carbynes generally react at either the carbyne carbon atom or the metal centre. However, the phospha- and arsalkeny-substituted carbynes exhibit nucleophilicity at the heteroatoms of their carbyne substituents. Alkylation (MeO₂SCF₃) occurs at the phosphorus and arsenic atoms to produce the salts [M≡CXMeC(NR₂)₂(CO)₂Tp*][O₂SCF₃] (X = P, As) in good yields.⁸⁸ The alkylation of the heteroatom is accompanied by strong shielding of the carbyne carbon atom and a significant decrease in s-orbital contribution to the M≡C–X bond.⁸⁸

Protonation similarly occurs at the phosphorus atom to give [W≡CPHC(NEt₂)₂(CO)₂Tp*]⁺, which undergoes facile rearrangement to the metallaphosphirene [W≡CHPC(NEt₂)₂(CO)₂Tp*]⁺, thereby adopting η²-bonding to the metal centre via the phosphorus and carbon atoms (Scheme 1.65).¹¹¹ Protonation of the corresponding arsenic analogues does not, however, lead to tractable products.⁸⁸ Facile oxidation with dioxygen at the phosphorus atom cleanly affords the orange carbyne complexes [M≡CP(O)₂C(NR₂)₂]- (CO)₂Tp*], which are functionalised at the methyldyne with an α-carbenium phosphinate substituent.¹⁷⁰
CHAPTER 1. ALKYLIDYNE COMPLEXES LIGATED BY POLYPYRAZOLYLBORATES

1. ALKYLIDYNE COMPLEXES LIGATED BY POLYPYRAZOLYLBORATES

Scheme 1.65. Reactivity of phospha- and arsaalkenyl alkylidyne complexes, \([M] = M(CO)_2\text{Tp}^*\), \(M = \text{Mo}, W\) \((E = \text{As}, R = \text{Me}, M = \text{Mo, W}; E = \text{P}, R = \text{Me, Et}; X = \text{BF}_4, \text{O}_3\text{SCF}_3)\).

Reaction of \([M\{\equiv\text{C}(\text{NR}_2)\}_2\}\text{CO}\text{Tp}^*\) with two molar equivalents of \(\text{AuCl(CO)}\) affords the trinuclear complex \([M\{\equiv\text{C}(\text{AuCl})\text{C}(\text{NR}_2)\}_2\}\text{CO}\text{Tp}^*\), in which the phosphorus atom of the carbyne substituent acts as donor to gold.\(^{110}\) Ligation of the two ‘\(\text{AuCl}^\cdot\)’ fragments via the phosphorus atoms exerts a significant electron-withdrawal from the ‘\(\text{M(CO)}_2^\cdot\)’ fragment and the resultant shift to higher energy of the \(v_{\text{CO}}\) bands (by ca. 50–60 cm\(^{-1}\)) is attended by high field shifts for the \(^{13}\text{C}\) nuclei of the carbyne ligand. A similar reaction with the arsenic analogue \([M\{\equiv\text{CAs}(\text{NMe}_2)\}_2\}\text{CO}\text{Tp}^*\) gives rise to As=C cleavage with resultant formation of the gold carbene complex \(\text{Au}_{2}\{\text{C(NMe}_2)\}_2\) and the functionalised cyclotriarsane \([\{M\{\equiv\text{CAs}\}\text{CO}\text{Tp}^*\}_2\}\) (Scheme 1.66).\(^{110}\) Spectroscopic evidence is consistent with the presence of a cyclotriarsane ring in which two metal–carbyne substituents are in a cis-disposition and the remaining one is on the opposite face of the ring. Formation of the cyclotriarsane ring decreased the \(\sigma\)-donor/\(\pi\)-acceptor capacity of the cyclotriarsane–triscarbyne ligand.\(^{110}\)

Scheme 1.66. \(\eta^1\)-Ligation vs pnictogen–carbon bond cleavage, \([M] = M(CO)_2\text{Tp}^*\), \(M = \text{Mo, W}\).

The increased reactivity of the arsaalkene with respect to the phosphaalkene may be due to a decreased HOMO/LUMO energy gap in the former case and the general decrease in C–As vs C–P bond strengths in analogous compounds.\(^{110}\)
[W(=COMe)(CO)₂Tp*] also reacts at the heteroatom substituent of the carbyne with nucleophiles attacking the Me group of the methoxide substituent, delivering Me⁺ and generating [W(CO)₂Tp*]⁻ via an S₈N₂ reaction.⁷⁹ The reactivity of the methoxycarbyne complex [W(=COMe)(CO)₂Tp*] differs from the reactivity of the methylthiocarbyne species [W(=CSMe)(CO)₂Tp*], which reacts with phosphines at the carbyne carbon to undergo nucleophilic displacement of the methylthiolate substituent to produce phosphonocarbyne compounds.⁷² The otherwise close structural similarities suggest that the difference in reactivity is due to the electronic differences between oxygen and sulfur.⁷⁹

The bimetallic complex [Mo{≡CFe(CO)₂Cp⁺}(CO)₂Tp*] undergoes photolytic insertion of CS₂ into the C–Fe bond with loss of one CO at Fe to form the dithiocarboxylate derivative which is chelated to iron in the product [Mo{≡CCS₂Fe(CO)Cp⁺}(CO)₂Tp*].⁷¹ Photolytic substitution of both CO ligands at Fe forms [Mo{≡CFe(L')₂Cp⁺}(CO)₂Tp*] derivatives (L' = PMe₃, CNt-Bu). These substitutions are accompanied by lowered frequency of the CO absorptions and the very low field carbide chemical shifts (> 450 ppm) in the ¹³C{¹H} NMR spectra.⁷¹

### 1.4.5 The poly(pyrazolyl)borate ligand

Whilst they are commonly employed as robust molecular scaffolds the poly(pyrazolyl) borate ligands are not always innocent. An unusual reaction occurs during the sequential treatment of [W(=CR)Br(CO)₃] (R = C₆H₄Me-4) with sulfur and K[Bp] to provide [W(κ²-S₂CR)(CO)₂-HB(pz)₂(SCH₂R)] (a, Chart 1.5) via reduction of the alkylidyne–tungsten linkage.¹⁵¹ The intermediacy of a thioacyl species is suggested en route to the bis(pyrazolyl)thiolatoborate complex and isolated examples have since followed this postulate.⁴⁸,¹⁵⁴

![Chart 1.5. Examples of unusual poly(pyrazolyl)borate ligands](image)

A second example involves the imido and oxo complexes [W(≡CHPh)Br(X)Tp] (X = Nt-Bu, N-1-adamantyl, N-C₆H₃Me₂-2,6, O) that are prepared from dihalocarbyne complexes and primary amines or water.¹³⁵ Subsequent oxidation of these alkylidenes with bromine produces a highly reactive, electron-deficient alkylidyne ligand which undergoes insertion into a σ-W–N bond of the tungsten tris(pyrazolyl)borate cage, affording complexes
[W\{κ³-H\{pz\}_2\{(C\textsubscript{6}H\textsubscript{3}N\textsubscript{2}C\textsubscript{6}H\textsubscript{5})\}Br\textsubscript{3}(X)\}] (b, Chart 1.5) via formal insertion of an alkylidyne group into the tungsten–(pyrazolyl nitrogen) bond. The \(^{13}\text{C}\{^{1}\text{H}\} NMR spectra show resonances in the range \(\delta\) 250–260 due to the former benzylidene carbons, which indicates the retention of a degree of multiple bonding with the metal centre.\(^{135}\) The crystal structures of two compounds of this type (\(X = N\text{-1-adamantyl and } X = O\)) were determined by X-ray crystallography, displaying unusual geometric features due to the strained nature of the tris(pyrazolyl)borate-substituted alkylidyne ligand.\(^{131}\)

The characteristic propensity for bis(pyrazolyl) and bis(methimazolyl)borates (Bm) to enter into agostic B–H–M interactions has been investigated. In the case of bis(pyrazolyl)borates, all examples of alkylidyne complexes to date do not show such an interaction. Bis(methimazolyl)borates are however more prone to such interactions, as has been demonstrated with the isolation of \([\text{Mo}(=\text{CR})(\text{CO})\text{Bm}]\) \((\text{R} = \text{C}_6\text{H}_2\text{Me}_2, 2,4,6)\) from the reaction of \([\text{Mo}(=\text{CR})\text{X}(\text{CO})\text{Bm}])_2\) \((L = \text{py}, \text{Hpz*}; \text{X} = \text{Br}, \text{Cl})\) with Na[Bm]. Attempts to prepare the corresponding tungsten derivative led instead to the isolation of the bis(chelate) complex \([\text{W}(\text{CO})(\text{Bm})\text{Bm}])_2\] in which one Bm ligand is bidentate-S,S’ coordinated whilst the second adopts a tridentate \(\kappa^3\)-H,S,S’ coordination mode.\(^{171}\)

Treatment of the salts bearing the neutral tris(pyrazolyl)methane ligand HC\{pz\}_3\[\text{M}(=\text{CR})(\text{CO})\text{Bm}\{\text{HC}(\text{pz}\textsubscript{3})\}]\{\text{BF}_4\}\] \((\text{M} = \text{W}, \text{M}; \text{R} = \text{alkyl, aryl})\) with NaOEt or LiBu deprotonates the bridgehead carbon of the ligand. The pyrazolyl rings allows for delocalisation of the charge from the bridgehead onto the rings and subsequently on to the metal centre. Consequent reaction with Au(\text{C}_6\text{F}_5)/(tht) or BF\textsubscript{3}:Et\textsubscript{3}O affords the neutral alkylidyne metal compounds \([\text{M}(=\text{CR})(\text{CO})\text{Bm}\{\text{C}_6\text{F}_5\text{AuC}(\text{pz}\textsubscript{3})\}]\) \((\text{M} = \text{W}, \text{Mo, R} = \text{C}_6\text{H}_4\text{Me}-4; \text{M} = \text{W}, \text{R} = \text{Me, xylyl})\) or \([\text{W}(=\text{CR})(\text{CO})\text{Bm}\{\text{F}_3\text{B}\text{C}(\text{pz}\textsubscript{3})\}]\) \((\text{R} = \text{Me, C}_6\text{H}_4\text{Me}-4)\), respectively, bearing poly(pyrazolyl)methane ligands that are modified at the bridgehead carbon atom.\(^{117,118}\) \([\text{W}(=\text{CMe})(\text{CO})\text{Bm}\{\text{F}_3\text{B}\text{C}(\text{pz}\textsubscript{3})\}]\) may also be prepared in lower yield from the reaction between \([\text{W}(=\text{CMe})\text{Br(\text{CO})_3}]\) and Li\{\text{F}_3\text{B}\text{C}(\text{pz}\textsubscript{3})\} in tetrahydrofuran.\(^{118}\)

### 1.4.6 Bi- and polymetallic compounds

Bi- and polymetallic compounds were mentioned briefly in Sections 1.4.3 and 1.4.4. Stone’s recognition of the synthetic utility of the isolobal relationship between alkynes and the M–C triple bond of carbyne metal complexes led to use of the complexes \([\text{M}(=\text{CR})(\text{CO})\text{Cp}^*]\) \((\text{M} = \text{W, Mo or Cr; R} = \text{alkyl or aryl}; \text{Cp}^* = \text{Cp, Cp*})\) as precursors for the synthesis of compounds containing heteronuclear metal–metal bonds.\(^{172-174}\) The M=Cr group is capable of functioning as a ligand towards low-valent metal fragments providing bi- and trimetallic complexes with bridging alkylidyne ligands. Typically, the low-valent metal fragments contain
ligands (alkene, CO, MeCN) that are readily displaced by the more powerful ligating properties of the $\text{M}≡\text{C}$ groups which typically act as $\mu$-$\text{CR}$ or $\mu_2$-$\text{CR}$ ligands. The poly(pyrazolyl)borate anions play a stabilising role in metal–alkylidyne chemistry and have allowed significant extension of the chemistry of cluster compounds containing bridging Group 6 alkylidyynes and it is this chemistry with which Section 1.4.6 is concerned. The structures of the various products obtained are generally similar to those previously reported using the Cp alkylidyynes as precursors but important differences in reactivity between the poly(pyrazolyl)borate and cyclopentadienyl analogues arise. The ‘$\text{M}≡\text{CR}$Tp’ fragment is a superior $\sigma$-donor and weaker $\pi$-acceptor than the Cp analogue,\(^\text{175}\) and qualitatively the Tp complexes appear to be more reactive towards low-valent metal species due to an increased stability of the products.\(^\text{40}\) The nature of the compounds containing heteronuclear metal–metal bonds formed from the Bp ligated alkylidyynes are generally similar to those previously prepared from the Tp analogues.\(^\text{46}\) Angelici’s thiocarbyne [W(≡CSMe)(CO)$_2$Tp] also forms heteronuclear complexes similar to those formed by the analogous alkyl and aryl carbynes ($R = \text{Me}, \text{C}_6\text{H}_4\text{Me}-4$), however, the latter appear to act as better ligands in forming heteronuclear complexes.\(^\text{176}\)

**Nickel and Platinum**

A characteristic reaction occurs between the platinum complex [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] and [W($\equiv$CR)(CO)$_2$Tp] (R = Me or C$_6$H$_4$Me-4, Tp$^x$ = Tp;\(^\text{39,40}\) R = C$_6$H$_4$Me-4, Tp$^x$ = pzTp;\(^\text{39,40}\) R = SMe, Tp$^x$ = Tp, L$'$ = PMe$_3$; Scheme 1.67) via displacement of the alkene, forming platinum–tungsten bimetallic compounds of the general formula [WPt($\mu$-CR)(CO)$_2$(L$'$)(PMe$_3$)Tp] (L$'$ = PMe$_3$, CO).

Protonation of the bridging tolylmethylidyne complex [MoPt($\mu$-CR)(CO)$_2$(P(OMe)$_3$)$_2$Tp] (R = C$_6$H$_4$Me-4) with HBF$_4$·Et$_2$O forms the Mo–Pt salt [MoPt($\mu$-$\sigma$-$\eta^2$-CHR)(CO)$_2$(P(OMe)$_3$)$_2$-Tp][BF$_4$] (Scheme 1.67) but, due to its poorer $\pi$-acceptor and better $\sigma$-donor properties, the ethylidyne complex merely decomposes to release the carbyne under the same conditions, presumably via ethylidyne–ethene rearrangement.\(^\text{175}\)

![Scheme 1.67. General formation of alkylidyne and alkylidene bridged M–Pt bimetallic complexes.](attachment:image.png)
An alternative route to cationic bridged alkylidyne complexes \([\text{MPt}(\mu\text{-CRR'})\text{(CO)}_2\text{(PR}^3\text{)}_2\text{Tp}]^+\) involves the direct regioselective addition of a Pt–R bond from \([\text{trans-Pt}R'(\text{PR}^3\text{)}_2(\text{acetone})][X]\) \((R' = \text{H, Me, CH}=\text{CH}_2; \text{PR}^3 = \text{PET}_3, \text{PMe}_2\text{Ph}; X = \text{BF}_4, \text{CF}_3\text{SO}_3)\) across the M–C triple bond of the alkylidyne ligand in complexes of the type \([\text{M}==\text{CR(CO)}_2\text{Tp}]\) \((R = \text{Ph, 2-furyl, C}_6\text{H}_4\text{Me}-4, \text{Me}; \text{M} = \text{W, Mo, Scheme 1.68}).^{42}

![Scheme 1.68. Formation of \([\text{PtW}\{\mu\text{-C(H)Ph}\}(\text{CO})_2(\text{PET}_3)_2\text{Tp}]\text{[BF}_4\text{]}\).](image)

The dinuclear products typically have a bridging CO ligand (evidenced by a low frequency \(\nu_{\text{CO}}\) at ca. 1840 cm\(^{-1}\)) and \(\mu\)-\(\eta^1\),\(\eta^1\)-alkylidene ligands so that the tungsten atoms have an 18-electron configuration. The molecular structure determination of \([\text{WPt}\{\mu\text{-C(H)Ne}_2\}-(\text{CO})_2(\text{PET}_3)_2\text{Tp}]\text{[BF}_4\text{]}\) confirmed the \(\mu\)-\(\eta^1\),\(\eta^1\) coordination with the nitrogen atom of the bridging (diethylamino)methylidyne ligand coordinated to the tungsten centre. In solution, the binuclear benzylidene bridged complex exists as a mixture of major and minor isomers \((3:1)\), with only the major isomer (in which a PET\(_3\)/CO ligand exchange has occurred) being present in the solid state.\(^{42}\) The bridging ethylidyne complex which has a 16-electron count at the tungsten centre was not sufficiently stable to permit complete characterisation.\(^{42}\)

Reaction of the dicarbonyl carbynes with the electron-deficient platinum reagent \([\text{Pt}\{\text{P(OMe)}_3\}_2(\text{C}_2\text{H}_4)]\) gives extremely unstable complexes of the form \([\text{MPt}(\mu\text{-CR})-(\text{CO})_2\{\text{P(OMe)}_3\}_2\text{Tp}]\) \((M = \text{Cr, Mo, W, R = C}_6\text{H}_4\text{Me}-4; M = \text{W, R = Me})\) along with the trimetallic complexes \([\text{M}_2\text{Pt}(\mu\text{-CR}_2(\text{CO})_4\text{Tp}_2]\) (Scheme 1.69).\(^{175}\) The trimetallic species presumably arise from reaction of the initially formed bimetallic compound with a second \([\text{M}==\text{CR}(\text{CO})_2\text{Tp}]\) fragment, which functions as a better ligand towards platinum(0) than the tertiary phosphines.\(^{175}\) For reaction of \([\text{W}==(\text{CMe})(\text{CO})_2\text{Tp}]\) with \([\text{Pt}(\text{PR}^3)_2(\text{C}_2\text{H}_4)]\) \((R = \text{Me or}
Et) and [Pt(PCy3)(C2H4)2] only the trimetallic complexes [M2M'(μ-CMe)2(CO)Tp2] are obtained.\(^{175}\)

![Scheme 1.69](image)

**Scheme 1.69.** Reaction of Tp-alkylidyne complexes with unsaturated d\(^{10}\) complexes, ML\(_n\) = [Ni(cod)\(_2\)], [Pt(C2H4)(P(OMe)3)\(_2\)], [Pt(C2H4)\(_2\)] (R = C\(_6\)H\(_4\)Me-4, Me, SMc).

Trimetal compounds [M\(_2\)M'(μ-CR)\(_2\)(CO)\(_4\)Tp\(_2\)] (M = W, R = Me, M' = Ni or Pt,\(^{175}\) M = Mo, Cr W, R = C\(_6\)H\(_4\)Me-4, M' = Pt,\(^{175}\) M = W, R = SMe, M' = Pt\(^{175}\)) comprising bis(alkylidyne) ‘bow-tie’ structures also arise by treating [M≡CR(CO)\(_2\)Tp] with the zero-valent metal alkene complexes [M(alkene)\(_3\)] (M' = Ni, Pt; alkene = ethylene (n = 3) or cod (n = 2)) in a 2:1 ratio. The \(^{13}\)C{\(^1\)H} NMR spectra show resonances in the range ca. \(\delta\) 300–340 that are characteristic for alkylidyne carbon nuclei bridging a metal–metal bond. The Tp ligand stabilises the NiW\(_2\) species relative to the Cp group, being comparable to Cp\(^*\) ligated complexes. The ferrocenyl tethered bis(alkylidyne) species [Mo\(_2\)Fe(μ-σ,σ':η\(^5\)-CC\(_6\)H\(_4\))\(_2\)(CO)\(_4\)Tp\(_2\)] reacts with [Pt(cod)\(_2\)] in a 1:1 ratio to yield the crystallographically characterised tetranuclear metal complex [Mo\(_2\)FePt(μ-σ,σ':η\(^5\)-CC\(_6\)H\(_4\))\(_2\)(CO)\(_4\)Tp\(_2\)].\(^{55}\)

X-ray diffraction studies of the bis(alkylidyne) ‘bow-tie’ structures typically show that the molecules have essentially linear M–M'–M spines with the two metal–metal bonds each bridged by an alkylidyne ligand and semi-bridged by a CO group. The two alkylidyne fragments lie on the same side of the M–M'–M axis.\(^{55,175}\) The disposition of the edge-bridging alkylidyne groups is such that the two dimetallacyclopropene rings which share a common vertex (M') are close to 90° with respect to one another.\(^{53}\) For the ferrocenyl tethered tetranuclear species, this angle is expanded to 140° due to constraints imposed by the ferrocene fragment.\(^{55}\)

The analogous Bp complexes [WPt(μ-CR)(CO)\(_3\)(cod)Bp] and [W\(_2\)M(μ-CR)(CO)\(_6\)Bp\(_2\)] (M = Ni or Pt, R = C\(_6\)H\(_4\)Me-4; M = Pt, R = Me) have been synthesised by treating the appropriate alkylidyne tungsten compound with [M(cod)\(_2\)] (M = Ni or Pt, Scheme 1.70).\(^{46}\) The reaction of [W≡CR(CO)\(_3\)Bp] with zero-valent [Pt(cod)\(_2\)] yields the bimetallic species [WPt(μ-
CR(CO)3(cod)Bp (R = C₆H₄Me-4). Subsequent reaction with PMe₃ or a second equivalent of alkylidyne displaces the cod to generate [W Pt(μ-CR)(CO)3(PMe₃)₂Bp] (which can also be prepared directly by reaction with [Pt(PMe₃)₂(C₂H₄)] or the trimetal complex [W₂Pt(μ-CR)₂(CO)₆Bp₂] (which can also be obtained by treating two equivalents of the alkylidyne with [Pt(cod)₂]), respectively. The trimetallic nickel complexes are similarly prepared.

Formation of the bimetallic species from the [Pt(cod)₂] starting material is unusual given that the analogous [W(≡CR)(CO)₂Cp'] (R = alkyl or aryl; Cp' = Cp or Cp*) and [W(≡CR)(CO)₂Tp] complexes always react to produce the trimetallic PtW₂ species, even if reactants are employed in a 1:1 ratio. Facile disproportionation of the Bp bimetallics in solution does, however, provide the trimetallic W₂Pt complexes.

Reaction of Angelici’s thiocarbyne [W(≡CSMe)(CO)₂Tp] with the Ni(I) dimer [Ni(CO)Cp]₂ generates the expected trinuclear metal complex containing a Ni₂W triangle [WNi₂(μ₃-CSMe)(CO)₂Cp₂Tp] (Scheme 1.71). The two infrared stretches evident at 1875 and 1806 cm⁻¹ are consistent with a semi-bridging functionality for the tungsten-carbonyls.

**Scheme 1.70.** Reaction of Bp-alkylidyne complexes with unsaturated d¹⁰ complexes, MLₙ = [Pt(cod)₂], [Ni(cod)₂] (R = C₆H₄Me-4, Me).

**Scheme 1.71.** Synthesis of a tungsten dinickel cluster.
Gold

The bi- and trimetallic tungsten–gold compounds [WAu(µ-CMe)(CO)\textsubscript{2}(PPh\textsubscript{3})Tp][PF\textsubscript{6}] and [W\textsubscript{2}Au(µ-CMe)\textsubscript{2}(CO)\textsubscript{4}Tp\textsubscript{2}][PF\textsubscript{6}] are prepared by treating [W(≡CMe)(CO)\textsubscript{2}Tp] with AuCl(L')(L' = PPh\textsubscript{3} or tht, respectively) in the presence of Tl[PF\textsubscript{6}] (Scheme 1.72).

The bimetallic complex displayed a \textsuperscript{13}C\textsubscript{\{H\}} NMR resonance for the µ-C at δ\textsubscript{C} 280.8, which is appreciably less deshielded than expected if the alkyldyne ligand were fully bridging the metal–metal bond. The Tp ligand focuses electron density at the tungsten, which increases the stability of this complex compared with the Cp analogue that readily disproportionates in solution to give [W\textsubscript{2}Au(µ-CMe)\textsubscript{2}(CO)\textsubscript{4}Cp\textsubscript{2}][PF\textsubscript{6}] and [Au(PPh\textsubscript{3})\textsubscript{2}][PF\textsubscript{6}].

The neutral alkyldyne metal compound [W(≡CMe)\textsubscript{2}(C\textsubscript{6}F\textsubscript{5})AuC(pz)\textsubscript{3}][CO\textsubscript{2}] reacts with Au(X)(tht) (X = Cl or C\textsubscript{6}F\textsubscript{5}) to afford neutral bimetallic species [WAu(µ-CMe)X(CO)\textsubscript{2}(C\textsubscript{6}F\textsubscript{5})AuC(pz)\textsubscript{3}] that retain the anionic ligand on the gold centre. The µ-C resonance for X = Cl (δ\textsubscript{C} 280.8) is again indicative of little perturbation of the W≡C group upon ligation of the AuX group.

In the formation of the trimetallic gold compounds [W\textsubscript{2}Au(µ-CMe)\textsubscript{2}(CO)\textsubscript{4}Tp\textsubscript{2}][PF\textsubscript{6}], which are analogous to the copper, silver, and gold salts [W\textsubscript{2}M(µ-CR)\textsubscript{2}(CO)\textsubscript{4}Cp\textsubscript{2}][X] previously reported (R = C\textsubscript{6}H\textsubscript{4}Me-4; M = Cu or Au, X = PF\textsubscript{6}; M = Ag, X = BF\textsubscript{4}), from AuCl(tht), the weakly coordinated tetrahydrothiophene is readily displaced by a second [W(≡CR)(CO)\textsubscript{2}Tp] \textsubscript{2}fragment that acts as better donor towards Au(I) than tht (but poorer than PPh\textsubscript{3}). The resonance for the bridging carbyne nucleus in the \textsuperscript{13}C\textsubscript{\{H\}} NMR occurs at δ\textsubscript{C} 277.8, which is approximately 20 ppm upfield of its toluidyne Cp analogue (δ\textsubscript{C} 295.8). Both carbonyl ligands are terminally bound to the tungsten atoms, in contrast to the Ni and Pt complexes discussed above in which there are two strongly semi-bridging carbonyl groups present.
Cobalt

Octacarbonyldicobalt and the alkylidyne molybdenum or alkylidyne tungsten Tp complexes react to afford a family of species of the type [MCo$_2$(µ$_3$-CR)(CO)$_8$Tp] ($M = W$, $R = Me$ or $C_6H_4Me-4$, $T_p = Tp$; $R = C_6H_4Me-4$, $T_p = pzTp$) with a trimetallatetrahedrane, µ-CMCo$_2$ core (Scheme 1.73). The cobalt octacarbonyl reaction providing the analogous Bp-ligated clusters [WC$_2$(µ$_3$-CR)(CO)$_9$Bp] ($R = C_6H_4Me-4$) proceeds in a similar manner as for the Tp analogues. [Mo{$CN$(i-Pr)$_2$}(CO)$_2$Tp], however, fails to react with [Co$_2$(CO)$_8$]. The Tp dicobalt–tungsten complexes, like their Cp analogues, exhibit rotational isomerism with respect to the ‘W(CO)$_2$Tp’ fragment above the CCo$_2$ plane.\(^\text{40}\)

![Scheme 1.73](image)

For alkynyl carbynes [M(≡CC≡CR)(CO)$_2$L] ($L = Tp$, Cp), two reactive sites are available for reaction with cobalt octacarbonyl. Treatment of the cyclopentadienyl complexes [M(≡CC≡Ct-Bu)(CO)$_2$Cp] with [Co$_2$(CO)$_8$] in light petroleum gives the trimetallatetrahedrane clusters [MCo$_2$(µ$_3$-CC≡Ct-Bu)(CO)$_8$Cp] ($M = Mo$ or $W$) in quantitative yield, structurally akin to the products obtained when $R = alkyl$ or aryl (Scheme 1.74). In contrast, reaction of [M(≡CC≡Ct-Bu)(CO)$_2$Tp] (Tp/W and Tp*/Mo) with [Co$_2$(CO)$_8$] afford, respectively, the µ-alkyne trimetal compounds [Co$_2$(µ-t-BuC$_2$C≡M(CO)$_2$Tp*)(CO)$_8$] ($M = W$, $T_p = Tp$; $M = Mo$, $T_p = Tp*$).\(^\text{52}\) The more bulky hydrotris(pyrazolyl)borate ligands reduce the reactivity of the alkylidyne M≡C bond, instead favouring reactivity at the unsaturated organic linkage and retaining the M≡C bonds (evident in the $^{13}$C-$^1$H NMR spectra by a resonance for $C_\alpha$ ca. 15 ppm downfield of that of the precursor). Treatment of the µ-alkyne trimetal compounds with dppe produces the symmetrically phosphine bridged product via replacement of a CO ligand on each Co metal centre.\(^\text{52}\)
CHAPTER 1. ALKYLYDENE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

1. ALKYLYDENE COMPLEXES LIGATED BY POLY(PYRAZOLYL)BORATES

Scheme 1.74. Reaction of propargyldiyne complexes with [Co$_2$(CO)$_8$], M = Mo or W.

Molybdenum

The metal alkylidyne complex [W(≡CMe)(CO)$_2$Tp] reacts with [Mo$_2$(CO)$_4$Cp$_2$] or [Mo(CO)$_3$(NCMe)$_3$] to afford the trimetal complexes [Mo$_2$W(µ$_3$-CMe)(CO)$_8$Cp$_2$Tp] and [MoW$_2$(µ-CMe)$_2$(µ-CO)$_3$(CO)$_4$Cp$_2$], respectively (Scheme 1.75). In the latter complex, one of the terminal carbonyl ligands of each tungsten centre is η$^2$-bound to the central molybdenum atom.

Scheme 1.75. Reaction of alkynylmethylidyne complexes with [Mo$_2$(CO)$_4$Cp$_2$] and [Mo(CO)$_3$(NCMe)$_3$].

For the alkynyl-substituted carbyne complexes [M(≡CC≡Ct-Bu)(CO)$_2$Tp], reaction with [Mo$_2$(CO)$_4$Cp$_2$] gives the µ-alkyne trimetal compound [Mo$_2${µ-t-BuCt-Bu≡C(W(CO)$_2$)Tp}$]$(CO)$_4$Cp$_2$] via addition across the organic C≡C rather than the M≡C bond due to steric shielding of the latter by the Tp ligands. The [Mo$_2${µ-t-BuCt-Bu≡C(W(CO)$_2$)Tp}$]$(CO)$_4$Cp$_2$] complex is structurally akin to the complex obtained with cobalt octacarbonyl (Scheme 1.74), but with the C≡C unit transversely bridging a Mo–Mo bond rather than a Co–Co linkage. Contrastingly, [W(≡CC≡Ct-Bu)(CO)$_2$Cp] reacts with the dimolybdenum reagent to give the trimetallatetrahedrane cluster [Mo$_2$W(µ$_3$-C≡Ct-Bu)(CO)$_8$Cp$_2$]. The $^{13}$C{°H} NMR spectrum of the complex [Mo$_2${µ-t-BuCt-Bu≡C(W(CO)$_2$)Tp}$]$(CO)$_4$Cp$_2$] shows a deshielded peak with tungsten coupling at $\delta$: 273.1, which unambiguously indicates that the compound possesses an intact
CHAPTER 1. ALKYLIDYNE COMPLEXES Ligated By POLY(PYRAZOLYLBORATES)

W≡C group that is unattached to another dimetal–ligand fragment. The molecule undergoes a dynamic process in solution,\(^{52}\) which is akin to the behaviour of other \(\mu\)-alkyne–dimolybdenum compounds.\(^{182,183}\)

**Rhodium**

The pyrazolylborate complexes \([W(=CR)(CO)\_2Tp]^{\text{3}}\) (\(R = \text{Me or } C\_6H\_4\text{Me-4}\)) are less reactive towards the low-valent rhodium species than their Cp analogues, requiring more forcing conditions (i.e., higher temperatures and longer reaction times) for reactions to proceed.

Cationic dimetal complexes \([WRh(\mu-CR)(CO)\_2(L')\_2Tp][X]\) (\(R = \text{Me, } C\_6H\_4\text{Me-4}, L' = \text{PPh}_3\), \(X = \text{PF}_6\); \(R = \text{Me}, L' = \frac{1}{2} \text{cod, } X = \text{BF}_4\)) arise from treatment of \([W(=CR)(CO)\_2Tp]\) with \([\text{Rh(PPh}_3\text{)}_2(\text{cod})][\text{PF}_6]\) and \([\text{Rh(THF)}_2(\text{cod})][\text{BF}_4]\) (the latter generated in situ from \([\text{Rh}_2(\mu-\text{Cl})_2(\text{cod})_2]\) and \(\text{AgBF}_4\), Scheme 1.76).\(^{177}\)

![Scheme 1.76](image.png)

**Scheme 1.76.** Synthesis of bimetallic tungsten–rhodium complexes with bridging alkyldyne groups. \(R = C\_6H\_4\text{Me-4, Me; } L' = \text{PPh}_3, X = \text{PF}_6; L' = \frac{1}{2} \text{cod, } X = \text{BF}_4\).

In their infrared spectra, each compound shows two bands in the CO stretching region with an absorption at approximately 1800 cm\(^{-1}\) indicating the presence of a semi-bridging carbonyl. Characteristic \(\mu\)-C resonances are seen in the \(^{13}\)C\(\{^1\text{H}\}\) NMR spectrum at ca. \(\delta_c 340\). The somewhat deshielded position indicates that in these compounds the W≡C bond is acting as a four-electron donor to the rhodium centre, allowing it to attain a 16- rather than 14-electron count.\(^{177}\) The reaction with NaI affords the neutral, iodo-bridged complexes \([WRh(\mu-CMe)-(\mu-I)(\mu-CO)(CO)(L')\_2Tp]\) (\(L' = \text{PPh}_3\) or \(\frac{1}{2} \text{cod}\)). A low frequency infrared stretch (ca. 1760 cm\(^{-1}\)) suggests that one carbonyl ligand now fully bridges the W–Rh bond. The resonances for the \(\mu\)-C nuclei at \(\delta_c 303.7\) and 294.7, respectively, are significantly less deshielded than those of the corresponding cations, which is in accord with the electronic saturation of the metal centres.\(^{177}\)
The reaction of the salt [WRh(µ-CR)(CO)$_2$(PPh$_3$)$_2$Tp][PF$_6$] (R = C$_6$H$_4$Me-4) with hydride donors leads to decomposition (with some evidence of hydride attack at the boron ligand), in contrast to the Cp version in which reaction with hydride produces the neutral complex via attack at the bridging carbon atom. Similarly, reaction with molecular hydrogen produces an uncharacterisable product, not the dihydrido complex [WRh(µ-CR)H$_2$(CO)$_2$(PPh$_3$)$_2$Cp][PF$_6$] that is produced with the Cp analogue.$^{177}$


Reaction of the complexes [W(=CR)(CO)$_2$Tp] (R = C$_6$H$_4$Me-4, Me) with [Rh(C$_2$H$_4$)$_2$(η$^5$-C$_5$H$_5$)] in toluene at 60 °C gives the trimetallic species [WRh$_2$(µ$_3$-CR)(µ-CO)(CO)$_2$(η$^5$-C$_5$H$_5$)$_2$Tp] (Scheme 1.77).$^{39,40}$ For [W(=CR)(CO)$_2$Tp] (R = C$_6$H$_4$Me-4), the alkene displacement reaction provides a mixture of the bi- and trimetallic complexes [WRh(µ-CR)(CO)$_2$(η$^5$-C$_5$H$_5$)$_2$Tp] and [WRh$_2$(µ$_3$-CR)(µ-CO)(CO)$_2$(η$^5$-C$_5$H$_5$)$_2$Tp], respectively, the latter of which could also be prepared by heating the alkylidyne compound with [Rh(CO)$_2$(η$^5$-C$_5$H$_5$)] at 100 °C. The analogous Bp complexes [WRh$_2$(µ$_3$-CMe)(µ-CO)(CO)$_2$(η$^5$-C$_5$H$_5$)$_2$Bp] have been synthesised by treating the appropriate alkylidyne tungsten compound with [Rh(L')$_2$(η$^5$-C$_5$H$_5$)] (L' = CO or C$_2$H$_4$) in toluene at reflux.$^{46}$ A parallel reaction of the hetero-substituted carbyne [W(=CSMe)-(CO)$_2$Tp] with two equivalents of [Rh(CO)$_2$(η$^5$-C$_5$H$_5$)] in refluxing tetrahydrofuran affords the crystalline µ$_3$-carbyne [WRh$_2$(µ$_3$-CSMe)(µ-CO)(CO)$_2$(η$^5$-C$_5$H$_5$)$_2$Tp], with a Rh$_2$W triangular arrangement of atoms akin to that of the Ni$_2$W cluster arising from reaction with [CpNi(µ-CO)$_2$]. In the rhodium–tungsten complex, methyltriflate is capable of alkylating the sulfur of the µ$_3$-CSMe group to provide what might be described as a thioether stabilised carbido ligand.$^{176}$

![Scheme 1.77. Synthesis of Rh$_2$W complexes from Tp-alkylidyne complexes. R = C$_6$H$_4$Me-4, Me, SME. (i) [Rh(C$_2$H$_4$)$_2$(η$^5$-C$_5$H$_5$)]; (ii) [Rh(CO)$_2$(η$^5$-C$_5$H$_5$)].](image-url)
Iron

Diiron nonacarbonyl and the alkylidyne molybdenum or alkylidyne tungsten Tp complex react to afford a family of species [MFe(µ-CR)(CO)₅Tp] (M = W, R = Me, C₆H₄Me-4; M = Mo, R = C₆H₄Me-4), with an unsaturated 32-valence electron count in which the M=C bond functions as a four-electron donor to iron. Treatment of [Mo(≡CR)(CO)₂Tp] (R = C₆H₄Me-4) initially gives a mixture of [MoFe(µ-CR)(CO)₆Tp] (n = 5 and 6, respectively), but the saturated molybdenum complex readily loses CO under N₂. The parallel reaction between bis(pyrazolyl)borate alkylidyne complexes and [Fe₂(CO)₉] similarly provides the 32-valence electron dimetal species [WFe(µ-CR)(CO)₆Bp]. These heteronuclear bimetallic complexes have a rich further chemistry, as summarised in Scheme 1.78.

Scheme 1.78. Synthesis and reactions of [LnMFe(µ-CR)] complexes (M = Mo or W; R = alkyl or aryl; Ln = (CO)₃₋₂Tp; Tp = Tp, n = 3 or Tp = Bp, n = 4).

Infrared spectra of the unsaturated heteronuclear tris(pyrazolyl)borate M–Fe complexes typically show five carbonyl associated bands, with a low frequency stretch (ca.1860 cm⁻¹) being characteristic of a semi-bridging carbonyl. The ¹³C{¹H} NMR spectra show characteristic deshielded resonances for the µ-C nucleus at δ ≈ 400. A crystal structure determination of [WFe(µ-C₆H₄Me-4)(CO)₅Tp] confirmed the presence of a semi-bridging carbonyl and the four-electron functionality of the M=C bond, with partially delocalised multiple bond character evident within the FeCW ring. The Fe–CO ligand transoid to the π-acidic bridging alkylidyne group lies furthest from the iron atom.
The behaviour of the poly(pyrazolyl)borate alkylidyne complexes towards \([\text{Fe}_2(\text{CO})_6]\) contrasts markedly with that of the Cp analogues. The complex \([\text{W}(=\text{CR})(\text{CO})_2\text{Cp}]\) \((R = \text{C}_6\text{H}_4\text{Me}-4)\) reacts with \([\text{Fe}_2(\text{CO})_6]\) to give a labile ‘\(\text{Fe}(\text{CO})_4\)’ complex that readily affords diiron–tungsten or ditungsten–iron clusters,\(^{186}\) while its \(\text{Cp}^*\) analogue, in the presence of \(\text{CO}\), exists in equilibrium with the electronically saturated complex \([\text{WFe}(\mu-\text{CR})(\text{CO})_3\text{Cp}]\).\(^{45}\) Conversion of \([\text{MFe}(\mu-\text{CR})(\text{CO})_2\text{L}]\) complexes to the saturated hexacarbonyl derivatives under an atmosphere of carbon monoxide is possible, but for \(L = \text{Tp}\) the equilibrium favours the tricarbonyl species and reversion to this occurs under nitrogen purge.\(^{39}\) For \(L = \text{Cp}\), the equilibrium favours the ‘\(\text{Fe}(\text{CO})_4\)’ adduct.\(^{184}\) The enhanced stability of the ‘\(\text{Fe}(\text{CO})_3\)’ species for \(L = \text{Tp}\) reflects the relatively greater \(\sigma\)-donor properties of the \(\text{Tp}\) ligand cf. \(\text{Cp}\), which would increase electron donation by the \(\text{M} = \text{C}\) system, thus facilitating its four-electron donor functionality. Steric effects may also have a role in determining whether ‘\(\text{Fe}(\text{CO})_3\)’ or ‘\(\text{Fe}(\text{CO})_4\)’ adducts are formed.

It is a characteristic feature that in these 32-valence electron complexes the resonances for the bridging alkylidyne carbon nuclei are approximately 80 ppm more deshielded than those of their 34-valence electron counterparts.\(^{46}\) There is no evidence for addition of a \(\text{CO}\) ligand to the analogous iron–tungsten bis(pyrazolyl)borate species in solution.\(^{46}\)

Treatment of the bimetallic complexes \([\text{MFe}(\mu-\text{CR})(\text{CO})_3\text{Tp}]\) with one equivalent of phosphine at room temperature readily gives the electronically unsaturated compounds \([\text{WFe}(\mu-\text{CR})(\text{CO})_4(L')\text{Tp}]\) \((M = \text{W}, R = \text{Me}, R = \text{C}_6\text{H}_4\text{Me}-4, L' = \text{PHPh}_2;\)^{185} \((M = \text{W}, R = \text{C}_6\text{H}_4\text{Me}-4, L' = \text{PMe}_3\) or \(\text{PEt}_3;\)^{184} \((M = \text{Mo}, R = \text{C}_6\text{H}_4\text{Me}-4, L' = \text{PMe}_3\) via carbonyl substitution at the iron centre and ultimate retention of the four-electron donor role of the \(\text{M} = \text{C}\) bond. The unsaturated cyclopentadienyl compounds \([\text{WFe}(\mu-\text{CR})(\text{CO})_3\text{Cp}]\) \((R = \text{C}_6\text{H}_4\text{Me}-4\) also react readily with phosphines via initial attack at the iron centre and there is little difference in reactivity between the \(\text{Cp}\) and \(\text{Tp}\) systems.\(^{184}\) The \(\text{Cp}\) complex \([\text{WFe}(\mu-\text{CR})(\text{CO})_4(\text{PMe}_3)_2\text{Cp}]\) reacts with \(\text{PMe}_3\) to produce the electronically saturated complex \([\text{WFe}(\mu-\text{CR})(\text{CO})_3(\text{PMe}_3)_2\text{Cp}],\) which can be thermally converted to \([\text{WFe}(\mu-\text{CR})(\mu-\text{CO})(\text{CO})_2(\text{PMe}_3)_2\text{Cp}]\) via release of \(\text{CO}\), with a phosphine bound to each metal centre.\(^{184}\) For \(\text{Tp}\), excess \(\text{PMe}_3\) gave a mixture of products including \([\text{W}(=\text{CR})(\text{CO})(\text{PMe}_3)\text{Tp}],\) but for the chelating phosphines \((L' = \text{dppm}, \text{dmpm}),\) initial coordination of one phosphorus at the iron generates \([\text{WFe}(\mu-\text{CR})(\text{CO})_4(\mu-L'-L')\text{Tp}]\) and subsequent loss of \(\text{CO}\) in solution provides \([\text{WFe}(\mu-\text{CR})(\mu-\text{CO})(\mu-L'-L')(\text{CO})_2\text{Tp}],\) in which the phosphine bridges the two metal centres (for \(\text{dmpm},\) the non-bridging form is not isolated).\(^{184}\)

The unsaturated dimetal compound \([\text{WFe}(\mu-\text{CR})(\text{CO})_6\text{Bp}]\) reacts similarly with bidentate phosphines affording \([\text{WFe}(\mu-\text{CR})(\mu-\text{CO})(\mu-L'-L')(\text{CO})_3\text{Bp}]\) \((L'-L' = \text{dppm}),\)^{46} Alkylation of the bridging carbonyls \((v_{\text{CO}} \text{ ca. } 1700 \text{ cm}^{-1})\) results in the cationic salts \([\text{WFe}(\mu-\text{CR})(\mu-\text{COMe})(\mu-L'-L')(\text{CO})_2\text{Tp}]\) \([\text{O}_2\text{SCF}_3],\) which feature two distinct alkylidyne bridges.\(^{184}\)
Heating $[\text{WFe}(\mu-\text{CR})(\text{CO})_4(\text{PHPh}_2)\text{Tp}]$ ($R = \text{C}_6\text{H}_4\text{Me}-4$) in toluene results in transfer of hydride from the secondary phosphine to the $\mu$-C atom to afford the complex $[\text{WFe}(\mu-\sigma,\eta^3-\text{CHR})-(\mu-\text{PPH}_2)(\mu-\text{CO})(\text{CO})_5\text{Tp}]$, having an 18-electron configuration at the iron centre (Scheme 1.79).\(^{185}\) In contrast, under similar conditions the corresponding ethylidyne complex yields the compound $[\text{WFe}(\mu-\text{PPH}_2)(\text{CO})_5\text{Tp}]$, presumably through decomposition of an unstable $\mu$-CHMe analogue which eliminates ethylene and then scavenges CO.\(^{185}\)

![Scheme 1.79. Reactivity of W–Fe bimetallic complexes containing the secondary phosphine PHPh₂.](image)

The unsaturated dimetal compounds $[\text{WFe}(\mu-\text{CR})(\text{CO})_n\text{L}]$ ($R = \text{C}_6\text{H}_4\text{Me}-4$, $\text{L} = \text{Tp}$, $n = 5$; $\text{L} = \text{Bp}$, $n = 6$) react with $R'C=CR'$ ($R' = \text{Me}$ or Ph) to afford the complexes $[\text{WFe}(\mu-\text{CRC}(R')-\text{C}(R'))(\text{CO})_5\text{L}]$.\(^{46}\) With diazomethane, the complex $[\text{WFe}(\mu-\text{trans-CH}=\text{C}(\text{H})R)-(\mu-\text{CO})(\text{CO})_5\text{Bp}]$ is produced,\(^{46}\) however the Tp complex does not react similarly with CH$_2$N$_2$.\(^{46}\)

The addition of sulfur to the bridging alkylidyne ligand forms heterobimetallic thioacyl complexes $[\text{MoFe}(\mu-\eta-\text{SCR})(\text{CO})_2\text{Tp}]$ ($R = \text{C}_6\text{H}_4\text{Me}-4$), along with trace amounts of the CO insertion product which decomposes into the thioacyl complex.\(^{41}\) The heterobimetallic thioaroyl complex can also be obtained from the direct reaction of $[\text{Mo}(\eta^2-\text{SCR})(\text{CO})_2\text{Tp}]$ ($R = \text{C}_6\text{H}_4\text{OMe}-4$) with $[\text{Fe}_2(\text{CO})_5]$ (Scheme 1.80).\(^{48,154}\)
Reaction of [Fe₂(CO)_₅] and [Mo{µ-CN(i-Pr)_₂}(CO)_₃Tp] similarly provides the thermally unstable complex [MoFe{µ-CN(i-Pr)_₂}(CO)_₅Tp], which reacts with sulfur to provide the heterobimetallic bridging thiocarbamoyl complex [MoFe{µ-SCN(i-Pr)_₂}(CO)_₅Tp].

Treatment of [FeW(µ-CR)(CO)_₅Tp] (R = C₆H₄Me-4, R = Me) with [Rh(CO)₂(η⁵-C₅H₅)] (vide supra) in diethyl ether at room temperature affords the black crystalline trimetallic complex [WF₉Rh(µ₃-CR)(µ-CO)(CO)_₅(η⁵-C₅H₅)Tp]. The ^{13}C{¹H} NMR spectrum shows four CO resonances in contrast to the Cp analogue, which has only one. Evidently, the Tp complexes have a higher energy barrier for dynamic behaviour. The trimetal compounds [WF₉Rh(µ₃-CR)(µ-CO)(CO)_₅(η⁵-C₅H₅)Tp] react with but-2-yne in toluene at 100 °C to give the alkylidyne- and alkynyl-bridged complexes [WF₉Rh(µ₃-CR)(µ-MeC₂Me)(CO)_₄(η⁵-C₅H₅)Tp]. The crystal structure shows three essentially equal N–W distances between the Tp ligand and the tungsten, which is consistent with the reduction in bond order of the M–C linkage.

For the rhodium-alkynyl-substituted carbyne complex [Rh{C≡CC≡W(CO)₃Tp}(CO)(PPh₃)] (Scheme 1.64), shielding of the M=C bond by the sterically cumbersome Tp ligands results in the reaction with [Fe₂(CO)_₅] proceeding via addition of two ‘Fe(CO)_₅’ units across the organic C≡C bond (Scheme 1.81). This is similar to the situation described by Stone for the reaction of simple alkynyl-substituted carbynes with [Mo(CO)₅Cp] and [Co₂(CO)_₈] (vide supra) and provides [Fe₂Rh{µ-C₃W(CO)₂Tp}(CO)₁₀(PPh₃)] in 52% yield; a rare example of a tricarbidoligand incorporated within a cluster framework.
The appearance of the tungsten alkylidyne resonance at \( \delta_c 254.6 \) in the \(^{13}\text{C}\{^1\text{H}\} \) NMR spectrum, together with crystallographic evidence, confirms that the \( \text{W}=\text{C}_3 \) unit remains intact and that it straddles one \( \text{Rh}–\text{Fe} \) bond (2.552(1) Å), contracting it relative to the other \( \text{Rh}–\text{Fe} \) separation (2.721(1) Å).\(^{163}\)

**Ruthenium**

The majority of complexes containing bonds between tungsten and ruthenium are structurally different from those having tungsten–iron bonds. Treatment of the compounds \([\text{W}(=\text{CR})(\text{CO})_2\text{Tp}] \) \( \text{(R} = \text{C}_6\text{H}_4\text{Me}-4) \) with a three-fold excess of \([\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)]\), a source of the fragment ‘\( \text{Ru}(\text{CO})_4 \)’, in light petroleum gives the tetranuclear metal cluster complex \([\text{WRu}_3(\mu_3-\text{CR})(\text{CO})_1\text{Tp}] \) (Scheme 1.82). The cluster has a \( \text{WRu}_3 \) core which is essentially tetrahedral, with one \( \text{Ru}_2\text{W} \) face capped by a triply bridging \( \mu_3-\text{CC}_6\text{H}_4\text{Me}-4 \) ligand. The \(^{13}\text{C}\{^1\text{H}\} \) NMR spectrum shows a resonance for the asymmetrically bridging \( \mu_3-\text{C} \) nuclei at \( \delta_c 329.6 \), which is roughly 30 ppm more deshielded than the corresponding shift for the \( \text{Cp} \) complex due partly to the greater donor ability of the \( \text{Tp} \)-alkylidyne fragment. The formation of a tetranuclear compound reflects the ease with which carbonyl–ruthenium fragments combine to form Ru–Ru bonds.\(^{187}\)

**Scheme 1.82** Formation of tetranuclear \( \text{WRu}_3 \) cluster containing a triply bridging alkylidyne ligand \( \text{(R} = \text{C}_6\text{H}_4\text{Me}-4) \).

Addition of the reagent \([\text{Ru}(\text{CO})_2(\text{THF})(\eta^5-7,8-\text{C}_2\text{B}_9\text{H}_{11})]\) to the compounds \([\text{M}(=\text{CR})(\text{CO})_2\text{Tp}]\) \( \text{(M} = \text{Mo, W}; \text{R} = \text{C}_6\text{H}_4\text{Me}-4) \) in dichloromethane affords the bimetallic species \([\text{RuM}(\mu-\text{CR})-(\text{CO})_4(\eta^5-7,8-\text{C}_2\text{B}_9\text{H}_{11})\text{Tp}]\), mentioned briefly in Section 1.41 (Scheme 1.83).\(^{153}\) The \( \text{Cp} \) analogues are very labile and have a predilection for insertion of their tolylmethylidyne ligands...
into an adjacent B–H bond of the carborane group. In contrast, the Tp complexes are stable in dichloromethane or toluene solution but are readily cleaved by donor molecules including tetrahydrofuran. X-ray diffraction studies established the molecular structure, revealing long Ru–W separations (ca. 3 Å) that are asymmetrically bridged by the tolylmethylidyne groups (µ-C–W$_{av}$ 1.92 Å vs µ-C–Ru$_{av}$ 2.21 Å). The chemical shifts of the µ-C nuclei (ca. δ$_C$ 290) differ little from the precursor alkylidynes and reflect the asymmetric bridging of the metal–metal bond by the tolylmethylidyne ligand.

The reaction of [RuM(µ-CR)(CO)$_4$(η$^5$-7,8-C$_2$B$_9$H$_{11}$)] with elemental sulfur or selenium gives the chalcoacyl compounds [RuM(µ-ECR)(CO)$_4$(η$^5$-7,8-C$_2$B$_9$H$_{11}$)] and appreciable amounts of the compounds [M(κ$^2$-S$_2$CR)(CO)$_2$Tp], which have previously been obtained from another route. X-ray crystallography established the structure displaying ‘Ru(CO)$_2$(η$^5$-7,8-C$_2$B$_9$H$_{11}$)’ and ‘W(CO)$_2$Tp’ units unusually bridged by a chalcoacyl group which is η$^2$-coordinated to the tungsten and bound to the ruthenium only through the chalcogen atom, i.e., with no direct metal–metal bond.

Dewhurst’s dimetallaoctatetra-1,3,5,7-ynes [Tp*(CO)$_2$W≡CC≡CC≡CC≡W(CO)$_2$Tp*] do not react at the M≡C multiple bond, instead participating in reactions at the more sterically accessible C≡C bonds of the WC$_6$W spine. With [RuHCl(CO)(L')(PPh$_3$)$_2$] (L' = PPh$_3$, CO), regioselective hydoruthenation of one C≡C bond provides the complexes [Ru{(C≡CC≡W(CO)$_2$Tp*)=CHC≡W(CO)$_2$Tp*Cl}(CO)$_n$(PPh$_3$)$_{4-n}$] (n = 1 or 2), containing hex-2-en-4-yn-3-yl-1,6-diyldiyne-bridges (Scheme 1.84).
Scheme 1.84 Regioselective hydoruthenation of dimetallaoctatetraynes, \([W] = W(CO)_2Tp^x\), where \(Tp^x = Tp, Tp^*\); \(L = PPh_3\).

With the zero-valent ruthenium complex \([Ru(CO)_2(PPh_3)_3]\), the bis(tricarbido) complexes \([Ru\{C_3W(CO)_2Tp^x\}_2(CO)_2(PPh_3)_2]\) involving cleavage of the C–C single bond of the WC₆W spine are formed via the adduct \([Ru\{\eta^2-Tp'(CO)_2WC_6W(CO)_2Tp^x\}(CO)_2(PPh_3)_2]\). This adduct, along with \([Ru\{C_3W(CO)_2Tp^x\}\{HgC_3W(CO)_2Tp^x\}(CO)_2(PPh_3)_2]\), is observed as an intermediate in the reactions of \([Ru(CO)_2(PPh_3)_3]\) with \([Hg\{C_3W(CO)_2Tp^x\}_2]\) that also ultimately provide the bis(tricarbido) complex (Scheme 1.85).

Scheme 1.85 Reaction of bis(tricarbido)mercurial resulting in C–C single bond scission, \([W] = W(CO)_2Tp^x\); \(L = PPh_3\). (1) r.t, 40 h for \(Tp^x = Tp^*\); or 65 °C, 70 h for \(Tp^x = Tp\).

Spectroscopic data for the \(\pi\)-alkynyl complex \([Ru\{\eta^2-Tp'(CO)_2WC_6W(CO)_2Tp^x\}(CO)_2(PPh_3)_2]\) confirm the presence of two chemically distinct ‘\(W(CO)_2Tp^x\)’ groups. The bis(tricarbido) complexes \(cis,cis,trans-[Ru\{C_3W(CO)_2Tp^x\}_2(CO)_2(PPh_3)_2]\) display single resonances for the Ru–CO, W–CO and alkylidyne carbon nuclei. The latter complex has been crystallographically characterised.
Zirconium and Titanium

Whilst a range of alkylidyne complexes \([M(\equiv CR)(CO)\_2Cp]\) react with \([M'(n-Bu)\_2Cp\_2]\) or \([M'Cl\_2Cp\_2]/Mg\) (\(M' = \text{Ti, Zr}\)) to provide the complexes \([\text{TiW}\_2\mu-\text{CC}_6\text{H}_4\text{OMe}-2](\mu-\text{CO})(\text{CO})\_3\text{Cp}\_3\) and \([\text{ZrM}\_2\mu-\text{CR}}\_2\text{Cp}\_3\] (\(M = \text{Mo, } R = \text{C}_6\text{H}_4\text{OMe}-2; \quad M = \text{W, } R = \text{Me, } \text{C}_6\text{H}_4\text{OMe}-2, \text{xylyl}\)), the corresponding poly(pyrazolyl)borate complex involving \([\text{Mo}(\equiv \text{CC}_6\text{H}_4\text{OMe}-2)(\text{CO})\_2\text{Tp}]\), whilst spectroscopically observable, was unstable and could not be isolated.\(^{189}\)

Cluster chemistry with alkylidyres co-ligated by the pyrazolylmethanes

Like the boron-based alkylidyne compounds, the tris(pyrazolyl)methane complexes have a rich chemistry involving polynuclear clusters.\(^{100,117,118}\) Both the salts and the neutral pyrazolylmethane complexes \([W(\equiv CR)(CO)\_2L]\)\(^{117}\) (\(R = \text{Me, } \text{C}_6\text{H}_4\text{Me}-4; \quad L = \text{HC}(\text{pz})_3, \quad x = +1\) per \(L; \quad L = \{(\text{C}_6\text{F}_5)\text{AuC}(\text{pz})_3\}, \quad x = 0; \quad R = \text{Me, } \text{C}_6\text{H}_4\text{Me}-4; \quad L = \{(\text{F}_3\text{B})\text{C}(\text{pz})_3\}, \quad x = 0\) afford a variety of mixed-metal complexes upon treatment with low-valent metal-ligand fragments, the structures and properties of which reflect those obtained for the closely related Tp analogues (vide infra) but with a charge higher by one unit per ligand for \(L = \text{HC}(\text{pz})_3\).\(^{100,117,118}\) In some instances, the Au–C bond of the derivatised neutral complexes are cleaved.\(^{117}\)
1.5 Concluding Remarks

The preceding discussion indicates that a substantial amount of alkylidyne chemistry supported by TpM and Tp*M scaffolds has been developed. Early work focused on perceived similarities between these ligands and variously substituted cyclopentadienyls and indeed much of the work described herein bears out this analogy. However, distinctions soon emerged, many of which can be traced to the steric profile of the scorpionate ligands and the geometric constraints that predispose their complexes to pseudo-octahedral six-coordination, especially in the case of Tp*. From an applications point of view, the added stability offered by the Tp* and Tp scaffolds has made it possible to carry out many carbyne ligand transformations that are not yet available to Cp derivatives. This has led to a far wider range of accessible carbyne substituents including many heteroatom examples. Amongst these, halocarbynes are unique to pyrazolylborate chemistry and the synthetic potential as precursors to exotic ‘C₁’ ligands is enormous.
<table>
<thead>
<tr>
<th>Compound</th>
<th>δ M=CR, ppm (J, Hz)</th>
<th>δ M(CO), ppm (J Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(=CC6H4Me-4)(CO)2Tp]</td>
<td>310.0</td>
<td>231.6</td>
<td>41</td>
</tr>
<tr>
<td>[Mo(=CMe)(CO)2Tp]</td>
<td>304.0</td>
<td>225.0</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CMe)(CO)2(NCCD3)Tp]</td>
<td>291.9</td>
<td>248.6</td>
<td>62g</td>
</tr>
<tr>
<td>[Mo(=CMe)(CO)(PMe3)Tp]</td>
<td>288.1 (2J(1H) 20)</td>
<td>243.0 (2J(1H) 10)</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CPr)(CO)2Tp]</td>
<td>310.6</td>
<td>225.6</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CPh)(CO)2Tp]</td>
<td>314.4</td>
<td>226.1</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC6H4Me-4)(CO)2Tp]</td>
<td>310.6</td>
<td>225.6</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC5H4OMe-4)(CO)2Tp]</td>
<td>314.4</td>
<td>226.1</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC4H3S-2)(CO)2Tp]</td>
<td>288.8</td>
<td>226.2</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)2Tp]</td>
<td>293.1</td>
<td>224.9</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(SMe)2Tp]</td>
<td>288.8</td>
<td>226.2</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(P(OMe)3)Tp]</td>
<td>293.1</td>
<td>224.9</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CPh)(CO)2Tp]</td>
<td>288.8</td>
<td>226.2</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC6H4Me-4)(CO)2Tp]</td>
<td>293.1</td>
<td>224.9</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC6H4Me-4)(CO)2(Tp)*]</td>
<td>288.9</td>
<td>225.8</td>
<td>62</td>
</tr>
<tr>
<td>[Mo(=CC6H4Me-4)(CO)(PPh3)Tp]</td>
<td>NR</td>
<td>NR</td>
<td>64</td>
</tr>
<tr>
<td>[Mo(=CC6H4OMe-4)(CO)2Tp]</td>
<td>294.2</td>
<td>226.0</td>
<td>48b</td>
</tr>
<tr>
<td>[Mo(=CC6H4OMe-4)(CO)2(Tp)*]</td>
<td>276.8</td>
<td>225.9</td>
<td>48b</td>
</tr>
<tr>
<td>[Mo(=CC6H4S-2)(CO)2Tp]</td>
<td>259.8</td>
<td>226.0</td>
<td>52</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)2Tp]</td>
<td>256.7</td>
<td>226.6</td>
<td>52</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(P(OMe)3)Tp]</td>
<td>256.7</td>
<td>226.6</td>
<td>52</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(P(OMe)3)Tp*]</td>
<td>301.3 / 298.7</td>
<td>224.20</td>
<td>60g</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(P(OMe)3)Tp*]</td>
<td>269.47</td>
<td>226.1</td>
<td>189b</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>229.3</td>
<td>226.1</td>
<td>369</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp*]</td>
<td>556</td>
<td>232.0 (1J(1H) 197)</td>
<td>68.89.120</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp*]</td>
<td>280.6 (1J(1H) 192)</td>
<td>224.5 (1J(1H) 169)</td>
<td>46</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp*]</td>
<td>293.9 (1J(1H) 189)</td>
<td>222.3 (1J(1H) 168)</td>
<td>30.4/0.2</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>295.2 (1J(1H) 189)</td>
<td>223.3 (1J(1H) 169)</td>
<td>150.68.156</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>289</td>
<td>223 (1J(1H) 168)</td>
<td>19</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>303.9</td>
<td>225 (1J(1H) 170)</td>
<td>150.66</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>295.1</td>
<td>225 (1J(1H) 168)</td>
<td>150.66</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>297</td>
<td>223 (1J(1H) 168)</td>
<td>150.66</td>
</tr>
<tr>
<td>[Mo(=CC=Ct-Bu)(CO)(PMe3)Tp]</td>
<td>293</td>
<td>223 (1J(1H) 168)</td>
<td>150.66</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta M=$CR, ppm ($J$, Hz)</td>
<td>$\delta M$(CO), ppm ($J$ Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------</td>
<td>-----------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>$[W(=CCHPh)(CO)_{2}T^\alpha]$</td>
<td>287.4 ($J_{CW}$ 189)</td>
<td>223.4 ($J_{CW}$ 166)</td>
<td>121</td>
</tr>
<tr>
<td>$[W(=CCH(\text{OH})Ph)(CO)_{2}T^\alpha]$</td>
<td>289 ($J_{CW}$ 187)</td>
<td>223.5, 223.4 ($J_{CW}$ 166)</td>
<td>67a</td>
</tr>
<tr>
<td>$[W(=CCH(\text{OH})(\text{CH}=\text{CHMe})<em>{2})(CO)</em>{2}T^\alpha]$</td>
<td>292 ($J_{CW}$ 188)</td>
<td>224.2, 224.1 ($J_{CW}$ 166)</td>
<td>67b</td>
</tr>
<tr>
<td>$[W(=CCH(\text{OH})PhMe)(CO)_{2}T^\alpha]$</td>
<td>291 ($J_{CW}$ 187)</td>
<td>224.3, 224.2 ($J_{CW}$ 166)</td>
<td>67b</td>
</tr>
<tr>
<td>$[W(=CCH(\text{O})Ph)(CO)_{2}T^\alpha]$</td>
<td>273</td>
<td>225</td>
<td>67b</td>
</tr>
<tr>
<td>$[W(=CCH_{2}CH=\text{CH}(\text{O})(\text{CH}=\text{CHMe})<em>{2})(CO)</em>{2}T^\alpha]$</td>
<td>288.0 ($J_{CW}$ 191)</td>
<td>223.0 ($J_{CW}$ 170)</td>
<td>67b, 185a</td>
</tr>
<tr>
<td>$[W(=CCH_{2}CH=\text{CH}PhMe)(CO)_{2}T^\alpha]$</td>
<td>301</td>
<td>224 ($J_{CW}$ 168)</td>
<td>65c, 6</td>
</tr>
<tr>
<td>$[W(=CCH_{2}CH=\text{CH}Ph)(CO)_{2}T^\alpha]$</td>
<td>289.4 ($J_{CW}$ 193)</td>
<td>224.7 ($J_{CW}$ 166)</td>
<td>65c, 6</td>
</tr>
<tr>
<td>$[W(=CCH_{2}Ph)(CO)_{2}T^\alpha]$</td>
<td>284.4 ($J_{CW}$ 193)</td>
<td>224.3 ($J_{CW}$ 165)</td>
<td>68</td>
</tr>
<tr>
<td>$[W(=CCH_{2}Ph)(CO)_{2}T^\alpha]$</td>
<td>277.3 ($J_{CW}$ 188)</td>
<td>225.5 ($J_{CW}$ 161)</td>
<td>68</td>
</tr>
<tr>
<td>$[W(=CCH_{2}Ph)(CO)_{2}T^\alpha]$</td>
<td>$E$: 278 ($J_{CW}$ 184)</td>
<td>225 ($J_{CW}$ 166)</td>
<td>67b, 121</td>
</tr>
<tr>
<td>$[W(=CCH_{2}Ph)(CO)_{2}T^\alpha]$</td>
<td>$E$: 280.2 ($J_{CW}$ 183)</td>
<td>223.0 ($J_{CW}$ 170)</td>
<td>67b, 121</td>
</tr>
<tr>
<td>$[W(=CCH_{2}Ph)(CO)_{2}T^\alpha]$</td>
<td>$Z$: 281.2 ($J_{CW}$ 183)</td>
<td>225.6 ($J_{CW}$ 166)</td>
<td>67b, 121</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>$E$: 285.2</td>
<td>225.0</td>
<td>121c</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>$Z$: 284.5</td>
<td>225.9</td>
<td>121c</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>276.5</td>
<td>224.6</td>
<td>65</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>276.9 ($J_{CW}$ 190)</td>
<td>224.6 ($J_{CW}$ 167)</td>
<td>64f</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>253.4 ($J_{CW}$ 200)</td>
<td>226.5 ($J_{CW}$ 164)</td>
<td>64f</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>247.3 ($J_{CW}$ 198)</td>
<td>226.1 ($J_{CW}$ 162)</td>
<td>64f</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>253.5 ($J_{CW}$ 202)</td>
<td>224.8 ($J_{CW}$ 168)</td>
<td>64f</td>
</tr>
<tr>
<td>$[W=CCMe=CHMe)(CO)_{2}T^\alpha]$</td>
<td>251.4</td>
<td>226.7 ($J_{CW}$ 164)</td>
<td>64f</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta$ M=CR, ppm ($J$, Hz)</td>
<td>$\delta$ M(CO), ppm ($J$, Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>------</td>
</tr>
<tr>
<td>[W(≡CC≡CPh)(CO)$_2$Tp$^+$]</td>
<td>247.3</td>
<td>227.3 ($J_{cw}$ 160)</td>
<td>61f</td>
</tr>
<tr>
<td>[W(≡CPh)(CO)$_2$Tp$^+$]</td>
<td>277.9</td>
<td>224.2</td>
<td>78</td>
</tr>
<tr>
<td>[W(≡CPh)Br$_2$Tp]</td>
<td>329.8</td>
<td></td>
<td>130,134</td>
</tr>
<tr>
<td>[W(≡CPh)Br$_2$Tp$^+$]</td>
<td>327.4 ($J_{cw}$ 208)</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)$_2$Bp]</td>
<td>284.7 ($J_{cw}$ 189)</td>
<td>224.6 ($J_{cw}$ 167)</td>
<td>46</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)$_2$Tp$^+$]</td>
<td>279.6</td>
<td>224.2 ($J_{cw}$ 168)</td>
<td>43</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)$_2$Tp$^+$]</td>
<td>282.3</td>
<td>224.2 ($J_{cw}$ 168)</td>
<td>43</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)$_2$Tp$^+$]</td>
<td>286.4 ($J_{cw}$ 190)</td>
<td>224.7 ($J_{cw}$ 170)</td>
<td>46</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)(PMe$_3$)Bp]</td>
<td>298.3</td>
<td>228.9, 224.5</td>
<td>46</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)(PMe$_3$)Bp]</td>
<td>272.0</td>
<td>248.6</td>
<td>46</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_5$Me-4)(CO)(PPh$_3$)Bp]</td>
<td>284.5</td>
<td>232.1, 226.5</td>
<td>46</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2)(CO)$_2$Tp]</td>
<td>286.4 ($J_{cp}$ 2.5)</td>
<td>246.2</td>
<td>50b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2)(CO)$_2$Tp]</td>
<td>280.5</td>
<td>225.1</td>
<td>43</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>$^<em>$fac: 294.5, $^</em>$mer: 284.5</td>
<td>225.3, 227.5</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>285.6</td>
<td>222.1, 211.2</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>287.5</td>
<td>221.7, 210.6</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>285.1 ($J_{cp}$ 8.9)</td>
<td>221.7, 210.6</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>288.6</td>
<td>226.8</td>
<td>43</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>326.5</td>
<td>246.8</td>
<td>107b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,6)(CO)$_2$(pic)Bp]</td>
<td>335.5</td>
<td>246.8</td>
<td>107b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,4,6)(CO)$_2$(pic)Bp]</td>
<td>$^<em>$fac: 295.0 ($J_{cw}$ 200), $^</em>$mer: 284.9 ($J_{cw}$ 194)</td>
<td>225.5 ($J_{cw}$ 169), 227.6, 221.9 ($J_{cw}$ 169, 169)</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,4,6)(CO)$_2$(pic)Bp]</td>
<td>284.4 ($J_{cp}$ 8.6)</td>
<td>227.1 ($J_{cp}$ 3.6), 213.4 ($J_{cp}$ 53.3)</td>
<td>43</td>
</tr>
<tr>
<td>[W(≡C$_2$H$_6$OMe-2,4,6)(CO)$_2$(pic)Bp]</td>
<td>278.2 ($J_{cp}$ 11)</td>
<td>249.9 ($J_{cp}$ 5.3)</td>
<td>40b</td>
</tr>
<tr>
<td>[W(≡CC$_2$H$_5$Cl)(CO)$_2$(pic)Bp]</td>
<td>288.5 ($J_{cw}$ 193)</td>
<td>249.9 ($J_{cp}$ 5.3)</td>
<td>107b</td>
</tr>
<tr>
<td><a href="CH$_3$%E2%88%92t-Bu">Re≡CPh</a>(CH$_3$−Bu)Tp]</td>
<td>289.3</td>
<td>226.3 ($J_{cp}$ 165)</td>
<td>91b</td>
</tr>
<tr>
<td><a href="CO">Re≡CC$_2$H$_5$Cl(O)H</a>(PMe$_3$)Tp]</td>
<td>308.2 ($J_{cp}$ 12.2)</td>
<td>206.3</td>
<td>91b</td>
</tr>
<tr>
<td><a href="CO">Re≡CC$_2$H$_5$OMe-2,6,4,6</a>$_2$(pic)Bp]</td>
<td>310.5 ($J_{cp}$ 9.8)</td>
<td>206.3</td>
<td>91b</td>
</tr>
<tr>
<td><a href="CO">Re≡CC$_2$H$_5$OMe-2,4,6</a>$_2$(pic)Bp]</td>
<td>NR</td>
<td>192.8</td>
<td>94b</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta M = CR$, ppm ($J$, Hz)</td>
<td>$\delta M$(CO), ppm ($J$, Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>$[\text{Ru}(\equiv \text{CCH}_2-t\text{-Bu})\text{Cl}(\text{PPh}_3)\text{Tp}]^+$</td>
<td>335.2 ($^{2}J_{CP}$ 16.5)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>$[\text{Ru}(\equiv \text{CCH}_{2-n}\text{-Bu})\text{Cl}(\text{PPh}_3)\text{Tp}]^+$</td>
<td>351.2 ($^{2}J_{CP}$ 17.5)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>$[\text{Ru}(\equiv \text{CCH}_2\text{Ph})\text{Cl}(\text{PPh}_3)\text{Tp}]^+$</td>
<td>341.4 ($^{2}J_{CP}$ 7.8)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>$[\text{Ru}(\equiv \text{CCH} = \text{CPh}_2)\text{Cl}{\text{P(i-Pr)}\text{Ph}_2}\text{Tp}]^+$</td>
<td>324.4 ($^{2}J_{CP}$ 5.2)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>$[\text{Ru}(\equiv \text{CCH} = \text{CPh}_2)\text{Cl}{\text{P(i-Pr)}\text{Ph}_2}\text{Tp}]^+$</td>
<td>328.5 ($^{2}J_{CP}$ 8.0)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>$[\text{Os}(\equiv \text{Ct-Bu})(\text{CHrt-Bu})\text{Tp}]^+$</td>
<td>326.4 ($^{2}J_{CP}$ 4.2)</td>
<td></td>
<td>98111</td>
</tr>
<tr>
<td>[Mo(≡CSiMe$_2$Ph)(CO)$_2$Tp$^*$]</td>
<td>360.4</td>
<td>227.8</td>
<td>89</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CSiMe}_3)(\text{CO})_2\text{Tp}]^*$</td>
<td>344.6 ($J_{CW}$ 160)</td>
<td>225.9 ($J_{CW}$ 154)</td>
<td>68</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CSiMe}_2\text{Ph})(\text{CO})_2\text{Tp}]^*$</td>
<td>339.0 ($J_{CW}$ 160)</td>
<td>226.1 ($J_{CW}$ 173)</td>
<td>89</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CO})$(CO)$_2$(CO)$_2$Tp$^*$]</td>
<td>218.0</td>
<td>225.4</td>
<td>70</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CO})$(CO)$_2$(CO)$_2$Tp$^*$]</td>
<td>218.8</td>
<td>225.5</td>
<td>70</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{COMo})(\text{CO})_2\text{Tp}]^*$</td>
<td>228.2 ($J_{CW}$ 235)</td>
<td>222.4 ($J_{CW}$ 164)</td>
<td>79</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{COMo})(\text{CO})_2\text{Tp}]^*$</td>
<td>219.3 ($J_{CW}$ 242)</td>
<td>222.9 ($J_{CW}$ 164)</td>
<td>70</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CO}(\text{C}_9\text{H}_4\text{Me}-4))(\text{CO})_2\text{Tp}]^*$</td>
<td>220.2 ($J_{CW}$ 245)</td>
<td>223.1 ($J_{CW}$ 164)</td>
<td>70</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CO}(\text{C}_9\text{H}_4\text{Me}-4))(\text{CO})_2\text{Tp}]^*$</td>
<td>220.5 ($J_{CW}$ 244)</td>
<td>222.9 ($J_{CW}$ 164)</td>
<td>78</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CO}(\text{C}_9\text{H}_4\text{NO}-4))(\text{CO})_2\text{Tp}]^*$</td>
<td>214.5 ($J_{CW}$ 247)</td>
<td>222.5 ($J_{CW}$ 161)</td>
<td>78</td>
</tr>
<tr>
<td>$[\text{W}(\equiv \text{CO}(\text{C}_9\text{H}_4\text{Cl}-4))(\text{CO})_2\text{Tp}]^*$</td>
<td>218.0</td>
<td>222.7</td>
<td>78</td>
</tr>
<tr>
<td>[Cr$(\equiv \text{CN}(t\text{-Pr})_2)$(CO)$_2$Tp$^*$]</td>
<td>256.4</td>
<td>239.2</td>
<td>81,82c</td>
</tr>
<tr>
<td>[Cr$(\equiv \text{CN}(t\text{-Pr})_2)$(CO)$_2$(N$_2$Bu)Tp$^*$]</td>
<td>254.6</td>
<td>242.8</td>
<td>81,82c</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CNH}(t\text{-Bu})$(CO)$_2$Tp$^*$]</td>
<td>251.6</td>
<td>228.2</td>
<td>83</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CNMe}(t\text{-Bu})$(CO)$_2$Tp$^*$]</td>
<td>253.7</td>
<td>228.7</td>
<td>83</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CN}(t\text{-Pr})_2)$(CO)$_2$Tp$^*$]</td>
<td>260.2</td>
<td>230.2</td>
<td>1906A</td>
</tr>
<tr>
<td>[Mo$(\equiv \text{CNMe}(t\text{-Bu})$(CO)$_2$Tp$^*$]</td>
<td>253.5</td>
<td>229.7</td>
<td>83</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta$ M=CR, ppm ($J$, Hz)</td>
<td>$\delta$ M(CO), ppm ($J$, Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>------------------------------------------------------</td>
<td>-----------------------------</td>
<td>--------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>[Mo(=CNMePh)(CO)$_2$Tp$^*$]</td>
<td>244.5</td>
<td>228.2</td>
<td>$^{83}$</td>
</tr>
<tr>
<td>[W(=CNMe)(CO)$_2$Tp$^*$]</td>
<td>249.0 ($^1J_{cw}$ 208)</td>
<td>225.5 ($^1J_{cw}$ 167)</td>
<td>$^{84j}$</td>
</tr>
<tr>
<td>[W(=CNMe)Br$_2$Tp$^*$]</td>
<td>267.1 ($^1J_{cw}$ 241)</td>
<td></td>
<td>$^{85}$</td>
</tr>
<tr>
<td>[W(=CNMe)I$_2$Tp$^*$]</td>
<td>265.5</td>
<td></td>
<td>$^{85}$</td>
</tr>
<tr>
<td>[W(=CNMe)($=$CNMe)$_2$Tp$^*$]</td>
<td>243.1 ($^1J_{cw}$ 232)</td>
<td></td>
<td>$^{85c}$</td>
</tr>
<tr>
<td>[W(=CNMe)($=$CNMe)$_2$(CNMe)Tp$^*$]</td>
<td>260.7</td>
<td></td>
<td>$^{58}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$(CNMe)Tp$^*$]</td>
<td>261.5</td>
<td></td>
<td>$^{85}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$(CO)$_2$Tp]</td>
<td>254.6</td>
<td>225.8</td>
<td>$^{85b}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$(CO)$_2$Tp$^*$]</td>
<td>248.6 ($^1J_{cw}$ 208)</td>
<td>225.6 ($^1J_{cw}$ 169)</td>
<td>$^{84j}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$(CNMe)$_2$Tp$^*$]</td>
<td>242.6 ($^1J_{cw}$ 231)</td>
<td></td>
<td>$^{85c}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$Br$_2$Tp$^*$]</td>
<td>266.5 ($^1J_{cw}$ 242)</td>
<td></td>
<td>$^{85}$</td>
</tr>
<tr>
<td>[W(=CNMe)$_2$I$_2$Tp$^*$]</td>
<td>263.8</td>
<td></td>
<td>$^{85}$</td>
</tr>
</tbody>
</table>

**CHALCO**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ M=CR, ppm ($J$, Hz)</th>
<th>$\delta$ M(CO), ppm ($J$, Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(=CSMe)(CO)$_2$Tp$^*$]</td>
<td>267.6</td>
<td>226.8</td>
<td>$^{75b}$</td>
</tr>
<tr>
<td>[Mo(=CSePh)(CO)$_2$Tp$^*$]</td>
<td>261.8</td>
<td>226.0</td>
<td>$^{185b}$</td>
</tr>
<tr>
<td>[Mo(=CTeMe)(CO)$_2$Tp$^*$]</td>
<td>266.2</td>
<td>225.6</td>
<td>$^{75b}$</td>
</tr>
<tr>
<td>[W(=CSMe)(CO)$_2$Tp]</td>
<td>264.4</td>
<td>224.7</td>
<td>$^{23,77b}$</td>
</tr>
<tr>
<td>[W(=CSMe)(SM)$_2$Tp]</td>
<td>268.3</td>
<td></td>
<td>$^{19}$</td>
</tr>
<tr>
<td>[W(=CSMe)(SM)(SPh)Tp]</td>
<td>271.1</td>
<td></td>
<td>$^{19}$</td>
</tr>
<tr>
<td>[W(=CSMe)(SM)(S)$_2$Me-(4)Tp]</td>
<td>270.8</td>
<td></td>
<td>$^{19}$</td>
</tr>
</tbody>
</table>

**HALO**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ M=CR, ppm ($J$, Hz)</th>
<th>$\delta$ M(CO), ppm ($J$, Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(=CCl)(CO)$_2$Tp$^{py,4Me}$]</td>
<td>211.6</td>
<td>222.4</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CCl)(CO)$_2$Tp$^{py}$]</td>
<td>208.7</td>
<td>224.0</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CCl)(CO)$_2$Tp$^{py,4Me}$]</td>
<td>208.2</td>
<td>224.3</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CCl)(CO)$_2$Tp$^{py,4Cl}$]</td>
<td>245.01</td>
<td>223.1</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CCI)(CO)$_2$tp$^*$]</td>
<td>213.5</td>
<td>223.6</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CBr)(CO)$_2$Tp$^*$]</td>
<td>202.5</td>
<td>223.9</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[Mo(=CBr)(CO)$_2$Tp$^{py}$]</td>
<td>201.9</td>
<td>224.0</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>[W(=CCI)(CO)$_2$Tp$^*$]</td>
<td>205.6</td>
<td>222.0</td>
<td>$^{36b}$</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta$ M=CR ppm ($J$, Hz)</td>
<td>$\delta$ M(CO) ppm ($J$, Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----</td>
</tr>
<tr>
<td>[W(=CBr)(CO)$_2$Tp$^*$]</td>
<td>197.97</td>
<td>221.88</td>
<td>366</td>
</tr>
<tr>
<td>[W(=CI)(CO)$_2$Tp$^*$]</td>
<td>183.2</td>
<td>223.3</td>
<td>68</td>
</tr>
<tr>
<td>PHOSPHONIO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[W(=CP$_3$)(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>251.1 ($J_{cw}$ 163) ($J_{cp}$ 15)</td>
<td>226.1 ($J_{cw}$ 163)</td>
<td>70</td>
</tr>
<tr>
<td>[W(=CPMe$_2$Ph)(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>245.9 ($J_{cw}$ 207)</td>
<td>223.0 ($J_{cw}$ 155)</td>
<td>70</td>
</tr>
<tr>
<td>[W(=CPPh$_3$)(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>242.1 ($J_{cw}$ 212)</td>
<td>224.5 ($J_{cw}$ 158)</td>
<td>70</td>
</tr>
<tr>
<td>PHOSPHA- AND ARSAALKENYL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mo(=CP=C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>337.5 ($J_{cp}$ 111.3)</td>
<td>229.5</td>
<td>87</td>
</tr>
<tr>
<td>[Mo(=CP=C(NB$_3$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>338.6 ($J_{cp}$ 116)</td>
<td>230.7</td>
<td>87</td>
</tr>
<tr>
<td>[Mo(=CP(Me)C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$][O$_3$SCF$_3$]</td>
<td>287.7 ($J_{cp}$ 94)</td>
<td>226.9</td>
<td>110</td>
</tr>
<tr>
<td>[Mo(=CP(Me)C(NEt$_2$)$_2$)(CO)$_2$Tp$^*$][O$_3$SCF$_3$]</td>
<td>286.7 ($J_{cp}$ 97)</td>
<td>227.2</td>
<td>110</td>
</tr>
<tr>
<td>[Mo(=CP(O)$_2$C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>312.6 ($J_{cp}$ 30)</td>
<td>226.5</td>
<td>169</td>
</tr>
<tr>
<td>[Mo(=CP(O)$_2$C(NB$_3$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>314.4 ($J_{cp}$ 28)</td>
<td>227.3</td>
<td>169</td>
</tr>
<tr>
<td>[Mo(=CP(O)$_2$C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>349.7</td>
<td>229.1</td>
<td>83</td>
</tr>
<tr>
<td>[Mo(=CAS=C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>301.9</td>
<td>225.7, 226.1</td>
<td>88</td>
</tr>
<tr>
<td>[W(=CP=C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>318.3 ($J_{cp}$ 101.2)</td>
<td>228.1</td>
<td></td>
</tr>
<tr>
<td>[W(=CP=C(NB$_3$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>319.0 ($J_{cp}$ 108.3)</td>
<td>229.4</td>
<td>87</td>
</tr>
<tr>
<td>[W(=CP(Me)C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$][O$_3$SCF$_3$]</td>
<td>273.0 ($J_{cp}$ 83.0)</td>
<td>225.5</td>
<td>110</td>
</tr>
<tr>
<td>[W(=CP(H)C(NB$_3$)$_2$)(CO)$_2$Tp$^*$][BF$_4$]</td>
<td>261.8 ($J_{cp}$ 90.9)</td>
<td>225.2</td>
<td>110</td>
</tr>
<tr>
<td>[W(=CP(Me)C(NB$_3$)$_2$)(CO)$_2$Tp$^*$][O$_3$SCF$_3$]</td>
<td>271.9 ($J_{cp}$ 85.6)</td>
<td>225.7</td>
<td>110</td>
</tr>
<tr>
<td>[W(=CP(O)$_2$C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>298.7 ($J_{cp}$ 46.2)</td>
<td>225.9</td>
<td>169</td>
</tr>
<tr>
<td>[W(=CP(O)$_2$C(NEt$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>299.9 ($J_{cp}$ 54.0)</td>
<td>226.5</td>
<td>169</td>
</tr>
<tr>
<td>[W(=CAS=C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$]</td>
<td>329.1</td>
<td>227.6 ($J_{cw}$ 183.3)</td>
<td>88</td>
</tr>
<tr>
<td>[W(=CAS(Mo)C(NMe$_2$)$_2$)(CO)$_2$Tp$^*$][O$_3$SCF$_3$]</td>
<td>283.2</td>
<td>225.3, 225.1</td>
<td>88</td>
</tr>
</tbody>
</table>
### Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta M=CR ), ppm (J, Hz)</th>
<th>( \delta M(CO) ), ppm (J, Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrMo{( \mu-\eta^6,\sigma-CC_3H_4(O\text{Me}-2))}(CO)Tp}</td>
<td>278.1</td>
<td>225.7, 225.5</td>
<td>536</td>
</tr>
<tr>
<td>[Mo{( \mu-\sigma,\pi^1-CC_2H_2}}(CO)Tp]</td>
<td>279.1</td>
<td>224.8</td>
<td>546</td>
</tr>
<tr>
<td>[Mo_2Fe{( \mu-\sigma,\pi^1-CC_3H_4}_2(CO)_4Tp}_2]</td>
<td>293.2</td>
<td>225.4</td>
<td>555</td>
</tr>
<tr>
<td>[Mo{( \equiv\text{Fe}(CO)_2Cp})(\equiv\text{Tp}}]</td>
<td>381</td>
<td>226.1</td>
<td>71</td>
</tr>
<tr>
<td>[Mo{( \equiv\text{CMe}(CO)_2C(N\text{Me}_2)_2}}(CO)(\equiv\text{Tp})]</td>
<td>280.9</td>
<td>226.1</td>
<td>109</td>
</tr>
<tr>
<td>[W{( \equiv\text{CP}(\text{AuCl})_2C(N\text{Me}_2)_2}_2}(CO)(\equiv\text{Tp})]</td>
<td>273.0</td>
<td>225.1</td>
<td>109</td>
</tr>
<tr>
<td>[[(\equiv\text{Mo}{( \equiv\text{CMe}}(CO)_2})(\equiv\text{Tp})]}_2]</td>
<td>310.6, 304.8</td>
<td>226.8, 226.4, 225.8</td>
<td>109</td>
</tr>
<tr>
<td>[{(\equiv\text{W} \equiv\text{Mo}{( \equiv\text{CMe}}(CO)_2})(\equiv\text{Tp})]}_2]</td>
<td>296.0, 291.5</td>
<td>225.4, 224.5</td>
<td>109</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO})\equiv\text{Mo} \equiv\text{CMe}(CO)\equiv\text{Tp}])</td>
<td>284.7</td>
<td>225.1</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO})\equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>287.5, W: 273.5</td>
<td>Mo: 225.0; W: 223.2</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{K}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>313.7, W: 298.1</td>
<td>Mo: 229.6; W: 231.4 ((J_{\text{CW}}) 172)</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>294.6, W: 281.0</td>
<td>Mo: 226.6, 225.3, 224.5, 223.3</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>298; W: 285 ((J_{\text{CW}}) 195)</td>
<td>Mo: 226; W: 224 ((J_{\text{CW}}) 170)</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{Mo} \equiv\text{CMe}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>252.8</td>
<td>228.1</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>246</td>
<td>226 ((J_{\text{CW}}) 160)</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>253</td>
<td>228</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>282.3, 274.3</td>
<td>Mo: 227; W: 226 ((J_{\text{CW}}) 162)</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>300.7</td>
<td>225.1</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>289.9 ((J_{\text{CW}}) 180)</td>
<td>223.2 ((J_{\text{CW}}) 160)</td>
<td>1506</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>Isomer 1: 298.0/</td>
<td>223.9, 223.8/</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>Isomer 2: 297.7</td>
<td>224.2, 223.8</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>Isomer 1: 297.6/</td>
<td>226.3, 223.1/</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>Isomer 2: 297.6/</td>
<td>226.3, 223.1</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>303.4</td>
<td>224.9 ((J_{\text{CW}}) 170)</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>285.0</td>
<td>226.8</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>276.4</td>
<td>225.1</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>283.2</td>
<td>226.0</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>283.2</td>
<td>226.5</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>248.9</td>
<td>230.1</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>243.7</td>
<td>228.7</td>
<td>1508</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>(E)</td>
<td>WC(_2)H(_2): 284.7; WC(_2): 278.6</td>
<td>121</td>
</tr>
<tr>
<td>([\equiv\text{Tp}(\equiv\text{CO}) \equiv\text{W} \equiv\text{CMe} \equiv\text{Mo}(\equiv\text{CO})\equiv\text{Tp}])</td>
<td>(Z)</td>
<td>WC(_2)H(_2): 287.0; WC(_2): 279.0</td>
<td>121</td>
</tr>
<tr>
<td>Compound</td>
<td>( \delta M=CR ), ppm (( J, \text{Hz} ))</td>
<td>( \delta M(CO) ), ppm (( J, \text{Hz} ))</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>K( [Tp^<em>(CO)_2W=C(CH)=iC=W(CO)_2Tp^</em>] )</td>
<td>306.1 (( J_{CW} 173 ))</td>
<td>229.6 (( J_{CW} 172 ))</td>
<td>161c</td>
</tr>
<tr>
<td>( [Tp(CO)_2W=CC=CC=CC=W(CO)_2Tp] )</td>
<td>NR</td>
<td>NR</td>
<td>167</td>
</tr>
<tr>
<td>( [Tp^<em>(CO)_2W=CC=CC=W(CO)_2Tp^</em>] )</td>
<td>242.8</td>
<td>227.4</td>
<td>167</td>
</tr>
<tr>
<td>( [Tp^*(CO)_2Mo=CC=W(CO)<em>2(Tp)</em>{172-PhC=CPh}(CO)Tp] )</td>
<td>325.2</td>
<td>226.3, 226.2</td>
<td>161b</td>
</tr>
<tr>
<td>( [Tp^*(CO)_2W=CCH=W(172-PhC=CPh)(CO)Tp] )</td>
<td>312.3</td>
<td>224.6, 224.5</td>
<td>161b</td>
</tr>
<tr>
<td>( [Tp^*(CO)_2Mo=CC=W(CO)<em>2(Tp)</em>{172-PhC=CPh}(CO)Tp] )</td>
<td>311.1</td>
<td>233.4, 229.7</td>
<td>161b</td>
</tr>
<tr>
<td>( [Tp^*(CO)_2Mo=CC=W(172-PhC=CPh)(CO)Tp] )</td>
<td>W: 342.7 (( J_{CW} 184 )),</td>
<td>W: 218.6 (( J_{CW} 130 )),</td>
<td>161b</td>
</tr>
<tr>
<td>( [Tp^*(CO)_2W=CC=W(CO)<em>2(Tp)</em>{172-PhC=CPh}(CO)Tp] )</td>
<td>Mo: 277.0 (( J_{CW} 43 ))</td>
<td>Mo: 234.1, 231.9</td>
<td>161b</td>
</tr>
<tr>
<td>( [Co_2{\mu-t-BuC_2C=W(CO)<em>2Tp}(CO)</em>{172-PhC=CPh}] )</td>
<td>269.1</td>
<td>227.4</td>
<td>161b</td>
</tr>
<tr>
<td>( <a href="CO">Co_2{\mu-t-BuC_2C=W(CO)_2Tp}</a>_{172-PhC=CPh}] )</td>
<td>263.2</td>
<td>224.7 (( J_{CW} 165 ))</td>
<td>161b</td>
</tr>
<tr>
<td>( <a href="%5Cmu-dppm">Co_2{\mu-t-BuC_2C=W(CO)_2Tp}</a>(CO)_{172-PhC=CPh}] )</td>
<td>278.5</td>
<td>227.4 (( J_{CW} 169 ))</td>
<td>161b</td>
</tr>
<tr>
<td>( <a href="CO">Mo_2{\mu-t-BuC_2C=W(CO)_2Tp}</a>(PPh_3)_{172-PhC=CPh}] )</td>
<td>272.9</td>
<td>233.1, 232.6, 228.0, 226.6, 226.2, 225.1 (4 CoCO, 2 WCO)</td>
<td>162</td>
</tr>
<tr>
<td>( <a href="CO">Rh(C=CC=W(CO)_2Tp)</a>(PPh_3)_2 )</td>
<td>258.3</td>
<td>227.3</td>
<td>161b</td>
</tr>
<tr>
<td>( <a href="CO">Rh(C=CC=W(CO)_2Tp)</a>(PPh_3)_2 )</td>
<td>256.7</td>
<td>226.2</td>
<td>161b</td>
</tr>
<tr>
<td>( <a href="CO">RhFe_2{\mu-C_1W(CO)_2Tp}</a>(PPh_3)_2 )</td>
<td>254.6</td>
<td>224.4</td>
<td>161b</td>
</tr>
<tr>
<td>( [Ir(C=CC=W(CO)_2Tp)]H(CO)(PPh_3)_2 )</td>
<td>262.6</td>
<td>227.9</td>
<td>161b</td>
</tr>
<tr>
<td>( [Ir(C=CC=W(CO)_2Tp)]H(CO)(PPh_3)_2 )</td>
<td>255.7</td>
<td>228.0</td>
<td>161b</td>
</tr>
<tr>
<td>( [Ir(C=CC=W(CO)_2Tp)]H(CO)(PPh_3)_2 )</td>
<td>260.6</td>
<td>228.2</td>
<td>161b</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>255.6</td>
<td>227.1 (( J_{CW} 168 ))</td>
<td>161b</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>258.6</td>
<td>227.5</td>
<td>161b</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>261.4</td>
<td>227.2</td>
<td>161b</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>261.4</td>
<td>227.7 (( J_{CW} 171.1 ))</td>
<td>161b</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>NR</td>
<td>NR</td>
<td>168</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>( +{\mu-t-BuC_2C=W(CO)_2Tp}(CO)(PPh_3)_2 )</td>
<td>253.9, 253.5</td>
<td>227.8, 227.2</td>
<td>168c</td>
</tr>
<tr>
<td>Compound</td>
<td>$\delta$ M=CR, ppm ($J$, Hz)</td>
<td>$\delta$ M(CO), ppm ($J$, Hz)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>-------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>[Ru{C(C=W(CO)2Tp*)=CHC=W(CO)2Tp*}]Cl(CO)(PPh3)2</td>
<td>WC$_3$: 287.9; WC$_2$: 241.6</td>
<td>227.9, 227.0</td>
<td>187c</td>
</tr>
<tr>
<td>[Ru{C(C=W(CO)2Tp*)=CHC=W(CO)2Tp*}]Cl(CO)(PPh3)2</td>
<td>WC$_3$: 287.9; WC$_2$: 241.6</td>
<td>227.7, 226.8</td>
<td>187c</td>
</tr>
<tr>
<td>[Ru{C(C=W(CO)2Tp*)}Cl(CO)(PPh3)2]</td>
<td>WC$_3$: 283.6; WC$_2$: 244.9</td>
<td>228.6, 227.4</td>
<td>187c</td>
</tr>
<tr>
<td>[W=CC=CAuPPh]3(CO)2Tp</td>
<td>255.8 ($J_{WC}$ 196)</td>
<td>222.6 ($J_{WC}$ 168)</td>
<td>165</td>
</tr>
<tr>
<td>[W=CC=CAuPPh]3(CO)2Tp</td>
<td>251.7</td>
<td>222.6 ($J_{WC}$ 164)</td>
<td>165</td>
</tr>
<tr>
<td>[$(PPh)2N</td>
<td>Au[C=CC=W(CO)2Tp*]$_2]$</td>
<td>253.6</td>
<td>225.8</td>
</tr>
<tr>
<td>[Hg[C=CC=W(CO)2Tp]$_2$]</td>
<td>246.7</td>
<td>225.6 ($J_{WC}$ 171)</td>
<td>165b</td>
</tr>
</tbody>
</table>

- $^{13}$C($^1$H) NMR data were obtained in CD$_2$Cl$_2$ solution at room temperature unless otherwise indicated. $^{2}$ CDCl$_3$, $^{3}$ C$_6$D$_6$, $^{4}$ DMSO-$d_6$, $^{5}$ THF-$d_6$, $^{6}$ Acetone-$d_6$, $^{7}$ CD$_3$CN, $^{8}$ - 40 °C. $^{9}$ 22 °C. $^{10}$ 20 °C. $^{11}$ Major isomer. $^{12}$ Minor isomer. $^{13}$ - 70 °C. $^{14}$ - 20 °C. NR = not reported.

List of abbreviations: Bp, bis(pyrazolyl)borate; Tp, tris(pyrazolyl)borate; Tp$^*$, tris(3-phenylpyrazolyl)borate; Tp*, tris(3,5-dimethylpyrazolyl)borate; Tp$^*$Me, tris(3,4,5-trimethylpyrazolyl)borate; Tp$^*$Cl, tris(4-chloro-3,5-dimethylpyrazolyl)borate; pzTp, tetrakis(pyrazolyl)borate; dppm, bis(diphenylphosphino)methane; pic, 4-picoline; fc, ferroceny; c, cis; t, trans.

$^{15}$ For Bp complexes fac and mer prefixes refer to the orientation of the bidentate Bp and alkylidyne fragments.
Appendix A.2, Table 1.2. Compilation of structural data for crystallographically characterised alkylidyne metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mo-C, Å</th>
<th>Mo-C-R, Å</th>
<th>Mo-N trans to Other M-N separations, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo} (=\text{C} \text{CMe})_{2} \text{Ph}) \text{(OMe)} { \text{NHC}_3 \text{H}_2 \text{(i-Pr)}_2-2,6 } \text{Tp}])</td>
<td>1.765(4)</td>
<td>177.2(4)</td>
<td>2.386(4)</td>
</tr>
<tr>
<td>([\text{Mo} (=\text{CCl}) \text{(CO)}_2 \text{Tp}])</td>
<td>1.798(9)</td>
<td>NR</td>
<td>2.250(7)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CtBu}) \text{(NHPh)}_2 \text{Tp}])</td>
<td>1.789(5)</td>
<td>166.5(4)</td>
<td>2.356(4)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CtBu}) \text{Cl(NHPh)}_2 \text{Tp}])</td>
<td>1.771(1)</td>
<td>174.7(8)</td>
<td>2.393(8)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{Tp}])</td>
<td>1.821(1)</td>
<td>168.0(8)</td>
<td>2.338(7)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.825(4)</td>
<td>173.5(3)</td>
<td>2.292(3)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.826(5)</td>
<td>173.9(4)</td>
<td>2.298(4)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.831(5)</td>
<td>168.7(4)</td>
<td>2.295(4)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.844(6)</td>
<td>176.4(5)</td>
<td>2.268(4)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.789(5)</td>
<td>177.1(1)</td>
<td>2.36(1)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.821(9)</td>
<td>168.1(5)</td>
<td>2.291(7)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.838(6)</td>
<td>167.9(4)</td>
<td>2.298(5)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.840(8)</td>
<td>162.1(2)</td>
<td>2.281(3)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.813(3)</td>
<td>166.8(2)</td>
<td>2.326(2)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.825(9)</td>
<td>165.2(4)</td>
<td>2.304(6)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.860(1)</td>
<td>177(1)</td>
<td>2.30(1)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.788(7)</td>
<td>171.6(5)</td>
<td>2.288(5)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.786(7)</td>
<td>178.8(6)</td>
<td>2.226(6)</td>
</tr>
<tr>
<td>([\text{W} (=\text{CCl}) \text{(CO)}_2 \text{pzTp}])</td>
<td>1.73(2)</td>
<td>161(2)</td>
<td>2.30(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYMETALLIC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mo{═CFe(CO)\textsubscript{2}Cp}(CO)\textsubscript{2}Tp\textsuperscript{*}]</td>
<td>1.819 (6)</td>
<td>172.2 (5)</td>
<td>2.291 (2)</td>
<td>2.216 (2), 2.207 (2)</td>
<td>71</td>
</tr>
<tr>
<td>[Mo{═CP(AuCl)\textsubscript{2}C(N\textsubscript{Me\textsubscript{2}})\textsubscript{2})(CO)\textsubscript{2}Tp\textsuperscript{*}]</td>
<td>1.819 (2)</td>
<td>160.6 (1)</td>
<td>2.260 (3)</td>
<td>2.218 (3), 2.190 (3)</td>
<td>109</td>
</tr>
<tr>
<td>[Tp\textsuperscript{<em>}(CO)\textsubscript{2}W\textsuperscript{═CCMe=CMeC=W(CO)\textsubscript{2}Tp\textsuperscript{</em>}}]</td>
<td>1.811 (2)</td>
<td>170.1 (1)</td>
<td>2.241 (1)</td>
<td>2.21 (1), 2.221 (1)</td>
<td>158</td>
</tr>
<tr>
<td>[Tp\textsuperscript{<em>}(CO)\textsubscript{2}W\textsuperscript{═CC=C=W(CO)\textsubscript{2}Tp\textsuperscript{</em>}}]</td>
<td>1.862 (3)</td>
<td>175.6 (3)</td>
<td>2.260 (3)</td>
<td>2.218 (3), 2.190 (3)</td>
<td>167</td>
</tr>
<tr>
<td>[Hg{═CC≡AuPPh\textsubscript{3}=W(CO)\textsubscript{2}Tp\textsuperscript{*}}]</td>
<td>1.834 (6)</td>
<td>177.4 (4)</td>
<td>2.034 (4)</td>
<td>2.203 (4), 2.206 (4)</td>
<td>165</td>
</tr>
<tr>
<td>[Bu\textsubscript{4}N]{Au{═CC≡W(CO)\textsubscript{2}Tp\textsuperscript{*}}]</td>
<td>1.823 (3)</td>
<td>173.1 (1)</td>
<td>2.18 (1)</td>
<td>2.20 (1), 2.22 (1)</td>
<td>165</td>
</tr>
<tr>
<td>[Hg{═CC≡W(CO)\textsubscript{2}Tp\textsuperscript{*}}]</td>
<td>1.849 (5)</td>
<td>174.9 (4)</td>
<td>2.267 (4)</td>
<td>2.210 (4), 2.202 (4)</td>
<td>166</td>
</tr>
</tbody>
</table>

* List of abbreviations: Bp, bis(pyrazolyl)borate; Tp, tris(pyrazolyl)borate; Tp\textsuperscript{*}, tris(3,5-dimethylpyrazolyl)borate; Tp\textsuperscript{Me}, tris(3,4,5-trimethylpyrazolyl)borate; pzTp, tetrakis(pyrazolyl)borate; dppm, bisdiphenylphosphinomethane; pic, 4-picoline.
### Appendix A.3, Table 1.3. Characteristic infrared absorptions for known alkylidyne metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{CO}}$, cm$^{-1}$</th>
<th>$k_{\text{CO}}$, N m$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(=CC$_2$H$_4$Me-4)(CO)$_2$Tp]</td>
<td>1997, 1913$^a$</td>
<td>15.44</td>
<td>41</td>
</tr>
<tr>
<td>[Cr(=CC$_2$H$_4$Me-4)(CO)$_2$Tp$^*$]</td>
<td>1987, 1909$^c$</td>
<td>15.33</td>
<td>47</td>
</tr>
<tr>
<td>[Mo($\equiv$CH)(CO)$_2$Tp$^*$]</td>
<td>2001, 1913$^j$</td>
<td>15.47</td>
<td>89</td>
</tr>
<tr>
<td>[Mo($\equiv$CMe)(CO)$_2$Tp$^*$]</td>
<td>1982, 1889$^b$</td>
<td>15.14</td>
<td>62</td>
</tr>
<tr>
<td>[Mo($\equiv$CEt)(CO)$_2$Tp$^*$]</td>
<td>1840$^f$</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>[Mo($\equiv$CH$_2$Bu)(CO)$_2$Tp]</td>
<td>1998, 1906</td>
<td>15.34</td>
<td>48</td>
</tr>
<tr>
<td>[Mo($\equiv$CH$_2$Bu)(CO)$_2$Tp$^*$]</td>
<td>1980, 1885$^b$</td>
<td>15.09</td>
<td>62</td>
</tr>
<tr>
<td>[Mo($\equiv$CH$_2$Bu)(CO)$_2$Tp$^*$]</td>
<td>1889</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)(CO)$_2$Tp$^*$]</td>
<td>1992, 1902</td>
<td>15.32</td>
<td>145</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)(CO)$_2$Tp]</td>
<td>1992, 1882$^b$</td>
<td>15.37</td>
<td>62</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)(CO)$_2$Tp]</td>
<td>1998, 1921$^d$</td>
<td>15.51</td>
<td>41.42</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)$_2$(CO)$_2$Tp]</td>
<td>1955, 1920$^f$</td>
<td>15.16</td>
<td>44</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)$_2$(CO)$_2$Tp]</td>
<td>1982, 1899$^f$</td>
<td>15.21</td>
<td>48</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)$_2$(CO)$_2$Tp]</td>
<td>1991, 1906</td>
<td>15.54</td>
<td>35</td>
</tr>
<tr>
<td>[Mo($\equiv$CPh)$_2$(CO)$_2$Tp]</td>
<td>1989, 1898, 1885$^b$</td>
<td>15.10</td>
<td>69</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>2015, 1940$^b$</td>
<td>15.80</td>
<td>69</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1975, 1892$^b$</td>
<td>15.10</td>
<td>68</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1916, 1819$^b$</td>
<td>14.09</td>
<td>120</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1992, 1903$^k$</td>
<td>15.32</td>
<td>89</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1986, 1891$^b$</td>
<td>15.18</td>
<td>46</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1976, 1881</td>
<td>15.03</td>
<td>39.404</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1983, 1899$^k$</td>
<td>15.22</td>
<td>2</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1995, 1910$^c$</td>
<td>15.40</td>
<td>67.158</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1968, 1867$^b$</td>
<td>14.86</td>
<td>66</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1968, 1876$^k$</td>
<td>14.93</td>
<td>67.158</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1960, 1862$^k$</td>
<td>14.76</td>
<td>66</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1969, 1875$^b$</td>
<td>14.93</td>
<td>67.158</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1963, 1864$^b$</td>
<td>14.80</td>
<td>121</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1958, 1862$^b$</td>
<td>14.74</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1967, 1866$^b$</td>
<td>14.84</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1971, 1872$^b$</td>
<td>14.92</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1969, 1873$^b$</td>
<td>14.91</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1991, 1876$^b$</td>
<td>14.95</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1965, 1865$^b$</td>
<td>14.83</td>
<td>67.158</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1964, 1865$^b$</td>
<td>14.81</td>
<td>66</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1964, 1867$^b$</td>
<td>14.83</td>
<td>66</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1965, 1868$^b$</td>
<td>14.84</td>
<td>121</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1969, 1876$^b$</td>
<td>14.93</td>
<td>121</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1976, 1880$^b$</td>
<td>15.02</td>
<td>68</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1965, 1868$^b$</td>
<td>14.84</td>
<td>121</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1967, 1872$^b$</td>
<td>14.87</td>
<td>68</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1974, 1876$^b$</td>
<td>14.97</td>
<td>68</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1999, 1918$^b$</td>
<td>15.50</td>
<td>67</td>
</tr>
<tr>
<td>[Mo($\equiv$C(CN)(Et)$_2$(CO)$_2$Tp]</td>
<td>1969, 1867$^b$</td>
<td>14.87</td>
<td>67</td>
</tr>
<tr>
<td>Compound</td>
<td>ν&lt;sub&gt;CO&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>k&lt;sub&gt;CO&lt;/sub&gt;, N m&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-------------------------------</td>
<td>------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>[W(=CC≡CHMe)(CO)₂Tp⁺]</td>
<td>1962, 1866&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.80</td>
<td>121</td>
</tr>
<tr>
<td>[W(=CC≡CMe)(CO)₂Tp⁺]</td>
<td>1965, 1862&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.80</td>
<td>121</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(CO)₂Tp⁺]</td>
<td>1953, 1868&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.75</td>
<td>65</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(OC₆H₄Me-4)(CO)₂Tp⁺]</td>
<td>1953, 1870&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.76</td>
<td>65</td>
</tr>
<tr>
<td>[W(=CC≡CMe)(CO)₂Tp⁺]</td>
<td>1991, 1906&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.34</td>
<td>61</td>
</tr>
<tr>
<td>[W(=CC≡CMe)(CO)₂Tp⁺]</td>
<td>1982, 1896&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.19</td>
<td>52</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(CO)₂Tp⁺]</td>
<td>1988, 1904</td>
<td>15.30</td>
<td>60</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(CO)₂Tp⁺]</td>
<td>1979, 1893&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.14</td>
<td>42</td>
</tr>
<tr>
<td>[W(=CC≡CH₂O-2)(CO)₂Tp⁺]</td>
<td>1987, 1905</td>
<td>15.30</td>
<td>42</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(CO)₂Tp⁺]</td>
<td>1990, 1915&lt;sup&gt;40&lt;/sup&gt;</td>
<td>15.40</td>
<td>78</td>
</tr>
<tr>
<td>[W(=CC≡CPh)(CO)₂Tp⁺]</td>
<td>1969, 1876&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.93</td>
<td>46</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1986, 1903</td>
<td>15.28</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1974, 1888&lt;sup&gt;4&lt;/sup&gt;</td>
<td>15.06</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1982, 1897&lt;sup&gt;4&lt;/sup&gt;</td>
<td>15.20</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1986, 1903</td>
<td>15.28</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1889, 1989</td>
<td>15.27</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1866&lt;sup&gt;f&lt;/sup&gt;</td>
<td>50</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1860&lt;sup&gt;f&lt;/sup&gt;</td>
<td>45</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-4)(CO)₂Tp⁺]</td>
<td>1976, 1886</td>
<td>15.07</td>
<td>39,40</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,6)(CO)₂Tp⁺]</td>
<td>1978, 1886</td>
<td>15.08</td>
<td>49</td>
</tr>
<tr>
<td>mer-[W(=CC≡CMe-2,6)(CO)₂(PMe₃Ph)Bp]</td>
<td>1992, 1903</td>
<td>15.32</td>
<td>49</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,6)(CO)₂Tp⁺]</td>
<td>1984, 1901&lt;sup&gt;40&lt;/sup&gt;</td>
<td>15.24</td>
<td>49</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂(pip)Bp]</td>
<td>1975, 1888</td>
<td>15.07</td>
<td>49</td>
</tr>
<tr>
<td>mer-[W(=CC≡CMe-2,4,6)(CO)₂(PMe₃Ph)Bp]</td>
<td>1993, 1905</td>
<td>15.35</td>
<td>49</td>
</tr>
<tr>
<td>mer-[W(=CC≡CMe-2,4,6)(CO)₂(PMe₃Ph)Bp]</td>
<td>1860&lt;sup&gt;49&lt;/sup&gt;</td>
<td>15.07</td>
<td>49</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂Tp⁺]</td>
<td>1975, 1888</td>
<td>15.07</td>
<td>107</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂Tp⁺]</td>
<td>1971, 1874&lt;sup&gt;49&lt;/sup&gt;</td>
<td>14.93</td>
<td>107</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂Tp⁺]</td>
<td>2076, 2010&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16.86</td>
<td>94</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂Tp⁺]</td>
<td>1996&lt;sup&gt;97&lt;/sup&gt;</td>
<td>15.43</td>
<td>97</td>
</tr>
<tr>
<td>[W(=CC≡CMe-2,4,6)(CO)₂Tp⁺]</td>
<td>1991&lt;sup&gt;97&lt;/sup&gt;</td>
<td>15.43</td>
<td>97</td>
</tr>
</tbody>
</table>

**SILYL**

| [Mo(=CSiMe₃Ph)(CO)₂Tp⁺]                       | 1997, 1911                    | 15.43                        | 89  |
| [W(=CSiMe₃)(CO)₂Tp⁺]                         | 1976, 1884<sup>f</sup>        | 15.05                        | 68  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1982, 1889                    | 15.14                        | 69  |

**ARYLOXY**

| [Mo(=COPh)(CO)₂Tp⁺]                          | 1982, 1889<sup>e</sup>        | 15.14                        | 70  |
| [Mo(=CO₂C₆H₄Me-4)(CO)₂Tp⁺]                   | 1980, 1887<sup>e</sup>        | 15.11                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1958, 1862<sup>i</sup>        | 14.74                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1967, 1870<sup>i</sup>        | 14.87                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1966, 1870<sup>i</sup>        | 14.86                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1965, 1866<sup>e</sup>        | 14.83                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1977, 1877<sup>i</sup>        | 15.01                        | 70  |
| [W(=C₂H₅Me)(CO)₂Tp⁺]                         | 1969, 1864<sup>b</sup>        | 14.84                        | 70  |

**AMINO**

<p>| [Cr{=CN(i-Pr)₂}(CO)₂Tp⁺]                     | 1953, 1856                    | 14.66                        | 81,82|
| [Cr{=CN(i-Pr)₂}(CO)(CN₃-Bu)Tp⁺]              | 1956, 1863&lt;sup&gt;j&lt;/sup&gt;        | 14.73                        | 81,82|
| [Mo(=CNMe₂)(CO)₂Tp⁺]                         | 1948, 1852&lt;sup&gt;j&lt;/sup&gt;        | 14.59                        | 83  |
| [Mo(=CNMe₂)(CO)₂Tp⁺]                         | 1939, 1884&lt;sup&gt;b&lt;/sup&gt;        | 14.76                        | 83  |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{\text{CO}}$, cm$^{-1}$</th>
<th>$k_{\text{CO}}$, N m$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo{CN(i-Pr)$_2$}(CO)$_2$Tp]</td>
<td>1937, 1835$^a$</td>
<td>14.37</td>
<td>180</td>
</tr>
<tr>
<td>[Mo{CNMe(r-Bu)}(CO)$_2$Tp$^*$]</td>
<td>1945, 1848$^b$</td>
<td>14.53</td>
<td>83</td>
</tr>
<tr>
<td>[Mo{CNMePh}(CO)$_2$Tp$^*$]</td>
<td>1963, 1856$^b$</td>
<td>14.74</td>
<td>83</td>
</tr>
<tr>
<td>[W{CNH$_2$}(CO)$_2$Tp]</td>
<td>1950, 1855</td>
<td>14.63</td>
<td>75</td>
</tr>
<tr>
<td>[W{CNHMe}(CO)$_2$Tp$^*$]</td>
<td>1943, 1837</td>
<td>14.44</td>
<td>75</td>
</tr>
<tr>
<td>[W{CNMePh}(CO)$_2$Tp$^*$]</td>
<td>1956, 1860</td>
<td>14.71</td>
<td>75</td>
</tr>
<tr>
<td>[W{CNMe$_2$}(CO)$_2$Tp$^*$]</td>
<td>1941, 1837</td>
<td>14.42</td>
<td>75</td>
</tr>
<tr>
<td>[W{CNMe$_2$}(CO)$_2$Tp$^*$]</td>
<td>1936, 1833</td>
<td>14.35</td>
<td>84</td>
</tr>
<tr>
<td>[W{CNH$_2$}(CO)$_2$Tp$^*$]</td>
<td>1938, 1831</td>
<td>14.35</td>
<td>75</td>
</tr>
<tr>
<td>[W{CNH$_2$}(CO)$_2$Tp$^*$]</td>
<td>1930, 1830</td>
<td>14.28</td>
<td>75</td>
</tr>
<tr>
<td>CHALCO</td>
<td>1836, 1833</td>
<td>14.35</td>
<td>42</td>
</tr>
<tr>
<td>[Et$_4$N][Mo{CS}(CO)$_2$Tp$^*$]</td>
<td>1886, 1794$^e$</td>
<td>13.68</td>
<td>73</td>
</tr>
<tr>
<td>[Et$_4$N][Mo{CSe}(CO)$_2$Tp$^*$]</td>
<td>1913, 1824$^b$</td>
<td>14.11</td>
<td>73</td>
</tr>
<tr>
<td>[Et$_4$N][Mo{CTe}(CO)$_2$Tp$^*$]</td>
<td>1924, 1840$^b$</td>
<td>14.31</td>
<td>73</td>
</tr>
<tr>
<td>[Mo{CSMe}(CO)$_2$Tp$^*$]</td>
<td>1987, 1904$^m$</td>
<td>15.29</td>
<td>189</td>
</tr>
<tr>
<td>[Mo{CSePh}(CO)$_2$Tp$^*$]</td>
<td>1988, 1914$^c$</td>
<td>15.38</td>
<td>73</td>
</tr>
<tr>
<td>[Mo{CTeMe}(CO)$_2$Tp$^*$]</td>
<td>1992, 1911$^m$</td>
<td>15.39</td>
<td>23,77</td>
</tr>
<tr>
<td>[W{CSMe}(CO)$_2$Tp$^*$]</td>
<td>1979, 1893$^g$</td>
<td>15.14</td>
<td>23</td>
</tr>
<tr>
<td>[W{CSeH$_2$}(CO)$_2$Tp$^*$]</td>
<td>1973, 1885</td>
<td>15.03</td>
<td>23</td>
</tr>
<tr>
<td>[W{CSeH$_2$}(CO)$_2$Tp$^*$]</td>
<td>1979, 1892$^g$</td>
<td>15.14</td>
<td>23</td>
</tr>
<tr>
<td>[W{CSc$_2$H$_4$(NO)$_2$-2,4}(CO)$_2$Tp$^*$]</td>
<td>1999, 1914$^g$</td>
<td>15.47</td>
<td>23</td>
</tr>
<tr>
<td>HALO</td>
<td>2006, 1925$^c$</td>
<td>15.61</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2003, 1925</td>
<td>15.58</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2002, 1922</td>
<td>15.55</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2005, 1921$^c$</td>
<td>15.57</td>
<td>36,37</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2005, 1920$^c$</td>
<td>15.56</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2010, 1929$^c$</td>
<td>15.67</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2010, 1929$^c$</td>
<td>15.67</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2008, 1924$^c$</td>
<td>15.62</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2007, 1923$^c$</td>
<td>15.60</td>
<td>36</td>
</tr>
<tr>
<td>[Mo{CCl}(CO)$_2$Tp$^*$]</td>
<td>2009, 1927$^c$</td>
<td>15.65</td>
<td>36</td>
</tr>
<tr>
<td>[W{CCl}(CO)$_2$Tp$^*$]</td>
<td>1991, 1902$^c$</td>
<td>15.31</td>
<td>36</td>
</tr>
<tr>
<td>[W{CCl}(CO)$_2$Tp$^*$]</td>
<td>1994, 1905$^c$</td>
<td>15.36</td>
<td>36</td>
</tr>
<tr>
<td>PHOSPHONIO</td>
<td>1992, 1907$^c$</td>
<td>15.35</td>
<td>68</td>
</tr>
<tr>
<td>[W{CPE$_3$}(CO)$_2$Tp$^*$]</td>
<td>2020, 1935</td>
<td>15.80</td>
<td>72</td>
</tr>
<tr>
<td>[W{CPC$_3$}(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>2020, 1933$^r$</td>
<td>15.78</td>
<td>70</td>
</tr>
<tr>
<td>[W{CPC$_3$}(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>2022, 1934$^r$</td>
<td>15.81</td>
<td>70</td>
</tr>
<tr>
<td>[W{CPC$_3$}(CO)$_2$Tp$^*$][PF$_6$]</td>
<td>2026, 1940$^r$</td>
<td>15.89</td>
<td>70</td>
</tr>
<tr>
<td>PHOSPHA- AND ARSAALKENYL</td>
<td>1946, 1864$^b$</td>
<td>14.66</td>
<td>87</td>
</tr>
<tr>
<td>[Mo{CP=C(NMe$_2$)$_2$}(CO)$_2$Tp$^*$]</td>
<td>1943, 1859$^b$</td>
<td>14.86</td>
<td>87</td>
</tr>
<tr>
<td>[Mo{CP=C(NMe$_2$)$_2$}(CO)$_2$Tp$^*$]</td>
<td>1997, 1915$^b$</td>
<td>15.46</td>
<td>110</td>
</tr>
<tr>
<td>[Mo{CP=C(NMe$_2$)$_2$}(CO)$_2$Tp$^*$]</td>
<td>1994, 1903$^b$</td>
<td>15.34</td>
<td>110</td>
</tr>
<tr>
<td>[Mo{CP=C(NMe$_2$)$_2$}(CO)$_2$Tp$^*$]</td>
<td>2005, 1918$^b$</td>
<td>15.54</td>
<td>169</td>
</tr>
<tr>
<td>[Mo{CP=C(NMe$_2$)$_2$}(CO)$_2$Tp$^*$]</td>
<td>2002, 1923$^b$</td>
<td>15.56</td>
<td>169</td>
</tr>
<tr>
<td>Compound</td>
<td>ν&lt;sub&gt;CO&lt;/sub&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>κ&lt;sub&gt;CD&lt;/sub&gt;, N m&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-------------------------------</td>
<td>---------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>[Mo{≡CAs=C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂}(CO)₂Tp*]</td>
<td>1947, 1863&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.66</td>
<td>88</td>
</tr>
<tr>
<td>[Mo{C≡C(Me)C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂}(CO)₂Tp*][O₃SCF₃]</td>
<td>1997, 1911&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.43</td>
<td>88</td>
</tr>
<tr>
<td><a href="CO">W≡CP=C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂</a>₂Tp*</td>
<td>1935, 1848&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.46</td>
<td>87</td>
</tr>
<tr>
<td>[W≡CP=C(NEt&lt;sub&gt;2&lt;/sub&gt;)₂(CO)₂Tp*]</td>
<td>1933, 1845&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.42</td>
<td>87</td>
</tr>
<tr>
<td>[W≡CP(C)(C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂)(CO)₂Tp*][O₃SCF₃]</td>
<td>1982, 1893&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.17</td>
<td>110</td>
</tr>
<tr>
<td><a href="CO">W≡CP(H)(CNEt&lt;sub&gt;2&lt;/sub&gt;)₂</a>₂Tp*[BF₄]</td>
<td>1986, 1897&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.23</td>
<td>110</td>
</tr>
<tr>
<td>[W≡CP(C)(CNEt&lt;sub&gt;2&lt;/sub&gt;)₂(CO)₂Tp*][O₅SCF₃]</td>
<td>1981, 1884&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.09</td>
<td>110</td>
</tr>
<tr>
<td>[W≡CP(O)(C)(C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂)(CO)₂Tp*]</td>
<td>1987, 1893&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.21</td>
<td>169</td>
</tr>
<tr>
<td>[W≡CP(O)(C)(CNEt&lt;sub&gt;2&lt;/sub&gt;)₂(CO)₂Tp*]</td>
<td>1989, 1894&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.23</td>
<td>169</td>
</tr>
<tr>
<td><a href="CO">W≡CAs=C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂</a>₂Tp*</td>
<td>1936, 1848&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.46</td>
<td>88</td>
</tr>
<tr>
<td><a href="CO">W≡CAs(Me)C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂</a>₂Tp*[O₃SCF₃]</td>
<td>1981, 1888&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.12</td>
<td>88</td>
</tr>
</tbody>
</table>

**POLYMETALLIC**

<p>| CrMo[(μ-η⁶:η¹-CC₆H₄(OMe-2))(CO)₂Tp]                                     | 2011, 1966, 1929, 1900&lt;sup&gt;b&lt;/sup&gt; | 53   |
| [Mo₂Fe(μ-σ, σ':η⁵-CC₆H₄)₂(CO)₄Tp₂]                                    | 1987, 1904                           | 55   |
| [Tp<em>CO]₂Mo[≡CF(CO)₂Cp]                                               | 1947, 1865                           | 71   |
| [Tp</em>CO]₂Mo[≡CP(AuCl)₂C(NMe&lt;sub&gt;2&lt;/sub&gt;)₂]                             | 2002, 1921                           | 109  |
| [(Mo≡CAs(CO))₂Tp*]                                                   | 1987, 1909                           | 109  |
| [(W≡CAs(CO)₂Tp*)]                                                    | 1972, 1887                           | 109  |
| [Tp<em>CO]₂W[≡CCH(Me)C≡Mo(CO)₂Tp</em>]                                      | 1894, 1878                           | 159  |
| [Tp<em>CO]₂W[≡CCH(Me)C≡Mo(CO)₂Tp</em>]                                      | 1896, 1874                           | 159  |
| [Tp<em>CO]₂W[≡CC(Me)C≡Mo(CO)₂Tp</em>]                                       | 1893, 1874                           | 159  |
| [Tp<em>CO]₂W[≡CC(Me)C≡Mo(CO)₂Tp</em>]                                       | 1983, 1897                           | 159  |
| [Tp<em>CO]₂W[≡CC(Me)C≡Mo(CO)₂Tp</em>]                                       | 1971, 1877                           | 159  |
| [Tp<em>CO]₂W[≡CC(CO)₂Tp</em>]                                               | 1985, 1904                           | 159  |
| [Tp<em>CO]₂Mo[≡CCH₂C≡Mo(CO)₂Tp</em>]                                        | 1976, 1879                           | 158  |
| [Tp<em>CO]₂W[≡CCH₂C≡Mo(CO)₂Tp</em>]                                         | 1963, 1867                           | 158  |
| [Tp<em>CO]₂W[≡CCH₂C≡Mo(CO)₂Tp</em>]                                         | 1969, 1866                           | 158  |
| [Tp<em>CO]₂W[≡CCH₂C≡Mo(CO)₂Tp</em>]                                         | 1964, 1869                           | 158  |
| [Tp<em>CO]₂W[≡CCH₂C≡Mo(CO)₂Tp</em>]                                         | 1963, 1864                           | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1890&lt;sup&gt;b&lt;/sup&gt;                    | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1977, 1956                           | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1869&lt;sup&gt;b&lt;/sup&gt;                    | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1957, 1869                           | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1963, 1875                           | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1901&lt;sup&gt;b&lt;/sup&gt;                    | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1987, 1958                           | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1878&lt;sup&gt;b&lt;/sup&gt;                    | 158  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1962, 1870                           | 121  |
| [Tp<em>CO]₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                      | 1962, 1870                           | 121  |
| [K(Tp<em>CO)₂W[≡CCH₃C≡CH=CH(CO)₂Tp</em>]                                    | NR                                 | 121  |
| [Tp<em>CO]₂W[≡CC≡CC≡CC≡W(CO)₂Tp]                                        | 1890                               | 167  |
| [Tp</em>CO]₂W[≡CC≡CC≡CC≡W(CO)₂Tp]                                        | 1901                               | 167  |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{CO}$, cm$^{-1}$</th>
<th>$k_{CO}$, N m$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Tp^*(CO)_2Mo=CCCH_2W(\eta^2-PhC=CPh)(CO)Tp]$</td>
<td>1943, 1921, 1855$^a$</td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>$[Tp^*(CO)_2W=CCCH_2W(\eta^2-PhC=CPh)(CO)Tp]$</td>
<td>1933, 1918, 1842$^b$</td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>$[Tp^*(CO)_2Mo=CC=W(\eta^2-PhC=CPh)(CO)Tp]$</td>
<td>1999, 1950, 1871$^c$</td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>$[Co_2(\mu-t-BuC_2C=Mo(CO)_2Tp^*)_2(CO)]_3$</td>
<td>2090, 2055, 2032, 1975, 1898</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>$[Co_2(\mu-t-BuC_2C=W(CO)_2Tp^*)(CO)]_3$</td>
<td>2089, 2053, 2029, 1978, 1902$^e$</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>$[Mo_2(\mu-t-BuC_2C=W(CO)_2Tp^*)(CO)]_4(OCp)_2$</td>
<td>2001, 1954, 1932, 1874, 1840</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>$[Rh(C=C=W(CO)_2Tp^*)(CO)(PPh_3)]_2$</td>
<td>1979, 1872, 14.98</td>
<td></td>
<td>162</td>
</tr>
<tr>
<td>$[Rh(C=C=W(CO)_2Tp^*)(CO)(PPh_3)]_2$</td>
<td>1965, 1882, 14.95</td>
<td></td>
<td>162</td>
</tr>
<tr>
<td>$[Fe_2Rh(\mu-C_5W(CO)<em>2Tp^*)(CO)</em>{10}(PPh_3)]_2$</td>
<td>1982, 1899, 15.21</td>
<td></td>
<td>162</td>
</tr>
<tr>
<td>$[Ir(C=C=W(CO)_2Tp^*)_2H(CO)(PPh_3)]_2$</td>
<td>1948, 1873, 14.75</td>
<td></td>
<td>162</td>
</tr>
<tr>
<td>$[Ru(C_2W(CO)_2Tp^<em>)(Hg_2C_2W(CO)_2Tp^</em>)_2(CO)(PPh_3)]_2$</td>
<td>1985, 1970, 1879, 1865</td>
<td></td>
<td>168</td>
</tr>
<tr>
<td>$[Ru(C_2W(CO)_2Tp^*)=CHC=W(CO)_2Tp^*Cl(CO)(PPh_3)]_2$</td>
<td>1998, 1876, 15.17</td>
<td></td>
<td>168</td>
</tr>
<tr>
<td>$[Ru(C_2W(CO)_2Tp^*)=CHC=W(CO)_2Tp^*Cl(CO)(PPh_3)]_2$</td>
<td>2003, 1867, 15.14</td>
<td></td>
<td>168</td>
</tr>
</tbody>
</table>

$^a$ Data were obtained in CH$_2$Cl$_2$ solution at room temperature unless otherwise indicated. $^b$ KBr. $^c$ Cyclohexane. $^d$ Light Petroleum. $^e$ Acetonitrile. $^f$ Neat. $^g$ CS$_2$. $^h$ Nujol. $^i$ THF. $^j$ Ether. $^k$ Hexane. $^l$ Pentane. $^m$ Unspecified. $^n$ CaF$_2$.

List of abbreviations: Bp, bis(pyrazolyl)borate; Tp, tris(pyrazolyl)borate; Tp$^{Me}$, tris(3-methylpyrazolyl)borate; Tp$^Ph$, tris(3-phenylpyrazolyl)borate; Tp$^{4To}$, tris(4-toly1pyrazolyl)borate; Tp$, tris(3,5-dimethy1pyrazolyl)borate; Tp$^{Me}$, tris(3,4,5-trimethylpyrazolyl)borate; Tp$^{Cl}$, tris(4-chloro-3,5-dimethylpyrazolyl)borate; pzTp, tetrakis(pyrazolyl)borate; dppm, bisdiphenylphosphinomethane; pic, 4-picoline.
REFERENCES

17. S. Trofimenko, Chemical Reviews (Washington, DC, United States) 1993, 93, 943.


CHAPTER TWO
CHEMISTRY OF ORGANYL ISOSELENOCYANATES WITH PLATINUM GROUP METALS
2.1 Introduction

Unsaturated organosulfur compounds have been known since the beginnings of organic chemistry and can be readily prepared for most organic functional groups. However, the larger size difference between the heavier congener of sulfur, selenium, and the first-row elements results in a diminished stability (and greater reactivity) of bonds to carbon, nitrogen, and oxygen, and there are consequently relatively few reports of selenium in multiple bonds to carbon.¹

Kinetic stabilisation of the otherwise reactive C–Se multiple bonds is frequently achieved by the incorporation of sterically bulky substituents.² Furthermore, the C–Se linkage may gain electronic stability by engaging the π-system of an additional heteroatom (oxygen, nitrogen, or sulfur) in a mesomeric interaction.² A final strategy for stabilisation of unsaturated organoselenium compounds involves coordination to transition-metals. However, the general instability of selenocarbonyl derivatives, R¹(R²)C=Se,² has limited their direct use in coordination chemistry and, in contrast to carbon monoxide, there is a lack of freely available carbon monochalcogenide molecules CE (E = S, Se, Te). Consequently, ligands containing unsaturated carbon–selenium bonds must typically be prepared by modification of a coordinated precursor.³ Historically, CSe₂ and CSSe have been employed in this role, though neither is conveniently accessible. A new approach to the organometallic and coordination chemistry of molecules containing unsaturated C–Se units was therefore an attractive goal.

This Chapter describes an attempt to expand upon the transition-metal chemistry of platinum group complexes containing unsaturated C–Se linkages by employing an organyl isoselenocyanate (SeCNR) as the unsaturated C–Se source molecule. Linford and Raubenheimer have comprehensively reviewed the reactions of organosulfur and organoselenium compounds mediated by transition-metals, including an extensive section focused specifically on the formation and reactions of unsaturated organosulfur and organoselenium organometallic compounds.⁴ Furthermore, Fischer has prepared a detailed review devoted entirely to metal complexes of ligands with multiple carbon–sulfur and carbon–selenium bonds, specifically chalcoaldehyde and chalcoketone complexes.² Accordingly, a general overview of the organometallic chemistry of complexes containing unsaturated organoselenium compounds will not be included here.

2.1.1 The isoselenocyanate ligand

Bonding interactions

In organic syntheses, organyl isoselenocyanates are often used as the synthetic equivalent for the unstable and difficult to access selenocarbonyl unit.⁵ Organyl isoselenocyanates formally
CHAPTER 2. CHEMISTRY OF ORGANYL ISOSELENOCYANATES WITH Pt GROUP METALS

comprise cumulated C=Se and C=N bonds, but in emphasising the aforementioned property it is often instructive to draw the polarised canonical form depicted on the left of Figure 2.1 (a). The structure of the SeCNR molecule is, however, more accurately described as intermediate between the two boundary forms shown on the right (b and c, Figure 2.1).

Due to the cumulated system of C=Se and C=N bonds and the presence of a terminal chalcogen donor atom, both $\eta^1$- and $\eta^2$-coordination modes are potentially available to the organyl isoselenocyanate molecule in mononuclear metal complexes (Chart 2.1). The $\eta^1$-mode (a, Chart 2.1) involves $\sigma$-donation from a lone pair of the chalcogen to an empty d orbital of the metal, while $\eta^2$-bonding (b and c, Chart 2.1) engages the $\pi$-orbitals of the heteroallenic ligand in cooperative $\sigma$-donor (to a vacant metal orbital) and $\pi^*$-acceptor (from a filled $\delta\pi$ metal orbital) roles.

Rosi and co-workers have performed theoretical studies on the interaction of transition-metals with heterocumulenes and, on this basis, have concluded that the $\eta^2$-bonding situation lies at the very extreme of the Dewar–Chatt–Duncanson model, i.e., being dominated by the retrodonation from the metal to the heterocumulene. Distortion of the unsaturated ligand upon coordination thus enhances stabilisation of the complex by increasing this interaction.

Transition-metal complexes
A survey of the literature reveals relatively few examples of metal complexes containing an intact SeCNR ligand. Furthermore, although two $\eta^2$-coordination modes (b and c, Chart 2.1) are possible, only the $\pi$-C=Se mode has been experimentally observed, with the resultant complexes exhibiting limited stability.
Step-wise formation of an unstable $\eta^1$-isoselenocyanate ligand was achieved within the protective coordination sphere of the transient salt $[\text{Re(SeCNMe)}(\text{CO})_2(\text{triphos})][\text{O}_3\text{SCF}_3]$ (triphos = (PPh$_2$CH$_2$)$_3$CMe). Displacement of the poorly coordinating triflate anion from $[\text{Re(O}_3\text{SCF}_3)(\text{CO})_2(\text{triphos})]$ with selenocyanate afforded the complex $[\text{Re(SeCN)(CO)}_2(\text{triphos})]$. Subsequent methylation of the coordinated selenocyanate ligand occurred at selenium to generate the thermodynamically favoured methylselenocyanate complex, $[\text{Re(SeCNMe)}(\text{CO})_2(\text{triphos})][\text{O}_3\text{SCF}_3]$, with a small amount (ca. 30%) of N-methylation generating the elusive methyl isoselenocyanate compound, $[\text{Re(SeCNMe)}(\text{CO})_2(\text{triphos})][\text{O}_3\text{SCF}_3]$. Complete and irreversible conversion of the unstable isoselenocyanate complex to the more stable compound occurred at ambient temperature within one hour (Scheme 2.1).

**Scheme 2.1.** Generation of an unstable $\eta^1$-isoselenocyanate complex of rhenium(I).

Quantitative displacement of the 3-hexyne ligand in the porphyrin complex $[\text{Ti}(3\text{-hexyne})(\text{TTP})]$ (TTP = meso-5,10,15,20-tetra-p-tolylporphyrinato dianion) with t-butyl isoselenocyanate rapidly affords the $\eta^2$-Se,C-isoselenocyanate complex $[\text{Ti}(\eta^2-\text{SeCNt-Bu})(\text{TTP})]$ (Scheme 2.2, top). This complex was, however, only a transiently observed intermediate, being slowly (over approximately four hours) converted to the selenido complex $[\text{Ti}(\equiv\text{Se})(\text{TTP})]$ through loss of the t-butyl isonitrile fragment.

The related porphyrin imido complexes $[\text{M}(\equiv\text{NR})(\text{TTP})]$ (M = Zr, Hf; R = 2,6-diisopropylphenyl) are similarly reported to participate in atom- and group-transfer reactions with heterocumulenes. With t-butyl isocyanate, a $[2+2]$ cycloaddition affords $N,O$-bound ureato metallacycles. However, a corresponding $N,Se$-bound selenoureato metallacycle was not isolable when t-butyl isoselenocyanate was employed. Instead, further

$^5$ Both the $N$- and $Se$-bound linkage isomers of the pseudohalide complex $[\text{Re(SeCN)(CO)}_2(\text{triphos})]$ were formed, however, transformation of the $N$-bound isomer to the more stable $Se$-bound isomer was achieved upon gentle heating.
reaction led to ejection of the carbodiimide product, \( t\text{-BuN} = C\text{=}NR \), with concomitant formation of a metal–selenido derivative (Scheme 2.2, bottom).

Prior to this, Walker and co-workers described the preparation of the (poorly characterised) \( \eta^3\text{-C,Se}-\text{isoselenocyanate complex} \ [\text{Pt}(\eta^3\text{-SeCNC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2] \), which displayed enhanced stability over the above example. This platinum complex was isolated as an air stable solid from the reaction between \([\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)] \) and \( p\text{-tolyl isoselenocyanate} \) in hexane (Scheme 2.3). With excess SeCNR in dichloromethane solution the instability of the SeCNR ligand was manifest, affording the complex \([\text{Pt}(\eta^2\text{-Se}_2\text{CNC}_6\text{H}_4\text{Me-4})(\text{CNC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)] \), which contains both diselenocarbonimidato and isonitrile ligands as a result of SeCNR disproportionation.
Summary
Due to a propensity for the C=Se bond to undergo reduction to the more stable C–Se single bond, complexes incorporating intact organyl isoselenocyanate ligands are rare. In order to further explore the coordination chemistry of SeCNR, a system is required that confers an enhanced stability to the π-C,Se interaction with transition-metals. Mesityl isoselenocyanate, bearing the bulky and thus kinetically stabilising 2,4,6-trimethylphenyl (Mes) substituent, should be ideally suited to this role.

2.1.2 Metal substrates for SeCNRmes coordination
Organyl isoselenocyanates might be expected to display bonding properties similar to those of the closely related cumulene carbon diselenide. Moreover, an obvious relationship exists between the heterocumulenic organyl isoselenocyanates and the corresponding sulfur compounds, SCNR. As such, the body of organometallic and coordination chemistry of arylphosphine complexes of ruthenium involving both CSe₂ and SCNR ligands provides a comparative background for parallel studies involving SeCNR.

The formation of π-bound organic isothiocyanate complexes of ruthenium and rhodium has been known since 1967.¹¹,¹² Treatment of the ruthenium(0) complex [Ru(CO)₂(PPh₃)₃] with a range of organic isothiocyanates yields the simple π-bound complexes [Ru(η²-SCNR)(CO)₂(PPh₃)₂] (R = Ph, Et, Me).¹² In the presence of excess isothiocyanate, it has also been established that sulfur abstraction occurs to yield isonitrile-dithiocarbonimidato complexes (Scheme 2.4), analogous to the situation described for Pt(η²-SeCN-C₆H₄Me-4)(PPh₃)₂ (vide supra, Scheme 2.3).

Similarly, facile reaction between carbon diselenide and [Ru(CO)₂(PPh₃)₃] occurs to provide the complex [Ru(CSe₂)(CO)₂(PPh₃)₂] (Scheme 2.4), which, like its carbon disulfide analogue, can be alkylated with MeI to afford the diselenomethoxyxycarbonyl complex.

Scheme 2.4. Reactivity of [Ru(CO)₂(PPh₃)₃] with isothiocyanates and carbon diselenide (R = Ph, E, Me).
[Ru(CSe₂Me)(CO)(PPh₃)₂]. Subsequent reaction with HCl proceeds via elimination of MeSeH to produce the selenocarbonyl complex [RuCl₂(CO)(CSe)(PPh₃)₂].

To investigate the possibility of obtaining ruthenium complexes incorporating an η²-bound mesityl isoselenocyanate ligand, a selection of ruthenium substrates were chosen that span the more common functional groups in organometallic chemistry, i.e., those with a vacant coordination site (Ru(0) and Ru(II)), innocent co-ligands, and reactive metal–ligand bonds (including metal hydride and metal σ-organyl complexes).
2.2 Ligand synthesis and characterisation

An effective and high yielding synthetic route to the mesityl isoselenocyanate ligand, SeCNMes (1), was first developed, the overall synthetic strategy of which is illustrated in Scheme 2.5.

Scheme 2.5. Reagents: (i) (CH₃CO)₂O(CHO), 5 °C; (ii) POCl₃, (i-Pr)₂NH, CH₂Cl₂, 0 °C; (iii) Se, DBU, THF (R = C₆H₂Me₃-2,4,6).

The precursor isocyanide 3 was obtained by a combination of the standard procedures devised by Huffman¹⁴ and Ugi,¹⁵ which involve the preparation and dehydration of the corresponding formamide 2. Classically, organyl isoselenocyanates have then be prepared by the addition of elemental selenium to a refluxing chloroform solution of the isonitrile.⁵ However, this method proved unsuccessful in the present case, even in the presence of triethylamine catalyst. A modified procedure was thus developed that involved heating a tetrahydrofuran solution of 3 with a slight excess of elemental selenium in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Rauchfuss has previously commented on the activating effect of strong nitrogen bases on elemental chalcogens¹⁶⁻²⁰ and it is likely that the role of the DBU in this synthesis, being a much stronger base than Et₃N (pK_ip (THF): DBU −3.78 vs. Et₃N 2.11)²¹ is to polarise the Se–Se bonds of the polymeric grey elemental selenium.

Perturbations of the physical properties of 3 upon the incorporation of selenium are minimal. The most discernible spectroscopic change is in the infrared spectrum, with the sharp, narrow ν CN stretch of 3, 2120 cm⁻¹, being replaced by a broader absorption in 1, ν SeCN(as) 2122 cm⁻¹, with a sharp shoulder at 2018 cm⁻¹. This absorption profile is characteristic of the cumulated double bond system of aryl isoselenocyanates.⁵

The ¹H NMR data for 3 and 1 are virtually identical. The ¹³C{¹H} NMR spectra are, however, more indicative of the differing chemical properties for these molecules. Nuclear quadrupole coupling in isonitriles is very low, indicating a near zero electric field gradient about nitrogen,

⁵ where pK_ip is the ion pair basicity and smaller or negative values are indicative of stronger bases.
which allows the measurement of natural abundance $^{14}\text{N}\cdots^{13}\text{C}$ spin–spin coupling constants.$^{22}$ For mesityl isocyanide, these values are $J_{\text{NC}} = 12.67$ Hz and $J_{\text{NC}} = 5.8$ Hz for C(2) and C(1), respectively (using the numbering scheme defined in Figure 2.2), which are typical of aryl isocyanides. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1, the resolution of this coupling is lost and the resonances due to these carbons display a broadened appearance. Moreover, the resonance due to C(1), the central carbon of the SeCN unit, has undergone an approximate 40 ppm upfield shift ($\Delta$; 167 in 3 vs 130 in 1). Both the low intensity and upfield chemical shift of this resonance are consistent with those found for other organic isoselenocyanates.$^{23,24}$ Furthermore, the shift is in agreement with the expected enhancement of shielding upon increasing the coordination number of carbon from one to two. The remaining carbon resonances of mesityl isoselenocyanate, like the proton resonances, are marginally altered from those observed for the precursor isocyanide.

![Molecular structure of a) CNMes and b) SeCNMes with 30% probability ellipsoids shown. Hydrogen atoms have been omitted.](image)

**Figure 2.2.** Molecular structure of a) CNMes and b) SeCNMes with 30% probability ellipsoids shown. Hydrogen atoms have been omitted.

Prior to this work, very limited structural data were available for organyl isoselenocyanates,$^{25}$ thus it seemed appropriate to establish a crystallographic benchmark for this functional group. Accordingly, both mesityl isocyanide and mesityl isoselenocyanate were crystallographically characterised. The results of this study are shown in Figure 2.2 and selected bond distances and angles are collected in Table 2.1. Comparable C(1)–N bond distances were found for mesityl isoselenocyanate (1.166(3) Å) and isonitrile (1.158(3) Å), with only a modest departure from linearity (ca. 10°) observed for the SeCN unit in 1. The short bond lengths (1.160(3) Å (N=C) and 1.731(2) Å (C-Se)) and large C–N–Se angle (167.6(3)°) for 1 are as expected for the significant $\pi$-interactions between these atoms in the cumulated SeCN linkage.
Table 2.1. Selected bond lengths (Å) and angles (°) for 1 and 3

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>Bond Angles, °</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1)–N</td>
</tr>
<tr>
<td>(3) SeCNMes</td>
<td>1.158(3)</td>
</tr>
<tr>
<td>(1) CNMes</td>
<td>1.166(3)</td>
</tr>
</tbody>
</table>

Isolation of O-Methyl-N-mesityl selenocarbamate (4)

The system of cumulated double bonds in organyl isoselenocyanates renders them highly reactive toward nucleophilic addition and cycloaddition reactions and these chemical properties have been reviewed. A characteristic reaction of SeCNR molecules occurs upon refluxing with primary alcohols, resulting in the formation of O-alkylselenocarbamates in high yields. Under conditions of basic catalysis, this reaction can be performed at room temperature. Thus it is perhaps unsurprising that the O-methylselenocarbamate MeO(CSe)NHMes, 4, was isolated from the attempted recrystallisation of SeCNMes from methanol prior to chromatographic removal of the DBU (Scheme 2.6).

Scheme 2.6. Formation of an O-alkyl selenocarbamate (R = C₆H₃Me₂-2,4,6, R' = Me).

The partial C–N multiple bond character that arises from π–π overlap between the sp² nitrogen and carbon centres of the selenoamide unit of 4 results in a significant barrier to rotation around the C–N bond such that both rotamers are evident in the ¹H and ¹³C{¹H} NMR spectra (ca. 1:2 ratio). Resonances for the selenoamide carbons are clearly distinguishable at δ : 193.9 and 196.5 for the major and minor isomers, respectively, and the orientational preference of 4 presumably favours the isomer in which the O-alkyl group is positioned trans to the bulky mesityl substituent.

Identification of 4 as the selenocarbamate ester was confirmed by the molecular structure determination, the results of which are summarised in Figure 2.3. The increased C(1)–N bond distance and decreased linearity of the C(1)–N–C(2) angle, in comparison to those of 1, are as expected upon the disruption of the heterocumulenic π-system. Due to the delocalised nature of the selenoamide linkage, the C(1)–N and C(1)–Se bond distances of 4 (1.326(2) and 1.836(2) Å, respectively) remain shorter and longer than formal C–N single and C–Se double bonds.
Figure 2.3. Molecular structure of 4 with 30% probability ellipsoids shown. Hydrogen atoms (excluding the amide proton) have been omitted. Selected bond lengths (Å) and angles (°): C(1)–N 1.326(2), C(1)–Se 1.836(2), C(1)–N–C(2) 124.9(2), Se–C(1)–N 122.6(1).

Selenocarbamates have not been extensively studied and while 4 could, in itself, prove to be an interesting ligand, its coordination chemistry was not pursued, partly because of the extreme instability reported for selenocarbamate metal complexes.27
2.3 Coordination chemistry of mesityl isoselenocyanate: Platinum(0)

Due to the scarcity of organometallic complexes of organyl isoselenocyanates and the limited and equivocal nature of the data reported for the complex \([\text{Pt}(\eta^2-\text{SeCN}_{6}\text{H}_{4}\text{Me}-4)(\text{PPh}_3)_2]\),\(^{10}\) initial confirmation of the ability of aryl isoselenocyanates to form stable \(\pi\)-coordinated complexes was desirable. Accordingly, Walker’s synthesis (Scheme 2.3, Section 2.1.1) was revisited using SeCNMes in the hope that more satisfactory characterisation might be possible since the more sterically encumbered SeCNMes ligand should be less prone to the further reactions that compromised the earlier study.

Treatment of a hexane suspension of \([\text{Pt(PPh}_3)_2(\text{C}_2\text{H}_4)]\) with mesityl isoselenocyanate afforded \([\text{Pt}(\eta^2-\text{SeCNMes})(\text{PPh}_3)_2]\), \(5\), in near quantitative yield. Coordination of the isoselenocyanate ligand to the platinum centre was confirmed by the observation of a strong absorption in the infrared spectrum at 1672 cm\(^{-1}\) attributable to the C–N stretch, which is shifted 450 cm\(^{-1}\) to lower energy than the C–N absorption of free \(1\) and comparable to those observed in the \(\pi\)-isothiocyanate complexes of ruthenium\(^{12}\) and platinum\(^{11}\).

The \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectrum of \(5\) exhibited two mutually coupled doublets, \(\delta 31.2\) and 25.1 (\(J_{\text{pp}} = 12.2\) Hz), with attendant \(^{195}\text{Pt}\)-satellites (33.8% natural abundance) of \(J_{\text{pp}} = 4409\) and 2694 Hz, respectively (Figure 2.4). Within tertiary phosphine complexes of platinum there exists an empirical correlation between the P–Pt bond length and the magnitude of the \(J_{\text{pp}}\) spin–spin coupling.\(^{28}\) On the basis of this, the signal at \(\delta 25.1\) (with the smaller \(J_{\text{pp}}\) coupling) was attributed to the phosphorus nucleus trans to carbon, in view of the strong trans influence of the imine group. The chemical shifts and coupling constants for the cis-phosphorus ligands in \(5\) are comparable to those found for the related complex \([\text{Pt}(\eta^2-\text{CSeS})(\text{PPh}_3)_2]\), which exhibited doublet resonances at \(\delta 33.4\) and 25.1 (\(J_{\text{pp}} = 12\) Hz, \(J_{\text{pp}} = 4574\) Hz and 2608 Hz, respectively).\(^{29}\)

The \(\pi\)-bound isoselenocyanate complex \(5\) proved unstable in solution, gaining a red colouration within three hours at ambient temperature. At this time, the \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectrum revealed a complete absence of resonances due to \(5\), consistent with complex decomposition.
The low temperature (−40 °C) $^{13}$C{$_1^H$} NMR spectrum of [Pt($\eta^2$-SeCNMes)(PPh$_3$)$_2$] revealed doublet signals for the platinum-coordinated imino and ipso carbons of the organic ligand. In principle, an AXX' pattern with associated platinum satellites should be resolved for each carbon due to coupling to both the $\textit{cis}$ and $\textit{trans}$ phosphorus ligands. However, only the larger phosphorus coupling (presumably that to the $\textit{trans}$ phosphorus) could be determined for each resonance, these being $^2J_{PC} = 113$ Hz for the imino carbon and $^4J_{PC} = 11$ Hz for the ipso centre. The $^2J_{PC}$ coupling for the imino carbon is comparable to that of 80.2 Hz measured for the $\eta^2$-$C,S$ carbon disulfide complex [Pt($\eta^2$-CS$_2$)(PPh$_3$)$_2$].\textsuperscript{30} Due to poor signal-to-noise ratio in the spectrum of 5, the appearance of the $^{195}$Pt satellites did not allow for accurate determination of $^1J_{PTC}$.

Compound 5 represents the first structurally characterised example of a transition-metal organyl isoselenocyanate complex and the results of the molecular structure determination are depicted in Figure 2.5.

The molecular structure determination of 5 reveals $\pi$-$C,Se$ coordination of a distinctly non-linear isoselenocyanate ligand to the platinum centre. The Pt–P bond distances (2.331(1) Å $\textit{trans}$ to Se, 2.259(1) Å $\textit{trans}$ to C) reflect the $\textit{trans}$ influence of the imine functionality and support the assignments made for the two $^{31}$P resonances in the $^{31}$P{$_1^H$} NMR spectrum. These structural features are in agreement with those observed for the $\eta^2$-$C,Se$ complex [Pd($\eta^2$-CSeS)$_2$(PPh$_3$)$_2$], in which the influence of the C=S ligand results in an elongated Pt–P bond for the $\textit{trans}$ disposed phosphine.\textsuperscript{25} In the case of 5, the isoselenocyanate unit is almost coincident with the P$_2$Pt plane (dihedral angle: 5.11°) and the mesityl ring of the organic ligand is oriented perpendicular to this P$_2$PtSeC complex core (dihedral angle: ca. 95°).
Figure 2.5. Molecular structure of 5 in a crystal of \(5 \cdot \text{C}_6\text{H}_6\) with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.331(1), Pt–P(2) 2.258(1), Pt–Se 2.448(4), Pt–C(1) 2.007(4), C(1)–Se 1.925(4), C(1)–N 1.236(5), Se–Pt–C(1) 50.0(1), Pt–Se–C(1) 53.0(1), P(1)–Pt–P(2) 102.23(4), Se–Pt–P(2) 152.16(3), C(1)–Pt–P(1) 155.0(1), C(1)–N–C(2) 122.2(4), Se–C(1)–N 138.1(3).

A comparison of data for free 1 and the coordinated SeCNMes ligand in 5 reveals that both the carbon–nitrogen and carbon–selenium bonds are significantly lengthened upon coordination. The C(1)–Se separation (1.925(4) for 5 vs 1.731(2) Å for 1) is consistent with a C–Se single bond description, being longer than the corresponding carbon–selenium bond distances observed for \([\text{Pd}(\eta^2\text{-CSe})\{(1,2-(\text{PPh}_2\text{CH}_2)\_2\text{C}_6\text{H}_4}\}]\) (1.80(2) Å)\(^{29}\) and the pentacarbonyl selenoaldehyde complex \([\text{W}(\eta^2\text{-SeCHPh})(\text{CO})_5]\) (1.864(13) Å)\(^{31}\) implying greater retrodonation to the ligand in 5 and subsequent weakening of the C–Se bond. The significant distortion of the heteroallene fragment in 5, Se–C–N: 122.2(4)°, 45° greater than that found for free 1, reflects the extent of π-retrodonation to the ligand\(^6\) and is markedly increased cf. the comparable E–C–E distortion in the related \([\text{Pd}(\eta^2\text{-CSe})\{(1,2-(\text{PPh}_2\text{CH}_2)\_2\text{C}_6\text{H}_4}\}]\) (140.7(11)°).\(^{29}\)
2.4 Attempted coordination of mesityl isoselenocyanate: Ru(0) and Ru(II) complexes

2.4.1 Reaction of SeCNMes with [Ru(CO)(L)(PPh₃)] (L = CO, CNMes)

Facile dissociative loss of one phosphine ligand from the complex [Ru(CO)₂(PPh₃)₃] provides a convenient entry into the chemistry of ruthenium(0)²² and previous reports have documented the use of this zero-valent precursor in the preparation of π-bound organyl isothiocyanate³² and carbon diselenide¹³ complexes (vide supra, Scheme 2.4). Equivalent coordination behaviour was anticipated for the mesityl isoselenocyanate ligand. However, reaction between the complex [Ru(CO)₃(PPh₃)] and 1 in benzene resulted in complete ligand decomposition, with C-Se cleavage of 1 resulting in the isonitrile-containing complex [Ru(CO)₂(CNMes)(PPh₃)₂], 6, being the only isolable product.

Monitoring of this reaction with ³¹P{¹H} NMR spectroscopy (C₆D₆, 25 °C) revealed the direct formation of 6 (δP 60.5) together with substantial amounts of triphenylphosphine selenide (C₆D₆: δP 35.9, ¹JPse = 756 Hz cf. literature data, CDCl₃: δP 35.9, ¹JPse = 732 Hz).³³ Small resonances due to free triphenylphosphine and minor, previously documented products arising from ligand redistribution, namely [RuH₂(CO)(PPh₃)₃]³⁴ and [Ru(CO)₃(PPh₃)₂],³⁵ were also observed.

It is of note that complexes of the form [M(²⁻E₂)(CO)₂(PPh₃)₂] (M = Ru, Os, E = S; M = Os, E = Se) are prepared from the reaction of one equivalent of [M(CO)₂(PPh₃)₂] with the respective elemental chalcogens.³⁶,³⁷ On the basis of ³¹P{¹H} NMR data for the related complexes [Ru(²⁻O₂)(CO)₂(PPh₃)₂] (C₆D₆: δP 32.9),³⁸ [Ru(²⁻Se₂)(CO)₂(PPh₃)₂] (CD₂Cl₂: δP 39.53),³⁹ and [RuH(SePh)(CO)₂(PPh₃)₂] (CD₂Cl₂: δP 36.98),³⁹ the formation of [Ru(²⁻Se₂)(CO)₂(PPh₃)₂] in the above situation cannot be excluded from the ³¹P{¹H} chemical shift data alone. However, the absence of any ⁷⁷Se satellites (natural abundance 7.58%) with a smaller, two-bond (²JPse) coupling would seem to suggest that this diselenido complex is not present in the reaction mixture.

Ligand cleavage also occurred during the reaction of 1 with the more electron-rich metal complex [Ru(CO)(CNMes)(PPh₃)₃] (7) (prepared via literature procedures described for the CNC₆H₄Me-4 analogue)⁴⁰ in which the increased basicity of the ruthenium centre was expected to enhance retrodonation to a π-bonded heteroallene ligand.⁶ Indeed, the reactions of [Ru(CO)(CNR)(PPh₃)₃] (R = t-Bu, C₆H₃Me₂-2,6) with sulfur based heterocumulenes O=S=E (E = O, NC₆H₄Me-4, N-SO₂C₆H₄Me-4) have been previously shown to afford the simple and stable ²⁻ES adducts, [Ru(²⁻ESO)(CO)(CNR)(PPh₃)₃].⁴¹
Monitoring of the reaction between \([\text{Ru}(\text{CO})(\text{CNMes})(\text{PPh}_3)_3]\) and 1 by \(^{31}\text{P}\{^{1}\text{H}\}\text{NMR}\) spectroscopy revealed replacement of the resonance due to \([\text{Ru}(\text{CO})(\text{CNMes})(\text{PPh}_3)_3]\) (\(\delta = 52.3\)) by smaller peaks due to \([\text{Ru}(\text{CO})(\text{CNMes})_2(\text{PPh}_3)_2]\) (8) (\(\delta = 54.5\)) and triphenylphosphine selenide, both of which arise from severing of the C-Se bond in 1. Additionally, the observation of a further set of resonances consistent with the previously reported dihydride complex \([\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]\)^{14} would seem to imply that 7 is highly susceptible to ligand redistribution and decomposition reactions.

Over the course of the reactions which led to the formation of \([\text{Ru}(\text{CO})(\text{CNMes})(\text{L})(\text{PPh}_3)_2]\) (L = CO, 6; CNMes, 8), the \(^{31}\text{P}\{^{1}\text{H}\}\text{NMR}\) monitoring revealed minor, short-lived, intermediates (\(\delta = 45.4\), L = CO; \(\delta = 43.5\), L = CNMes) that were not observed in parallel studies with CNMes. Formulation of these intermediate complexes as the transiently formed \(\eta^2\)-C,Se adducts \([\text{Ru}(\eta^2\text{-SeCNMes})(\text{CO})(\text{L})(\text{PPh}_3)_2]\) is supported by analogy with comparable data for the \(\pi\)-bound alkyne complex \([\text{Ru}(\eta^2\text{-PhC}=\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]\) (\(\text{C}_6\text{D}_6\): \(\delta = 42.5\)).^{42} However, the instability of these complexes precluded their isolation or further characterisation.

**Deliberate preparation and characterisation of \([\text{Ru}(\text{CO})(\text{CNMes})(\text{L})(\text{PPh}_3)_2]\) (L = CO, 6; CNMes, 8)**

Verification of the product arising from the reaction of \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) with mesityl isoselenocyanate as \([\text{Ru}(\text{CO})_2(\text{CNMes})(\text{PPh}_3)_2]\) (6) was achieved by comparison with an authentic sample prepared directly from 3 and the corresponding zero-valent ruthenium complex. The singlet resonance in the \(^{31}\text{P}\{^{1}\text{H}\}\text{NMR}\) spectrum of 6 (\(\delta = 60.5\)) was consistent with trigonal bipyramidal geometry incorporating axial phosphine ligands. Moreover, the chemical shift resembles that observed for the related complex \([\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]\) (\(\text{C}_6\text{D}_6\): \(\delta = 56.3\)), for which the stereochemistry is unequivocally known.\(^{35}\) The trans disposition of the phosphine ligands was further confirmed by the virtual triplet multiplicity of the aryl phosphine resonances in the \(^{13}\text{C}\{^{1}\text{H}\}\text{NMR}\) spectrum. The infrared spectrum of \([\text{Ru}(\text{CO})_2(\text{CNMes})(\text{PPh}_3)_2]\) exhibits three absorptions [IR (Nujol): 2031 (v\(_{\text{CN}}\)), 1893, 1952 (v\(_{\text{CO}}\)) cm\(^{-1}\)], with the two carbonyl peaks of equal intensity, which is again consistent with an equatorial disposition of the isonitrile and carbonyl ligands.\(^{49}\)

**Metal-assisted decomposition of SeCNR**

In solution, sterically driven dissociation of a phosphine ligand from the tris(triphenylphosphine) complexes \([\text{Ru}(\text{CO})(\text{L})(\text{PPh}_3)_3]\) (L = CO, CNMes) generates the reactive ‘\(\text{Ru}(\text{CO})(\text{L})(\text{PPh}_3)_2\)’ species.\(^{32}\) From the above results it can be concluded that in the presence of mesityl isoselenocyanate the liberated phosphine rapidly reacts with this source of
selenium, forming mesityl isonitrile and triphenylphosphine selenide. Such deselenation of isoselenocyanates by trivalent phosphorus compounds is a well-established phenomenon that has been found to follow second-order kinetics\textsuperscript{43} and can be represented by the equilibrium shown in Equation 2.1 for SeCNMes.

In the absence of a transition-metal this equilibrium lies in favour of the intact isoselenocyanate molecule. The $^{31}\text{P}^{t\text{H}}$ NMR spectroscopic monitoring ($C_6D_6$, 25 °C) of the reaction between 1 and one equivalent of PPh$_3$ revealed that the ratio of the selenium abstraction product, PPh$_3$Se, to PPh$_3$ was approximately 1:8 after five minutes, corresponding to an immediate, 11\% conversion of triphenylphosphine to triphenylphosphine selenide ($K_{eq}$ for SeCNMes = 1.7 $\times$ 10$^{-2}$). No further changes were observed over a 48 hour period.

\[
\text{Ph}_3\text{P} + \text{SeCNMes} \rightleftharpoons \text{Ph}_3\text{PSe} + \text{CNMes} \quad \text{(Eq 2.1)}
\]

In contrast, in the presence of the zero-valent ruthenium complexes [Ru(CO)(L)(PPh$_3$)$_3$] (L = CO, CNMes) complete decomposition of SeCNMes occurs, and while the reaction is too rapid for kinetic measurements, it is nevertheless clear that the selenium transfer reaction is metal-assisted. Deselenation of free 1 and subsequent incorporation of the released isonitrile ligand into the ruthenium coordination sphere would drive the equilibrium shown in Equation 2.1 to the right. A more likely alternative, however, involves selenium abstraction from a transiently formed $\pi$-isoselenocyanate adduct, for which there is spectroscopic evidence (vide supra). Indeed, the activation of $\eta^2$-C,Se-heterocumulenic complexes by trivalent phosphorus compounds has literature precedent, and relevant examples are summarised in Scheme 2.7. Nevertheless, it should be noted that spontaneous selenium extrusion from an $\eta^2$-C,Se-isoselenocyanate ligand due to weakening of the C-Se bond through extensive $\pi^*$-acceptance from the metal, independent of the action of phosphine, cannot be excluded.

Scheme 2.7. Reaction of $\eta^2$-C,Se bound transition-metal complexes with triphenylphosphine.
In the presence of one equivalent of triphenylphosphine, carbon diselenide complexes of chromium(0) and manganese(II) are deselenated to provide the corresponding selenocarbonyl complexes.\textsuperscript{44} Similarly, the chalcocarbonyl complexes [Co(CE)(PR\textsubscript{3})Cp] (E = S, Se; PR\textsubscript{3} = PMe\textsubscript{3}, PMe\textsubscript{2}Ph) are formed by selenium abstraction from [Co(\eta\textsuperscript{2}-SeCE)(PR\textsubscript{3})Cp] with PPh\textsubscript{3}.\textsuperscript{45} Conversely, the complex [Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] reacts with CSe\textsubscript{2} to form the ruthenium(0) heteroallene complex [Ru(\eta\textsuperscript{2}-CSe\textsubscript{2})(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] with concomitant generation of one equivalent of free triphenylphosphine to which the \pi-bound complex is inert.\textsuperscript{13} The experimentally observed instability of [Ru(\eta\textsuperscript{2}-SeCNMes)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] under identical reaction conditions can be explained, in part, in terms of the low nucleophilicity of isonitriles towards selenium. This property is most readily exemplified by the base-catalysis required to promote reaction between isonitriles and selenium in isoselenocyanate syntheses.\textsuperscript{5} Furthermore, the molecular structure determinations of the atom-transfer partners, CNMes and SeCNMes, did not show vastly different geometric parameters for the C–N and Se–C–N units, which is consistent with a minimal reorganisational energy requirement upon selenium incorporation and, by extension, extrusion.

2.4.2 Reaction of SeCNMes with [Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})]

The liberation of one equivalent of triphenylphosphine from [Ru(CO)(L)(PPh\textsubscript{3})\textsubscript{2}] (L = CO, CNMes) to provide a reactive metal species appears problematic for maintaining the integrity of the isoselenocyanate ligand. Facile loss of the weakly bound ethylene ligand from [Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})] generates the reactive metal species ‘Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}’ without releasing PPh\textsubscript{3} and should therefore, in principle, provide favourable conditions for the formation of an \eta\textsuperscript{2}-coordinated isoselenocyanate complex. Nevertheless, the only product formed in isolable quantities from the reaction between 1 and [Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4})] in benzene solution was the previously observed complex 6. In situ monitoring of the reaction mixture (\textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy) revealed a resonance due to the known complex [Ru(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}] (\delta \sim 56.3),\textsuperscript{35} in addition to signals attributable to 6, PPh\textsubscript{3}Se, and a small amount of the transiently formed \pi-adduct [Ru(\eta\textsuperscript{2}-SeCNMes)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (\delta \sim 45.4). The presence of [Ru(CO)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}] in this reaction mixture was indicative of facile ligand redistribution reactions, the occurrence of which may account for the generation of free triphenylphosphine required for the (unexpected) formation of PPh\textsubscript{3}Se in this case.

Whilst the five-coordinate ruthenium isonitrile complexes, [Ru(CO)(CNMes)(PPh\textsubscript{3})\textsubscript{3}] (7), [Ru(CO)\textsubscript{2}(CNMes)(PPh\textsubscript{3})\textsubscript{2}] (6) and [Ru(CO)(CNMes)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (8), are all previously unreported compounds, the intention was to preserve the C–Se interaction. Thus, ruthenium(0) systems were sought in which the selenium-acceptor PPh\textsubscript{3} was not available.
2.4.3 Towards ruthenium(0) complexes that are devoid of a labile phosphine ligand

The results described above for platinum indicate that in systems in which 1 is not in solution with free triphenylphosphine, stable isoselenocyanate complexes may be accessible. Synthesis of the ruthenium ethylene complex \([\text{Ru}(\text{CO})_2(\text{dppe})(\text{C}_2\text{H}_4)]\) was therefore sought, in which the multiple donor sites of the chelating 1,2-bis(diphenylphosphino)ethane (dppe) ligand should suppress ligand dissociation reactions.

**Preparation and characterisation of \([\text{Ru}(\text{CO})_2(\text{dppe})(\text{PPh}_3)]\) (9)**

The potential to prepare the zero-valent ruthenium species 9 from \([\text{Ru}_2(\mu-1,2-(\text{NH})_2\text{C}_4\text{H}_4)(\text{CO})_6(\text{PPh}_3)_2]\) or \([\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]\) has previously been described, but the detailed synthetic procedure and full characterisation of the product were not communicated. In this study, \([\text{Ru}(\text{CO})_2(\text{dppe})(\text{PPh}_3)]\) was prepared by a modification of the multi-step approach traditionally employed for generating \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\), as outlined in Scheme 2.8.

```
\[
\begin{align*}
\text{H}_3\text{PPh}_3 &\quad \text{Cl} \quad \text{(i)} \quad \left[ \begin{array}{c} 
\text{H}_3\text{PPh}_3 \\
\text{OC}
\end{array} \right] \\
\text{OC} &\quad \text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PPh}_3 &\quad \text{NCMe} \quad \text{(ii)} \quad \left[ \begin{array}{c} 
\text{H}_3\text{PPh}_3 \\
\text{OC}
\end{array} \right] \\
\text{OC} &\quad \text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PPh}_3 &\quad \text{NCMe} \quad \text{(iii)} \quad \left[ \begin{array}{c} 
\text{H}_3\text{PPh}_3 \\
\text{OC}
\end{array} \right] \\
\text{OC} &\quad \text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{P} &\quad \text{Ru} \quad \text{CO} \\
\text{L} &\quad \text{L'} \\
\text{Ph}_2\text{P} &\quad \text{Ru} \quad \text{CO} \\
\text{L} &\quad \text{L'}
\end{align*}
\]

**Scheme 2.8.** Reagents: (i) 3 NaBF₄, MeCN, heat; (ii) CO(g), CH₂Cl₂; (iii) MeOH, KOH, dppe, heat (fac-9: L = CO, L' = PPh₃; mer-9: L = PPh₃, L' = CO).

Structural characterisation of 9 revealed trigonal bipyramidal geometry for ruthenium with the three phosphorus donors occupying meridional sites, as shown in Figure 2.6. The trans-P–Ru–P angle, 177.08(4)°, differs markedly from that which was reported for \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) by Hiraki and co-workers, in which the compression of the P–Ru–P angle (156°) alleviates steric repulsion between the equatorial and apical PPh₃ ligands and the complex geometry is strongly distorted towards square pyramidal. Lavigne has subsequently reported a different structure for \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) involving trans disposed carboxyls and equatorial phosphine ligands with essentially perfect \(D_{3h}\) symmetry [OC–Ru–CO: 178.31(11)°, P–Ru–P₃a: 119.9(3)°].

\[^5\] The single crystal of \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) contained two independent molecules in its asymmetric unit with slightly different conformations. Data quoted here represent the average of reported values.
Figure 2.6. Molecular structure of 9 with 30% probability ellipsoids. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Ru–P(1) 2.351(1), Ru–P(2) 2.328(1), Ru–P(3) 2.268(1), Ru–C(1) 1.865(5), Ru–C(2) 1.894(5), C(1)–O(1) 1.186(5), C(2)–O(2) 1.154(5), P(2)–C(3) 1.835(4), P(3)–C(4) 1.851(4), C(3)–C(4) 1.530(6), P(1)–Ru–P(2) 177.08(4), P(1)–Ru–P(3) 99.78(4), P(2)–Ru–P(3) 82.65(4), P(1)–Ru–C(1) 86.8(1), P(2)–Ru–C(1) 90.6(1), P(3)–Ru–C(1) 122.2(2), P(1)–Ru–C(2) 89.1(1), P(2)–Ru–C(2) 91.4(1), P(3)–Ru–C(2) 114.7(1), C(1)–Ru–C(2) 122.9(2), Ru–C(1)–O(1) 174.9(4), Ru–C(1)–O(1) 174.0(4).

Deformations from the idealised geometry for [Ru(CO)₂(dppe)(PPh₃)] are minimal, with inter-ligand angles that deviate less than 8° from those expected for a perfect trigonal bipyramid. The observed distortions in the molecular structure of 9 can be largely attributed to the steric bulk and geometric constraints of the chelating diphosphine ligand. Geometrical features of the bidentate ligand in 9 are typical of those found for other dppe complexes of Group 8 metals.⁴８,⁴⁹ The P–Ru–P bite angle, 82.65(4)°, of the five-membered chelate ring is comparable to that of [Ru(CO)₃(dppe)] (81.98(4)°),⁴⁹ and the P–C–C–P torsion angle, 53.8°, of the puckered dppe ligand falls within the expected range.⁴¹,⁴⁹

The Ru–P separation for the equatorial phosphine ligand, 2.2675(11) Å, is somewhat shorter (> 9 σ) than those of the apical phosphorus donors, consistent with the equatorial coordination sites being more spacious (cf. VSEPR model), thus allowing a closer approach. The longest Ru–P separation in the complex (2.3512(11) Å) is that to the axial triphenylphosphine ligand, the implication being that in the presence of an extraneous donor it is this phosphorus ligand that will dissociate and be replaced. The ruthenium carbonyls show minor deviations from linearity (174.9(4) and 174.0(4)°) and although the two Ru–CO separations display some
variance (Ru–C(1) 1.865(5) Å vs Ru–C(2) 1.894(5) Å), the difference is at the limit of significance (6 σ) and is unlikely to have chemical ramifications.

The $^{31}$P{¹H} NMR spectrum of 9 shows two non-equivalent phosphorus environments. The resonance at $\delta$ 56.3 is attributed to the triphenylphosphine ligand and is split into a triplet ($^{2}J_{pp} = 83$ Hz) by coupling to the two equivalent dppe-P atoms, which give rise to a corresponding doublet signal at $\delta$ 69.1. The inability of the chelating dppe ligand to bridge the 120° angle between two equatorial sites renders an isomer with bis-axial carbonyl ligands and equatorial phosphines, as was observed in Lavigne's structural determination of [Ru(CO)$_2$(PPh$_3$)$_3$], unlikely. The equivalence of the dppe-P atoms on the NMR time scale is thus suggestive of facile fluxionality of the pentacoordinate complex (Berry pseudorotation), and presumably arises from interconversion of the possible facial and meridional arrangements of the phosphorus donor atoms. The solid-state infrared spectrum of 9 contains three carbonyl absorptions at 1930, 1897, and 1853 cm$^{-1}$, further confirming that the bulk material contains more than one geometric isomer, though only one of these was observed in the crystallographic study.

It should be noted that complex 9 prepared by this route is contaminated with approximately 12% of another material that is characterised by three inequivalent phosphorus resonances (each a doublet) in the $^{31}$P{¹H} NMR spectrum of the crude material ($\delta$ 80.7, $^{2}J_{pp} = 238$ Hz; 66.1, $^{2}J_{pp} = 13$ Hz; and 60.4, $^{2}J_{pp} = 238$ Hz). The magnitudes of the measured coupling constants, 238 and 13 Hz, are consistent with the coupling of trans and cis phosphines, respectively (a third anticipated cis phosphorus coupling was not observed). Furthermore, the $^{1}$H NMR spectrum of the crude material exhibited two small resonances characteristic of metal–hydrides at $\delta$–9.51 (dt, $^{2}J_{ph} = 78$ Hz, $^{2}J_{p2H} = 23$ Hz) and –7.47 (q, $^{2}J_{ph} = 25$ Hz), in which the larger coupling of 78 Hz was attributed to coupling with a trans disposed phosphine ligand. (NB: finer splitting structure was evident on both hydride peaks but due to the low signal-to-noise ratio accurate values of $J$ could not be determined). On the basis of these spectroscopic data — in addition to experimental observations during the synthesis of the closely related complex [Ru(CO)$_2$(PPh$_3$)$_3$], which is often accompanied by the generation of [RuH$_2$(CO)(PPh$_3$)$_3$] — the second product was formulated as the dihydride complex [RuH$_2$(CO)(dppe)(PPh$_3$)], bearing a meridional configuration of the three phosphorus ligands and cis-dihydrides, as depicted in Figure 2.7. Spectroscopic data are in agreement with those previously reported for [RuH$_2$(CO)(dppe)(PPh$_3$)] by Garrou and later by Onishi.
While ethylene replaces one phosphine ligand of the tris(triphenylphosphine) ruthenium complex \([\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]\) in a reaction driven by the alleviation of steric pressures, an analogous triphenylphosphine/ethylene substitution reaction was not detected with the chelating 1,2-bis(diphenylphosphino)ethane complex (9). Furthermore, the strong \([\text{MH}]^+\) response observed for 9 in the mass spectrum suggests a remarkable stability towards fragmentation. Thus, it may be surmised that the pinning back of two phosphine donors in the dppe chelate of \([\text{Ru}(\text{CO})_2(\text{dppe})(\text{PPh}_3)]\) reduces steric pressures sufficiently to disfavour phosphine labilisation.

The instability of the \(\eta^2\)-C-Se coordination mode of SeCNR ligands in solution has been established. Accordingly, it is necessary that any synthesis of \([\text{Ru}(\eta^2\text{SeCNR})\text{(CO)}_2\text{(dppe)}]\) result in a pure crystalline form of the complex in situ. In July 2006, an alternative synthesis of 9 from \([\text{Ru}(\text{CO})_3\text{(dppe)}]\) was described by Duckett and co-workers. Subsequent investigations into the activity of this complex revealed that reaction proceeded via one of two routes. Photochemically, dissociation of a carbonyl ligand was the dominant process whereas thermal conditions led to displacement of the PPh\(_3\) ligand. Thus, thermal activation of the triphenylphosphine ligand in \([\text{Ru}(\text{CO})_2\text{(dppe)}(\text{PPh}_3)]\) may yet provide an avenue for the isolation of \([\text{Ru}(\text{CO})_2(\text{dppe})(\text{C}_2\text{H}_4)]\) and, by extension, \([\text{Ru}(\eta^2\text{SeCNR})\text{(CO)}_2\text{(dppe)}]\).

### 2.4.4 Reaction of SeCNMes with \([\text{RuHCl(\text{CO})(PPh}_3)_3]\)

The insertion of unsaturated molecules into reactive metal–ligand bonds is a characteristic and important reaction in organometallic chemistry and alkyl and aryl isothiocyanates have been shown to undergo insertion reactions with platinum group metal–hydrides (including the complex \([\text{RuHCl(\text{CO})(PPh}_3)_3]\)) to yield the corresponding N-alkyl or N-arylthioformamide chelates (Scheme 2.9).  

![Scheme 2.9. Insertion of SCNR into the Ru–H bond of [RuHX(CO)(PPh)\(_3\)] (R = Ph, X = Cl, Br, CF\(_3\)CO\(_2\); R = C\(_6\)H\(_4\)Me-4, Et, X = Cl).](image)
The reaction of SeCNMes with one molar equivalent of the hydridocarbonyl complex [RuHCl(CO)(PPh₃)₃] did not, however, proceed similarly, instead resulting in SeCNMes ligand degradation and quantitative formation of the new complex [RuHCl(CO)(CNMes)(PPh₃)₂]. In situ monitoring of the reaction mixture by $^{31}$P{¹H} NMR spectroscopy (CD₂Cl₂, 25 °C) revealed an equal product distribution of [RuHCl(CO)(CNMes)(PPh₃)₂] ($\delta_p$ 43.8) and Ph₃PSe ($\delta$ 36.3, $J_{PSe}$ = 736 Hz), with no evidence for an intermediate π-complex.

The ligand degradation which occurs with [RuHCl(CO)(PPh₃)₃] is akin to that observed for the zero-valent ruthenium complexes described above, with the major product being one in which mesityl isonitrile, generated from the removal of selenium from mesityl isoselenocyanate, has replaced a readily dissociated phosphine ligand, in this case due to the strong trans effect of the metal-hydride.

**Deliberate preparation and characterisation of [RuHCl(CO)(CNMes)(PPh₃)₂]** (10)

Following Roper’s original report of the synthesis of [RuHCl(CO)(CN₆H₄Me-4)(PPh₃)₂],McCleverty and co-workers reported a series of analogues of the form [RuHCl(CO)(CNR)(PPh₃)₂] (R = t-Bu, i-Pr, C₆H₄Cl-4) obtained by treating [RuHCl(CO)(PPh₃)₃] with CNR. An authentic sample of the complex [RuHCl(CO)(CNMes)(PPh₃)₂] (10) could be similarly obtained by stirring [RuHCl(CO)(PPh₃)₃] with one equivalent of CNMes in dichloromethane. The resultant white product displayed infrared absorptions due to the coordinated isonitrile and carbonyl ligands at 2142 and 1953 cm⁻¹, respectively, which are comparable to the values reported by Roper (R = CN₆H₄Me-4: 2140, 1935, 1922 cm⁻¹) and McCleverty (R = i-Pr: 2168, 1952 cm⁻¹).

The high-field resonance in the $¹H$ NMR spectrum ($\delta_1 = 5.58$), diagnostic of the metal-hydride, shows a triplet multiplicity, which is characteristic of coupling to two equivalent phosphorus nuclei. The magnitude of the measured coupling constant for this resonance, $J_{PH} = 19.9$ Hz, is comparable to that reported for the $p$-tolyl isonitrile complex [RuHCl(CO)(CN₆H₄Me-4)-(PPh₃₂)] ($^3J_{PH} = 19$ Hz). The single phosphorus environment observed in the $^{31}$P{¹H} NMR spectrum of 10 ($\delta = 43.6$) is furthermore consistent with equivalent, trans disposed phosphine ligands, and is as expected due to replacement of the equatorial phosphine ligand trans to the metal-hydride.
2.4.5 Reaction of SeCNMes with [Ru(CH=CH-i-Pr)Cl(CO)(PPh₃)₂]: a reactive metal-σ-organyl bond

The metal–carbon σ-bonds of ruthenium–alkenyl complexes [Ru(CR'−CHR)Cl(CO)(PPh₃)₂] display a high reactivity towards unsaturated molecules. With the activated alkyne dimethylacetylenedicarboxylate, bis-insertion reactions give rise to complexes containing a butadienyl ligand that is further coordinated through a pendant ester group. Similarly, insertion of carbon disulfide leads to the formation of alkenylthiocarboxylate ligands, while reactions with sulfur dioxide provide alkenylsulfinate complexes (Scheme 2.10).}

![Scheme 2.10. Reactivity of ruthenium–alkenyl complexes towards heteroallenenes.](image)

Corresponding insertion behaviour for the heterocumulenic mesityl isoselenocyanate was not, however, observed. The σ-alkenyl complex [Ru(CH=CH-i-Pr)Cl(CO)(PPh₃)₂] instead reacts with SeCNMes to give the electronically saturated isonitrile/alkenyl complex [Ru(CH=CH-i-Pr)Cl(CO)(CNMes)(PPh₃)₂], which arises from degradation of the isoselenocyanate molecule. Monitoring of the reaction by $^{31}$P{¹H} NMR spectroscopy (CD₂Cl₂, 25 °C) revealed the complete and rapid conversion of the 16-electron species [Ru(CH=CH-i-Pr)Cl(CO)(PPh₃)₂] ($\delta = 31.5$) to the isonitrile complex [Ru(CH=CH-i-Pr)Cl(CO)-(CNMes)(PPh₃)₂] ($\delta = 25.9$), in addition to the formation of a small amount of Ph₃PSe. The origin of the free triphenylphosphine in this system is uncertain; however, contamination by residual triphenylphosphine liberated during the preparation of [Ru(CH=CH-i-Pr)Cl(CO)(PPh₃)₂] from the tris(triphenylphosphine) complex [RuHCl(CO)(PPh₃)₃] would seem most likely.

Storage of the NMR sample at ambient temperature for 24 hours resulted in the deposition of a small amount of elemental selenium and the $^{31}$P{¹H} NMR spectrum at this time revealed the appearance of two new resonances ($\delta = 53.4$ and 33.7). Ruthenium vinyl complexes of the form [Ru(CR=CHR')Cl(CO)(PPh₃)₂] (R = H, R' = SiMe₃; R = R' = Ph; R = H, R' = CO₂Et) have
previously shown a propensity to participate in carbonyl insertion and halide substitution reactions with isonitriles,\textsuperscript{61,62} and it is suggested that similar further reactions may be occurring with 12, though the products were not pursued.

**Preparation and characterisation of \([\text{Ru(CH=CH-iPr)Cl(CO)(PPh}_3\text{)}_2]\) (12) and \([\text{Ru(CH=CH-iPr)Cl(CO)(CNMes)(PPh}_3\text{)}_2]\) (11)**

In a procedure analogous to that reported by Santos for other alkynes,\textsuperscript{58} the cis-insertion of isopropyl acetylene into the metal–hydride bond of \([\text{RuHCl(CO)(PPh}_3\text{)}_3]\) affords the novel, five-coordinate alkenyl product \([\text{Ru(CH=CH-iPr)Cl(CO)(PPh}_3\text{)}_2]\) (12) with concomitant elimination of one phosphine molecule. The $^1H$ NMR spectrum of 12 reveals two doublet resonances attributable to the alkenyl protons (δ$_H$ = 7.46 and 5.44), with the magnitude of the proton–proton coupling, $^3J_{HH} = 12.3$ Hz, being characteristic of the *trans* configuration of the vinyl group.\textsuperscript{63} The lower field resonance also shows some triplet structure due to coupling to the two mutually *trans*, chemically equivalent phosphorus nuclei, though this coupling was not resolved.

Results of the molecular structure determination of the 16-electron complex 12 are summarised in Figure 2.8 and Table 2.2, revealing a distorted octahedral geometry with a vacant coordination site *trans* to the $\sigma$-vinyl ligand. The Cl–Ru–CO angle of 162.6(2)$^\circ$ approaches the *trans* P–Ru–P angle between the axial phosphine ligands (169.17(2)$^\circ$) and is expanded far beyond the 140.8(4)$^\circ$ inter-ligand angle that was observed for the related complex \([\text{Ru(CPh=CHPh)Cl(CO)(PPh}_3\text{)}_2]\), in which the geometry is best described as distorted trigonal bipyramidal.\textsuperscript{58} The compression of the *trans*-ligand angles from linearity can be related to the distortion of the *cis*-ligand pairs towards the vacant coordination site and, subsequently, away from the vinyl ligand.

**Table 2.2. Selected bond lengths (Å) and angles (°) for \([\text{Ru(CH=CH-iPr)Cl(CO)(PPh}_3\text{)}_2]\) (12)$^5$**

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru–P(1)</td>
<td>2.3631(5)</td>
</tr>
<tr>
<td>Ru–P(2)</td>
<td>2.3613(5)</td>
</tr>
<tr>
<td>Ru–C(1)</td>
<td>2.017(2)</td>
</tr>
<tr>
<td>Ru–C(10)</td>
<td>1.776(3)</td>
</tr>
<tr>
<td>Ru–Cl</td>
<td>2.422(2)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>1.314(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, °</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–Ru–P(2)</td>
<td>169.17(2)</td>
</tr>
<tr>
<td>P(1)–Ru–Cl</td>
<td>98.93(5)</td>
</tr>
<tr>
<td>P(1)–Ru–C(10)</td>
<td>99.45(2)</td>
</tr>
<tr>
<td>P(2)–Ru–Cl</td>
<td>88.45(5)</td>
</tr>
<tr>
<td>P(2)–Ru–C(10)</td>
<td>89.47(2)</td>
</tr>
<tr>
<td>P(1)–Ru–C(1)</td>
<td>93.90(6)</td>
</tr>
</tbody>
</table>

\textsuperscript{5} The CO and Cl ligands were disordered with respect to one another. Bond lengths and angles involving these atoms represent the averaged values for the two refined structural models.
The predisposition of the 16-electron complex 12 towards adopting six-coordinate octahedral geometry may account for the observed reactivity towards SeCNMes, which is in full accord with this preorganisation, i.e., cleavage of the C-Se bond of 1 affords a CNMes unit which then fills the vacant coordination site trans to the σ-organyl ligand. Roper has suggested a similar regioselectivity for incoming ligands with the related σ-aryl complex \([\text{Ru}(C_6H_4Me-4)\text{Cl}(\text{CO})-\text{(PPh}_3)_2]\).\(^{64}\)

A genuine sample of the complex \([\text{Ru}(\text{CH} = \text{CHt-Pr})\text{Cl}(\text{CO})(\text{CNMes})(\text{PPh}_3)_2]\), 11, was prepared by reaction of 12 with one equivalent of mesityl isocyanide in a manner similar to that described by Werner and co-workers for the synthesis of \([\text{Ru}(\text{CH}=\text{CHR'})\text{Cl}(\text{CO})(\text{CNR''})(\text{PR}_3)_2]\) (R = i-Pr, R' = Ph, R'' = CNCH\text{H}_2C\text{H}_5; R = Ph, R' = Ph, R'' = Me).\(^{63}\) As expected, the molecular structure determination of 11 (Figure 2.9) reveals an octahedral ruthenium centre with the CNMes ligand located trans to the vinyl group. Pertinent bond lengths and angles are summarised in Table 2.3.

Comparison of the structural data for 12 and 11 reveals expanded inter-ligand angles (Cl-Ru-CO and P-Ru-P: 176.85(10)° and 173.17(3)° for 11 vs 162.6(2)° and 169.172(18)° for 12) and a comparative lengthening of the ruthenium-ligand bonds, as expected in order to accommodate the increased steric demands upon going from a five- to six-coordinate metal.
Table 2.3. Selected bond distances (Å) and angles (°) for [Ru(CH=CH-i-Pr)Cl(CO)(CNMes)(PPh₃)₂] (11)

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th></th>
<th>Bond Angles, °</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru–P(1)</td>
<td>2.3971(9)</td>
<td>P(1)–Ru–P(2)</td>
<td>173.17(3)</td>
</tr>
<tr>
<td>Ru–P(2)</td>
<td>2.3904(9)</td>
<td>Cl–Ru–C(10)</td>
<td>176.9(1)</td>
</tr>
<tr>
<td>Ru–C(1)</td>
<td>2.110(3)</td>
<td>C(1)–Ru–C(11)</td>
<td>172.7(1)</td>
</tr>
<tr>
<td>Ru–C(10)</td>
<td>1.839(3)</td>
<td>C(1)–Ru–Cl</td>
<td>91.79(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(2)–Ru–C(11)</td>
<td>98.3(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(1)–Ru–C(10)</td>
<td>95.36(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(2)–Ru–Cl</td>
<td>91.6(1)</td>
</tr>
</tbody>
</table>

The elongation (10 σ) of the ruthenium–isonitrile bond compared to the adjacent ruthenium–carbonyl bond (2.019 (3) Å vs 1.839(3) Å) reflects the relative trans influences of the vinyl and chloride ligands, as well as the reduced π-acidity of isonitriles relative to carbonyl ligands. The Ru–C(1) bond length of 11, 2.110(3) Å, is longer (6 σ) than that in the five-coordinate complex 12, 2.017(2) Å, and falls within the typical range observed for Ru–C bonds in six-coordinate mononuclear ruthenium σ-vinyl complexes.⁶⁵

Figure 2.9. Molecular structure of [Ru(CH=CH-i-Pr)Cl(CO)(CNMes)(PPh₃)₂] (11) with 30% probability ellipsoids shown. Hydrogen atoms (excluding those of the vinyl linkage) have been omitted.
Infrared data for the complex 11 revealed an absorption due to the C–N stretching mode of the isonitrile ligand ($\nu_{CN} 2116 \text{ cm}^{-1}$) in addition to an intense $\nu_{CO}$ absorption at 1957 cm$^{-1}$, some 30 cm$^{-1}$ to higher energy than that in the coordinatively unsaturated alkenyl complex, 12 ($\nu_{CO} 1928 \text{ cm}^{-1}$). Furthermore, an upfield shift of the $^{31}P\{^1H\}$ NMR resonance for 11 ($\delta_p 25.9$ cf. $\delta_p 31.5$ for 12) was noted, with the position of the singlet resonance of 11 being in good agreement with data for the related complexes $[\text{Ru}(\text{CH} = \text{CHPh})\text{Cl}(\text{CO})(\text{CNr-Bu})(\text{PPh}_3)_2]$ (CDCl$_3$: $\delta_p 26.95$) and $[\text{Ru}\{\text{C} = \text{CPh} = \text{CHPh}\}\text{Cl}(\text{CO})(\text{CNR})(\text{PPh}_3)_2]$ (CDCl$_3$: $\delta_p 28.1$, R = t-Bu; 28.1, R = C$_6$H$_3$Me$_2$,6) The $^1H$ NMR spectrum revealed the characteristic signals of the vinylic protons ($\delta_1, 7.43, 5.48, J_{HH,\text{trans}} = 17.1$ Hz),§ which were only slightly displaced from those of the unsaturated complex 12. A comparison of the $^{13}C\{^1H\}$ NMR spectroscopic and X-ray crystallographic data for free 3 and the coordinated CNMes in 11 reveals a high degree of congruency, suggesting that the properties of the CNMes molecule are not substantially altered upon coordination to ruthenium.

§ For comparative purposes, $\delta_1$ data are reported from C$_6$D$_6$ in contrast to that appearing in the experimental section which is reported from CD$_2$Cl$_2$. 
2.5 Summary and conclusions

As early as 1889, it was proposed that organic isoselenocyanates could easily lose selenium. The mesityl isoselenocyanate ligand, once obtained, appears indefinitely stable in isolation, however, virtually every attempt to deploy it as a substrate for organotransition metal chemistry has led to metal-mediated cleavage into selenium and the constituent isocyanide.

Experimental data from the preceding sections are summarised in Scheme 2.11. Mesityl isoselenocyanate does not parallel the reactivity of organyl isothiocyanates or carbon diselenide with aryl phosphine complexes of ruthenium to afford stable \( \eta^2 \)-C\(_E\) \( (E = S, \text{Se}) \) complexes. Rather, activation of the heterocumulene occurs, yielding unstable adducts that undergo further reaction involving cleavage of the C–Se bond, with subsequent selenium extrusion and retention of the CNMes unit within the coordination sphere of ruthenium.

\[
\begin{align*}
\text{Ru(CO)(PPh}_3\text{)}_2L^1\text{L}^2\text{L}^3 & \rightarrow \text{Ru(CO)(CNMes)(PPh}_3\text{)}_2L^1\text{L}^4 \\
\text{L}^1 & = \text{H} \\
\text{L}^2 & = \text{Cl} \\
\text{L}^3 & = \text{PPh}_3 \\
\text{L}^4 & = \text{Cl}
\end{align*}
\]

Scheme 2.11. Attempted coordination of SeCNMes with Ru(0) and Ru(II) complexes.

A comparison of the molecular structures and spectroscopic data for the group-transfer partners 1 and 3 reveals that the incorporation of the selenium atom brings about only minor changes within the molecule. The remarkable fragility observed for the C–Se bond in mesityl isoselenocyanate can thus be linked, in part, to the small reorganisational energy required upon ligand cleavage.

The coordination and organometallic chemistry of organyl isoselenocyanates remains relatively unexplored, being restricted to the formation of the somewhat unstable \( \pi \)-bound platinum complexes \([\text{Pt}(\eta^2\text{-SeCNR})(\text{PPh}_3)_2] \) \( (R = p\text{-tolyl}^\text{10} \text{ Mes}, 5) \). The d orbitals of zero-valent platinum are lower in energy than those of ruthenium and, accordingly, the dominant retrodonation component of the synergic bonding between transition-metals and heterocumulenes\(^6\) is less effective for platinum. In the case of the more \( \pi \)-basic ruthenium, it would appear that retrodonation ensues to such an extent that the population of the C–Se \( \pi^* \) orbital severely weakens this bond, leading to facile cleavage. The thermodynamic benefit of forming strong \((\sigma + 2\pi)\) bonds to the resulting isonitrile no doubt provides a contribution to the driving force and, if the process were intra- rather than intermolecular, product development (M–CNR formation) might also provide a kinetic impetus.
While the preceding prognosis for the organometallic chemistry of organyl isoselenocyanates might seem discouraging, the potential to exploit the activation of the mesityl isoselenocyanate by transition-metals presents itself and the possibility of employing SeCNMes as an air stable and yet highly soluble single-atom selenium delivery reagent is explored in the following Chapter.
REFERENCES

CHAPTER THREE
SELENOAROYL COMPLEXES OF MOLYBDENUM
3.1 Introduction
This Chapter describes the metal-mediated cleavage of the Se–C bond of mesityl isoselenocyanate in reactions with molybdenum alkylidyne complexes. The delivery of a single atom equivalent of selenium to Group 6 metal–carbon triple bonds via this route affords the first structurally characterised examples of mononuclear selenoaroyl complexes.

3.1.1 Chalcoacyl complexes
Acyl complexes [LnM{C(=O)R}] are of great importance in organometallic chemistry, particularly as intermediates in reactions involving the coordinative activation of carbon monoxide. Not surprisingly, given this relationship between acyls and carbonyl ligands, the corresponding chemistry of chalcoacyls [LnM{C(=E)R}] (E = S, Se, Te) is far less mature, a corollary of the far smaller number of chalcocarbonyl complexes [LnM(CE)] that are known. The bonding of chalcoacyl ligands in transition-metal complexes may be depicted in a number of ways, i.e., the acyl unit may behave as a monodentate ligand in a manner similar to a simple σ-organyl group (a, Chart 3.1), exhibit dihapto coordination with the chalcogen providing a further two valence electrons to the metal (b, Chart 3.1), or display a combination of η¹- and η²-coordination when bridging metal centres in polymetallic assemblies (c, Chart 3.1).

![Chart 3.1](image)

3.1.2 Synthesis of chalcoacyl complexes
Mononuclear chalcoacyl complexes
While metal derivatives of acyl, carbamoyl (carboxamido) and related ligands are common, analogues based upon the replacement of oxygen by the heavier chalcogens [LnM{C(=E)R}] (E = S, Se or Te) remain quite rare, with the rarity increasing upon descending Group 16. The majority of acyl and aroyl complexes arise from migratory insertion processes involving carbonyl and σ-organyl ligands, nucleophilic attack at coordinated CO or attack by nucleophilic metals on acylum ‘RCO’⁺ synthetic equivalents (acid chlorides, acid anhydrides etc).
comparative lack of studies involving S, Se and Te reflects the lack of suitable synthetic strategies to the requisite cis-chalcocarbonyl/σ-organyl precursors, which are rare for sulfur and remain unknown for selenium and tellurium. In a similar manner, suitably electrophilic selenocarbonyl and tellurocarbonyl complexes remain extremely rare, limiting strategies based on attack by carbanionic nucleophiles whilst the availability of chalcoacylium synthetic equivalents decreases dramatically down Group 16.

Nevertheless, the chemistry of the thiocarbonyl ligand, developed to date, in many respects surpasses that of carbon monoxide, displaying a greater propensity for nucleophilic attack (at C), electrophilic attack (at S) and migratory insertion. In each case, this may be related to the smaller HOMO/LUMO gap of the free diatomic. Roper and co-workers have described several instances in which the rearrangement of octahedral Group 8 σ-aryl/thiocarbonyl complexes has afforded dihapto-thioacyl derivatives (Scheme 3.1).

The facility of these migrations is no doubt in part driven by the formation of a strong M–S bond (“HSAB”) in the bidentate thioacyl, for which a metallathiirene canonical form may also contribute to the bonding description. By way of contrast, the complex [Os(C₆H₄Me-4)Cl(CO)₂(PPh₃)₂] does not undergo this migration, supporting this contention.

An alternative synthetic route to thioacyl complexes involving the oxidative addition of an acyl chloride to a transition-metal precursor was described by Angelici and co-workers for the preparation of the thioester complex [Fe{C(S)OMe}(CO)₂Cp]. The reaction between methyl chlorothioformate and the carbonyl ferrate [Fe(CO)₅Cp] occurred at room temperature to afford the complex [Fe{C(S)OMe}(CO)₂Cp] in 43% yield (Scheme 3.2), with the infrared spectrum of the isolated compound exhibiting a characteristic absorption attributable to the C=S unit of the monodentate thioacyl ligand at approximately 1200 cm⁻¹.
CHAPTER 3. SELENOAROYL COMPLEXES OF MOLYBDENUM

Scheme 3.2. Preparation of a thioacyl complex $[\text{Fe}\{\text{C(S)OMe}\}(\text{CO})_2\text{Cp}]$ from the oxidative addition of an acyl chloride.

Additionally, novel cationic alkyl thioacyl complexes of the form $[\text{Co}\{\eta^2-\text{SC(CHR)}\}(\text{PMe}_3)\text{Cp}]^+$ ($R = \text{alkyl}$) have been prepared from $\beta$-protonation of the corresponding mononuclear thioketenes $[\text{Co}(\eta^2-\text{SC} = \text{CR}_2)(\text{PMe}_3)\text{Cp}][\text{X}]$ ($X = \text{BF}_4$ or $\text{BPh}_4$) (Scheme 3.3).\(^8\) This strategy is limited to the use of isolable free thioketene precursors, requiring sterically demanding carbon substituents for kinetic stabilisation. Free seleno- and telluroketenes have yet to be isolated.

Chalcoacyl complexes have also been obtained from nucleophilic substitution reactions of the electrophilic chlorocarbene complex $[\text{Os}\{\text{C(R)Cl}\}_2\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ ($R = \text{C}_6\text{H}_4\text{Me}-4$), which reacts with hydrochalcogenides $\text{HE}^-$ ($E = \text{S, Se or Te}$) via chloride displacement to yield dihapto-thio-, -seleno- and -telluroacyl derivatives $[\text{Os}(\eta^2-\text{ECR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$.\(^9,10\) Were it not for the reluctance of the complex $[\text{Os}(R)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ to exist in the isomeric $\eta^2$-toluoyl form $[\text{Os}(\eta^2-\text{OCR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, this would have provided the only complete set of analogous chalcoaroyl complexes. The aforementioned preparative route is paralleled by the reaction of the chloroaminocarbene complex $[\text{Ru}\{=\text{C(NMe}_2\text{)Cl}\}_2\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ with $\text{HE}^-$ to form dihapto-chalcocarbainoyl complexes (Scheme 3.4).\(^11\)

Scheme 3.3. Preparation of thioacyl complexes $[\text{Co}\{\eta^2-\text{SC(CHR)}\}(\text{PMe}_3)\text{Cp}]^+$ ($R = \text{alkyl}$) from protonation of a coordinated thioketene precursor.

Scheme 3.4. Treatment of chlorocarbene complexes $[\text{M}\{\text{C(R)Cl}\}_2\text{Cl}_2(\text{CO})(\text{PPh}_3)_2]$ with hydrochalcogenides ($M = \text{Os}, R = \text{C}_6\text{H}_4\text{Me}-4$; $M = \text{Ru}, R = \text{NMe}_2$; $E = \text{S, Se, Te}$).
The \( \eta^2 \)-thio-, -seleno- and -telluroacyl complexes of osmium \([\text{Os}(\eta^2\text{-ECR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\) (E = S, Se or Te; R = C\(_6\)H\(_4\)Me-4) may alternatively be obtained by the addition of elemental chalcogens to the M=C bond of the alkylidyne complex \([\text{Os}(=\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\) (Scheme 3.5).\(^9\)\(^{10}\)

\[\text{Scheme 3.5. Chalcogen addition to alkylidynes of Group 8 metals (E = O, S, Se, Te; R = C\(_6\)H\(_4\)Me-4).}\]

**Bridging chalcoacyl complexes**

Coordination to bi- or polynuclear ensembles often confers stability upon otherwise unstable and/or highly reactive small molecules and bridging chalcoacyl ligands including the rare seleno- and telluroacyl derivatives have been described for a number of polynuclear species.\(^{12}\)

As discussed in Chapter 1 (Section 1.4.6), bimetallic species of the type \([\text{MRu}(\mu-\text{CR})(\text{CO})_4(\eta^5\text{-7,8-C}_2\text{B}_{11}H_{11})\text{Tp}]\) (M = Mo or W; R = C\(_6\)H\(_4\)Me-4) containing a \(\mu\)-alkylidyne ligand react with elemental sulfur or selenium to give bridging chalcoacyl compounds in which the chalcoacyl ligand is \(\eta^2\)-coordinated to the Group 6 metal but bound to the ruthenium centre in an \(\eta^1\)-E (E = S or Se) manner.\(^{13}\) The addition of sulfur,\(^{14-16}\) selenium\(^{14,16}\) or tellurium\(^{12}\) to bridging alkylidyne complexes of the type \([\text{MFe}(\mu-\text{CR})(\text{CO})_5\text{L}]\) (R = aryl; L = Cp or Tp) similarly affords binuclear thio- seleno- and telluroacyl derivatives, however, in this case the chalcoacyl ligand transversely bridges a metal–metal bond (Scheme 3.6).

Just as electrophilic attack at mononuclear thiketene complexes affords thioacyl derivatives, the reaction of \([\text{Fe}_2(\mu-S\text{C=CR}_2)(\text{CO})_6]\) (CR\(_2\) = C\(_6\)H\(_4\)Me\(_2\)-2,2,6,6) with hydride donors provides the anionic bridging thioacyl ferrate \([\text{Fe}_2(\mu-S\text{CHR}_2)(\text{CO})_6]\), which could be converted to the
neutral and structurally characterised derivatives \([\text{Fe}_2\text{Au}(\mu-\text{SCCHR}_2)(\text{CO})_6(\text{PPh}_3)]\) and \([\text{Fe}_2(\mu-\text{SCCHR}_2)(\text{NO})(\text{CO})_4(\text{PPh}_3)]\). \(^{17}\)

### 3.1.3 Structural properties of \(\eta^2\)-chalcoacyls

A survey of the literature reveals a relatively small number of structurally characterised chalcoacyl complexes and the pertinent structural features for selected examples of \(\eta^2\)-derivatives are summarised in Table 3.1.

**Table 3.1. Structural data for selected \(\eta^2\)-chalcoacyl complexes\(^a\)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths, (\text{Å})</th>
<th>Bond Angles, °</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M–C</td>
<td>M–E</td>
<td>C–E</td>
</tr>
<tr>
<td><strong>MONONUCLEAR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zr((\eta^2)-SCR(^3))CICp(_2)]</td>
<td>2.298(8)</td>
<td>2.615(3)</td>
<td>1.623(8)</td>
</tr>
<tr>
<td>[Mo((\eta^2)-SCR(^3))(CO)(_2)Tp]</td>
<td>2.000(3)</td>
<td>2.567(1)</td>
<td>1.679(3)</td>
</tr>
<tr>
<td>[W((\eta^2)-SCR(^3))((\eta^2)-C(S)HPh)(S(_2)CNET(_2))(CO)]</td>
<td>2.040(6)</td>
<td>2.542(2)</td>
<td>NR</td>
</tr>
<tr>
<td>[Os((\eta^2)-SCR(^3))(_2)O(CF(_3))(_2)(CO)(PPh(_3))]</td>
<td>1.97(4)</td>
<td>2.520(8)</td>
<td>1.76(4)</td>
</tr>
<tr>
<td>[Os((\eta^2)-SCR(^3))Cl(CO)(PPh(_3))]</td>
<td>1.961(3)</td>
<td>2.498(1)</td>
<td>1.695(3)</td>
</tr>
<tr>
<td>[Os((\eta^2)-SCR(^3))(_2)Cl(CO)(PPh(_3))]</td>
<td>1.927(13)</td>
<td>2.542(3)</td>
<td>1.66(2)</td>
</tr>
<tr>
<td>[Co((\eta^2)-SCR(^5))(PMe(_3))Cp][BF(_4)]</td>
<td>1.854(3)</td>
<td>2.257(1)</td>
<td>1.629(3)</td>
</tr>
<tr>
<td>[Os((\eta^2)-TeCR(^8))Cl(CO)(PPh(_3))]</td>
<td>1.913(7)</td>
<td>2.823(1)</td>
<td>2.090(7)</td>
</tr>
</tbody>
</table>

| POLYNUCLEAR | | | |
| [WFe\(_2\)(\(\mu\)-SCR\(^2\))(CO)\(_6\)Cp] | 2.195(8) | 2.439(2) | 1.755(8) | 44.1(2) | 74.3(3) | 22 |
| [WRu(\(\mu\)-SCR\(^3\))(CO)\(_4\)(L)Tp] | 1.970(4) | 2.500(1) | 1.753(4) | 44.2(1) | 84.1(2) | 13 |

\(^a\) Ref. R\(_1\) = C\(_6\)H\(_5\)Me\(_2\)-2,2,6,6; R\(_2\) = C\(_6\)H\(_3\)S-2; R\(_3\) = NET\(_2\); R\(_4\) = CH(t-Bu)\(_2\); R\(_5\) = C\(_6\)H\(_4\)Me-4; R\(_6\) = C\(_6\)H\(_4\)Cl-4; R\(_7\) = CH=CHMe; R\(_8\) = Ph; R\(_9\) = Me; L = \(\eta^5\)-7,8-C\(_3\)B\(_9\)H\(_11\); \(^b\) Structural parameters from this work. NR = not reported.

The bidentate chalcoacyl ligands of each complex show essentially similar structural features. In all cases, the \(\eta^1\)-thioacyl is considered to occupy a single coordination site, a formalism that is supported by the small bite angle (E–M–C < 45°) and the perpendicular geometry (M–C–E typically 80–90°) exhibited by the coordinated ligand.\(^{2,3}\) The acyl carbon is trigonally hybridised with an E–C–R (R = chalcoacyl substituent) angle that is close to ideal (ca. 120°). Metal–carbon separations are shorter than corresponding M–C single bonds and reflect varying degrees of multiple bonding, while the C–E separations are generally longer than C–E double bonds, consistent with a reduction in the C–E bond order. From the established bond lengths and angles it thus appears that the \(\eta^2\)-thioacyl bonding in the mononuclear complexes can be described most accurately by invoking a three-membered metallacyclopentene ("metallathiirene") ring (Chart 3.1 b).\(^{23}\) Structural dimensions for the \(\eta^2\)-acyl ligand in polynuclear metal complexes closely resemble those observed for the mononuclear derivatives.
Prior to this work, geometrical parameters for mononuclear seleno- and telluroacyl complexes were not available. Thus, data for the tellurobenzoyl complex [Os(\eta^2-TeCPh)Cl(CO)(PPh_3)_2]^{9,10} (13) (crystallographically characterised during the course of this work) are presented here as a representative example of heavier chalcoacyl coordination (Figure 3.1). Although new, the compound was prepared in a manner identical to that previously described for the originally reported 4-tolyl derivative.

**Figure 3.1.** Molecular structure of one of the two independent molecules in a crystal of 13 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Os-P(1) 2.3989(17), Os-P(2) 2.4064(17), Os-C(1) 1.913(7), Os-Te 2.8225(8), C(1)-Te 2.090(7), C(1)-C(11) 1.454(9), P-Os-P 174.90(6), OC-Os-Cl 98.6(2), Cl-Os-Te 108.99(4), OC-Os-C(11) 108.99(4), Te-Os-C 47.8(2), Os-C-Te 89.5(3), Te-C(1)-C(11) 126.8(5).

Geometric features within the telluroacyl ligand are in general agreement with the structural properties of \eta^2-thioacyls discussed above, with the C–Te vector lying perpendicular to the Os–C bond (Os–C–Te: 89.5(3)°) and a typically acute bite angle of 47.8(2)°, though the latter dimension is expanded beyond that seen for the related thioacyl complexes due to the larger size of the tellurium atom. The osmium-carbon separation in 13, 1.913(7) Å, is consistent with multiple bond character but, as expected, remains longer than the Os–C triple bond distance of the alkylidyne complex [Os(\equivCC_6H_4Me-4)Cl(CO)(PPh_3)_2] (1.77(2) Å).^{9}

The telluroacyl ligand lies within the equatorial plane defined by the carbonyl and chloride ligands and the aromatic acyl substituent is sandwiched between two phenyl groups of the adjacent triphenylphosphine ligands to maximise π–π stacking interactions. The orientation of
the \( \eta^2 \)-telluroacyl unit with respect to the remaining equatorial ligands of the pseudo-octahedral metal centre is characteristic of the geometry adopted by Group 8 chalcoacyl complexes, i.e., with the \( \pi \)-donor chalcogen atom being \textit{trans} to the \( \pi \)-acid CO ligand and the \( \pi \)-acidic acyl carbon being opposite the \( \pi \)-donor halide.\(^{6,21}\)

### 3.1.4 Spectroscopic properties of chalcoacyl complexes

Comparative spectroscopic data for a range of Group 6 alkylidyne, thioaroyl and dichalcocarboxylato complexes co-ligated by Tp are collected in Table 3.2. From the \( ^{13}\text{C} \{ ^1\text{H} \} \) NMR data it can be seen that the resonance for the thioacyl carbon appears in the low-field region of the spectrum characteristic of M–C multiple bonding, with the extent of shielding being somewhat dependent upon the electron-donating ability of the acyl substituent. Corresponding data for the dichalcocarboxylato complexes reveal a comparative insensitivity to the nature of both the incorporated chalcogen atoms and the carbon substituent, with a less than 2 ppm variance noted over the range of compounds surveyed (\( R = \text{C}_6\text{H}_4\text{Me}-4, \text{C}_6\text{H}_4\text{OMe}-4, \text{C}_4\text{H}_3\text{S}-2; \quad \text{EE}' = \text{OS}, \text{S}_2, \text{SeS} \)). Nevertheless, infrared data for the dichalcocarboxylate complexes \([\text{LnM}(\kappa^2_{\text{E}}\text{E}_2\text{CR})]\) are diagnostic of the net electron-releasing nature of the \( \pi \)-basic ligand. The compounds chosen for comparison are those based on the ‘\( \text{Mo(CO)}_2\text{Tp} \)’ fragment which is employed extensively in the work to be described.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( ^{13}\text{C} { ^1\text{H} } ) NMR ( \delta ) CE, ppm</th>
<th>( \nu_{\text{CO}} ), cm(^{-1} )</th>
<th>( k_{\text{CO}} ), N m(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="=CC%5Ctext%7BH%7D_4%5Ctext%7BMe%7D-4">Mo</a></td>
<td>293.1</td>
<td>1998, 1921</td>
<td>15.51</td>
</tr>
<tr>
<td><a href="=CC%5Ctext%7BH%7D_4%5Ctext%7BOMe%7D-4">Mo</a></td>
<td>294.2</td>
<td>1991, 1906</td>
<td>15.34</td>
</tr>
<tr>
<td><a href="=%5Ctext%7BC%7D_4%5Ctext%7BH%7D_3%5Ctext%7BS%7D-2">Mo</a></td>
<td>276.8</td>
<td>1996, 1913</td>
<td>15.43</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BSe%7D%7D%5Ctext%7BC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BMe%7D-4">Mo</a></td>
<td>280.4</td>
<td>1979, 1893</td>
<td>15.14</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BSe%7D%7D%5Ctext%7BC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BOMe%7D-4">Mo</a></td>
<td>278.0</td>
<td>1976, 1891</td>
<td>15.10</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BSe%7D%7D%5Ctext%7BC%7D_4%5Ctext%7BH%7D_3%5Ctext%7BS%7D-2">Mo</a></td>
<td>261.6</td>
<td>1980, 1897</td>
<td>15.18</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BO%7D%7D%5Ctext%7BSCC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BMe%7D-4">Mo</a></td>
<td>251.6</td>
<td>1959, 1855</td>
<td>14.70</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BS%7D%7D%5Ctext%7BS%7D_%7B%5Ctext%7BC%7D%7D%5Ctext%7BC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BMe%7D-4">Mo</a></td>
<td>249.1</td>
<td>1953, 1871</td>
<td>14.77</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BS%7D%7D%5Ctext%7BS%7D_%7B%5Ctext%7BC%7D%7D%5Ctext%7BC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BOMe%7D-4">Mo</a></td>
<td>250.9</td>
<td>1965, 1890</td>
<td>15.01</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BSe%7D%7D%5Ctext%7BSeSCC%7D_6%5Ctext%7BH%7D_4%5Ctext%7BOMe%7D-4">Mo</a></td>
<td>249.7</td>
<td>1943, 1861</td>
<td>14.62</td>
</tr>
<tr>
<td><a href="%5Ckappa%5E2_%7B%5Ctext%7BSe%7D%7D%5Ctext%7BSeSCC%7D_4%5Ctext%7BH%7D_3%5Ctext%7BS%7D-2">Mo</a></td>
<td>249.6</td>
<td>1945, 1857</td>
<td>14.60</td>
</tr>
</tbody>
</table>

\( ^6 \) Data reproduced from reference [19], \( \text{E} = \text{O}, \text{S}, \text{Se}; [\text{Mo}] = \text{Mo(CO)}_2\text{Tp} \).

For each chalcoacyl complex, the infrared spectrum shows two carbonyl-associated absorptions, with the lower frequency absorption being significantly more intense. Comparative data for the corresponding dichalcocarboxylate ligands reveals a reversal of this characteristic intensity profile, with a stronger absorption being observed for the higher energy stretch.\(^\text{14}\) This reversal
CHAPTER 3. SELENOAROYL COMPLEXES OF MOLYBDENUM

of intensities arises from changes in the intercarbonyl angle on proceeding from the dihapto-chalcocarboxylate ligand, a point which will be revisited below.

3.1.5 The addition of selenium to unsaturated M–C bonds

As noted above, the only complete set of heavier chalcocarboxyl complexes previously reported arose from the addition of elemental chalcogens to an osmium alkylidyne. This transformation is relevant to the results to be discussed below and, accordingly, a brief overview of the addition of chalcogens, in particular selenium, to metal–carbon multiple bonds is now provided.

\( M=C \) double bonds

Elemental selenium reacts slowly with the \( M=C \) double bond in the electron-rich methyldiene complex \([\text{Os}(=\text{CH}_2)(\text{NO})\text{Cl}(\text{PPh}_3)_2]\) to give the \( \pi \)-coordinated selenoformaldehyde compound \([\text{Os}(\eta^2-\text{Se}=\text{CH}_2)(\text{NO})\text{Cl}(\text{PPh}_3)_2]\), a reaction which proceeds in a similar manner for sulfur and selenium, but not for oxygen.\(^{24}\) The cationic selenoformaldehyde complex \([\text{Re}(\eta^2-\text{Se}=\text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^+\) is similarly formed from reaction of the electrophilic \([\text{Re}(=\text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^+\) with triphenylphosphine selenide or potassium selenocyanate (Scheme 3.7).\(^{25}\)

\[
\begin{array}{c}
\text{Cp} \quad \text{Re} \quad \text{Se} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{Ph}_3\text{P} \quad \text{NO} \\
\end{array} \quad \xrightarrow{\text{2+ Se}^-} \quad \begin{array}{c}
\text{Cp} \quad \text{Re} \quad \text{Se} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{Ph}_3\text{P} \quad \text{NO} \\
\end{array} + \begin{array}{c}
\text{Cp} \quad \text{Re} \quad \text{X} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{Ph}_3\text{P} \quad \text{NO} \\
\end{array}
\]

Scheme 3.7. Synthesis of the rhenium selenoformaldehyde complex \([\text{Re}(\eta^2-\text{Se}=\text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^+\) (\( X = \text{Ph}_3\text{P} \) or \( \text{NC}^- \)).

With aryl(phenyl)carbene complexes \([\text{M}(=\text{CPhR})(\text{CO})_3] \) (\( M = \text{Cr} \) or \( \text{W} \); \( R = C_6H_4X-4, \ X = \text{H}, \text{Me}, \text{Br}, \text{OMe}, \text{CF}_3 \) or \( \text{NMe}_2 \)), the phenyl isoselenocyanate acts as a nucleophilic selenium-atom donor to yield \( \eta^1\)-diphenylselenoketone pentacarbonyl complexes \([\text{M}(\eta^1-E=\text{CPhR})(\text{CO})_5] \) via selenium insertion into the metal–carbon double bond (Scheme 3.8).\(^{26}\) It is also possible to isolate selenobenzaldehyde complexes \([\text{M}(\eta^1-\text{Se}=\text{CHR})(\text{CO})_3] \) (\( R = C_6H_4X-4; \ M = \text{Cr}, \text{W}, \ X = \text{H}, \text{OMe} \) or \( \text{CF}_3 \)) from the reaction of the corresponding pentacarbonyl carbene complexes with the pseudohalide selenocyanate.\(^{27}\) Notably, in these cases, as distinct from the osmium and rhenium examples, \textit{monodentate} coordination of the selenoaldehyde occurs, with complete cleavage of the \( W=C \) bond.
Contrastingly, selenium adds across but does not cleave the M=C bond of 
\[ \text{[Rh(=C=CHR)}\{P(\text{-Pr})_{\text{3}}\}Cp\} \] (R = H, Me, Ph) to afford \( \eta^2 \)-selenoketene complexes (Scheme 3.9).\(^{28,29}\)

\[ \text{[Rh(=C=CHR)}\{P(\text{-Pr})_{\text{3}}\}Cp\} \] (E = S, Se, Te; R = H, Me, Ph).

**M≡C triple bonds**

The addition of chalcogens to the metal–carbon triple bonds of alkylidyne complexes takes one of two courses, depending on the metal centre. The isolation of the complete set of chalcoaroyl complexes \[ \text{[Os(} \eta^2 \text{-ECR)}\text{Cl(CO)(PPh}_{\text{3}})\text{]} \] (E = S, Se or Te) through the addition of elemental chalcogens to the Group 8 alkylidyne complex \[ \text{[Os(CR)}\text{Cl(CO)(PPh}_{\text{3}})\text{]} \] described by Roper (Scheme 3.5)\(^9,10\) established the viability of chalcoaroyl ligands, however, this approach has not proven to be generally applicable. Stone showed that the addition of elemental sulfur or selenium to Group 6 analogues instead transformed the carbynes to the corresponding dichalcocarboxylate complexes \[ \text{[M(} \eta^2 \text{-} \text{E}_{\text{2}} \text{-CR)}\text{L}_{\text{2}}\text{Cp}\} \] (E = S or Se; M = Mo, R = CH\text{2}t-Bu, L = P(OMe)\text{3}; M = W, R = C\text{6}H\text{4}Me-4, L = CO) (Scheme 3.10).\(^30\) The 2:1 adducts were the only isolable products arising from the treatment of Group 6 alkylidynes with elemental chalcogens, even when steric hindrance around the metal centre was increased, e.g., in the complexes \[ \text{[M(=C}C\text{6}H\text{3}Me\text{-2,6)}\text{(CO)}\text{2Cp}^*\} \] (M = Mo or W),\(^31\) or when the milder sulfur transfer reagent cyclohexene episulfide was employed.\(^32\)
Nevertheless, it was subsequently demonstrated that propylene sulfide may serve as a single sulfur atom transfer reagent, allowing access to mononuclear thioaroyl complexes of molybdenum and tungsten (Scheme 3.11).

\[
\text{Scheme 3.11. Preparation of thioaroyl complexes of Group 6 metals } [\text{LnM}(\eta^2-\text{SCR})] \quad (M = \text{Mo or W}; \quad R = \text{aryl}; \quad \text{Ln} = \text{Br(CO)}_2\text{bipy or (CO)}_2\text{Tp}).
\]

The synthetic challenge would therefore appear to lie in identifying an analogous system that allows for the controlled transfer of a single selenium atom to mononuclear Group 6 alkylidyne complexes. Organic solvent soluble reagents capable of transferring a single selenium atom are rare as organoselenium compounds are, in general, unstable and often display oxidative- and photo-sensitivity. Furthermore, these compounds are frequently malodorous and noxious. Therefore, new approaches to Se-delivery reagents would appear to be an attractive goal. Given that the preceding Chapter described a number of reactions in which mesityl isoselenocyanate extruded elemental selenium in the presence of various metal complexes, it was envisaged that the C–Se fragility of SeNCMmes might be constructively exploited towards this end.
3.2 Crystallographic study of [Mo(≡CC₄H₃S-2)(CO)₂Tp] (Tp* = Tp, 14, or Tp*, 15)

The work in this and subsequent Chapters is concerned with the reaction of selenium-containing ligands with Group 6 alkylidyne complexes co-ligated by poly(pyrazolyl)borates. Accordingly, crystallographic studies of the known compound [Mo(≡CC₄H₃S-2)(CO)₂Tp]¹⁴,¹⁹ (14) and the previously undescribed complex [Mo(≡CC₄H₃S-2)(CO)₂Tp*] (15) were performed, as these were the substrates chosen for the work to follow.

Results of the crystallographic studies for 14 and 15 are summarised in Figures 3.2 and 3.3 and selected bond lengths and angles are collected in Table 3.3. The [Mo(≡CC₄H₃S-2)(CO)₂Tp] molecule lies on a crystallographic mirror plane with the thiophene group being orthogonal to and equally disordered across this plane. The Tp* complex [Mo(≡CC₄H₃S-2)(CO)₂Tp*] shows a similar disordering of the thienyl group, albeit unequal in this case. The rotational disorder around the Cₓ–C(thienyl) bond is a commonly observed phenomenon for this functional group and has been noted previously.³⁵ Indeed, positional disorder of the 2-thienyl group proved to be a recurrent feature in crystallographic studies of many of the complexes to be described. Nevertheless, due to the high yield of the alkylidyne synthesis and the comparative ease of the requisite two-site refinement, this obstacle did not discourage further investigations involving [Mo(≡CC₄H₃S-2)(CO)₂Tp*] (Tp* = Tp, Tp*).

Figure 3.2. Molecular structures of a) 15 and b) 14 with 30% probability ellipsoids shown. Hydrogen atoms and solvate molecules have been omitted. Only one orientation of the disordered thiophene unit is shown (for 15 this corresponds to the major orientation).
Table 3.3. Selected bond lengths (Å) and angles (°) of [Mo(≡C₆H₄S-2)(CO)₂Tp]¹

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>14</th>
<th>15</th>
<th>Bond Angles, °</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)</td>
<td>1.809(4)</td>
<td>1.810(3)</td>
<td>Mo–C(1)–C(11)</td>
<td>172.7(3)</td>
<td>168.5(4)</td>
</tr>
<tr>
<td>Mo–N(21)</td>
<td>2.287(3)</td>
<td>2.311(3)</td>
<td>N(21)–Mo–N(31)</td>
<td>81.44(8)</td>
<td>83.50(10)</td>
</tr>
<tr>
<td>Mo–N(31)</td>
<td>2.217(2)</td>
<td>2.235(3)</td>
<td>N(21)–Mo–N(41)</td>
<td>81.44(8)</td>
<td>80.52(10)</td>
</tr>
<tr>
<td>Mo–N(41)</td>
<td>2.217(2)</td>
<td>2.226(3)</td>
<td>N(31)–Mo–N(41)</td>
<td>81.01(11)</td>
<td>82.60(10)</td>
</tr>
<tr>
<td>Mo–C(20)</td>
<td>2.000(3)</td>
<td>1.991(4)</td>
<td>C(20)–Mo–C(30)</td>
<td>89.58(19)</td>
<td>84.67(15)</td>
</tr>
<tr>
<td>Mo–C(30)</td>
<td>2.000(3)</td>
<td>1.995(4)</td>
<td>Mo–C(20)–O(20)</td>
<td>178.8(3)</td>
<td>173.6(3)</td>
</tr>
<tr>
<td>C(20)–O(20)</td>
<td>1.146(4)</td>
<td>1.147(4)</td>
<td>Mo–C(30)–O(30)</td>
<td>178.8(3)</td>
<td>176.0(3)</td>
</tr>
<tr>
<td>C(30)–O(30)</td>
<td>1.146(4)</td>
<td>1.153(5)</td>
<td>C(20)–O(20)</td>
<td>178.8(3)</td>
<td>176.0(3)</td>
</tr>
<tr>
<td>N(21)–N(22)</td>
<td>1.364(4)</td>
<td>1.374(4)</td>
<td>C(30)–O(30)</td>
<td>178.8(3)</td>
<td>176.0(3)</td>
</tr>
<tr>
<td>N(31)–N(32)</td>
<td>1.362(3)</td>
<td>1.379(4)</td>
<td>N(21)–N(22)</td>
<td>178.8(3)</td>
<td>176.0(3)</td>
</tr>
<tr>
<td>N(41)–N(42)</td>
<td>1.362(3)</td>
<td>1.381(4)</td>
<td>N(31)–N(32)</td>
<td>178.8(3)</td>
<td>176.0(3)</td>
</tr>
</tbody>
</table>

¹ Tp = Tp 14, Tp* 15. For 14, N₄₁/₄₂ = N₁₁/₃₂, C₃₀ = C₂₀, O₃₀ = O₂₀.

Figure 3.3. Space-filling representations of [Mo(≡C₆H₄S-2)(CO)₂Tp] (Tp = Tp, Tp*) along (||) and perpendicular (⊥) to the B–Mo vector (Tp = grey; Mo = pink; C₆ = blue; C₆H₄S-2 = cyan; CO = white and red).
Structural features of 14 and 15 are in good agreement with the generally observed trends for hydrotris(pyrazolyl)borate alkylidyne complexes that were discussed in Chapter 1, Section 1.3.2. Each of the 2-thienylmethylidyne complexes displays distorted octahedral geometry at the molybdenum centre and the Mo–C bond lengths are distinctly insensitive to the nature of the facially-capping ligand (1.809(4) Å for 14 vs 1.810(3) Å 15). The valence angle across Cα is essentially linear for each of the complexes (172.2(3)° for 14 and 168.5(4)° for 15), with that of 15 showing minimal distortion despite the enhanced steric profile of the Tp* ligand that is clearly evident in the space-filling representations of the Tp and Tp* complexes (Figure 3.3).

The familiar elongation (28 σ) of the pyrazolyl-N–molybdenum separation trans to the alkylidyne ligand is noted, in addition to a slight lengthening of the N–N and Mo–N bonds for the Tp* ligand of 15 relative to the corresponding separations for the Tp complex 14 (δav 0.015 Å). This discrepancy is further manifest in the enlarged sum of angles for the three six-membered chelate rings (246.6° for 15 vs 243.9° for 14) and is an expression of the greater steric profile of the Tp* ligand.

A further point of contrast between the two structures that arises from the relative donor properties of the tripodal pyrazolylborate ligands (Tp* > Tp) is the marginally contracted Mo–CO separations for the Tp* complex (1.991(4) and 1.995(4) Å for 15 vs 2.000(3) for 14) together with the enhanced bend of the carbonyl ligands (Mo–C–O: 173.6(3) and 176.0(3)° for 15 vs 178.8(3)° for 14), which is consistent with increased back-donation to the metal carbonyls in the case of [Mo(≡CC₄H₇S-2)(CO)₂Tp*], though these variations lie at the limits of statistical significance.
3.3 Synthesis of mononuclear selenoaroyl complexes

The potential for aryl isoselenocyanates to serve as selenium-donor agents has been demonstrated on one occasion (vide supra, Scheme 3.8). Moreover, the facile metal-mediated cleavage of the C-Se bond of mesityl isoselenocyanate was extensively documented in Chapter 2. As such, it was anticipated that mesityl isoselenocyanate may serve as an effective single-atom selenium transfer reagent for the synthesis of mononuclear Group 6 selenoacyl complexes.

Treating the complex \([\text{Mo}(=\text{CC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\)\(^{14,19}\) with SeCNMes in hexane at reflux over a period of 4 hours provided no less than three discrete products (Scheme 3.12), which were separated by cryostatic chromatography (−20 °C, silica gel). The major blue product (isolated in ca. 30% yield) was formulated as the desired selenoaroyl \([\text{Mo}(=\text{SeCC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) (16). The isolation of 16 allows direct comparison of associated spectroscopic data with those of the thioaroyl analogue \([\text{Mo}(=\text{SCCC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) (17).\(^{14,19}\)

\[
\begin{align*}
\text{14} + \text{SeCNMes} & \rightarrow \text{hexane} \\
\text{15} & \rightarrow \text{heat} \\
\text{16,CNMes,18,19} & \rightarrow \text{heat}
\end{align*}
\]


The infrared spectrum of 16 (Table 3.5) revealed two v\(_{\text{CO}}\) absorptions at 1988 and 1909 cm\(^{-1}\), to lower frequency of those for the alkylidyne precursor (1996, 1913 cm\(^{-1}\)). The intensity profile is similar to that of 17 (1980, 1897 cm\(^{-1}\)) with the higher frequency absorption being the less intense of the pair, but the v\(_{\text{CO}}\) absorptions for 16 are moved to marginally higher frequency. The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum of 16 includes a resonance at \(\delta = 264.5\) attributable to the selenoaroyl carbon, to higher field of that for 14 (\(\delta = 276.8\)) but falling within the range observed for the molybdenum thioaroyl complexes \([\text{Mo}(=\text{SCR})(\text{CO})_2\text{Tp}]\) (R = C\(_6\)H\(_3\)S-2, C\(_6\)H\(_4\)OMe-4 and C\(_6\)H\(_4\)Me-4) (\(\delta = 260–280\), Table 3.2).\(^{19}\) The room temperature \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra for 16 indicate a single environment for the three pyrazolyl arms, with three broad singlets due to the \(\text{H}^1\), \(\text{H}^4\) and \(\text{H}^5\) protons. The chemical equivalence of the pyrazolyl rings of the tridentate ligand suggests that the molecule is fluxional on the \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR time scales. A similar fluxionality was observed for the related acyl, thioacyl and thiocarbamoyl complexes, \([\text{Mo}(=\text{OCR})(\text{CO})_2\text{Tp}]\) (R = Me or Ph),\(^{36}\) \([\text{Mo}(=\text{SCCC}_6\text{H}_4\text{OMe-4})(\text{CO})_2\text{Tp}]\),\(^{19}\) and \([\text{Mo}(=\text{SCNMe}_2)(\text{CO})_2\text{pzTp}]\),\(^{37}\) respectively.

The three \(\text{H}^4\) protons of the Tp ligand's pyrazolyl arms appear as a broad singlet at \(\delta = 6.26\), clearly distinct from the remaining aromatic resonances of the complex. At lower temperatures
(-40 °C, Figure 3.4), these resonances appear as two triplets in a 1:2 ratio, consistent with the molecule containing a plane of symmetry that includes the acyl ligand, as was observed for the related complexes [Mo(η²-OCR)(CO)₂Tp] (R = Me or Ph)³⁶ and the thiocarbamoyl complex [Mo(η²-SCNMe₂)(CO)₂pzTp].³⁷ Coalescence of the resonances occurred at 28 °C, with the singlet resonance developing finer structure upon further heating, though signs of complex decomposition were evident above 50 °C.

![Figure 3.4. ¹H NMR spectrum of 16 in CD₃CN at -40 °C with variable temperature study (-30 to 70 °C) showing coalescence of TpH⁴ resonances inset.](image)

From the coalescence temperature ($T_c$), an energy barrier ($ΔG^\ddagger$) for the fluxional process of 62 kJ mol⁻¹ can be calculated according to the modified Gutowsky equation (Equation 3.1).³⁸

$$ΔG^\ddagger = RT_c [22.96 + \ln(T_c / \delta ν)]$$

(Eq 3.1)

The equivalence of the three arms of the Tp ligand suggests that the fluxional process is not associated with a simple oscillation of the dihapto-acyl ligand, i.e., if the pyrazolylborate ligand were stereochemically rigid a 1:2 ratio of the signals would be expected at all times, irrespective of the dynamic behaviour exhibited by the selenoacyl, though the simultaneous occurrence of such a process cannot be excluded.³⁶,³⁷ In light of the inertness of 16 towards ligand substitution reactions (vide infra) and the apparent lack of spectroscopic evidence for acetonitrile-$d_3$ coordination, a process involving dissociation of one pyrazolyl arm and Berry pseudo-rotation of the penta-coordinate intermediate is not favoured. Instead, the chemical equivalence is accounted for by invoking a Bailar twist of the complete pyrazolylborate ligand. In the case of the related complex [Mo(η²-SCNMe₂)(CO)₂pzTp], Lalor and co-workers similarly suggested
that rotation of the entire pyrazolylborate ligand about the B–Mo axis was responsible for the chemical equivalence of the coordinated pyrazolyl arms. 37

The molecular geometry of 16 (Figure 3.5) confirms the formulation of the complex and reveals a ground-state geometry in which the plane of the selenoaroyl ligand approximately (but not crystallographically) bisects the N–Mo–N and OC–Mo–CO angles, which is consistent with the 1:2 intensity of the pyrazolyl ligands observed in the low temperature 1H NMR spectrum. Thus, the limiting solution structure mirrors that found in the solid state. Relevant bond lengths and angles of 16 are summarised in Table 3.4. For comparative purposes, data for the isostructural thioaroyl complex [Mo(η2-SCC4H3S-2)(CO)2Tp]14,19 (17) are also presented. This complex had been previously reported but without any structural characterisation. Accordingly, a crystallographic study was also undertaken.

If the selenoacyl ligand is relegated to a single coordination site, the metal atom can be regarded as quasi-six-coordinate and the geometry at the molybdenum centre thus approximates to octahedral, with the shortest molybdenum–pyrazolyl separation being that trans to the chalcogen atom (2.199(2) Å vs 2.229(2) and 2.227(2) Å), as has been observed for two related Group 6 η2-acyl complexes. 39 The geometry of the ‘Mo(CO)2Tp’ unit is otherwise unremarkable and interest instead focuses on the η2-selenoacyl ligand, for which no structural precedent exists. The small bite angle (43.42(8)°) and orientation of the acyl ligand (Mo–C–Se 88.73(12)°) are as expected and are nearly identical to those found for the corresponding η2-thioaroyl analogue [Mo(η2-SCC4H3S-2)(CO)2Tp]14,19 (17) (40.81(8)° and 88.08(12)°, respectively). The Mo–C(1) bond length of 1.995(3) Å for 16 clearly indicates multiple bonding.

Figure 3.5. Molecular structure of a) 16 in a crystal of 16·CH2Cl2 and b) viewed orthogonal to the pseudo-molecular mirror plane. 30% displacement ellipsoids are shown and hydrogen atoms have been omitted. Only the major orientation of the disordered thiophene unit is shown.
character and is consistent with the expected reduction of the Mo–C bond order to two. Multiple bonding is also evident for the C(1)–Se separation (1.849(3) Å), which falls within the range observed for π-C,Se seleno-aldehyde, -ketone and -ketene complexes (1.805–1.960 Å). The Mo–Se distance of 16 (2.6897(4) Å) approaches that observed for more conventionally bound Se donors such as the Mo–Se single bond separation of 2.585(1) Å observed for the selenolato [Et₄N][Mo(CO)(SeC₆H₅)(S₂C₂Me₂)]⁶¹ and is indicative of a significant bonding interaction between the molybdenum centre and the selenium atom. Thus, geometric parameters for the coordinated selenoaroyl unit would appear to point towards substantial contributions from both the metallaselenirene and η²-selenoacyl valence bond descriptions depicted in Chart 3.1 b.

A second product isolated from the reaction in modest yield is the diselenocarboxylate complex [Mo(κ²-Se₂CC₆H₃S-2)(CO)₂Tp] (19). Spectroscopic data for the teal blue complex 19 (Table 3.5) are comparable to those of the related compounds [Mo(κ²-Se₂CCH₂t-Bu){P(OMe)₃}₂Cp] and [W(κ²-Se₂CC₆H₄Me-4)(CO)₂Cp] with a low field resonance at δ₁ 251.6 being readily attributable to the carbon atom of the Se₂C unit (cf. δ₁ 251.6 for [Mo(κ²-Se₂CCH₂t-Bu)(CO)₂Cp] and 251.9 for [W(κ²-Se₂CC₆H₄Me-4)(CO)₂Cp]) and a single resonance for the carbonyl ligands at δ₁ 209.0, which, like that for the Cα carbon nucleus, appears to much higher field than the corresponding resonance for the selenoaroyl complex 16 (δ₁ 230.4). The solution CO stretching absorptions of 19, 1939 and 1860 cm⁻¹, show the expected intensity profile and are at 50 cm⁻¹ lower energy than those observed for 16. This is consistent with the diselenocarboxylate unit being overall electron-releasing, due to potent π-basicity and no π-acid capability.

The Cambridge Crystallographic Data Base currently includes some 33 structures involving four-membered L₄MSe₂C chelates based on Se₂C=O, Se₂C=NCN, Se₂C=Se, Se₂C=C(CN)₂ and (numerous) Se₂CN₄R₂ ligands. Remarkably, however, no structural data currently exist for diselenocarboxylato complexes, L₄MSe₂CR. Accordingly, a crystallographic study of complex 19 was undertaken, the results of which are summarised in Figure 3.6 and which confirm the formulation. The geometry of the seven-coordinate complex may be described as distorted octahedral with one face being capped by a somewhat bent CO ligand (hence the intensity reversal in νCO-associated infrared data, vide supra). The equatorial plane is defined by the diselenocarboxylate unit and two arms of the pyrazolylborate ligand and gross structural features appear to be in good agreement with those observed for the related dithiocarboxylato complexes [Mo(κ²-S₂CCH₂t-Bu)(CO)₂Cp] and [W(κ²-S₂CC₆H₄Me-4)(CO)₂Cp], which exhibit E–M–E angles of ca. 68° and E–C–E angles of ca. 110° compared with 69.64(4) and 108.8(5)°, respectively, for 19. Nevertheless, while the identity of the complex was unambiguously
confirmed by this study, the precision of the model was low such that data may only be interpreted with caution, thus precluding a more detailed discussion.

Notably, treating 16 with elemental selenium or alternatively further SeCNMes led to incorporation of a second equivalent of selenium to generate 19, though the reaction with SeCNMes was much slower than the corresponding reaction with elemental selenium and did not reach completion within three weeks. The reaction of 16 with Li₂Se₂ similarly afforded the diselenocarboxylate complex, albeit in low yield.

![Figure 3.6. Preliminary molecular structure of 19 viewed approximately across the MoN₂Se₂ plane. 30% probability ellipsoids are shown. Hydrogen atoms have been omitted. Only the major orientation of the disordered thiophene unit is shown. Selected bond lengths (Å) and angles (°): Mo–Se(1) 2.6068(16), Mo–Se(2) 2.6437(13), C(1)–Se(1) 1.851(9), C(1)–Se(2) 1.837(10), C(1)–C(11) 1.417(15), Mo–N(21) 2.219(9), Mo–N(31) 2.228(8), Mo–N(41) 2.304(8), Mo–C(20) 1.981(12), C(20)–O(20) 1.162(13), Mo–C(30) 1.958(11), C(30)–O(30) 1.153(12), Se(1)–Mo–Se(2) 69.64(4), Se(1)–C(1)–Se(2) 108.8(5), Se(1)–C(1)–C(11) 127.3(8), Se(2)–C(1)–C(11) 123.9(8).]

The final product from the reaction was obtained as purple crystalline solid in ca. 30% yield and is a second example of a selenoaroyl complex [Mo(η²-SeCC₄H₃S-2)(CO)(CNMes)Tp] (18), which is akin to 16 but in which one carbonyl ligand has been replaced by an isonitrile group. The formulation of 18 followed from spectroscopic data (Table 3.5), which included a strong infrared absorption at 2099 cm⁻¹ that was diagnostic of the νCN stretch of a coordinated isonitrile ligand in addition to resonances attributable to the mesityl substituent in the ¹H NMR spectrum (δH 6.80, 2.22 and 1.93). Moreover, in the ¹³C{¹H} NMR data a resonance consistent with the terminal carbon of a coordinated isonitrile was evident at δC 186.4, in addition to the signals for the acyl carbon nuclei and the single carbonyl ligand at δC 267.6 and 239.5, respectively, the latter appearing at a relatively deshielded position compared with that of the chemically
equivalent carbonyls of 16 ($\delta_c$ 230.4). Finally, $^1$H NMR data are indicative of inequivalence of the three limbs of the Tp ligand, as expected for a complex with $C_1$ symmetry. A single crystal X-ray analysis provided unambiguous confirmation of the formulation of 18 as $[\text{Mo(}\eta^2\text{-SeCC}_4\text{H}_3\text{S-2})(\text{CO})(\text{CNMes})\text{Tp}]$ and results are summarised in Figure 3.7 and Table 3.4.

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>17</th>
<th>16</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)</td>
<td>2.000(3)</td>
<td>1.995(3)</td>
<td>1.975(3)</td>
</tr>
<tr>
<td>Mo–E</td>
<td>2.5677(8)</td>
<td>2.6897(4)</td>
<td>2.6605(5)</td>
</tr>
<tr>
<td>C(1)–C(11)</td>
<td>1.433(4)</td>
<td>1.432(5)</td>
<td>1.437(6)</td>
</tr>
<tr>
<td>Mo–N(21)</td>
<td>2.192(2)</td>
<td>2.199(2)</td>
<td>2.214(3)</td>
</tr>
<tr>
<td>Mo–N(31)</td>
<td>2.224(2)</td>
<td>2.229(2)</td>
<td>2.221(3)</td>
</tr>
<tr>
<td>Mo–N(41)</td>
<td>2.224(2)</td>
<td>2.227(2)</td>
<td>2.238(3)</td>
</tr>
<tr>
<td>Mo–C(20)</td>
<td>1.980(3)</td>
<td>1.996(4)</td>
<td></td>
</tr>
<tr>
<td>Mo–C(50)</td>
<td></td>
<td></td>
<td>2.066(4)</td>
</tr>
<tr>
<td>Mo–C(30)</td>
<td>1.980(3)</td>
<td>1.995(3)</td>
<td>1.975(3)</td>
</tr>
<tr>
<td>C(20)–O(20)</td>
<td>1.148(3)</td>
<td>1.059(4)</td>
<td></td>
</tr>
<tr>
<td>C(50)–N(50)</td>
<td>1.138(3)</td>
<td>1.133(3)</td>
<td>1.158(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, °</th>
<th>17</th>
<th>16</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)–C(11)</td>
<td>142.0(2)</td>
<td>143.0(3)</td>
<td>149.3(4)</td>
</tr>
<tr>
<td>C(1)–Mo–E</td>
<td>40.81(8)</td>
<td>43.42(8)</td>
<td>44.48(10)</td>
</tr>
<tr>
<td>Mo–C(1)–E</td>
<td>88.08(12)</td>
<td>88.73(12)</td>
<td>87.63(14)</td>
</tr>
<tr>
<td>E–C(1)–C(11)</td>
<td>129.8(2)</td>
<td>128.3(3)</td>
<td>122.9(3)</td>
</tr>
<tr>
<td>Mo–C(20)–O(20)</td>
<td>179.5(2)</td>
<td>178.3(3)</td>
<td></td>
</tr>
<tr>
<td>Mo–C(50)–N(50)</td>
<td></td>
<td></td>
<td>177.6(3)</td>
</tr>
<tr>
<td>Mo–C(30)–O(30)</td>
<td>177.0(3)</td>
<td>179.4(2)</td>
<td>177.8(3)</td>
</tr>
</tbody>
</table>

$^6$ L = CO, E = S, 17, E = Se, 16; L = CNMes, E = Se, 18.
CHAPTER 3. SELENOAROYL COMPLEXES OF MOLYBDENUM

Figure 3.7. Molecular structure of 18 with 30% displacement ellipsoids shown. Hydrogen atoms and dichloromethane solvate have been omitted. Only the major orientation of the disordered thienyl unit is represented.

Geometric parameters within the selenoaroyl ligand of 18 are remarkably close to those for 16 despite the presumed increase in \( \pi \)-basicity of the molybdenum upon CO/CNMes substitution. The Mo–C(1) and C(1)–Se separations at 1.975(3) and 1.866(3) Å, respectively, show only marginal changes relative to the corresponding distances in 16, i.e., a 7 \( \sigma \) shortening of the Mo–C(1) bond and a 6 \( \sigma \) lengthening of the C(1)–Se separation. The Mo–Se bond (2.6605(5) Å) is, however, dramatically contracted (> 60 \( \sigma \)) and these structural parameters are consistent with an enhanced contribution to the ground state structure from the metallaselenirene resonance form similar to that shown on the right in Chart 3.1 b.

The substitution of a carbonyl ligand in 16 with the bulky CNMes in 18 increases electron density at the metal centre, which in turn leads to increased back-bonding to the remaining carbonyl ligand. Accordingly, the Mo–CO distance for 18 is clearly shorter than those of the \( \text{cis}-(\text{CO})_2 \) selenoaroyl (1.975 (3) Å for 18 vs 1.995(3) and 1.996(4) Å for 16), whilst the C–O bond distances show the opposite trend (1.158(5) Å for 18 vs and 1.133(3) and 1.059(4) Å for 16).

Interestingly, treating 18 with elemental selenium did not afford the isonitrile substituted diselenocarboxylate complex \([\text{Mo}(\kappa^2-\text{Se}_2\text{CC}_2\text{H}_3\text{S}-2)(\text{CO})(\text{CNMes})\text{Tp}]\) which would be analogous to 19, presumably due to the increased steric bulk of the CNMes vs CO ligand, which
disfavours the formation of the seven coordinate complex. Whilst this somewhat remote steric bulk does not impinge directly upon the coordination sphere, it may be expected to hinder approach of the isoselenocyanate.

Table 3.5. IR and $^{13}$C$^{1}{^1}$H NMR data for alkylidyne, selenoacyl and diselenocarboxylate complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{13}$C$^{1}{^1}$H NMR, ppm</th>
<th>IR, cm$^{-1}$</th>
<th>$k_{CO}$, N m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(14)</td>
<td>$\delta$C$_a$ 276.8, $\delta$CO 225.9</td>
<td>v$_{CN}$ 1996, 1913</td>
<td>15.43</td>
</tr>
<tr>
<td>(20)</td>
<td>$\delta$C$_a$ 293.1, $\delta$CO 224.9</td>
<td>v$_{CO}$ 1993, 1909</td>
<td>15.38</td>
</tr>
<tr>
<td>(15)</td>
<td>$\delta$C$_a$ 271.1, $\delta$CO 225.7</td>
<td>v$_{CN}$ 1998, 1904</td>
<td>15.30</td>
</tr>
<tr>
<td>(16)</td>
<td>$\delta$C$_a$ 264.5, $\delta$CO 230.4</td>
<td>v$_{CN}$ 1988, 1909</td>
<td>15.34</td>
</tr>
<tr>
<td>(21)</td>
<td>$\delta$C$_a$ 288.2, $\delta$CO 230.8</td>
<td>v$_{CN}$ 1988, 1905</td>
<td>15.31</td>
</tr>
<tr>
<td>(22)</td>
<td>$\delta$C$_a$ 258.5, $\delta$CO 229.0</td>
<td>v$_{CN}$ 1981, 1900</td>
<td>15.21</td>
</tr>
<tr>
<td>(18)</td>
<td>$\delta$C$_a$ 267.6, $\delta$CO 239.5</td>
<td>v$_{CN}$ 2099</td>
<td>1885</td>
</tr>
<tr>
<td>(23)</td>
<td>$\delta$C$_a$ 292.4, $\delta$CO 240.3</td>
<td>v$_{CN}$ 2102</td>
<td>1879</td>
</tr>
<tr>
<td>(19)</td>
<td>$\delta$C$_a$ 251.6, $\delta$CO 209.0</td>
<td>v$_{CN}$ 1939, 1860</td>
<td>14.58</td>
</tr>
</tbody>
</table>

$^a$ Infrared data measured in CH$_2$Cl$_2$ solution and $^{13}$C$^{1}{^1}$H NMR spectra measured in CD$_2$Cl$_2$ solution unless otherwise stated as follows: $^b$CDCl$_3$.

In a manner similar to the synthesis of 16 and 18, the analogous selenoaroyl complexes [Mo($\eta^3$-SeCC$_6$H$_4$Me-4)(CO)$_2$Tp] (21) and [Mo($\eta^3$-SeCC$_6$H$_4$Me-4)(CO)(CNMes)Tp] (23) were prepared from the alkylidyne precursor [Mo(=CC$_6$H$_4$Me-4)(CO)$_2$Tp]$_{14,19}$ (14). A minor purple band suspected to correspond to the diselenocarboxylate complex [Mo($\kappa^2$-SeCC$_6$H$_4$Me-4)(CO)$_2$Tp] was evident during the chromatographic separation of 21 and 23, but was not formed in significant quantities to allow for the collection of useful characterisation data. Spectroscopic data for the selenotoluoyl complexes 21 and 23 are comparable to those obtained for the corresponding thienyl derivatives (Table 3.5), though an approximate 25 ppm deshielding is noted for the C$_a$ resonances ($\Delta$C 288.2 for 21 and 292.4 for 23 vs 264.5 for 16 and 267.6 for 18). It is not clear whether this reflects an increase in $\pi$-base character for the selenoaroyl ligand bearing the p-tolyl substituent, or if it is a corollary of the tolyl group being more sterically demanding than the 2-thienyl substituent (5 vs 6-membered ring). It is of note that the selenoaroyl complex 21 displayed decreased stability relative to the thienyl derivative, with significant decomposition occurring during the acquisition of $^{13}$C$^{1}{^1}$H NMR data. After 12 h in dichloromethane-$d_2$ solution (ambient temperature), resonances consistent with both reformation of the precursor carbyne ($\Delta$C$_a$ 294.9) and a compound tentatively identified as the diselenocarboxylate ($\Delta$C$_a$ 250.3) were apparent, in addition to the major resonances associated with 21.
A single crystal X-ray diffraction study of the substituted selenotoluoyl complex $[\text{Mo}(\eta^2-\text{SeCC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{CNMes})\text{Tp}]$ (23) was performed and the results are illustrated in Figure 3.8. The selenoaroyl and isonitrile ligands lie in essentially the same position as found for 18 with structural dimensions within the acyl ligand showing only moderate deviations from those found for 18. A statistically insignificant increase in the Mo–C(1) separation (4 \(\sigma\)) and slight contraction of the Se–C(1) separation (5 \(\sigma\)) are accompanied by a significantly elongated Mo–Se distance (33 \(\sigma\)), which together imply increased $\eta^2$-selenoacyl character for the ground state structure of 23 relative to that for 18 (Chart 3.1b), an interpretation supported by the modest opening of the Mo–C(1)–C(11) angle by some 2–3°.

![Figure 3.8. Molecular structure of 23 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond lengths (\(A\)) and angles (°): Mo–C(1) 1.988(3), Mo–Se 2.6755(4), C(1)–Se 1.854(2), C(1)–C(11) 1.450(2), Mo–N(21) 2.227(2), Mo–N(31) 2.197(2), Mo–N(41) 2.233(2), Mo–C(30) 1.967(3), C(30)–O(30) 1.122(3), Mo–C(50) 2.075(2), C(50)–N(50) 1.153(3), Mo–C(1)–C(11) 145.41(19), C(1)–Mo–Se 43.83(7), Mo–C(1)–Se 88.23(11), Se–C(1)–C(11) 126.25(19).](image)

A point of contrast between the substituted selenoacyl complexes 23 and 18 and the corresponding dicarbonyl analogue 16 is apparent in the relative trans influences of the selenoacyl, carbonyl, and isonitrile ligands. For Group 6 \textit{cis}-(CO)$_2$ acyl complexes, the shortest metal–pyrazolyl separation is typically that trans to the chalcogen donor atom\textsuperscript{39} however, the Mo–N separations trans to the acyl and isonitrile ligands for 18 are statistically equivalent and, in the case of 23, the shortest Mo–N separation is that trans to the isonitrile unit (2.197(2) \(A\)).

Unlike the \textit{p}-tolyl substituted derivative, alkylidyne bearing the sterically bulky mesityl and xylyl substituents were unreactive towards mesityl isoselenocyanate, which is most likely due to shielding of the metal–carbon triple bond by the sterically cumbersome alkylidyne substituents. The alternative interpretation, a destabilisation of the resulting selenoacyl, appears less likely given reversible selenium addition/extrusion might be expected to result in eventual
consumption of the isoselenocyanate, however this was not appreciably observed. Hill and co-workers noted a similar reactive reticence for these alkylidyne complexes in attempts to form the mononuclear thioaroyl complexes by treatment with methyl thiirane.\textsuperscript{19}

A notable difference in reactivity between the Tp and Tp* co-ligated thienyl carbynes, 14 and 15, was observed in their reactions with SeCNMes (1). The former gave the CNMes substituted selenoaroyl and diselenocarboxylate products, 18 and 19, in addition to the desired complex 16, while the latter yielded only the selenoaroyl complex [Mo(\(\eta^2\)-SeCC\(_4\)H\(_3\)S-2)(CO)\(_2\)Tp\*)] (22). The difference in reactivity between the Tp and Tp* complexes may be attributed to electronic effects, with the electron-releasing methyl groups in the Tp* ligand reducing the reactivity of the M=C bond towards nucleophilic attack by SeCNMes relative to the Tp complex. Additionally, the steric bulk of the Tp* ligand may serve to hinder both the ligand substitution process and the incorporation of two equivalents of selenium into the metal–carbon bond that would allow for the formation of the tris(3,5-dimethylpyrazolyl)borate complexes analogous to 18 and 19, respectively. The general reluctance of the Tp* ligand (vs Tp) to accommodate coordination numbers above 6 is a recurrent feature of the chemistry reviewed in Chapter 1.

Spectroscopic data for [Mo(\(\eta^2\)-SeCC\(_4\)H\(_3\)S-2)(CO)\(_2\)Tp\*)] (22) (Table 3.5) are comparable to those of 16, but reflect the greater donor ability of the Tp* relative to the Tp co-ligand. The two \(v_{\text{CO}}\) absorptions at 1981 and 1900 cm\(^{-1}\) are to marginally lower frequency than those of the alkylidyne precursor 15 (1998, 1904 cm\(^{-1}\)) and the Tp analogue 16 (1998, 1909 cm\(^{-1}\)) and show the characteristic acyl intensity profile. The selenoaroyl carbon nucleus resonates at \(\delta\) 258.5. In contrast to the fluxional process evident for 16 (vide supra), \(^1\)H and \(^{13}\)C{\(^1\)H} NMR spectra for 22 indicate a 1:2 intensity pattern for the arms of the Tp* ligand, consistent with stereochemical rigidity for this unit due to stronger binding of the N donors with the metal centre and the greater steric hurdles associated with a Bailar twist process (see Figure 3.3).

A crystallographic study provided confirmation of the geometry of 22 and the results are summarised in Figure 3.9. The \(\eta^2\)-ligand is aligned in the same manner found for 16, 21 and 18, such that the selenoaroyl defines an approximate molecular mirror plane, which is consistent with the observed equivalence of the two carbonyl ligands and two of the pyrazolyl arms in the \(^1\)H and \(^{13}\)C{\(^1\)H} NMR spectroscopic data. The geometry of the selenoacyl ligand in 22 is statistically equivalent to that of 16, excluding a modest (9 \(\sigma\)) contraction of the Mo–Se separation. (NB: The disparity of the Se–C(1)–C(11) angle (124.8(3) vs 128.3(3)\(^\circ\)) reflects the differing orientation of the thienyl unit. For the alternate orientation of 22, related to the structure represented in Figure 3.9 by a 180\(^\circ\) rotation around the C(1)–C(11) bond, this angle is 127.8(3)\(^\circ\)).
Figure 3.9. Molecular structure of 22 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): Mo–C(1) 1.995(2), Mo–Se 2.6867(3), C(1)–Se 1.846(3), C(1)–C(11) 1.424(6), Mo–N(21) 2.220(2), Mo–N(31) 2.222(2), Mo–N(41) 2.256(2), Mo–C(20) 2.057(3), Mo–C(30) 2.012(3), C(20)–O(20) 1.021(4), C(30)–O(30) 1.084(3), Mo–C(1)–C(11) 146.5(3), C(1)–Mo–Se 43.39(7), Mo–C(1)–Se 88.67(10), Se–C(1)–C(11) 124.8(3).
3.4 Proposed mechanism for selenium delivery from SeCNMes

As a solid, the isoselenocyanate ligand is indefinitely stable to both air and light. Moreover, in the absence of a transition-metal, SeCNMes (1) is thermally robust, showing no sign of decomposition in 1,1,2,2-tetrachloroethane-\(d_2\) solution under argon at 70 °C over a period of several weeks. Thus, the Se–C bond scission that allows for the isolation of the mononuclear selenoacyl complexes under the conditions described herein (Scheme 3.12) must be metal-mediated and not involve free selenium. Similar conclusions followed from the results discussed in Chapter 2.

While allowing access to the previously inaccessible mononuclear Group 6 selenoaroyls, product selectivity from this methodology is low and attempts to optimise the procedure for the exclusive preparation of any of the compounds have been met with little success, though formation of the substituted selenoacyl derivatives 18 and 23 can be somewhat limited by employing gentler reaction conditions. Indeed, the formation of 18 and 23 from treatment of the corresponding alkylidyne \([\text{Mo}(\equiv\text{CR})(\text{CO})_2\text{Tp}]\) \((R = \text{C}_4\text{H}_3\text{S}-2, \ 14 \ \text{and} \ \text{C}_6\text{H}_4\text{Me}-4, \ 20)\) with SeCNMes is mechanistically significant in that isolated 16 does not react with CNMes under the conditions of the synthesis of 16, 18 and 19, i.e., complex 16 is not an intermediate in the formation of 18. It is, however, not clear whether the substitution complex \([\text{Mo}(\equiv\text{CC}_4\text{H}_3\text{S}-2)(\text{CO})(\text{CNMes})\text{Tp}]\) (24) serves as an intermediate en route to 18. Complexes of the type \([\text{M}(\equiv\text{CR})(\text{CO})_2\text{L}]\) \((\text{M} = \text{Mo or W}; \ \text{L} = \text{Cp, Cp*}, \ \text{Tp or Tp*})\) are generally inert to associative ligand substitution at the 18-electron centre under mild (non-photolytic) conditions, but treatment of 14 with CNMes in hexane at reflux afforded 24 in low isolated yield (16%). The structure assigned to 24 was supported by characteristic \(v_{\text{CN}}\) and \(v_{\text{CO}}\) absorptions in the solution infrared spectrum at 2083 and 1899 cm\(^{-1}\), respectively, that may be compared to spectroscopic data for the related aminocarbonyne complex \([\text{Cr}(\equiv\text{CNi-Pr}_2)(\text{CO})(\text{CNt-Bu})\text{Tp*}]\) \((v_{\text{CN}} \ 2093 \ \text{cm}^{-1} \ \text{and} \ v_{\text{CO}} \ 1826 \ \text{cm}^{-1})\). Furthermore, the \(^{13}\text{C}\{^{1}\text{H}\}\) NMR spectrum of 24 revealed \(C_1\) symmetry, with each of the arms of the Tp ligand showing chemically distinct environments and characteristic resonances for the carbon nuclei of the alkylidyne, carbonyl, and coordinated isonitrile being evident at \(\delta_c\ 271.8, \ 237.9\) and 188.2, respectively. These \(^{13}\text{C}\{^{1}\text{H}\}\) NMR data may be compared directly to corresponding signals for 18 \((\delta_c\ 267.6, \ 239.5\ \text{and} \ 186.4)\), in which the presence of a coordinated isonitrile has been crystallographically confirmed (vide supra), and the related isonitrile/carbonyl alkylidyne complex \([\text{Cr}(\equiv\text{CNi-Pr}_2)(\text{CO})(\text{CNt-Bu})\text{Tp*}]\) \((\delta_c\ 254.6, \ 242.8\ \text{and} \ 191.8, \ \text{respectively})\).

The reaction course leading to the selenoaroyl complexes does not lend itself to direct kinetic observation due to the over-all complexity of the reaction mixture and the elevated temperatures utilised, however parallels can nevertheless be drawn from related systems. The incorporation of
both components of selenium delivery reagents of the type X-Se containing a polarised X-Se bond (X = leaving group) into metal complexes has been previously observed in one instance. Generation of the cationic selenoformaldehyde complex \([\text{Re}(\eta^2-\text{Se} = \text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^+\) from treatment of the electrophilic methylidene species \([\text{Re}(-\text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^-\) with \(\text{Ph}_3\text{PSe}\) or \(\text{NCSe}^-\) was accompanied by formation of an equimolar proportion of the heteroalkyl complex \([\text{Re}(\text{NO})(\text{CH}_2\text{X})(\text{PPh}_3)\text{Cp}]^-\) (Scheme 3.7, vide supra). The reaction was proposed to involve initial nucleophilic attack at the methylidene carbon and subsequent formation of the complex \([\text{Re}(\eta^2-\text{Se} = \text{CH}_2)(\text{NO})(\text{PPh}_3)\text{Cp}]^+\) by loss of the leaving group X (X = \(\text{Ph}_3\text{P}, \text{CN}^-\)). Attack of this liberated nucleophile on the starting methylidene complex was suggested to account for concomitant formation of the heteroalkyl species. From the observation of a 50:50 product distribution, it may be inferred that both attack by selenocyanate and subsequent \(\text{CN}^-\) or \(\text{Ph}_3\text{P}\) elimination are significantly slower than attack by these stronger nucleophiles upon further methylidene complex. The insertion of a single chalcogen atom into the M=C bond of aryl(phenyl)carbene complexes from the corresponding organyl isothio- and isoselenocyanates (Scheme 3.8, vide supra) was similarly suggested to involve initial nucleophilic attack of the chalcogen at the electrophilic carbene carbon, though attack by the \(\pi\)-electrons was not excluded.

The reaction of \([\text{Ru}(=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\) with the heteroallene \(\text{CS}_2\) results in the generation of both thiocarbonyl and thioacyl ligands in the complex \([\text{Ru}(\eta^2-\text{SCPh})\text{Cl}(\text{CS})(\text{PPh}_3)_2]\) and is suggested to proceed via a metallacyclobuten-thione intermediate (Scheme 3.13).

\[
\text{Scheme 3.13. Preparation of ruthenium(II) thiobenzoyl complexes.}
\]

A number of cycloaddition reactions across the C-Se double bond of isoselenocyanates are also known and in the present case, it is suspected that the reaction proceeds via an analogous metallacyclobuten-imine (Scheme 3.14, 25), which serves as a common intermediate to account for the formation of both \([\text{Mo}(\eta^2-\text{SeCR})(\text{CO})_2\text{Tp}]\) and \([\text{Mo}(\eta^2-\text{SeCR})(\text{CO})(\text{CNMes})\text{Tp}]\). Isonitrile extrusion from 25 or competitive CO dissociation (disfavoured at lower temperatures) followed by metallacycle collapse with retention of the isonitrile within the coordination sphere would account for the formation of both \([\text{Mo}(\eta^2-\text{SeCR})(\text{CO})_2\text{Tp}]\) (16, 21 and 22) and \([\text{Mo}(\eta^2-\text{SeCR})(\text{CO})(\text{CNR})\text{Tp}]\) (18 and 23), respectively. From this model, the slow reaction
observed between the isolated selenoaroyls and a second equivalent of SeCNMe₂ can be explained in terms of a lowered propensity for cycloaddition across the Mo=C bond.

The reduction or elimination of isonitrile substitution products when the steric bulk of either the alkylidyne or pyrazole substituents is increased is therefore rationalised as resulting from increased steric pressures in the metallacylobuten-imine that accelerate isonitrile extrusion relative to decarbonylation.

A key point is the regioselectivity of [2+2] Mo=C/C=A (A = Se vs NMes) cycloaddition in that no evidence for the formation of selenocarbonyl or iminoacyl complexes was obtained, although Templeton has demonstrated the viability of the latter class of ligand in the related complex [Mo(η²-MeCNt-Bu)(CO)₂Tp*] (see Chapter 1).

3.4.1 Isolation of the novel η¹-vinyl complex [Mo{CN(R')C(=NR')SeC(=NR')C-(C₄H₃S-2)}₂(CO)₂Tp] (R' = Mes) 26

Product selectivity from the treatment of 14 with SeCNMe₂ in dichloromethane solution was enhanced by employing gentler reaction conditions (i.e., ambient temperature and the exclusion of light) and a prolonged reaction time (50 h), affording 16 as the major isolated product (43%) in addition to a small amount of the substituted derivative 18 (5%). Interestingly, an orange product 26 not previously observed was also isolated in modest yield (15%) following chromatography. The gross formulation of 26 followed from mass spectral data for which a molecular ion consistent with the unusual empirical formula 'Mo(=CC₄H₃S-2)Se(CO)₂(CNMe)₂Tp' was observed. ¹H and ¹³C{¹H} NMR spectroscopic data for 26 included resonances associated with three inequivalent mesityl groups and three distinct pyrazolyl environments as well as unique signals for each of the carbonyl carbons, implying C₁
symmetry for the complex. The \(^1\)H NMR resonances associated with the mesityl units were broad, suggesting restricted rotation around the associated C–N bonds, the presence of which was inferred from the infrared data for the compound that included, in addition to two carbonyl associated absorptions at 2004 and 1985 cm\(^{-1}\), a cluster of absorptions of medium intensity near 1600 cm\(^{-1}\). A resonance at \(\delta_C 241.2\) and a high field signal at \(\delta_C 37.3\) were indicative of Mo–C multiple bonding and alkyl character (respectively) for the corresponding carbon nuclei. A broad, low intensity resonance at \(\delta_C 137.5\) was reminiscent of those found for the central carbon of organyl isoselenocyanates\(^{52,53}\) such as 1 (\(\delta_C 130\)). Unfortunately, these data did not unequivocally indicate the nature of the complex formed and, accordingly, the identity of 26 was unambiguously determined by a crystallographic study.

The molecular structure of 26 (Figure 3.10) identified the compound as [Mo\{CN(Mes)C(=NMes)SeC(=NMes)C(C_2H_5S-2)}(CO)_2Tp\], revealing the formation of the unusual cyclic \(\eta^2\)-vinyl ligand incorporating the elements of two molecules of CNMes, an isoselenocyanate unit and the alkylidyne moiety. If the \(\eta^2\)-vinyl ligand is considered as occupying a single coordination site the geometry around the molybdenum may be described as distorted octahedral. The C\(_\alpha\)–C\(_\beta\)\(^8\) vector of the vinyl ligand is aligned parallel to one OC–M–N axis (OC–Mo–C\(_\alpha\)–C\(_\beta\) torsion angles of 178.7 and 92.9\(^\circ\) for CO\(_{30}\) and CO\(_{20}\), respectively), which directly contrasts with the orientation of the vinyl unit observed for the related but simpler complex [W(\(\eta^2\)-CPh=CPh)(CO)_2Tp\(^*\)] reported by Templeton in which the vinyl ligand approximately bisects the OC–M–CO angle.\(^{54}\) Nevertheless, the orientation found for 26 is comparable to that of the Cp complex [Mo(\(\eta^2\)-C(Ph)=CPh)]\{P(OMe)_3\}_2Cp\] described by Green in which the C\(_\alpha\)–C\(_\beta\) vector is oriented such that there is one parallel and one perpendicular Mo–P bond.\(^{55}\)

Structural features of the \(\eta^2\)-vinyl moiety include Mo–C separations (Mo–C\(_\alpha\) 2.003(3) Å and Mo–C\(_\beta\) 2.245(3) Å) that are appropriate for Mo–C double and single bonds, respectively, and a C\(_\alpha\)–C\(_\beta\) (1.434(4) Å) bond order that is close to unity. These parameters are typical of the \(\eta^2\)-vinyl moiety and are consistent with structural data for the related complex [W(\(\eta^2\)-CPh=CPh)(CO)_2Tp\(^*\)], which exhibits W–C\(_\alpha\), W–C\(_\beta\) and C\(_\alpha\)–C\(_\beta\) separations of 1.990(8), 2.263(8) and 1.405(11) Å, respectively.\(^{54}\) For \(\eta^2\)-vinyl complexes, the MC\(_\alpha\)C\(_\beta\)R\(_\alpha\) and C\(_\beta\)R\(_\alpha\)R\(_\beta\) planes are typically oriented orthogonal to one another\(^{55}\) and 26 conforms with this trend, displaying an R\(_\alpha\)C\(_\alpha\)C\(_\beta\)R\(_\beta\) torsion angle of –82.4\(^\circ\). Using the formalism adopted by

\(^8\) For the purposes of the following discussion, C\(_\alpha\) refers to the carbon atom doubly bonded to molybdenum and C\(_\beta\) represents the singly bound vinyl carbon. For torsion angles, the substituents of each of these carbons are referred to as R\(_\alpha\) [N(70)] and R\(_\beta\) (thienyl) and R\(_\beta\) (selenazinan ring), respectively.
Green, the thienyl \((R_{\beta})\) substituent may be described as being pseudo-axial with respect to the \(\text{MC}_\alpha C_{\beta}\) ring with an \(\text{Mo}--\text{C}_{\beta}--\text{R}_{\beta}\) angle of 116.0(2)° that is contracted some 10° beyond that of the quasi-equatorial disposed first atom of the \(\text{C}(=\text{NR}')\text{SeC}(=\text{NR}')\text{NR}'\) chain \((R_{\beta})\) of the selenazinan ring \((\text{Mo}--\text{C}_{\beta}--\text{R}_{\beta} 126.3(2)°)\).

An inspection of the remaining structural parameters of the ligand sphere reveals a distinct (>170°) compression of the trans-inter-ligand angle formed by the two cis pyrazole ligands aligned parallel to the vinyl unit \((\text{N}(41)--\text{Mo}--\text{C}(30) 154.8(1)°)\) relative to that of the perpendicular ligand pair \((\text{N}(31)--\text{Mo}--\text{C}(20) 172.1(1)°)\). The enhanced distortion for the parallel ligand pair can be rationalised on steric grounds and is clearly evident in the illustration of the inner coordination sphere of 26 in b, Figure 3.10, which emphasises the strong adherence to typical \(\eta^2\)-vinyl geometry by the coordinated 1,3-selenazinan ring. The greater departure from linearity for the trans-interligand angle involving \(\text{N}(41)\) likely reflects intramolecular repulsive interactions between this proximal pyrazolyl arm and the bulky \(C_{\beta}\) substituents on \(C(1)\), though the aromatic groups have been omitted for clarity in the depiction shown in b.

The most interesting feature is, however, the \(\eta^3\)-heterocyclic ring itself (Figure 3.11), which must accommodate the normal structural requirements of the internal \(\eta^2\)-bound vinyl unit. The six atoms of the heterocyclic system roughly define a plane from which the \(C_{\beta}\) or \(C(1)\) carbon shows the greatest departure due to its \(\text{sp}^3\) character. The exocyclic \(\text{C}--\text{N}\) imine bonds emanate from this selenazinan unit and are statistically equivalent \((1.252(4)\) and \(1.254(4)\) Å), with \(\text{C}--\text{N}--\text{C(Mes)}\) substituent angles of 117.9(3) and 122.5(3)° that are as expected for this functionality. The mesityl groups radiate from this extended planar region with the planes defined by each of the three aromatic rings being positioned essentially orthogonal to that of the heterocyclic system. The plane of the thienyl unit is similarly orthogonal to that of the heterocyclic moiety, however, this substituent rides below the plane in a rudder-like fashion \((\text{C}(50)--\text{C}(1)--\text{C(thienyl)} 116.2(3),\) and \(\text{C}(70)--\text{C}(1)--\text{C(thienyl)} 117.2(3)°)\) (a, Figure 3.11). Structural parameters within the three mesityl units and the thienyl ring are unexceptional.
Figure 3.10. a) Molecular geometry of [Mo(CN(Mes)C(=NMes)SeC(=NMes)C(C_4H_S-2){(CO)}_2Tp]} (26) and b) depiction of the inner coordination sphere with aromatic rings omitted. 30% displacement ellipsoids are shown and hydrogen atoms have been omitted. Selected bond distances (Å): Mo–C(1) 2.245(3), Mo–C(70) 2.003(3), Mo–N(21) 2.246(3), Mo–N(31) 2.232(3), Mo–C(20) 1.961(4), Mo–C(30) 2.011(4), C(20)–O(20) 1.152(4), C(30)–O(30) 1.144(4), C(70)–C(1) 1.434(4), C(1)–C(50) 1.496(4), C(50)–Se 1.966(3), Se–C(60) 1.937(3), C(60)–N(70) 1.430(4), N(70)–C(70) 1.349(4), C(50)–N(50) 1.252(4), C(60)–N(60) 1.254(4). Selected bond angles (°): N(21)–Mo–N(31) 82.2(1), N(21)–Mo–N(41) 78.7(1), N(31)–Mo–N(41) 82.0(1), N(31)–Mo–C(20) 172.1(1), N(41)–Mo–C(30) 154.8(1), C(20)–Mo–C(30) 85.6(1), Mo–C(70)–C(1) 79.7(2), Mo–C(1)–C(70) 61.4(2), C(1)–Mo–C(70) 38.9(1), Mo–C(1)–C(11) 116.0(2), Mo–C(1)–C(50) 126.3(2), Mo–C(70)–N(70) 152.2(3), C(11)–C(1)–C(50) 116.2(3), C(11)–C(1)–C(70) 117.2(3), C(1)–C(50)–Se 112.7(2), C(50)–Se–C(60) 100.7(1), Se–C(60)–N(70) 117.8(2), C(60)–N(70)–C(70) 121.9(2), C(60)–N(60)–C(61) 117.9(3), C(50)–N(50)–C(51) 122.5(3).
Within the cyclic unit, the C–N bond distances suggest a degree of electron density localisation in the Cα–Rα bond, with the C(60)–N(70) separation being 20σ longer than C(70)–N(70) (1.430(4) Å vs 1.349(4) Å), consistent with the anticipated constructive conjugation of the Cα (i.e., C(70)) substituent with the coplanar η²-vinyl unit. Nevertheless, this Cα–N bond distance remains elongated by some 24σ relative to the exocyclic C=N imine separations. The two C–Se bonds of the 1,3-selenazinan ring also reveal slightly disparate distances with the N2C–Se separation (1.937(3) Å) being ca. 10σ shorter than the CNC–Se bond (1.966(3) Å). The remaining internal separation of the cyclic ligand, Cβ–Rβ (1.496(4) Å), is essentially consistent with a C–C single bond separation.

The plausible mechanism for the formation of 26 is outlined in Scheme 3.15 and follows from the premise that under the gentle reaction conditions described, the production of 16 is accompanied by the accumulation of a significant quantity of liberated CNMes. The reaction between the alkylidyne complex 14 and the excess isocyanide that presumably follows is reminiscent of the room temperature reaction between xyllyl isonitrile and alkylidyne complexes of the type [M(=CR){P(OMe)3}2Cp] (M = Mo or W, R = CH3-t-Bu; M = Mo, R = CH3-i-Pr).
described by Green and co-workers, in which two molecules of the isocyanide combined with the carbyne substituent to form the 1,3-bis(imino)-substituted η3-allyl complexes \([\text{M} \{\eta^3-\text{R'NC}=\text{CC(R)C}=\text{NR'}\}(\text{CNR'})_2\text{Cp}]\) \((\text{R'} = \text{xylyl})\).\textsuperscript{56} Thus, by analogy with Green’s related system, a plausible mechanism (Scheme 3.15) for the formation of 26 can be suggested to involve the following steps: (i) ready reaction of the accumulated isonitrile with 14 to form the η2-iminoketenyl complex A; (ii) rearrangement of A to an unsaturated σ-iminoketenyl complex B; (iii) attack by a second molecule of CNMes at the 15-electron metal centre to afford the isonitrile-substituted complex C; (iv) migratory insertion of the coordinated isonitrile into the Mo–C bond of the σ-iminoketenyl and (v) subsequent isomerisation of D to the thermodynamically favoured bis(imino)-substituted η3-allyl complex E. From this point, parallels with Green’s system can no longer be drawn, however, the reported molecular structure of the η3-allyl complex \([\text{Mo} \{\eta^3-\text{R'NC}=\text{CC(}CH_3\text{-Bu)C}=\text{NR'}\}(\text{CNR'})_2\text{Cp}]\) \((\text{R'} = \text{xylyl})\) revealed a significant bend across the central nitrogen atoms \((123^\circ)\), implying the development of nucleophilic character for these nitrogens.\textsuperscript{56} Thus, two final mechanistic steps can be envisaged that ultimately result in the requisite addition of a molecule of SeCNMes to E: (vi) intermolecular nucleophilic attack by one of the imine nitrogens of E at the central carbon atom...
of an intact SeCNMes molecule to generate the zwitterionic species F bearing an internal Se-nucleophile; (vii) reaction between the nucleophilic selenium atom and an allylic carbon atom resulting in intramolecular cyclisation to furnish the unusual heterocyclic \( \eta^2 \)-vinyl ligand of complex 26.

### 3.4.2 Catalytic activation of elemental selenium by CNMes

The reaction of 14 with elemental selenium slowly provides a mixture of 16 and 19, though in contrast to literature reports (Section 3.1.5, vide supra),\(^3\) the selenoaryl complex 16 is by far the dominant species produced when gentle reaction conditions are employed (dichloromethane, stirring). The Tp* thienylmethylidyne complex 15 similarly adds one equivalent of selenium to the M–C triple bond when treated with \( 1/\alpha \text{Se}_n \) to afford 22, with no evidence for a seven-coordinate diselenocarboxylate derivative. The reluctance of the Tp* complex to undergo addition of a second equivalent of selenium may be rationalised on the basis of both steric and electronic grounds (vide supra). In the case of the Tp co-ligated alkylidyne species, it is perhaps pertinent to note that in the preparation of mononuclear thioacyl complexes by treatment of the corresponding alkylidyynes with methyl thiirane, it was observed that reaction with the thienyl substituted alkylidyne species was considerably accelerated relative to the corresponding reaction progress involving the tolyl and anisyl derivatives.\(^4\) The explanation offered for this was the modest decrease in the steric bulk of the five-membered ring of the carbyne substituent of 14, however, upon examination of spectroscopic data for the series of complexes [Mo(=CR)(CO)₂Tp] (R = C₆H₄Me-4, C₆H₄OMe-4 or C₄H₃S-2) in which a vastly altered shielding of the resonance for \( \text{C}_\alpha \) is evident (\( \delta_{\text{C}_\alpha} \) 293.1, \( ^{14} \)C 294.2, \( ^{19} \)C 276.8, \( ^{14} \)C, \( ^{19} \)C respectively, Table 3.2), an additional possibility presents itself involving altered electronics of the M–C bond. The relatively upfield resonance for the \( \text{C}_\alpha \) nucleus of 14 suggests perhaps an increased localisation of electron density at this carbon and enhanced nucleophilicity for the M–C multiple bond. It should be noted that whilst the operation of thiirane as a sulfur transfer reagent would most likely involve the sulfur acting as a nucleophile, the nature(s) of the intermediates and transition states for C–S and C–Se bond formation starting with the elements are by no means clear. Elemental sulfur can act as a nucleophile, electrophile or sulfanyl radical, whilst the nature of the active form of selenium under essentially heterogeneous conditions remains obscure.

Nevertheless, while the reaction between 14 and elemental selenium is rather sluggish, both the base catalysed (DBU) reaction of elemental selenium and CNMes to provide SeCNMes (1), and the reaction of 1 with 14 are comparatively rapid. It therefore seemed plausible that CNMes may activate elemental selenium in a pseudo-catalytic manner and this was indeed found to be
the case. The reaction of 14 with elemental selenium in the presence of DBU and CNMes (5 mol %) quickly provided 16, 19, and 18, however, the eventual accumulation of 18 prevents the CNMes from being a true catalyst (Scheme 3.16). Interestingly, comparable results were obtained in the absence of DBU, which appears to lend support to the notion that 18 may arise from reaction between SeCNMes and 24, the latter being generated from 14 and accumulated CNMes at the elevated reaction temperatures.

Scheme 3.16. Pseudo-catalytic activation of selenium. (i) $\frac{1}{10}$ Se, 5 mol % CNMes. [Mo] = Mo(CO)Tp, R = C$_4$H$_3$S-2, R' = Mes.
3.5 Preparation of $\eta^2$-selenolatocarbenes \([\text{Mo}(\eta^2-R\text{SeCC}_2\text{H}_3\text{S}-2)(\text{CO})(\text{L})\text{Tp})[\text{X}] \ (R = \text{Me}, \text{X} = \text{BF}_4, \text{L} = \text{CO} \ (27) \text{ or CNMes} \ (28); R = \text{Ph}, \text{X} = \text{PF}_6, \text{L} = \text{CO} \ (29))\)

The reactivity of $\eta^2$-thioacyl complexes towards electrophiles is dominated by attack at the heteroatom to afford the corresponding bidentate thiolatocarbene complexes (Scheme 3.17).$^{2,3,19,33}$ The $\text{S}$-alkylation of Roper’s Group 8 $\eta^2$-thioaryloyl complexes is slow and requires the potent alkylating agent methyl triflate,$^{2,3}$ whilst mononuclear Group 6 thioaroyls are readily alkylated by Meerwein’s reagent $[\text{Et},\text{O}][\text{BF}_4]$.$^{19,33}$

\[
\begin{align*}
\text{L}_3\text{M} & \quad \text{RX} \quad \text{RX} \\
& \quad \left[ \begin{array}{c}
\text{R} \quad \text{R}^+ \\
\text{S} \quad \text{S} \\
\end{array} \right]
\end{align*}
\]

Scheme 3.17. Generic alkylation of $\eta^2$-thioacyl complexes.

An alternative preparative route to bidentate thiolatocarbene complexes described by Angelici and co-workers involves protonation of the thiomethylidyne complex $[\text{W}(\equiv\text{CSMe})(\text{CO})_2\text{Tp}]$ at the carbyne carbon atom, which affords the purple complex $[\text{W}(\eta^2-\text{MeSCH})(\text{CO})_2\text{Tp}]^+$.\(^{57}\) As mentioned in Chapter 1, the formation of this complex may be reversed by treatment with base to regenerate the mercaptocarbyne, albeit in low recovered yields (Scheme 3.18).\(^{57}\)

\[
\begin{align*}
\text{TP} & \quad \text{W} = \text{Me} \\
& \quad \text{CO} \quad \text{CO} \quad \text{Me} \\
& \quad \text{TP} \\
& \quad \text{HX} \quad \text{base} \\
& \quad \left[ \begin{array}{c}
\text{M} \quad \text{S} \\
\text{OC} \quad \text{OC} \\
\text{Me} \\
\end{array} \right] \\
& \quad \text{Nu} \quad \text{Nu} \\
& \quad \text{Me} \quad \text{Me} \\
& \quad n^+ \\
\end{align*}
\]

Scheme 3.18. Synthesis and reactions of the thiolatocarbene complex $[\text{W}(\eta^2-\text{MeSCH})(\text{CO})_2\text{Tp}]^+$ ($\text{X} = \text{CF}_3\text{SO}_3, \text{BF}_4, \text{CF}_3\text{CO}_2$; base = $\text{NaH}, \text{K}_2\text{CO}_3, \text{Et}_3\text{N}$; $\text{Nu} = \text{PR}_3$ or $\text{py}$, $n = 1$; $\text{Nu} = \text{SR}^-$, $\text{H}^-$ or $\text{Me}^-$, $n = 0$).

Similarly, the addition of dimethyl(methylthio)sulfonium salts to Group 6 alkylidyne complexes $[\text{M}(\equiv\text{CR})(\text{CO})_2\text{L}]$ ($\text{M} = \text{Mo}$ or $\text{W}$; $\text{R} = \text{alkyl}$, aryl or $\text{SMe}$; $\text{L} = \text{Cp}$ or $\text{Tp}$) results in electrophilic attack of an $\text{SMe}^+$ unit at the metal–carbon triple bond, providing the $\eta^2$-thiolatocarbene derivatives $[\text{M}(\eta^2-\text{MeSCR})(\text{CO})_2\text{L}]$ in good yields.$^{19,58,59}$ Group 6 dihapto-thiolatocarbenes display a rich chemistry, with nucleophilic (Nu) addition at the carbene carbon atom providing a number of stable adducts of the form $[\text{M}(\eta^2-\text{R'SCR(Nu)})_2(\text{CO})_2\text{L}]^+$ ($\text{Nu} = \text{PR}_3$, $\text{py}$, $\text{SR}^-$, $\text{H}^-$ or $\text{Me}^-$) in which the MCS metallacyclic motif is retained (Scheme 3.18).$^{19,33,59-61}$

While a number of bidentate thiolatocarbene complexes are known for Group 6,$^{19,33,57-59}$ the analogous selenolatocarbenes are without precedent. Accordingly, alkylation of the
mononuclear selenoaroyl complexes was attempted in order to probe the viability of the corresponding \( \eta^2 \)-alkylselenolatocarbene complexes.

Employing a variation of the strategy used for the preparation of \( \eta^2 \)-thiolatocarbenes from mononuclear thioaroyl complexes (vide infra), the selenoaroyl complex 16 was treated with trimethylxonium tetrafluoroborate in diethyl ether solution, leading to a slow color change (7 days) from blue to yellow and precipitation of \([\text{Mo}(\eta^2-\text{MeSe})\text{Tp})\text{CO})_2\text{BF}_4\] (27) as a vivid yellow solid in near quantitative yield (92%) (Scheme 3.19). While no other \( \eta^2 \)-selenolatocarbene complexes are known, there is significant published spectroscopic precedent for the analogous thiolatocarbenes and comparison of the data for 27 (Table 3.6) with those of the related sulfur analogue \([\text{Mo}(\eta^2-\text{EtSC})\text{Tp})\text{CO})_2\text{BF}_4]\) is possible.

The infrared spectrum of 27 (Table 3.6) features two carbonyl absorptions at 2055 and 1981 cm\(^{-1}\) that are at comparable frequencies to those of the related \( \eta^2 \)-thiolatocarbenec complex \([\text{Mo}(\eta^2-\text{EtSC})\text{Tp})\text{CO})_2\text{BF}_4\] (2053, 1986 cm\(^{-1}\)), but to significantly higher frequency than the precursor 16 (1988, 1909 cm\(^{-1}\)), implying a reduction in back-donation to the metal carbonyls upon Se-alkylation. The \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectrum of 27 includes a resonance attributable to the carbene carbon at \( \delta_c \) 243.8, to higher field of that for 16 (\( \delta_c \) 264.5) and comparable to the chemical shift observed for \([\text{Mo}(\eta^2-\text{EtSC})\text{Me})\text{CO})_2\text{Tp})\text{BF}_4\] (248.1). The two metal carbonyls give rise to unique resonances (\( \delta_c \) 217.8 and 217.5), at relatively shielded positions compared with those of 16 (\( \delta_{\text{CO}} \) 230.4) supporting the decrease in back-donation to the metal carbonyls that was inferred from infrared spectral data. Similarly, each of the arms of the Tp ligand show distinct chemical environments, as was observed for the related salt \([\text{W}(\eta^2-\text{MeSC})\text{Me})\text{CO})_2\text{TP})\text{O}_2\text{SCF}_3\], in which resonances were evident for each of the unique carbonyl ligands (\( \delta_{\text{CO}} \) 216.3 and 215.3) and inequivalent pyrazolyl arms. In the \( ^1\text{H} \) and \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectra of 27, a sharp singlet corresponding to the SeMe group is observed at \( \delta_h \) 2.39 and \( \delta_c \) 17.7. Angelici and co-workers similarly observed only a single SMe
environment for the coordinated sulfur of the $\eta^2$-dithiolatocarbene salt $[W(\eta^2{-}\text{MeSCSMe})(\text{CO})_2\text{Tp}][\text{O}_2\text{SCF}_3]$ ($\delta_3 3.36$ and $\delta_c 29.1$). If pyramidal inversion at the chalcogen were occurring, two resonances would be expected for the isomeric pair and the absence of these suggests that inversion is rapid at ambient temperature or that only one isomer is present.

The molecular geometry of 27 in the solid state (Figure 3.12 a) revealed that the $\eta^2$-C-Se connectivity of the acyl ligand is retained upon Se-methylation, with the plane defined by the SeCR ($R = \text{thienyl}$) unit approximately bisecting the molecule, though the perpendicular Se-methyl substituent ($C_\alpha$-Se-C(methyl) 101.13(18)$^\circ$) destroys the pseudo-mirror symmetry (for relevant bond distances and angles see Table 3.7). Pertinent structural changes are noted within the MoCSe metallacycle upon methylation, including a significant shortening (ca. 1.20 $\sigma$) of the Mo-Se separation (2.6424(4) Å) and a modest contraction (8 $\sigma$) of the Mo-C bond distance (1.971(3) Å) relative to the corresponding structural dimensions for 16 (2.6897(4) and 1.995(3) Å, respectively), which is consistent with an enhancement of carbene character for the latter linkage. The $C_\alpha$-Se distance (1.908(3) Å), though considerably shorter than the Se-Me distance (1.962(4) Å), is elongated relative to the corresponding separation for 16, as is anticipated upon Se-alkylation of the $\eta^2$-selenoacyl ligand.

![Figure 3.12. Molecular structure of a) the complex cation 27+ viewed along the pseudo-molecular mirror plane and b) the complex cation 29+ in a crystal of [29][PF$_6$]-CH$_2$Cl$_2$ with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Only the major orientation of the disordered thiophene unit is shown for each.](image-url)

Treatment of 18 with [Me$_3$O][BF$_4$] similarly produces the $\eta^2$-selenolatocarbene salt $[\text{Mo}(\eta^2{-}\text{MeSeCC}_4H_2S-2)(\text{CO})(\text{CNMe})\text{Tp}][\text{BF}_4]$ (28) (Scheme 3.19), though the reaction
progress is more rapid than for 16, taking only 2 (cf. 7) days to reach completion. The faster reaction noted for 18 implies a greater relative nucleophilic character for the selenium atom in 18, which is unsurprising in light of the more electron-rich nature of complex 18 that results from isonitriles being poorer \( \pi \)-acids than CO.

Formulation of the salt 28 follows from the spectroscopic data (Table 3.6), which are highly consistent with those of 27, though the altered nature of the ligand field must be taken into account. The infrared data for 28 include two strong absorptions at 2144 and 1968 cm\(^{-1}\), characteristic of \( \nu_{CN} \) and \( \nu_{CO} \), respectively, which are to higher energy than the corresponding data for the selenoaroyl complex 18 (2099 and 1885 cm\(^{-1}\)). Both \(^1\)H and \(^{13}\)C\{\(^1\)H\} NMR data for 28 show two sets of resonances of differing intensities (4:1) that are off-set by approximately 1 ppm relative to one another, which suggests the presence of two isomeric forms of 28, however, coalescence of these resonances was not observed up to 55 °C. Due to the chiral nature of the complex a definitive explanation for this phenomenon cannot be offered on the basis of available spectroscopic data. Nevertheless, two likely fluxional processes can be conceived that would lead to the two isomers, namely a pyramidal inversion of the selenium atom giving rise to a pair of inverters that differ in the relative orientation of the Se-methyl group with respect to the CNMes and CO ligands. Alternatively, rotation of the entire \( \eta^1\)-MeSeCR (\( R = C_4H_3S-2 \)) ligand about an axis from the metal to the centre of the C–Se bond would afford anti and syn isomers. The latter is expected to be a higher energy process and is thus the favoured explanation. Nevertheless, a third isomerisation process involving cleavage of the Mo–Se bond and rotation about the Mo–C bond, whilst less likely, cannot be dismissed on the basis of available data.

### Table 3.6. Infrared and \(^{13}\)C\{\(^1\)H\} NMR data for \([\text{Mo}(\eta^2-R'SeCR)(CO)(L)Tp][X]\)^a

<table>
<thead>
<tr>
<th>Complex</th>
<th>(^{13})C{(^1)H} NMR, ppm</th>
<th>IR, cm(^{-1})</th>
<th>(v_{CN})</th>
<th>(v_{CO})</th>
<th>(k_{CO}), N m(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(27)</td>
<td>[Mo((\eta^2)-MeSeCC,H,S-2)(CO)(_2)Tp][BF(_4)]</td>
<td>243.8</td>
<td>217.8, 217.5</td>
<td>2055, 1991</td>
<td>16.53</td>
</tr>
<tr>
<td>(28)</td>
<td>[Mo((\eta^2)-MeSeCC,H,S-2)(CO)(CNMes)Tp][BF(_4)]</td>
<td>246.8</td>
<td>229.6b, 228.7c</td>
<td>2144, 1968</td>
<td>n.a.</td>
</tr>
<tr>
<td>(29)</td>
<td>[Mo((\eta^2)-PhSeCC,H,S-2)(CO)(_2)Tp][PF(_6)]</td>
<td>237.7</td>
<td>216.9, 216.8</td>
<td>2056, 1994</td>
<td>16.56</td>
</tr>
</tbody>
</table>

\(^a\) Infrared data measured in CH\(_2\)Cl\(_2\) solution and \(^{13}\)C\{\(^1\)H\} NMR measured in CD\(_2\)Cl\(_2\) solution. \(^b\) Major and \(^c\) minor products. \( R = Me, X = BF\(_4\), L = CO, 27, \) or CNMes, 28; \( R = Ph, X = PF\(_6\), L = CO, 29. \n
Direct treatment of 14 with phenylselenenyl chloride activated by AgPF\(_6\) (synthetically equivalent to ‘PhSe\(^+\)/PF\(_6\)-’) in dichloromethane solution affords, following filtration and precipitation with diethyl ether, the vivid yellow phenylselenolatocarbene salt [Mo(\(\eta^2\)-PhSeCC,H,S-2)(CO)\(_2\)Tp][PF\(_6\)] (29) in quantitative yield, thus avoiding the intermediacy of complex...
The formulation of 29 followed from spectroscopic data (Table 3.6), these being generally similar to those for 27. Thus, two carbonyl infrared absorptions are observed at 2056 and 1994 cm\(^{-1}\), at similar frequency as those of 27 (2055 and 1991 cm\(^{-1}\)), suggesting only slightly enhanced \(\pi\)-acidity for the selenolato-carbene ligand of 29 relative to the methyl substituted derivative 27. The resonance for the carbene carbon is observed at \(\delta\) 237.7 and two unique signals for the metal carboxyls are apparent at \(\delta\) 216.9 and 216.8. The \(^1\)H and \(^{13}\)C\(^{13}\)H\(^{13}\) NMR spectra of 29 clearly indicate a single environment for the Se-phenyl substituent.

The molecular geometry of 29 was confirmed by an X-ray crystallographic study (Figure 3.12 b) and important bond lengths and angles are listed in Table 3.7. The alignment and orientation of the bidentate selenolato-carbene ligand mirrors that found for 27 such that the Se-C\(_\alpha\) bond defines a vector that approximately bisects the OC-Mo-CO angle, with the phenyl substituent positioned perpendicular to this vector (C\(_\alpha\)-Se-C(phenyl) 104.46(12)\(^\circ\)). As for 27, the carbenoid carbon is syn to the carbonyl ligands and though the alternate orientation in which the thienyl substituent would be sandwiched between cis-pyrazolyl rings might be expected to have constructive CH-\(\pi\) interactions, the solid state orientational preference likely reflects the alleviation of possible steric strain between the cis-carboxyls and the orthogonal phenyl/methyl unit of the selenolato-carbene ligand.

A comparison of the geometric parameters within the dihapto-selenolato-carbene ligand of 29 with those of 27 reveals a shortening (23 \(\sigma\)) of the Mo-Se bond separation (2.6329(4) vs 2.6434(4) \AA\) for 27) and a modest contraction (8 \(\sigma\)) of the C\(_\alpha\)-Se distance (1.935(3) \AA),
consistent with a more tightly bound $\eta^2$-selenolatocarbene ligand for 29. The remaining structural dimensions of 27 and 29 are similar and call for no further comment.

3.5.1 Treatment of $\eta^2$-selenolatocarbene complexes with nucleophiles

As mentioned above, Angelici’s $\eta^2$-thiolatocarbene [W($\eta^2$-MeSCH)(CO)$_2$Tp]$^+$ is a synthetically versatile complex, displaying reactivity towards a variety of nucleophilic mercaptides and phosphines. The majority of these transformations yield simple adducts by nucleophilic addition to the carbene carbon atom (Scheme 3.18), though treatment with HS$^-$ and PhCH$_2$S$^-$ provides a mixture of [W($\equiv$CSMe)(CO)$_2$Tp] and [W($\eta^2$-MeSCHSMe)(CO)$_2$Tp]$^+$.

Similarly, instead of the anticipated thiolatomethyl complex [W($\eta^2$-CH$_3$SMe)(CO)$_2$Tp], the complex [W($\eta^2$-MeSCH)(CO)$_2$Tp]$^+$ reacts with a number of hydride donors to afford this same combination of products. The bidentate methylthiolatocarbene complexes described by Hill and co-workers similarly serve as useful precursors for a number of transformations (Scheme 3.20).

The reactivity of the bidentate pheryl seleniumatocarbene complex [Mo($\eta^2$-PhSeC$_6$H$_5$S-2)(CO)$_2$Tp][PF$_6$] (29) towards the nucleophiles Li[HBEt$_3$], PMe$_3$ and Li[C≡CC$_6$H$_4$Me-4] was investigated. In all cases, reaction failed to provide stable adducts arising from nucleophilic addition to the carbene carbon. Instead, in each example an instantaneous colour change for the reaction mixture from bright yellow to orange was noted, which was correlated to a suspected loss of the “PhSe$^+$” unit and concomitant regeneration of the
alkylidyne species [Mo(≡CC₄H₂S-2)(CO)₂Tp] (14), an assumption that was supported by infrared data that were consistent with those of 14 in addition to thin layer chromatography of the reaction mixture vs an authentic sample of 14. Indeed, in the case of Li[HBE₃], 14 was isolated in 79% recovered yield following chromatographic purification, which is in direct contrast to the reaction that occurred between the analogous thiolatocarbene salts [Mo(η²-SCR)(CO)₂Tp][BF₄] (R = C₆H₄OMe-4 and C₄H₂S-2) and Li[HBE₃] to cleanly afford the thioloalkyl complexes [Mo(η²-SCR)(CO)₂Tp].¹⁹

Re-formation of the metal–carbon triple bond by reversal of the ‘PhSe⁺’ addition upon reaction of 29 with nucleophiles resembles similar behaviour that was documented for Angelici’s related dithiolatocarbene cation [W(η²-SCSMe)(CO)₂Tp⁺], which reacted with Na[Mo(CO)₅Cp] or Na[Mn(CO)₅] to quantitatively and rapidly form [W(≡CSMe)(CO)₂Tp] and [Mo(SMe)(CO)₅Cp] or [Mn(SMe)(CO)₅], respectively.⁵⁹ This reaction was proposed to proceed by either initial attack by the metallate anions (M⁻) (M⁻ = Mo(CO)₅Cp⁻ or Mn(CO)₅⁻) at the carbene carbon and subsequent elimination of an M-SMe unit or direct attack of the metal anion on the sulfur atom.⁵⁹ In the present case, given that the phenylselenolatocarbene 29 does not similarly contain two PhSe units and dissociation is nevertheless observed, initial attack at the chalcogen seems most likely. Furthermore, the argument that the cation [W(η²-SCSMe)(CO)₂Tp⁺] was synthesised by electrophilic addition of an Me⁺ unit to a metal–carbon triple bond and that it may therefore act as a sulfonylum ion (Me⁺S⁻) source for stronger nucleophiles⁵⁹ can be extended to the current situation involving 29, which was similarly generated and may thus deliver PhSe⁺ ions to nucleophilic reagents (Nu) to regenerate [Mo(≡CC₄H₂S-2)(CO)₂Tp] and, presumably, Nu–SePh.

The fate of the selenium atom was unambiguously determined in the reaction between 29 and Li[C≡CC₆H₄Me-4] and the result confirms that the chalcogen atom is the most reactive site for initial nucleophilic attack. Two independent [M⁺] responses were evident for the crude reaction product in a ramped EI experiment,§ with mass spectral data for the more volatile compound featuring a cluster of ions with isotopic distributions and a fragmentation pattern that was consistent with the formulation of this molecule as the alkynyl selenoether PhSeC≡CC₆H₄Me-4 (m/z (%) 272.0 (85) [M⁺], 192.1 (100) [M – Ph]⁺, 115.0 (50) [M – SePh]⁺). The second compound exhibited a molecular ion and associated daughter peaks that were characteristic of the alkylidyne species [Mo(≡CC₄H₂S-2)(CO)₂Tp] (14) (m/z (%) 462.0 (20) [M⁺], 434.0 (40) [M – CO]⁺, 406.0 (100) [M – 2CO]⁺).

§ This experiment employs an incremental heating technique for sample vaporisation such that for a mixture of compounds, providing the components are of sufficiently different volatilities, independent [M⁺] responses may be detected for each.
These results indicate that the disparate behaviour documented for \([\text{Mo}(\eta^2\text{-MeECC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}][\text{BF}_4]\) \((E = S \text{ or } \text{Se})\) towards \(\text{Li[HBE}_3\text{t}]\) is due to the electrophilic site for the chalcogenolatocarbenes being altered upon substitution of selenium for sulfur, i.e., the site of reactivity moves from the carbene carbon to the heteroatom for \(E = \text{Se}\), with nucleophilic attack at the selenium atom and subsequent dissociation of the newly formed selenoether being the favoured reaction route (Scheme 3.21). This is perhaps not surprising, given the increased accessibility of hyper-valency upon descending a main group.

\[
\text{Scheme 3.21. Proposed routes for nucleophilic addition to } \eta^2\text{-chalcogenolatocarbenes } (R = \text{C}_4\text{H}_3\text{S}-2; \text{ML}_n = \text{Mo(CO)}_2\text{Tp}; \text{Nu} = \text{nucleophile}; E = S, R' = \text{Me}; E = \text{Se}, R' = \text{Ph}).
\]
3.6 Attempted preparation of \([\text{Mo}(\eta^2-\text{TeCC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) from \(\text{Et}_3\text{P} / \text{Te}\)

Phosphine tellurides \(\text{R}_3\text{P} \text{Te} \) are well known to act as soluble tellurium sources and triethylphosphine telluride has attracted particular attention in this role.\(^{63-71}\) Through phosphine activation, Te has been chemically transported to a variety of reagents for insertion into metal–metal and metal–carbon bonds under relatively mild conditions.\(^{63-71}\) Group 6 alkylidyne species are unreactive towards elemental tellurium, presumably reflecting a kinetic phenomenon,\(^{19}\) and accordingly preparation of the telluroaroyl complex \([\text{Mo}(\eta^2-\text{TeCC}_4\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) via \(\text{Et}_3\text{P}\) activation of Te was attempted (Scheme 3.22).

![Scheme 3.22](image)

**Scheme 3.22.** Reagents and conditions: (i) \(\times \text{PEt}_3, \frac{1}{14} \text{Te}_{\text{ex}} \) hexane \(69 \, ^\circ\text{C}\); toluene \(110 \, ^\circ\text{C}\); (ii) \(\text{PEt}_3\), toluene \(110 \, ^\circ\text{C}\)

Reaction between \(14\) and one equivalent of tellurium in the presence of excess triethylphosphine (toluene reflux) proceeded with complete consumption of \(14\). Nevertheless, the reaction failed to afford the desired telluroaroyl species. In addition to forming \(\text{TePET}_3\) (\(\delta_{\text{r}} = 0.37,\) Mp. \(77-79 \, ^\circ\text{C}\) cf. literature data \(\delta_{\text{r}} (-40 \, ^\circ\text{C}) 0.3,\) Mp. \(76-78 \, ^\circ\text{C}\)\(^{62}\) the only other species isolated from the reaction in high yield was a burgundy coloured solid corresponding to the simple carbonyl substitution product \([\text{Mo}(\equiv\text{CC}_4\text{H}_3\text{S}-2)(\text{CO})(\text{PEt}_3)\text{Tp}]\) \((30)\).

The characterisation of \(30\) calls for little comment, featuring a single \(\nu_{\text{CO}}\) absorption in the infrared spectrum at \(1870 \, \text{cm}^{-1}\) and \(^1\text{H}\) and \(^{13}\text{C}\)\(^{1}\text{H}\) NMR data that are consistent with a \(C_1\) symmetric metal centre. The resonance for the alkylidyne carbon appears as a doublet at \(\delta_{\text{C}} 264.2\) with \(^2J_{\text{PC}}\) coupling of \(19.2 \, \text{Hz}\) and the sole metal carbonyl similarly resonates as a doublet, albeit with a smaller \(^2J_{\text{PC}}\) coupling of \(9.6 \, \text{Hz}\). A singlet is evident at \(\delta_{\text{r}} 36.8\) in the \(^3\text{P}\)\(^{1}\text{H}\) NMR for the phosphorus nucleus, with this resonance reflecting the electron donor properties of the alkyl phosphine’s substituents. These data (other than substituent dependent \(\delta_{\text{r}}\)) are entirely comparable to those of the related monophosphine complexes \([\text{Mo}(\equiv\text{CBu})(\text{CO})\{\text{P(OEt})_3\text{Tp}]\) (\(\delta_{\text{C}} 304.2, \, ^2J_{\text{CP}} = 31 \, \text{Hz}; \, \delta_{\text{C}} 240.7, \, ^2J_{\text{CP}} = 15 \, \text{Hz}; \, \delta_{\text{C}} 185.9; \, \nu_{\text{CO}} 1889 \, \text{cm}^{-1}\)))\(^{73}\) and \([\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})(\text{PPh}_3)\text{Tp}]\) (\(\delta_{\text{C}} 275.4, \, ^2J_{\text{CP}} = 12.5 \, \text{Hz}; \, \delta_{\text{C}} 246.2; \, \delta_{\text{C}} 52.9; \, \nu_{\text{CO}} 1860 \, \text{cm}^{-1}\)\))).\(^{74}\)
3.7 Binuclear selenoaroyl complexes

As discussed in Chapter 1 (Section 1.4.6), the metal–carbon triple bond present in transition metal carbyne complexes is isobal with the C=C bond of alkynes and is capable of acting as a ligand towards a variety of low-valent metal fragments, allowing for the preparation of a wide array of polynuclear clusters.\(^{75-77}\)

One such example for which there is extensive literature precedent is the facile reaction that occurs between alkylidyne complexes of the type \([M(≡CR)(CO)\text{L}] (M = \text{Cr, Mo or W}; \text{R} = \text{Me, Ph, C}_6\text{H}_4\text{NMe}_2-4, \text{C}_6\text{H}_4\text{Me}-4\) or \(\text{C}_6\text{H}_3\text{Me}_2-2,6; \text{L} = \text{Cp, Cp* or Tp})\) and diiron nonacarbonyl (a source of ‘Fe(CO)\(_n\)’ fragments in solution) to afford the corresponding alkylidyne-bridged bimetallic species \([M\text{Fe}(µ-CR)(CO)\text{L}]\ (n = 4, \text{L} = \text{Cp}; n = 3, \text{L} = \text{Cp* or Tp})\).\(^{42,78-80}\)

Elemental chalcogens may add to the bridging carbyne ligand of these bimetallic compounds to form stable heterobimetallic chalcocarbonyl complexes \([M\text{Fe}(µ-ECR)(CO)\text{L}] (E = \text{S, Se or Te})\) (vide supra) (a, Scheme 3.23).\(^{12,15,16,22,42}\) Hill and co-workers have demonstrated a complementary reactivity for the mononuclear thioaroyl complexes \([\text{Mo}(η^2-SCR)(CO)\text{L}]\ (R = \text{C}_6\text{H}_4\text{Me}-4, \text{C}_6\text{H}_4\text{OMe}-4)\), which when treated with \([\text{Fe}_2(CO)\text{L}]\) similarly afford the corresponding heterobimetallic thioaroyl species \([\text{MoFe}(η^2-SCR)(CO)\text{L}]\) (b, Scheme 3.23).\(^{19,33}\)

It was thus of interest to determine whether the selenoaroyl complexes displayed analogous behaviour towards bridge-assisted metal–metal bond formation.

![Scheme 3.23](image)

\(\text{L}_n\text{M} = \text{Mo(CO)}\text{L}, \text{R} = \text{C}_6\text{H}_4\text{Me}-4\). \text{Reagents and conditions: (i) [Fe}_2(CO)\text{L}], \text{Et}_2\text{O};\) (ii) \(\frac{1}{3}\text{S}_\text{S}, \text{Et}_2\text{O};\) (iii) \(\text{SC}_2\text{H}_6, \text{CH}_2\text{Cl}_2\).

3.7.1 Preparation and characterisation of \([\text{MoFe}(µ-CC}_4\text{H}_3\text{S-2})(\text{CO})\text{L}]\ (31)

Following the well established synthetic protocol developed by Stone and co-workers for related derivatives,\(^{42,78-80}\) the new heteronuclear iron–molybdenum compound \([\text{MoFe}(µ-CC}_4\text{H}_3\text{S-2})(\text{CO})\text{L}]\ (31)\) was cleanly prepared from the reaction between diiron nonacarbonyl and the parent 2-thienyl carbyne (14) in diethyl ether (a, Scheme 3.24). The infrared spectrum of 31, isolated as a black microcrystalline solid, featured the expected five carbonyl absorption bands (2048s, 1987m, 1965m, 1925w, 1860w(br) cm\(^{-1}\)), with the low frequency absorption being indicative of a semi-bridging carbonyl ligand. The absorption profile may be compared
with that of the closely related complex \([\text{WFe}(\mu-\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_6\text{Tp}]\) \(2048\text{s}, 1988\text{s}, 1954\text{m}, 1925\text{m}, 1863\text{m cm}^{-1}\), in which a similarly low energy band was observed.\(^7\) The \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum of 31 includes a resonance attributable to the bridging carbyne carbon at \(\delta\ 392.1\) that is considerably more downfield than that of the parent carbyne 14 (\(\delta\ 276.8\)), but characteristic of the formal four-electron donor role for the \(\text{M}^+\text{C}\) bond of the class of compounds \([\text{MFe}(\mu-\text{CR})(\text{CO})_6\text{L}]\). The \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra of 31 are consistent with mirror symmetry about the \(\text{Mo}(\mu-\text{C})\text{Fe}\) unit, with a 2:1 pattern evident for the arms of the pyrazolylborate ligand. Two resonances are evident in the carbonyl region of the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum of 31, with the more deshielded signal (\(\delta\ 230.4\)) being assigned to the molybdenum carbonyls and that at \(\delta\ 213.5\) being attributed to the ‘\(\text{Fe(CO)}_3\)’ group, suggesting that rapid site exchange of the terminal carbonyl ligands of the Fe atom is occurring.

The molecular geometry of 31 was confirmed by an X-ray crystallographic study (Figure 3.13), which revealed an Mo–Fe separation \((2.603(2) \text{ Å})\) that was significantly shorter than the corresponding distance in the saturated bimetallic complex \([\text{MoFe}(\mu-\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_6\text{Cp}]\) \((2.832(1) \text{ Å})\),\(^8\) but comparable to the M–Fe separation of the analogous 32 valence electron species \([\text{WFe}(\mu-\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_6\text{Tp}]\) \((\text{W–Fe 2.612(2) Å})\).\(^7\) The substantial elongation (32 \(\sigma\)) noted for the Mo–C separation \((2.019(9) \text{ Å})\) relative to the Mo–C triple bond of the precursor 14 \((1.809(4) \text{ Å})\) is as expected upon reduction of this unit to a formal Mo=C double bond.

Figure 3.13. Molecular structure of one of the two independent molecules of 31 in a crystal of \((31)_2\cdot\text{CH}_2\text{Cl}_2\) with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Mo–C(1) 2.019(9), Fe–C(1) 1.815(9), Mo–Fe 2.603(18), Mo–N(21) 2.229(8), Mo–N(31) 2.208(9), Mo–N(41) 2.182(8), Mo–C(20) 1.941(13), Mo–C(30) 1.989(13), C(20)–O(20) 1.186(13), C(30)–O(30) 1.186(13), C(40)–Fe(40) 1.823(12), Fe–C(50) 1.778(14), Fe–C(60) 1.737(14), Mo–C(1)–C(11) 136.5(8), Fe–C(1)–C(11) 138.1(8), Mo–C(1)–Fe 85.3(4), Mo–Fe–C(1) 50.6(3), Fe–Mo–C(1) 44.0(3), Mo–C(20)–O(20) 172.2(10), Mo–C(30)–O(30) 172.2(11), C(20)–Mo–C(30) 86.8(5), C(40)–Fe–C(50) 96.8(5), C(40)–Fe–C(60) 100.3(5), C(50)–Fe–C(60) 92.2(6).
These data are indicative of substantial multiple bond character within the Mo(µ-C)Fe dimetallacyclopropene ring. As is typically observed for the ‘Fe(CO)₃’ fragment, the three iron carbonyl groups of 31 are linear and essentially orthogonal to one another, with the ligand trans to the α-acidic bridging carbyne unit being furthest from the iron atom (1.823(12) vs 1.778(14) and 1.737(14) Å) as a result of the strong trans influence of this unit.

3.7.2 Preparation and characterisation of [MoFe(µ-SeCC₄H₃S-2)(CO)₅Tp] (32)

By treating a suspension of 31 with one equivalent of elemental selenium in diethyl ether it was possible to prepare the heterobimetallic bridging selenoaryl complex [MoFe(µ-SeCC₄H₃S-2)(CO)₅Tp] (32) (a, Scheme 3.24), which was isolated as a golden-orange solid following chromatographic purification. The product 32 is analogous to the previously reported compounds [MFe(µ-SeCC₄H₄Me₂-2,6)(CO)₅Cp] (M = Cr, Mo or W) and [MoFe(µ-SCC₄H₆Me-4)(CO)₅Tp]. Indeed, the three carbonyl absorptions in the infrared spectrum of 32 (2053s, 1985s, 1845w cm⁻¹) are essentially identical to those of [MoFe(µ-SCC₄H₆Me-4)(CO)₅Tp] (2058s, 1985s, 1859w cm⁻¹), but to marginally lower frequencies.

While the ¹³C{¹H} NMR spectrum of the precursor bimetallic species 31 features a characteristically downfield resonance for the µ-CC₄H₃S-2 nucleus (δC 392.1), the corresponding resonance for the µ-SeCC₄H₃S-2 carbon of 32, expected to be weak, was not unambiguously detected, though for the related compounds [MFe(µ-SeCC₄H₄Me₂-2,6)(CO)₅Cp] (M = Mo or W) this signal appears at δC 126.5 and 112.9, respectively. Four peaks were apparent in the carbonyl region of the spectrum of 32, with the two signals to lower field (δC 231.6 and 227.3) being due to the molybdenum carbonyls and the remaining two resonances (δC 211.0 and 208.7) being attributed to the Fe(CO)₃ unit, which contrasts with the single Fe(CO)₃ environment that was observed for 31 and suggests that rotation of this group has become slow on the NMR timescale. A similar pattern for the carbonyl ligand resonances was observed in the ¹³C{¹H} NMR spectrum of the related complex [MoFe(µ-SCC₄H₆Me-4)(CO)₅Tp] (δC 232.5, 227.3, 210.4, 208.4).

The molecule 32 has no symmetry element, giving rise to a 1:1:1 intensity pattern for the arms of the Tp ligand in both the ¹H and ¹³C{¹H} NMR spectroscopic data. Of further note amongst the ¹H NMR data of 32 is the broadness of the thienyl associated resonances at ambient temperature, which suggests that the molecule is fluxional on the ¹H NMR timescale. Only at temperatures below -10 °C do the thienyl resonances become sharp and it seems likely that the fluxionality is due to rotation about the µ-SeC=C₄H₃S-2 bond of the bridging acyl ligand.
Figure 3.14. Molecular structure of 32 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted.

Table 3.8. Selected bond lengths (Å) and angles (°) of 32

<table>
<thead>
<tr>
<th>Bond Distances, Å</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)</td>
<td>2.178(2)</td>
<td>Mo–Fe</td>
</tr>
<tr>
<td>Fe–C(1)</td>
<td>1.974(2)</td>
<td>Mo–N(21)</td>
</tr>
<tr>
<td>Se–C(1)</td>
<td>1.914(2)</td>
<td>Mo–N(31)</td>
</tr>
<tr>
<td>Mo–Se</td>
<td>2.5472(3)</td>
<td>Mo–N(41)</td>
</tr>
<tr>
<td>Fe–Se</td>
<td>2.3453(4)</td>
<td>C(1)–C(11)</td>
</tr>
<tr>
<td>Mo–C(O) (20, 30)</td>
<td>1.977(2), 2.000(2)</td>
<td></td>
</tr>
<tr>
<td>C–O (20, 30)</td>
<td>1.157(3), 1.143(3)</td>
<td></td>
</tr>
<tr>
<td>Fe–C(O) (40, 50, 60)</td>
<td>1.833(3), 1.778(3), 1.786(3)</td>
<td></td>
</tr>
<tr>
<td>Fe–C(20)</td>
<td>2.572(2)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, °</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)–C(11)</td>
<td>138.62(16)</td>
<td>Mo–Se–C(1)</td>
</tr>
<tr>
<td>Fe–C(1)–C(11)</td>
<td>133.66(17)</td>
<td>Se–Mo–C(1)</td>
</tr>
<tr>
<td>Se–C(1)–C(11)</td>
<td>122.79(16)</td>
<td>Se–Fe–C(1)</td>
</tr>
<tr>
<td>Mo–C(1)–Fe</td>
<td>84.48(8)</td>
<td>Fe–Se–C(1)</td>
</tr>
<tr>
<td>Mo–C(1)–Se</td>
<td>76.70(8)</td>
<td>Mo–Fe–Se</td>
</tr>
<tr>
<td>Fe–C(1)–Se</td>
<td>74.19(8)</td>
<td>Fe–Mo–Se</td>
</tr>
<tr>
<td>Mo–Fe–C(1)</td>
<td>50.86(6)</td>
<td>Mo–Se–Fe</td>
</tr>
<tr>
<td>Fe–Mo–C(1)</td>
<td>44.66(6)</td>
<td>C(20)–Mo–C(30)</td>
</tr>
<tr>
<td>Mo–C–O (20, 30)</td>
<td>165.4(2), 176.6(2)</td>
<td></td>
</tr>
<tr>
<td>OC–Fe–C(O) (40/50, 40/60, 50/60)</td>
<td>92.04(12), 102.88(13), 93.04(13)</td>
<td></td>
</tr>
<tr>
<td>Mo–C(20)–Fe</td>
<td>74.54(7)</td>
<td></td>
</tr>
</tbody>
</table>
Complex 32 was crystallographically characterised, providing the first structural study of a selenoacyl ligand bridging a heteronuclear metal–metal bond. Results of the study are summarised in Table 3.8 and the molecular structure is illustrated in Figure 3.14, confirming the addition of a selenium atom to one face of the Mo(µ-C)Fe plane of 31 such that the selenoacyl ligand transversely bridges the metal–metal bond. The molecular core is chiral, with both enantiomers co-crystallising in the centrosymmetric space group.

As was anticipated from the low frequency infrared absorption (1845 cm⁻¹), the molecular geometry of 32 reveals that one carbonyl ligand perceptibly semi-bridges the Mo–Fe vector, having a diagnostically short Fe–CO separation (2.572(2) Å) and displaying a significant departure from linearity (Mo–C–O 165.4(2)°). The thienyl substituent adopts an orientation approximately parallel to the Fe–Mo vector, which presumably reflects a degree of electronic conjugation between the aromatic ring and the selenoacyl linkage, though the C(1)–C(11) bond separation at 1.461(3) is unremarkable. The remaining geometrical features of the ‘Fe(CO)₅’ and ‘Mo(CO)₅Tp’ units are unexceptional.

Of most interest in the molecular structure of 32 is the geometry of the Mo(µ-CSe)Fe core, which includes a C–Se separation of 1.914(2) Å that is significantly (ca. 25 σ) longer than that of the mononuclear selenoaroyl complex 16 (1.849(3) Å) and approaches a single bond description. The Mo–Fe separation of 32 (2.7949(4) Å) is appreciably longer than the metal–metal separation noted for the unsaturated precursor µ-alkyldyne species (31) at 2.6032(18) Å, but is highly consistent with that of the related complex [W(µ-TeCC₆H₄Me-4)(CO)₅Cp] (2.7844(7) Å)¹² Furthermore, the Mo–Cµ and Fe–Cµ bond lengths of 2.178 (2) and 1.974(2) Å, respectively, may be compared with corresponding data for the thio- and telluroaroyl complexes [Mo(µ-SCC₆H₄Me-4)(CO)₅Cp] (Mo–Cµ 2.153(2) Å and Fe–Cµ 1.942(2) Å)¹⁵ and [W(µ-TeCC₆H₄Me-4)(CO)₅Cp] (W–Cµ 2.127(5) Å and Fe–Cµ 1.937(5) Å).¹²

Surprisingly, the reaction between the selenoaroyl complex 16 and [Fe₂(CO)₉] (Scheme 3.24 b) does not mirror the corresponding chemistry of the analogous thioaroyl complexes (vide supra, Scheme 3.24 a), i.e., instead of affording the desired bridged bimetallic chalcocarboxyl complex 32, monitoring of the reaction progress via thin layer chromatography revealed the presence of a number of transiently formed species with the eventual accumulation over a period of 7 days of a major maroon product, accompanied by considerable decomposition to 14 (31%). Chromatographic separation of the dominant species 33 allowed for the unambiguous identification of the major reaction product as the previously described selenido complex.
[Fe₂Se₂(CO)₈] (33) (IR (CH₂Cl₂): 2056, 2038, 2012 cm⁻¹ cf. literature data IR (CCl₄): 2058, 2040, 2018 cm⁻¹; further confirmed by a unit cell determination). R₃M = Mo(CO)₂Tp, R = C₆H₄S-2. Reagents and conditions: (i) [Fe₂(CO)₉], Et₂O; (ii) 1/8 Se₈, Et₂O; (iii) SeCNMes, CH₂Ch; (iv) [Fe₂(CO)₉], CH₂Ch.

Scheme 3.24. Bridging selenido ligands have been previously generated from the reaction between elemental selenium and the trimetallic alkylidyne species [MFe₂(μ-CR)(μ-CO)(CO)₈Cp] (M = Mo or W; R = C₆H₄Me-4 or Me) to afford [MFe₂(μ-CR)(μ-Se)(CO)₇Cp] (Scheme 3.25) and a corresponding trimetallic intermediate might be implicated in the current situation involving the formation of 33 from [Mo(q)²-SeCC₆H₃S-2)(CO)₂Tp] (16) and [Fe₂(CO)₈]. However, given that 32 is stable, it would appear more likely that the coordination of the ‘Fe(CO)₉’ fragment occurs at the selenium of the selenoacetyl resulting in abstraction prior to Fe–Mo bond formation. Conglomeration of the ‘SeFe(CO)₉’ and ‘Fe(CO)₉’ fragments would then be expected to ultimately provide the stable trirron diselenide cluster product. That the reaction between [Fe₂(CO)₈] and 16 fails to yield the bimetallic selenoaroyl species 32 when the corresponding reaction with the thiaoaroyl complex was successful may simply reflect the greater relative fragility of the C–Se bond when occupying a bridging site. Indeed, this property was somewhat demonstrated during the reaction of the bidentate selenolatocarbenes with a range of nucleophilic reagents (vide supra).

Scheme 3.25. M = W, E = S, R = C₆H₄Me-4 or Me; M = W, E = Se, R = C₆H₄Me-4 or Me; M = Mo, E = Se, R = C₆H₄Me-4.
3.8 Summary and conclusions

Mesityl isoselenocyanate has been successfully employed as a stoichiometric selenium delivery reagent, allowing for the first isolation of mononuclear Group 6 selenoaroyl complexes of the type \( \text{Mo}(\eta^2\text{-SeCR})(\text{CO})_2\text{Tp}^* \) (\( R = \text{C}_6\text{H}_3\text{S}-2 \), \( \text{Tp}^* = \text{Tp} \), \( \text{16} \) or \( \text{Tp}^\star \), \( \text{22} \); \( R = \text{C}_6\text{H}_4\text{Me}-4 \), \( \text{Tp}^* = \text{Tp} \), \( \text{21} \)) and \( \text{Mo}(\eta^2\text{-SeCR})(\text{CO})(\text{CNMes})\text{Tp} \) (\( R = \text{C}_6\text{H}_3\text{S}-2 \), \( \text{18} \); \( R = \text{C}_6\text{H}_4\text{Me}-4 \) \( \text{23} \)). It is proposed that selenium delivery via this route proceeds via a cycloaddition of the Mo=CR and C-Se multiple bonds to provide a common metallacyclobuten-imine intermediate from which CNMes loss (favoured by steric pressures) or CO extrusion (favoured at higher temperatures) affords the mononuclear selenoaroyl products \( \text{M}(\eta^2\text{-SeCR})(\text{CO})_2\text{Tp}^* \) and \( \text{Mo}(\eta^2\text{-SeCR})(\text{CO})_2\text{Tp} \text{CNMes}\text{Tp} \), respectively. Enhancement of the selectivity for the \( \text{cis} \)-dicarbonyl complexes may be imparted by employing gentler reaction conditions, though the excess isonitrile liberated via this route undergoes eventual reaction with the alkylidyne species to afford the \( \eta^2 \)-vinyl compound \( \text{Mo}[\text{CN(Mes)C(==NMes)SeC(==NMes)C(C}_6\text{H}_3\text{S}-2)](\text{CO})_2\text{Tp} \) (\( \text{26} \)), with the novel cyclic ligand incorporating the elements of two molecules of mesityl isonitrile, one intact mesityl isoselenocyanate ligand and the alkylidyne group.

Mesityl isonitrile serves to pseudo-catalytically activate elemental selenium towards selenoaroyl formation, though the eventual accumulation of the isonitrile substituted species \( \text{Mo}(\eta^2\text{-SeCR})(\text{CO})_2\text{TP} \text{CNMes}\text{Tp} \) prevents the CNMes from being described as a true catalyst.

The reactivity of the selenoaroyl complexes is dominated by the selenium atom. With \( [\text{Me}_3\text{O}][\text{BF}_4] \), alkylation occurs at the nucleophilic selenium to afford the bidentate methylselenolatocarbene salts \( \text{Mo}(\eta^2\text{-RSeCC}_6\text{H}_3\text{S}-2)(\text{CO})\text{L}^\star\text{Tp}] [\text{X}] \) (\( R = \text{Me} \), \( X = \text{BF}_4 \), \( L = \text{CO} \), \( \text{27} \) or \( \text{CNMes} \), \( \text{28} \)). The corresponding phenyl analogue (\( R = \text{Ph} \), \( X = \text{PF}_6 \), \( L = \text{CO} \), \( \text{29} \)) could be prepared directly in comparable yields by electrophilic attack of a PhSe\(^+\) equivalent from PhSeCl on the M-C triple bond of the starting alkylidyne complex \( \text{14} \). The behaviour of the bidentate phenylselenolatocarbene complexes towards a range of nucleophilic reagents is similarly dominated by reaction at the chalcogen atom, with reversal of the PhSe\(^+\) addition and regeneration of the alkylidyne species \( \text{Mo}(==\text{CC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp} \) being observed.

While the bimetallic selenoaroyl complex \( \text{MoFe}(\mu\text{-SeCC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp} \) (\( \text{32} \)) could be prepared by the addition of elemental selenium to the bridging carbyne ligand of the complex \( \text{MoFe}(\mu\text{-CC}_6\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp} \) (\( \text{31} \)), the reaction of the isolated selenoaroyl complex \( \text{16} \) with \( [\text{Fe}_2(\text{CO})_9] \) failed to yield \( \text{32} \), instead resulting in selenium extraction by the iron centre to afford the previously described iron–selenium cluster \( [\text{Fe}_2\text{Se}_2(\text{CO})_9] \) (\( \text{32,84} \)) and the parent carbyne \( \text{14} \) as the major isolated products.
CHAPTER 3. SELENOAROYL COMPLEXES OF MOLYBDENUM

REFERENCES


CHAPTER FOUR
TUNGSTEN—ALKYNE COMPLEXES
4.1 Introduction

This Chapter reports the synthesis and spectroscopic and structural properties of a series of four-electron \((4e^-)\) donor alkyne complexes of the type \([W(\eta^2-\text{PrEC} \equiv \text{CPh})(\text{CO})_2\text{Tp}^*][\text{BF}_4]^-\) \((E = \text{O, S, Se, Te, 34-37})\) (Chart 4.1). The neutral complex \([W(\eta^2-\text{PrSeC} \equiv \text{CPh})\text{Cl}(\text{CO})\text{Tp}^*]\). 38, has also been prepared. The isolation of the complete series of heteroalkyne complexes bearing varying \(\pi\)-donor chalcogenolate substituents (whilst keeping all other factors constant) described herein is unique and the resulting augmentation of the \(\pi\)-system has enabled the first direct assessment of the role of the heteroatom in the metal–ligand \(\pi\)-framework.

\[
\begin{array}{c|ccc}
\text{E} & \text{L} & n \\
\hline
\text{O} & \text{CO} & 1 \\
\text{S} & \text{CO} & 1 \\
\text{Se} & \text{CO} & 1 \\
\text{Te} & \text{CO} & 1 \\
\text{Se} & \text{Cl} & 0 \\
\end{array}
\]

Chart 4.1.

4.1.1 Four-electron donor alkyne complexes co-ligated by hydrotris(pyrazolyl)borates

Group 6 transition-metal complexes with four-electron donor alkyne ligands possess a rich and varied chemistry, in particular those based on pseudo-octahedrally coordinated metals with \(d^3\)-electronic configurations.\(^1\) A prevalent feature of these \(4e^-\)-donor alkyne complexes is the presence of one (or more) \(\pi\)-acidic carbonyl ligand(s) and an extensive series of divalent, Group 6 metal complexes of the type \([L_n\text{M(\eta^2-RC} \equiv \text{CR}')(\text{L})(\text{CO})\text{Tp}^*]\) has been characterised. A large amount of alkyne based chemistry, primarily from Templeton et al., has been reported for poly(pyrazolyl)borate complexes of Group 6, i.e., \([\text{M(\eta^2-RC} \equiv \text{CR}')(\text{L})(\text{CO})\text{Tp}^*]\) \((\text{M} = \text{Mo, W})\) and the merits and special features of the poly(pyrazolyl)borate co-ligands (as discussed in Chapter 1) and the flexible electron donor capacity of the alkyne ligand, \(4e^- \leftrightarrow 3e^- \leftrightarrow 2e^-\), due to its filled \(\pi_L\) orbital (vide infra) have allowed these complexes to support a variety of ligand transformations, exerting both stereo- and regioselective control over the reaction outcome.\(^2-22\)

Neutral complexes bearing hydrocarbon alkynes, \([W(\eta^2-\text{RC} \equiv \text{CR}')(\text{L})(\text{CO})\text{Tp}^*]\) \((R = R' = \text{Me; R} = \text{Ph, R} = \text{H, Me})\), are readily synthesised via thermal decarboxylation of \([W(\text{CO})_3\text{Tp}^*]^-\) with the appropriate alkyne, as described by Feng et al.\(^3\) Iodide abstraction in the presence of silver salts generates the reactive complex \([W(\text{CO})_3\text{Tp}^*]^+\), which undergoes facile carbonyl displacement in the presence of alkynes to yield the cationic derivatives \([W(\eta^2-\text{RC} \equiv \text{CR}')(\text{L')}(\text{CO})\text{Tp}^*]^+\) \((L' = \text{CO, CNMe; R = R'} = \text{Me, Ph; R = Ph, R} = \text{Me, H; CMe = CH}_2\) and \([W(\eta^2-\text{PhC} \equiv \text{CMc})(\text{L'})(\text{CO})\text{Tp}^*]^+\) \((L' = \text{P(OMe)}_3\), CNMe).\(^3\) The cationic complexes can be similarly prepared from oxidation of the 17-electron radical \([W(\text{CO})_3\text{Tp}^*]\) by
ferrocenium salts in the presence of the corresponding alkyne. Molybdenum analogues have been similarly prepared, though are far less studied.  

4.1.2 Heteroalkyne complexes of Group 6 metals  

**Heteroalkyne formation via coupling of C₁ ligands**

Whilst synthetic methods for the preparation of Group 6 complexes of the type $[\text{M}(\eta^2-\text{RC}≡\text{CR}')\text{(L)(CO)Tp}^*] \quad (R, R' = \text{H, alkyl or aryl})$ are well established there were, until recently, surprisingly few reports of the direct preparation of analogues in which the alkyne bears heteroatom substituents. Complexes of the type $[\text{LnM}(\eta^2-\text{RC}≡\text{CAR}')\text{(CO)}] \quad (M = \text{Mo, W; A} = \text{heteroatom})$ have typically been synthesised through the coupling of carbyne and carbonyl (C₁) ligands, a topic that has been reviewed in detail by Mayr, to provide ketenyl complexes that undergo subsequent electrophilic addition at the oxygen atom (Scheme 4.1). A variety of heteroalkyne complexes containing hydroxyl and alkoxy alkenes have been prepared in this manner and, accordingly, some have invoked an ‘oxyalkyne’ canonical form to describe the bonding in ketenyl ligands.

![Scheme 4.1. Generic formation of an alkyne complex via alkylation of a ketenyl ligand (E = O, S, Se).](image-url)

Treatment of ketenyl complexes with Lawesson’s oxygen–sulfur exchange reagent, $(\text{S}_2\text{PC}_6\text{H}_4\text{Me-4})_2$, or Woollins’ oxygen–selenium transfer agent, $(\text{PPh})_4\text{Se}_8$, affords thio- and selenoketenyl complexes that can be similarly alkylated to provide complexes of thiolato- and selenolatoalkynes. Furthermore, the nucleophilicity of the ketenyl oxygen may be exploited in a reaction with $\text{Cl}_2\text{PPh}_3$, leading to the formation of a chloroalkyne complex, $[\text{W}(\eta^2-\text{ClC}≡\text{CC}_6\text{H}_4\text{Me-4})\text{Cl(CO)Tp}]$, which also serves as a precursor to a thiketenyl complex via reaction with NaSH in the presence of PMe₃Ph (Scheme 4.2).
Angelici and co-workers have previously used a similar approach to prepare a complex containing the unusual alkyne MeOC≡CSMe from a hetero-C$_1$ precursor.$^{29}$ Reaction of the thiomethylidyne complex $[\text{W}(=\text{CSMe})(\text{CO})_2\text{Tp}]$ with P$\text{Et}_3$ provided the $\eta^2$-ketenyl derivative $[\text{W}(\eta^2-C,C'-\text{OCCSMe})(\text{CO})(\text{P} \text{Et}_3)\text{Tp}]$, which upon O-methylation gave the alkyne complex $[\text{W}(\eta^2-\text{MeOC=CSMe})(\text{CO})(\text{P} \text{Et}_3)\text{Tp}]$ (Scheme 4.3).

Complexes containing the rare alkoxyethynylphosphines, $[\text{W}(\eta^2-\text{MeOC=CR'}_2\text{Ph})(\text{OC}_6\text{H}_4\text{NO}_2-4)(\text{CO})\text{Tp}^*][\text{OTf}]$ (R' = Me, Ph), have been formed similarly from nucleophile-induced carbonyl-carbyne coupling of phosphonium carbyne precursors and subsequent methylation of the resulting ketenyl complex at the oxygen atom, as shown in Scheme 4.4.$^{30}$
The formation of bis(alkylamino)acetylene ligands of the form R(H)NC≡CN(H)R by reductive coupling of two isonitrile ligands was reported by Lippard and co-workers in 1977. These reductive coupling reactions were interpreted in terms of the addition of two electrons and two protons, equivalent to the net addition of H₂. Recent observations by Filippou, however, show that the nucleophile-induced coupling of two carbyne (C₂) ligands to give a coordinated alkyne, as shown in Scheme 4.5, is also the C–C bond forming step in the acid-induced carbyne–isocyanide coupling reaction that gives coordinated (alkylamino)alkynes, and the reductive isocyanide–isocyanide coupling reaction of [MX(CNR)₆]⁺ complexes, or that which provides the bis(alkylamino)alkyne compounds [M{η²-R(H)NC-CN(H)R}X(CNR)₆]⁺ (M = Mo, W; X = halogen; R = alkyl).

![Scheme 4.5. Nucleophile-induced coupling of carbyne ligands (M = Mo, W).](image)

Related to this work is the base-induced reverse C₁-coupling reaction reported for the low-valent, carbonyl-free complex [W{η²-PhC≡CNH(t-Bu)}Br₂(CNR)₃] (R = Et, t-Bu). Nucleophilic attack of the η²-bromoalkyne ligand of the complex [W(η²-PhC≡CBr)Br₂(CNR)₃] (R = Et, t-Bu) by the amines t-BuNH₂ and Et₂NH afforded the 1-aminoalkyne complexes [W{η²-PhC≡CNH(t-Bu)}Br₂(CNR)₃] and [W(η²-PhC≡CNEt₂)Br₂(CNt-Bu)₃], respectively. Subsequent cleavage of the alkyne C≡C bond of the complex [W{η²-PhC≡CNH(t-Bu)}Br₂(CNR)₃] via treatment with phenyl lithium afforded the carbyne complexes [W(=CPh)Br(CNt-Bu)(CNR)₃] (R = Et, t-Bu), generating two C₁ fragments from a coordinated alkyne precursor (Scheme 4.6).

![Scheme 4.6. Base-induced alkyne cleavage in W(II) complexes (R = i-Bu, Et; NHR'₂ = t-BuNH₂, Et₂NH).](image)
Alternative preparative routes

Lalor and co-workers have shown that alkylation of the anionic cyano(alkyl)carbene complexes \([\text{Mo}^-\{\text{C}((\text{CN})(\text{R}))_2(\text{CO})_2\text{Tp}^*\}]^- (\text{R} = \text{C}((\text{CN})_2)(\text{C}_6\text{H}_4\text{Br}-4), \text{C}((\text{CN})_2)(\text{C}_6\text{H}_5\text{I})) \) results in formation of green, cationic \(N,N\)-dimethylaminoalkyne complexes.\(^{37}\) The alkyne ligand behaves as a 4-e\(^-\) donor in these complexes and while the compounds have not been crystallographically characterised, available spectroscopic data suggests that the keteneimmoniumyl resonance form shown on the right in Scheme 4.7 makes a significant contribution to the ground state structure.

\[
\begin{align*}
\text{Scheme 4.7. Formation of } N,N\text{-dimethylaminoalkyne complexes.}
\end{align*}
\]

A number of higher oxidation state (d\(^2\)) heteroalkyne complexes have been described by Dehnicke, generally being prepared directly from reaction between a metal chloride precursor and the free alkyne.\(^{38-42}\) The molybdenum and tungsten [M(VI)] complexes prepared in this manner include solvated complexes of the symmetrical alkynes EtEC=CEt (E = Te, Se, Equation 4.1)\(^{39}\) and the phenylethynyl derivates, \(n\)-BuEC=CPh (E = Se, Equations 4.2,\(^{40}\) 4.5;\(^{41}\) E = Te, Equation 4.3),\(^{42}\) in addition to bimetallic complexes of the latter containing bridging chloride ligands (Equation 4.4).\(^{40,42}\)

\[
\begin{align*}
\text{[WCl}_4(\text{SEt}_2)_2] + \text{EtEC}=\text{CEt} + \text{THF} &\rightarrow \text{[W(}\eta^2\text{-EtEC}=\text{CEt}Cl}_4(\text{THF})] + 2 \text{SEt}_2 & \text{(Eq 4.1)} \\
\text{[MoCl}_4(\text{SEt}_2)_2] + n\text{-BuSeC}=\text{CPh} &\rightarrow \text{[Mo(}\eta^2\text{-n-BuSeC}=\text{CPh}Cl}_4(\text{SEt}_2)] + \text{SEt}_2 & \text{(Eq 4.2)} \\
\text{[WCl}_4] + 2 n\text{-BuTeC}=\text{CPh} + 2 \text{Cl}_2\text{Et} + \text{THF} &\rightarrow \text{[W(}\eta^2\text{-n-BuTeC}=\text{CPh}Cl}_4(\text{THF})] + 2 \text{Cl}_2\text{Et} & \text{(Eq 4.3)} \\
\text{[WCl}_4] + 2 n\text{-BuEC}=\text{CPh} + 2 \text{Cl}_2\text{Et} &\rightarrow \text{[W(}\eta^2\text{-n-BuEC}=\text{CPh}(\mu\text{-Cl})_2\text{Cl}_2]_2 + 2 \text{Cl}_2\text{Et} & \text{(Eq 4.4)} \\
\text{[W(}\eta^2\text{-n-BuSeC}=\text{CPh}(\mu\text{-Cl})_2\text{Cl}_2]_2 + 2 \text{MeCN} &\rightarrow 2 \text{[W(}\eta^2\text{-n-BuSeC}=\text{CPh}Cl}_4(\text{NCMe})] & \text{(Eq 4.5)}
\end{align*}
\]

Recently, the cationic bis(benzylthio)acetylene complex \([\text{W(}\eta^2\text{-RSC}=\text{CSR})(\text{CO})_2\text{Tp}^*][\text{PF}_6]\) (R = benzyl) was prepared by Seidel\(^{24}\) directly from the free alkyne in a procedure analogous to that reported by Feng et al. involving iodide abstraction from [WI(CO)_3Tp*].\(^3\) Subsequent
reductive cleavage of one benzyl group yielded the thioketenyl complex 
\[ W(\eta^2-C,C'-SCCSR)(CO)_2Tp^* \] and a number of polymetallic complexes involving this 
compound were described, with the alkyne-1-thiolato-ligand acting as an \( \eta^2-C,C'-\eta^1-S \) bridge 
between the metal centres.\(^{24,43}\) Removal of both benzyl groups and chelate-binding 
(µ-\( \eta^2-C,C'-\eta^2-S,S' \)) of the resultant acetylenedithiolate unit has also been reported, providing 
complexes of the type \([\{Tp^*(CO)_2W\}(μ-C_2S_2)L(Ru(Cp))] \) \((L = PPh_3, CNC_6H_3Me_2-2,6).\(^{44}\) The 
coordination chemistry of \([W(\eta^2-RSC=CSR)(CO)_2Tp^*][PF_6] \) is summarised in Scheme 4.8.

\[
\text{Scheme 4.8. Reagents: (i) RSC=CSR, AgPF_6 (R = benzyl); (ii) CoCp; (iii) [M][BF_4]_n (M = Cu, n = 2,}
\text{m = 1; M = Ni or Pd, n = 4, m = 2); (iv) C_8K, THF; (v) [RuCp(L)][PF_6] (L = PPh_3, CNC_6H_3Me_2-2,6).}
\]

The \textit{cis}-bent structure adopted by bis(diphenylphosphino)ethyne in 
\([W(\eta^2-Ph_2PC=CPPh_2)(S_2CNEt_2)_2(CO)] \) similarly facilitates the formation of a variety of 
polymetallic transition-metal complexes via coordination of the two phosphorus centres 
(Chart 4.2).\(^{45,46}\)
4.1.3 Metal–alkyne bonding

Metal–alkyne bonding in the d\(^4\) metal complexes \([M(\eta^2-RC=CR')(L)(CO)Tp^*]\) is often described in terms of a ‘four-electron’ interaction. The bonding within the MC\(_2\) plane may be viewed as analogous to that of metal–olefin bonding within the context of the classic Dewar–Chatt–Duncanson model, i.e., donation from the filled \(\pi\) orbital parallel to the metal–alkyne plane (\(\pi_\|\)) to a vacant metal \(\sigma\) acceptor orbital and retrodonation of metal \(d\pi\) electron density into the corresponding anti-bonding orbital (\(\pi_\|^*\)) (Figure 4.1). For a \(d^4\) configuration, this interaction may be supplemented by donation from the filled \(\pi\) orbital that is orthogonal to the MC\(_2\) plane (\(\pi_\perp\)) to the empty \(\tau_2\) \(d\pi\) orbital. (NB: For \(d^n\) counts with \(n > 4\), this may actually provide a destabilising influence, favouring co-ligand dissociation or alkyne rearrangements, as often encountered for later transition-metal centres).

![Figure 4.1. Metal–alkyne orbital interactions.](https://example.com/figure4.1.png)

The synergic \(\pi_\| \rightarrow M\sigma\) and \(Md\pi \rightarrow \pi_\|^*\) interactions are important in determining the equilibrium geometry of the coordinated alkyne, with two basic structural modifications to the carbon skeleton occurring upon coordination to a transition-metal; specifically, an increase of the C–C alkyne bond distance, which reflects the bond weakening caused by population of the anti-bonding orbital (\(Md\pi \rightarrow \pi_\|^*\)), and distortion from linearity to give a cis-bent structure. However, it is the interaction of the filled alkyne \(\pi_\perp\) orbital with a vacant metal \(d\pi\) orbital that truly tunes the bonding in the \(d^4\) complexes,\(^3\) thus an assessment of the effect of heteroatom substituents on this secondary \(\pi\)-interaction is desirable.

The incorporated chalcogen is the sole variable in the series of complexes to be described, \([W(\eta^2-i-PrEC=CPh)(CO)Tp^*]^-\) (\(E = O, S, Se, Te\)), and is expected to be sufficiently distal with respect to the MC\(_2\) plane that the impact of the larger atomic size upon descending Group 16 should be negligible, thus allowing direct assessment of the influence of the \(\pi\)-basicity of the heteroatom substituent upon the metal–ligand \(\pi\)-framework.
4.2 Influence of heteroatom substituents on alkyne bonding

To provide a benchmark against which to assess the effect of chalcogen variation upon the properties of the resultant alkyne complexes, calculations were performed for the parent alkynes MeEC=CMe (E = O, S, Se, Te). Geometries were optimised at the HF: 3-21G level and orbital energies calculated at the MP2 level for these optimised geometries. It should first be noted, however, that in contrast to ethyne itself, the π-orbitals do not form degenerate pairs. Rather these interact to different extents with a lone pair of the chalcogen such that the frontier orbitals are each affected to varying degrees.

The calculations (HF: 3-21G) predict that on descending Group 16, the level of the HOMO will be raised in energy and that of the LUMO decreased, leading to a reduction in the HOMO/LUMO energy gap, as depicted in Figure 4.2. In contrast, the energy of the HOMO−1 level is virtually unperturbed and changes in the LUMO+1 are modest.

![Figure 4.2. Calculated Frontier Orbital Energies for free alkynes MeEC=CMe (E = O, S, Se, Te) (---HOMO−1; --- HOMO; --- LUMO; --- LUMO+1).](image)

These results can be interpreted in terms of the extent of chalcogen ‘character’ for the frontier orbitals (due to π-conjugation with the chalcogen lone pairs). The orbital representations for the model alkynes MeEC=CMe (E = O, Se) in Figure 4.3 serve to illustrate this property. (NB: For the following discussion it is assumed that the metal–alkyne axis is ‘z’, the empty t_{2g} orbital d_{yz} and the full t_{2g} orbitals d_{x^2} and d_{xy}, according to the schematic included at the base of Figure 4.3).

Changes in the topology of the π* (LUMO+1) orbital are modest upon going from O to Se and are unlikely to contribute to differences in the reactivity or bonding of the heteroalkyne complexes. While this empty orbital has δ-symmetry with respect to the metal–ligand vector and, in principle, is available to act as a δ-acid with the filled d_{xy} orbital, this interaction may be
Figure 4.3. Frontier orbitals (HF: 3-21G) for free alkynes \( \text{MeE}=\text{COME} \) (\( E = \text{O, Se} \)). The orbitals are designated by the descriptors (\( \pi_x \))\(^y\) where \( x \) indicates the \( \pi \)-bonding (\( x = b \)) or anti-bonding (\( x = * \)) nature; \( y \) indicates the orientation of an orbital either coplanar (\( \| \)) or orthogonal (\( \perp \)) to the \( \text{MC}_2 \) plane were a metal to coordinate and \( z \) denotes the orbital occupancy.
effectively discounted due to the poor orbital overlap typical of δ-bonding. Furthermore, being the highest energy orbital, the interactions of the π* orbital with the metal will be weak.

Similarly, changes in the properties of the metal complexes upon going from the oxygen- to the selenium-containing alkyne are unlikely to arise from the σ-bonding interaction (π_{1}^{\text{b}^2}, HOMO–1). Changes in the energy and topology of this orbital are negligible, gaining marginally more chalcogen character upon replacement of oxygen with selenium. The removal of electron density from this orbital by coordination to a metal centre would be expected to lead to a weakening of the C–C bond and a strengthening of the C–Se bond, which is otherwise an anti-bonding component of this orbital in the free molecule.

The stabilisation of the LUMO orbital (π_{1}^{\text{b}^0}) upon the incorporation of the heavier chalcogens suggests that the π-acidity of this orbital will be increased. From the representation in Figure 4.3 it can be seen that this orbital assumes more chalcogen character, though it is unlikely that in bonding to a transition metal the influence of the chalcogen could be separated from the other synergetic effects.

The energy of the π-donor HOMO (π_{1}^{\text{b}^2}) orbital appears to be the most affected by chalcogen substitution, showing an increase in energy that suggests the π-basicity of the alkyne becomes more efficient upon the successive replacement of oxygen by its heavier congeners. The orbital reveals a highly altered topology, assuming more chalcogen character upon substitution of oxygen with selenium. As for the HOMO–1, removal of electron density from this orbital by coordination to a metal centre should lead to a weakening of the C–C bond and a strengthening of the C–Se bond.

In summary, the greatest influence of chalcogen substitution in a coordination complex is upon the metal–ligand π-framework, i.e., the π_{1}^{\text{b}^2} and π_{1}^{\text{b}^0} orbitals, which operate in opposite directions (π-donor and π-acceptor roles, respectively). Nevertheless, upon coordination of the alkyne, the interaction of each of these orbitals with a metal center should serve to increase the strength of the M–C and C–E bonding interactions at the expense of the C–C linkage. The overall implication of these results is thus an increase in the strength of alkyne bonding as heavier chalcogens are incorporated into the ligand but because the π-acid and π-base interactions with the HOMO and LUMO orbitals oppose one another, they may well cancel each other out in terms of net effects on metal electron density.
4.3 Synthesis

The salts \( \text{[W}(\eta^2-\text{Pr}EC=\text{CPh})(\text{CO})_2\text{Tp}^*])\text{[BF}_4^-(E = \text{O, S, Se, Te}) \) were prepared by iodide abstraction from \( \text{[WI(CO)}_3\text{Tp}^*] \) with \( \text{Ag}^+ \) in the presence of free alkyne in a procedure analogous to that described by Feng et al. (Scheme 4.9).\(^3\) The \( 4e^- \) description of the resulting alkyne complexes is compatible with the replacement of two two-electron donor ligands from the seven-coordinate \( d^4 \) metal precursor. In contrast to the thioether complexes reported by Angelici for the preparation of the related complex \( \text{[Ru}(\eta^2-\text{MeSC}≡\text{CSMe})(\text{PMe}_3)\text{Cp}]^+ \), there is no evidence for intermediate coordination of the chalcogenide or corresponding byproducts, though initial coordination via the chalcogen is most likely, followed by rapid rearrangement.\(^47\)

![Scheme 4.9. Reagents: (i) AgBF\(_4\); (ii) RC=CR', CH\(_2\)Cl\(_2\); (iii) [Bu\(_4\)N]X, CH\(_2\)Cl\(_2\); (iv) RC=CR', C\(_6\)H\(_5\)Me (X = I, Cl; R = Ph, R' = E-\text{-}i\text{-Pr}; R = E-\text{-}i\text{-Pr} Ph, R' = Ph (E = O, S, Se, Te).](image)

The neutral complex \( \text{[W}(\eta^2-\text{Pr}EC=\text{CPh})\text{Cl(CO)}\text{Tp}^*] \) was synthesised cleanly by treatment of the salt 36 with excess \( [\text{Bu}_4\text{N}]\text{Cl} \) in dichloromethane. Attempts to similarly prepare the corresponding iodide analogue using \( [\text{Bu}_4\text{N}]\text{I} \) were unsuccessful, and afforded only the chloride complex 38, the chloride ligand being derived from the solvent. Incorporation of a solvent-derived chloride ligand similarly occurred during the reaction of \( \text{[W}(\eta^2\text{CNEt}_2)(\text{CO})_2\text{Tp}^*] \) with 2-butyne-1,4-diol in refluxing 1,2-dichloroethane, which affords \( \text{[W}(\eta^2\text{HOCH}_2\text{C}=\text{CCH}_2\text{OH})\text{Cl(CO)}\text{Tp}^*] \).\(^48\) It should, however, be noted that dichloromethane is a far less reactive solvent than 1,2-dichloroethane and that Connelly has reportedly prepared related iodide or bromide complexes of hydrocarbon alkynes in dichloromethane without any indication of chloride incorporation.\(^23\)

Attempts to synthesise the chiral complex 38 by thermal decarboxylation of \( \text{[WI(CO)}_3\text{Tp}^*] \) in the presence of alkyne were unsuccessful, with a variety of products being evident via thin layer chromatography, although none was sufficiently predominant to allow isolation. In the case of diphenylacetylene, Templeton and co-workers have suggested that unfavourable steric interactions between the alkyne and bulky \( \text{Tp}^* \) ligands prevent the formation of \( \text{[W}(\eta^2\text{PhC}=\text{CPh})\text{Cl(CO)}\text{Tp}^*] \).\(^3\) Given the isolation of 38 from an alternative route, steric inhibition seems unlikely in the present case. The activation of C–Se bonds by metal centres has
been shown in other Chapters in this thesis and it would appear that reactions involving C–Se bond cleavage follow the initial selenoether coordination under the forcing conditions required for decarbonylation.

The asymmetric nature of the alkynyl chalcoethers allows for the formation of a pair of geometrical isomers that differ in the alkyne orientations. Adopting Templeton’s syn and anti nomenclature for alkyne substituents, one possible isomer has the phenyl group assuming the anti position (i.e., oriented towards the Tp* ligand) and the heteroatom substituent lying syn (i.e., away from Tp*). The alternate phenyl down isomer is that in which the relative positions of the chalcoether and phenyl group are interchanged, as depicted in Chart 4.3.

![Chart 4.3](image)

The salt \([W(\eta^2-i-PrOC=Ph)(CO)Tp^*][BF_4]\) was formed as an approximate 50:50 mixture of two isomers, 34 and 34′ (where ′ indicates the phenyl up isomer), related by 180° rotation of the alkyne. Similarly, \([W(\eta^2-i-PrSeC=Ph)Cl(CO)Tp^*]\) formed as a mixture of the phenyl up and phenyl down isomers, 38 and 38′, in a 59:41 ratio. Pure samples of 38 and 38′ were obtained by solvent-dependent recrystallisation but, once separated, interconverted appreciably at room temperature in dichloromethane solution (over ca. 12 hours). Each of the isomers of \([W(\eta^2-i-PrSeC=Ph)Cl(CO)Tp^*]\) has been structurally characterised, confirming the position of the alkyne substituents with respect to the Tp* ligand, and (immediate) \(^{1}H\) NMR spectroscopic analysis of the crystalline samples used confirmed the presence of a single isomer in each case; thus the two isomers interconvert but this is not observable on the \(^{1}H\) NMR timescale.

All of the alkyne complexes are the vivid green colour typical of \([W(\eta^2-RC=CR)(L)(CO)Tp^*]\) complexes, with the exception of the tellurium analogue, 37, which shows a dramatic break from pattern being bright orange. The complexes have been fully characterised by infrared, NMR, and UV-visible spectroscopy, as well as by single crystal X-ray diffraction, providing unique insight into the effect of the heteroatom substituent upon alkyne bonding.

---

\(^{\dagger}\) In this case, anti and syn nomenclature is with respect to the ligands CO and L (where L = Cl or CO).
4.4 Structural characterisation

The molecular structures of the W(II) alkyne complexes show generally similar gross structural features that agree with those established by previous studies of d⁴ alkyne complexes.¹ The geometry around the tungsten atom in these complexes is distorted octahedral with the alkyne oriented in the upright position and considered to occupy a single coordination site.

4.4.1 Molecular structures of the salts \([\text{W}(\eta^2-\text{Pr}EC\text{Ph})(\text{CO})_2\text{Tp}^\ast][\text{BF}_4]\) (E = O, S, Se, Te)

Each of the salts 34-37 was characterised crystallographically and the molecular geometries are depicted for representative examples in Figures 4.4, 4.5, 4.7, 4.8 and 4.10. Selected intramolecular bond lengths and angles appear in Table 4.1.

![Molecular structure of the complex cation 36+](image)

Figure 4.4. Molecular structure of the complex cation 36+ with 30% probability ellipsoids. Hydrogen atoms have been omitted.

For the salts 35–37, the orientation that is observed in the molecular structure has the heteroatom in the *anti* position, sandwiched between two *cis*-pyrazolyl rings (*phenyl down*) (Figure 4.4). For \([\text{W}(\eta^2-\text{PrOC}\text{Ph})(\text{CO})_2\text{Tp}^\ast][\text{BF}_4]\), 34', (Figure 4.5) a differing solid state orientation of the alkyne fragment was observed in which the phenyl group of the alkyne is directed towards the pyrazolyl ligand. Templeton has suggested that this is a favourable orientation for phenyl-substituted alkynes due to a weakly attractive π-interaction between the aromatic rings.⁶⁹ In the related selenolatoalkyne complex \([\text{W}(\eta^2-\text{MeSeC}\text{CC}_6\text{H}_4\text{Me-4})\text{(PPh}_3)(\text{CO})\text{Tp}^\ast]^+\), the chalcogen group is again positioned proximal to the pyrazolyl rings.²⁷ On this basis, an extension of the trend proposed by Templeton¹⁶ for preferential proximity to the pyrazolyl rings (R > Ph ≥ H > Me) to E–R > Ph ≥ H > Me is suggested, though the origin of this phenomenon remains unclear.
In the cationic \( \text{cis-W(CO)}_2 \) complexes \( 34-37 \), the alkyne is aligned such that the \( \text{C=C} \) bond defines a vector that approximately bisects the \( \text{OC-W-CO} \) angle. This is clearly shown in the molecular drawing of the complex cation \( 35^+ \) in Figure 4.7, which is projected along the metal–boron axis. For \( 34-37 \), the acute angle formed by the two carboxyls with the tungsten centre reflects the energy advantage of increasing overlap of the empty \( \pi^* \) orbitals of the carboxyl ligands with the filled \( \text{d}_{x^2-y^2} \) orbital on the tungsten (according to the coordinate system defined in Figure 4.6).\(^{1,49}\) Furthermore, the orientation of the alkyne along the \( \text{W(CO)}_2 \) bisector plane ensures that the \( \pi \)-accepting \( \pi_{\|}^* \) orbital overlaps with the filled metal \( \text{d}_{xz} \) orbital while \( \pi_{\perp} \) encounters the vacant \( \text{d}_{yz} \) orbital.

Figure 4.5. Molecular structure of the complex cation \( 34^+ \) with 30% probability ellipsoids. Hydrogen atoms have been omitted.

Figure 4.6. Qualitative molecular orbital scheme of \( \text{d}_{\pi} \) metal orbitals of a \( [\text{W(\eta}^2-\text{RC=CR})(\text{CO})_2\text{Tp}^*]^- \) complex.\(^{49}\)
Figure 4.7. Molecular structure of the complex cation $35^+$ viewed along the metal–boron axis with 30% probability ellipsoids. Hydrogen atoms have been omitted.

Table 4.1. Structural data for cationic alkyne complexes $[W(\eta^2-i\text{-Pr}EC\text{Ph})(\text{CO})_2\text{Tp}^+][\text{BF}_4]^-$

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>34$^+$</th>
<th>35</th>
<th>36</th>
<th>37</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–N$_{21}$</td>
<td>2.203(2)</td>
<td>2.205(2)</td>
<td>2.190(3)</td>
<td>2.197(3)</td>
</tr>
<tr>
<td>W–N$_{31}$</td>
<td>2.213(2)</td>
<td>2.194(2)</td>
<td>2.195(3)</td>
<td>2.198(3)</td>
</tr>
<tr>
<td>W–N$_{41}$</td>
<td>2.186(2)</td>
<td>2.175(2)</td>
<td>2.166(3)</td>
<td>2.175(3)</td>
</tr>
<tr>
<td>W–C$_{20}$</td>
<td>2.015(3)</td>
<td>2.029(3)</td>
<td>2.010(4)</td>
<td>2.014(4)</td>
</tr>
<tr>
<td>W–C$_{30}$</td>
<td>2.054(3)</td>
<td>2.042(3)</td>
<td>2.039(4)</td>
<td>2.041(4)</td>
</tr>
<tr>
<td>W–C$_{\text{Ph}}$</td>
<td>2.050(3)</td>
<td>2.048(4)</td>
<td>2.055(4)</td>
<td>2.052(4)</td>
</tr>
<tr>
<td>W–C$_{\text{E}}$</td>
<td>2.050(3)</td>
<td>2.058(4)</td>
<td>2.046(4)</td>
<td>2.057(4)</td>
</tr>
<tr>
<td>C= C</td>
<td>1.335(4)</td>
<td>1.342(4)</td>
<td>1.338(6)</td>
<td>1.332(5)</td>
</tr>
<tr>
<td>C–C$_{\text{C}(\text{Pr})}$</td>
<td>1.447(4)</td>
<td>1.457(4)</td>
<td>1.447(5)</td>
<td>1.456(5)</td>
</tr>
<tr>
<td>C–E(i–Pr)</td>
<td>1.290(4)</td>
<td>1.676(3)</td>
<td>1.823(4)</td>
<td>2.029(4)</td>
</tr>
<tr>
<td>E–C(i–Pr)</td>
<td>1.497(4)</td>
<td>1.840(3)</td>
<td>1.988(5)</td>
<td>2.185(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, $^\circ$</th>
<th>34$^+$</th>
<th>35</th>
<th>36</th>
<th>37</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$<em>{31}$–W–C$</em>{20}$</td>
<td>164.8(1)</td>
<td>164.3(1)</td>
<td>162.3(1)</td>
<td>162.9(1)</td>
</tr>
<tr>
<td>N$<em>{41}$–W–C$</em>{30}$</td>
<td>173.3(1)</td>
<td>168.58(9)</td>
<td>171.1(1)</td>
<td>171.6(1)</td>
</tr>
<tr>
<td>C$<em>{20}$–W–C$</em>{30}$</td>
<td>86.1(1)</td>
<td>89.0(1)</td>
<td>87.8(2)</td>
<td>87.0(2)</td>
</tr>
<tr>
<td>C$<em>{20}$–W–C$</em>{20}$</td>
<td>72.7(1)</td>
<td>77.2(1)</td>
<td>76.8(2)</td>
<td>77.3(2)</td>
</tr>
<tr>
<td>C$<em>{20}$–W–C$</em>{30}$</td>
<td>81.5(1)</td>
<td>81.04(10)</td>
<td>81.0(2)</td>
<td>80.3(1)</td>
</tr>
<tr>
<td>C= C–C$_{\text{Ph}}$</td>
<td>144.5(3)</td>
<td>133.7(2)</td>
<td>141.7(4)</td>
<td>140.9(4)</td>
</tr>
<tr>
<td>C= C–E</td>
<td>149.3(3)</td>
<td>135.7(3)</td>
<td>135.7(3)</td>
<td>137.6(3)</td>
</tr>
<tr>
<td>C–E–C(i–Pr)</td>
<td>119.9(3)</td>
<td>109.2(1)</td>
<td>102.7(2)</td>
<td>99.1(2)</td>
</tr>
</tbody>
</table>

$^a(*)$ indicates phenyl up isomer; C$_{\text{C}(\text{Pr})}$ = C(alkyne) proximal to carbonyl ligands.
The cis-dicarbonyl angles for 34–37 range from 86–89°, closely approximating the idealised value of 90°, which suggests that the $t_{2g}$ orbitals should be near degenerate. Nevertheless, preferential stabilisation of one of the two filled $d\pi$ orbitals is evident in the selective contraction of the W–C separation for one carbonyl ligand ($C_{20}$). Furthermore, the orientation of the alkyne ligand between the metal carbonyls is notably distorted towards alignment with this W–CO axis, as revealed by the molecular representation of the complex cation $[W(\eta^2-i-PrTeC=CPh)(CO)_2Tp^*]^{+}$ (37) in Figure 4.8 (viewed along the metal–alkyne vector). In the related complex $[W(\eta^2-PhC=CMe)(CO)_2Tp^*]^{+}$ bearing a hydrocarbon alkyne, the OC–W–CO angle is somewhat smaller (82.9°) and the alkyne orientation is such that it lies on the molecular mirror plane between the carbonyls. The orientational bias found in 34–37 can be attributed to a constructive interaction between the $\pi$-system of the more proximal carbonyl ligand ($C_{20}$) and that of the alkyne, which is mediated by contribution from the heteroatom. The geometry of Seidel's analogous compound $[W(\eta^2-RSC=CSR)(CO)_2Tp^*][PF_6]$ ($R$ = benzyl), bearing the symmetrically substituted 1,2-bis(benzylthiolato)acetylene mirrors that exhibited by 34–37, with the alkyne SCCS plane asymmetrically dividing the OC–W–CO angle.

![Figure 4.8](image)

**Figure 4.8.** Molecular structure showing the inner-coordination sphere of the complex cation 37$^+$ viewed along the metal–alkyne axis. 30% probability ellipsoids are shown. Hydrogen atoms and pyrazolyl rings have been omitted.
The dihedral angles between the C–C vector of the alkyne ligand and the W–C axis of each of the two metal carbonyls (Table 4.2) serve to quantify the extent of this distortion for each of the complexes. The distortion from the conformation in which the alkyne ECCR plane lies symmetrically between the two metal carbonyls is most notable for the alkoxyalkyne complex (34'). The alkyne ligand in 34' displays an obvious propensity towards lying parallel to the W–C 20 axis (dihedral angle 20.3°), a geometry which is commonly found for cis-[M(\(\eta^2\)-RC≡CR')(L)(CO)Tp*] structures when the remaining cis ligand is a π-donor.1

It should be noted that there are few previous examples of heteroalkyne complexes with a W(CO)_2 unit against which to assess these effects. Previous tungsten alkoxy, thiolato and selenolato alkyne complexes have been prepared from ketenyls, which requires the incorporation of a new ligand (typically a phosphine) as CO itself is not able to induce CR/CO coupling. A solitary exception is Seidel's [W(\(\eta^2\)-RSC≡CSR)(CO)_2Tp*][PF_6] (R = benzyl) but, due to the symmetrical nature of the RSC≡CSR alkyne, the bonding, as expected, shows much less bias.

### Table 4.2. Alkyne orientation

<table>
<thead>
<tr>
<th>Complex</th>
<th>Torsion Angle: C(alkyne)–ct–W–CO, °</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_20</td>
</tr>
<tr>
<td>(34')</td>
<td></td>
</tr>
<tr>
<td>(35)</td>
<td></td>
</tr>
<tr>
<td>(36)</td>
<td></td>
</tr>
<tr>
<td>(37)</td>
<td></td>
</tr>
<tr>
<td>(36')</td>
<td></td>
</tr>
<tr>
<td>(38)</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{ct} = \text{centroid}\); \(\text{a} \) Torsion angle: C(alkyne)–ct–W–Cl.

Orbital interactions for alkyne bonding to divalent tungsten are well known to involve both \(\pi^*\) acceptance and \(\pi\) donation (see Figure 4.1) and contributions from the π-donor chalcogen atoms are consequently significant. The carbon–carbon triple bond is not, however, a highly sensitive indicator of \(\pi\) donation, and while a modest C–C contraction is noted (C–C separation: S > Se > Te), the C–C bond lengths for 34–37 are remarkably consistent, ranging from 1.332–1.342 Å. The slight elongation of the C–C triple bond for [W(\(\eta^2\)-i-PrSC=CPh)(CO)_2Tp*] and [W(\(\eta^2\)-i-PrSeC=CPh)(CO)_2Tp*] is most likely an
expression of the delocalisation of electron density in the C–C bonding orbital towards the heterogroup.

\[
\begin{align*}
\text{Figure 4.9.} \text{ Resonance contributions to ground state bonding for tungsten–alkyne complexes } \\
\text{[W(\eta^2-i-PrEC=CPPh)(CO)Tp*][L_nW = (L)(CO)Tp*]: E = O, S, Se, Te; L = CO; n = 1; or E = Se; L = Cl; n = 0].}
\end{align*}
\]

The relatively short W–C(alkyne) distances fall within the narrow range of 2.05 ± 0.01 Å and are consistent with multiple bond character for the W–C(alkyne) linkages. In the salts 34 and 37, the two W–C(alkyne) separations do not differ significantly from one another, suggesting considerable contribution to the ground state bonding from the bis(carbenoid) resonance form B (Figure 4.9). A similar equality of W–C bonds was observed for the d^2 complex [W(\eta^2-n-BuTeC=CPPh)Cl(THF)]. For the sulfur and selenium containing salts, 35 and 36, the alkyne coordination is less symmetric, with crystallographic data (W–C bond lengths and C=C–R angles) for [W(\eta^2-i-PrSC=CPPh)(CO)Tp*][BF_4], 35, consistent with a substantial contribution from the ketene-like valence bond description C (Figure 4.9).

Retrodonation from the metal to the vacant π* orbital drives the deformation of the carbon skeleton upon coordination. For 34–37, the delocalisation of electron-density towards the heterogroup must also be taken into account. For the phenyl down structures, the deviation from linearity for the C=C–E angle, ca. 45°, is larger than the more common 40° distortion characterising bound hydrocarbon alkynes. The greater bend may result from the relief of steric repulsion between the chalcoether fragment and the proximal pyrazolyl rings. Furthermore, E–C(alkyne) separations are noticeably contracted compared to the E–C(alkyl) distances, with the latter typical of E–C(sp^3) bonds. The short E–C(alkyne) separations are consistent with multiple bond character for this linkage and the compression of the C=C–E angle may reflect resultant sp^2-character for the alkyne carbon. Structural properties for the phenyl up isomer of [W(\eta^2-i-PrOC=CPPh)(CO)Tp*][BF_4] frequently depart from those of the phenyl down isomers and the C=C–E bond angle (149.3(3)°) is dilated by 13° relative to the corresponding angle in the phenyl down rotamers. The C=C–R angle is similarly expanded, though to a lesser extent.
Distortion of the alkyne ligand upon coordination extends beyond the cis-bent angle of the substituents. Deformations from planarity are evident along the coordinated i-PrEC=CR ligand spine, as quantified by the inter-plane angles collected in Table 4.3. The chalcogenoether substituents are minimally distorted (< 8°) from the WC2 plane, however, there is significant torsion between the phenyl group and the WC2 chelate ring (up to 20°). Nevertheless, there appears to be no discernible, systematic trend for the deformations across the alkyne series and it is suggested that efficient packing of these molecules via stacking of the aromatic moieties may be the driving force leading to the distortions observed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Alkyne plane,°</th>
<th>WC2:chalcloether,°</th>
<th>WC2:phenyl,°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34')</td>
<td>W[t(2)-i-PrOC=CR(CO)2]TP*[BF4]</td>
<td>6.7</td>
<td>175.6</td>
</tr>
<tr>
<td>(35)</td>
<td>W[t(2)-i-PrSC=CR(CO)2]TP*[BF4]</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>(36)</td>
<td>W[t(2)-i-PrSeC=CR(CO)2]TP*[BF4]</td>
<td>0.1</td>
<td>-5.4</td>
</tr>
<tr>
<td>(37)</td>
<td>W[t(2)-PrSeC=CR(CO)2]TP*[BF4]</td>
<td>-1.5</td>
<td>-7.6</td>
</tr>
<tr>
<td>(38)</td>
<td>W[t(2)-PrSeC=CR(CO)2]Cl(CO)TP*</td>
<td>5.6</td>
<td>-6.9</td>
</tr>
<tr>
<td>(38')</td>
<td>W[t(2)-PrSeC=CR(CO)2]Cl(CO)TP*</td>
<td>2.9</td>
<td>172.5</td>
</tr>
</tbody>
</table>

Torsion angles: °C(ipso)-C-C-E; °W-ct-E-C; °W-ct-C(ipso)-C(ortho); ct = centroid.

The Tp* ligand occupies three facial coordination sites and, as is typical of poly(pyrazolyl)borate complexes, the W–N separations are highly sensitive to the electronic influence of the trans disposed ligands. Of note for the cis-W(CO)2 tungsten alkyne fragments is the N–W separation trans to C20O, which is much larger than the N–W separation trans to the adjacent carbonyl ligand. The N–N bond lengths (av. 1.375 Å) and sum of the N–W–N angles (av. 249°) are typical of the tris(pyrazolyl)borate ligand and unremarkable, other than to note that the N–W–N bite angle of the pyrazolyl arms that form the anti pocket is somewhat larger (av. 86.6°) relative to those involving the trans pyrazolyl arm (av. 81.4°).

The Tp* chelation influences many of the metal–ligand angles in this series of complexes, however, geometric manifestations of the alkyne bonding are also important. The influence of the tungsten–alkyne multiple bonding is reflected in the systematic distortion of cis donor atoms away from the alkyne ligand. For the complex cations 34–37, alkyne bonding drives this distortion such that the trans disposed ligand pair that are most closely aligned with the alkyne (N31–W–C20) are swept an average of 8° further back from the alkyne than the perpendicular pair (N41–W–C30). The inner-coordination sphere of 37 represented in Figure 4.10 in which peripheral atoms have been omitted illustrates the relative distortions of the trans disposed ligand pairs from the alkyne, which can be rationalised on steric grounds.
4.4.2 Molecular structure of the chiral molecule $[W(\eta^2-i-PrSeC\equiv CPh)Cl(CO)Tp^*]$  

Both rotational isomers of $[W(\eta^2-i-PrSeC\equiv CPh)Cl(CO)Tp^*]$ were crystallographically characterised and molecular geometries for the phenyl down and phenyl up isomers are depicted in Figures 4.11 and 4.13, respectively. Selected intramolecular bond distances and angles are listed in Table 4.4.

The C≡C bond distance of the chiral complex $[W(\eta^2-i-PrSeC\equiv CPh)Cl(CO)Tp^*]$ is independent of the relative orientation of the alkyne ligand (38 1.316(4) and 38' 1.314(4) Å), but is substantially contracted relative to the corresponding distance of the salt $[W(\eta^2-i-PrSeC\equiv CPh)-(CO)_2Tp^*][BF_4]^{-}$ (1.338(6) Å). Moreover, the W–C(alkyne) separations were notably disparate, with the carbon–tungsten separation for the syn carbon atom being notably elongated, a trend commonly observed for $\eta^2$-alkyne complexes of Group 6 metals.
CHAPTER 4. TUNGSTEN—ALKYNE COMPLEXES

Figure 4.11. Molecular structure of the phenyl down isomer of the chiral complex [W(η²-i-PrSeC=CPh)Cl(CO)Tp*], 38, with 30% probability ellipsoids shown. Hydrogen atoms have been omitted.

Table 4.4. Structural data for the rotational isomers of the complex [W(η²-i-PrSeC=CPh)Cl(CO)Tp*]

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>38</th>
<th>38'</th>
<th>Bond Angles, °</th>
<th>38</th>
<th>38'</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–N₂₁</td>
<td>2.220(2)</td>
<td>2.239(2)</td>
<td>N₃₁–W–C₂₀</td>
<td>165.69(10)</td>
<td>167.10(10)</td>
</tr>
<tr>
<td>W–N₃₁</td>
<td>2.245(2)</td>
<td>2.250(2)</td>
<td>N₄₁–W–Cl</td>
<td>163.06(6)</td>
<td>163.35(6)</td>
</tr>
<tr>
<td>W–N₄₁</td>
<td>2.184(2)</td>
<td>2.184(2)</td>
<td>C₂₀–W–Cl</td>
<td>92.57(9)</td>
<td>92.12(9)</td>
</tr>
<tr>
<td>W–C₂₀</td>
<td>1.971(3)</td>
<td>1.982(3)</td>
<td>C₃₁–W–C₂₀</td>
<td>72.79(12)</td>
<td>73.20(12)</td>
</tr>
<tr>
<td>W–Cl</td>
<td>2.4322(7)</td>
<td>2.4323(7)</td>
<td>C=C–Ph</td>
<td>140.8(3)</td>
<td>144.5(2)</td>
</tr>
<tr>
<td>W–CPh</td>
<td>2.041(3)</td>
<td>2.031(2)</td>
<td>C=C–Se</td>
<td>131.0(2)</td>
<td>145.3(2)</td>
</tr>
<tr>
<td>W–CSe</td>
<td>2.032(3)</td>
<td>2.062(2)</td>
<td>C–Se–i-PrC</td>
<td>104.7(13)</td>
<td>102.84(13)</td>
</tr>
<tr>
<td>C=C</td>
<td>1.316(4)</td>
<td>1.314(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–Cₚₚₒ</td>
<td>1.482(4)</td>
<td>1.455(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–Se(i-Pr)</td>
<td>1.852(3)</td>
<td>1.855(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se–C(i-Pr)</td>
<td>1.978(3)</td>
<td>1.978(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* ('') indicates phenyl up isomer; Cₚₚₒ = C(alkyne) proximal to carbonyl ligand.

The alkyne is oriented such that it bisects two of the pyrazolyl rings and lies approximately parallel to the W–CO axis (as depicted in Figure 4.12). This orientation optimises π-acid and π-donor interactions of the alkyne with the dₓ orbitals on the tungsten, while the parallel carbonyl ligand (COₚ) can interact with both filled dₓ orbitals.¹
The alkyne is more closely aligned with the tungsten–carbonyl axis in the phenyl up isomer of \([W(\eta^2-iPrSeC=CH)Cl(CO)Tp^*]\) \(\text{38}'\), the implication being that bonding interactions are optimised in this orientation. Indeed, the alkyne/carbonyl torsion angle \(\left(12.7^\circ, \text{Table 4.2}\right)\) closely mirrors that seen for the related complexes \([W(\eta^2-PhC=CH)(\kappa S-S_2CNET_2)(CO)Tp^*)]^6\) at \(12.7^\circ\) and \(12.0^\circ\), respectively. Exact alignment is, however, prevented by conflict between the alkyne substituents and the pyrazolyl arms, and this seems to be more marked for the phenyl down rotamer.

Geometric parameters for both \(\text{38}\) and \(\text{38}'\) reveal a reduction in the \(W-CO\) separation (ca. 0.03 Å) and a concomitant increase of the \(N-W\) separation \(\text{trans}\) to \(C_2O\) upon replacement of the \(\text{cis}\)-carbonyl ligand in the precursor \(\text{36}\) with a \(\pi\)-basic chloride ligand. An elongation of the \(\text{Se–C(alkyne)}\) distance and reduction in the \(\text{Se–C(alkyne)}\) vs \(\text{Se–C(alkyl)}\) bond length disparity relative to corresponding data for \(\text{36}\) is noted, but the \(\text{Se–C(alkyne)}\) distances for \(\text{38}\) and \(\text{38}'\) (av. 1.853 Å) nevertheless remain indicative of double bond character.\(^{27}\) Through this (partial) multiple bonding, one of the chalcogen lone pairs is effectively ‘tied up’ with the alkyne \(\pi_1\) orbital and the resultant \(sp^2\)-hybridised geometry of the chalcogen atom relegates the remaining lone pair and the alkyl substituent to the plane defined by the \(WC_2\) chelate. It is noteworthy that the relative orientation of the chalcogen lone pair and the alkylchalco substituent for the phenyl down isomeric structure \(\text{38}\) is such that it is the alkyl group that is directed towards the pyrazolyl rings while in the phenyl up geometric isomer \(\text{38}'\) it is the lone pair on the chalcogen that is directed towards the metal–ligand framework. This same trend can be identified for the rotational isomers of the salts \([W(\eta^2-iPrEC=CPH)(CO)_2Tp^*][BF_4]\) (\(E = O\) vs \(E = S, \text{Se}, \text{Te}\)) (vide supra), with the orientation in \(\text{34}'\) matching that of \(\text{38}'\).

A constructive interaction between the free chalcogen lone pair and a vacant \(\pi^*\)-orbital on the \(\text{syn}\) carbonyl ligand in the phenyl up rotamers may account for this phenomenon, compromising conjugation of the chalcogen with the alkyne \(\pi\)-system. This effect can be somewhat substantiated by the elongated \(W-C_2\) separation for \(\text{38}', 1.982(3)\) Å, relative to the
corresponding distance in 38. 1.971 (3) Å, which is indicative of decreased acceptance of electron density through back-bonding with the metal centre. Furthermore, the $C_{\text{syn}}$–W–C$_{20}$ angle observed for 34' at 72.71(14)$^\circ$ is contracted relative to the corresponding bite angle (average 77$^\circ$) for the cationic complexes 35–37 displaying phenyl down geometry. Such a constructive interaction would also account for the large degree of bias in the orientation of the alkyne ligand between the metal carbonyls noted above for the alkoxyalkyne complex.

Support for the existence of a constructive, through-space interaction between the chalcogen lone pair and a vacant $\pi^*$-orbital in $[W(\eta^2-RC=CR')(L')(CO)Tp^*]$ complexes containing $\text{syn}$-chalcoether substituents can be found in the literature. In Templeton's related complex $[W(\eta^2-\text{MeOCCPMe}_2\text{Ph})(\text{OC}_6\text{H}_4\text{NO}_2-4)(CO)Tp^*][\text{OTf}]$, the alkoxy alkyne substituent is positioned $\text{syn}$ to the carbonyl ligand with the oxygen lone pair directed towards the carbonyl. Similarly, in Seidel's analogous 1,2-bis(benzylthioliato)acetylene complex $[W(\eta^2-RSCCSR)(CO)Tp^*][\text{PF}_6]$ ($R = \text{benzyl}$), it is the lone pair on the $\text{syn}$-benzylthioliato unit which is directed towards the metal–ligand scaffold.43

![Figure 4.13. Molecular structure of the phenyl up isomer of the chiral complex $[W(\eta^2-i-\text{PrSeC}≡\text{CPh})\text{Cl(CO)Tp}^*]$, 38', with 30% probability ellipsoids. Hydrogen atoms have been omitted.](image-url)

The trend observed in the distortion of cis ligands away from the alkyne for 34–37 (vide supra) is reversed in the neutral complex $[W(\eta^2-i-\text{PrSeC}≡\text{CPh})\text{Cl(CO)Tp}^*]$, with the perpendicular pair of trans disposed ligands ($N_{31}$–W–Cl) swept an average of 3$^\circ$ further back from the alkyne than the parallel pair ($N_{31}$–W–C$_{20}$). Furthermore, the bend-back of the C≡C–Se alkyne substituent in the phenyl up isomer of $[W(\eta^2-i-\text{PrSeC}≡\text{CPh})\text{Cl(CO)Tp}^*]$ is expanded by
approximately 14° compared to its *phenyl down* counterpart (C=E: 145.3(2)° for 38' vs 131.0(2)° for 38), and differs little from the 40° deformation characteristic of hydrocarbon alkynes. The similarity of the C=Ph and C-Se bend-back angles observed for 38' is compatible with the chalcogen exerting its bonding influences via a through-space interaction with the proximal carbonyl rather than through the π-system of the C-Se backbone.
4.5 Spectroscopic properties

Infrared and NMR spectroscopic data for the alkyne complexes are summarised in Table 4.5. Two-dimensional HMBC experiments were used to unambiguously distinguish between the alkyne carbon resonances and methine protons of isopropyl substituents, when obscured by methyl resonances of the Tp* ligand, were located via $^1$H–$^1$H COSY studies.

The [W($\eta^2$-i-PrEC=CPh)(CO)$_2$Tp*][BF$_4$] salts exhibit two strong infrared absorptions near 2050 and 1975 cm$^{-1}$ attributed to the metal carboxyls, with the higher frequency absorption assigned to the symmetric $A_1$ mode and the lower frequency absorption to the antisymmetric $B_1$ mode. The lower energy band is the more intense of the two, a phenomenon typical of such complexes. $^3$ Conjugation of the C=C bond with an electron-donating substituent increases available electron density for $\pi_d$-donation to the metal centre, and a subsequent increase in $\pi$-back-bonding to the $\pi$-acidic metal-carbonyls is observed. Comparison of the CO force constants ($k_{CO}$)$^4$ with those of W(II) complexes of 2-butyne (16.39)$^3$ and diphenylacetylene (16.45)$^3$ confirm that replacement of an alkyl or aryl group by a $\pi$-donor chalcogen substituent increases the net donor capacity of the alkyne. All other things remaining equal, from the values of $k_{CO}$ for the cationic series 34–37, it can be seen that the strength of W–CO bonding, and by implication the basicity of the alkyne ligands, increases in the order E = O < S < Se < Te.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1$^3$C{1$^1$H} NMR $\delta$, ppm</th>
<th>IR $\nu_{C=O}$, cm$^{-1}$</th>
<th>IR $\nu_{C=C}$, cm$^{-1}$</th>
<th>IR $k_{CO}$ (N m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(34)</td>
<td>[W($\eta^2$-i-PrOC=CPh)(CO)$_2$Tp*][BF$_4$]</td>
<td>215.1 187.6 237.8</td>
<td>1681 2054, 1978</td>
<td>16.42</td>
</tr>
<tr>
<td>(34')</td>
<td></td>
<td>216.1 211.0 213.2</td>
<td>1718 2049 1975</td>
<td>16.35</td>
</tr>
<tr>
<td>(35)</td>
<td>[W($\eta^2$-i-PrSC=CPh)(CO)$_2$Tp*][BF$_4$]</td>
<td>215.5 198.5 221.1</td>
<td>1715 2047, 1974</td>
<td>16.33</td>
</tr>
<tr>
<td>(36)</td>
<td>[W($\eta^2$-i-PrSeC=CPh)(CO)$_2$Tp*][BF$_4$]</td>
<td>216.5 199.4 219.1</td>
<td>1717 2043, 1970</td>
<td>16.26</td>
</tr>
<tr>
<td>(37)</td>
<td>[W($\eta^2$-i-PrTeC=CPh)(CO)$_2$Tp*][BF$_4$]</td>
<td>217.8 200.8 201.4</td>
<td>1715 2043, 1970</td>
<td>16.26</td>
</tr>
<tr>
<td>(38)</td>
<td>[W($\eta^2$-i-PrSeC=CPh)Cl(CO)TP*]</td>
<td>241.3 199.7 193.2</td>
<td>16.26</td>
<td></td>
</tr>
<tr>
<td>(38')</td>
<td></td>
<td>238.4 209.5 188.6</td>
<td>1715 1907</td>
<td>16.26</td>
</tr>
</tbody>
</table>

* Unless otherwise stated, data were collected in CH$_2$Cl$_2$ or CD$_2$Cl$_2$; ('') denotes phenyl up isomer; $^b$Ph–C=E, C=C–E; $^c$ Nujol.

In the infrared spectrum, absorbances diagnostic of the Tp* ligand occur near 2570 and 1540 cm$^{-1}$, corresponding to $\nu_{BH}$ and $\nu_{CN}$, respectively. Donation from both $\pi_d$ and $\pi_b$, as well as acceptance of metal d$\pi$ electron density into $\pi^*_d$, all contribute to reduction of the C–C bond order and weak absorptions at ca. 1700 cm$^{-1}$ have been assigned to $\nu_{C=C}$, some 500 cm$^{-1}$ to lower frequency than in the free alkynes ($\nu_{C=C} =$ 2180 cm$^{-1}$). The position observed for this stretch is in agreement with the 1712 cm$^{-1}$ absorption observed for Lator's related
CHAPTER 4. TUNGSTEN–ALKYNE COMPLEXES

N,N-dimethylaminoalkyne Mo(II) complexes [Mo(η²-RC=CNMe₂)(CO)₂Tp*]⁺ (R = C(CN)(CH₃)(C₆H₄Br-4), C(CN)(CH₃)(1-C₁₀H₂)₅), in which there is suggested to be significant contribution from an η²-C,C'-ketene resonance form (Scheme 4.7). Similarly low energy absorptions for the C–C alkyne stretch are evident in Dehnicke’s d⁵ complexes of alkynyl chalcogen compounds. It is notable that other than the alkoxy derivative, the position of this band is remarkably insensitive to variation of the chalcogen. The lower value for the alkoxy derivative presumably reflects the greater orbital overlap between oxygen and carbon compared with the heavier chalcogens, with greater delocalisation of the C=O and C–O (partially) multiple bond linkages.

Both the ¹³C{¹H} and ¹H NMR spectra for the cationic complexes 34–37 exhibit 2:1 patterns for the coordinated 3,5-dimethylpyrazolyl groups, indicating equivalence of the scorpionate arms trans to the CO ligands on the NMR time scale and consistent with the cis-W(CO)₂ bisector orientation of the alkyne ligand observed in the molecular structure determinations. Single environments are observed for the alkyne substituents in compounds 35–37, [W(η²-i-PrEC=CPH(CO)₂Tp*)[BF₄]] (E = S, Se, Te), suggesting facile alkyne rotation or that only a single alkyne orientation is populated (vide infra). While two orientations of the alkyne ligand are commonly observed among tungsten(II) complexes of the type [W(η²-RC=CR')(L)(CO)Tp*] bearing terminal acetylenes (R = H, R' = Ph, MeC=CH₂) (L = π-donor), complexes with the internal acetylene PhC=CMé tend to favour a single alkyne orientation. In the case of the cationic alkyloalkyne complex [W(η²-i-PrOC=CPH(CO)₂Tp*)[BF₄]], pair-wise signals are observed in the ¹H and ¹³C{¹H} NMR spectra, most clearly apparent from the presence of two methine septets at δH 3.96 and 5.53. These resonances are attributed to the geometric isomers 34 and 34', present in an approximately 1:1.15 ratio by integration, in which the orientation of the alkyne differs by a 180° rotation. Unambiguous assignment of the resonances of each isomer was possible by a combination of one- and two-dimensional NMR techniques. Furthermore, proximity to the pyrazolyl rings shifts ¹H NMR signals to higher field allowing the more shielded CH(i-Pr) methine resonance at δH 3.96 to be attributed to the phenyl down rotamer, 34, and that at δH 5.53, for which there is a slight orientational preference, to rotamer 34’, bearing a syn chalcog ether substituent.

The ¹³C{¹H} NMR spectra of the salts [W(η²-i-PrEC=CPH(CO)₂Tp*)[BF₄]] (E = S, Se, Te) reveal alkynyl carbon resonances ranging from 188–240 ppm, typical of 4e⁻ donor alkynes. In the compounds investigated by Templeton et al., alkynyl carbons close to Tp* have been found to exhibit downfield chemical shifts. In accordance with this, the ¹³C{¹H} NMR spectra of the
phenyl down isomer of 34 exhibits a resonance for i-PrOC≡CPh (C1) (sandwiched between the pyrazolyl arms), which is deshielded by 50 ppm relative to the i-PrOC≡CPh (C2) resonance. Of note is the persistence of the downfield chemical shift for C1 in the phenyl up orientation, 34', in which for a hydrocarbon alkyne the relative shielding of alkyne positions is expected to be interchanged. Not surprisingly, influences from the π-donor chalcogen dominate over electronic shielding effects caused by proximity to the Tp* ligand. Furthermore, the differences in chemical shift for the alkyne carbons, δC1−C2, diminishes as the shielding of C1 increases with the increasing π-basicity of the chalcogen substituent, i.e., δC1−C2: 22.6, 35, 19.7, 36, and 0.6 ppm, 37. The metal carbonyl resonances are similarly influenced by the donor strength of the chalcogen, exhibiting a slight downfield trend in chemical shift for the series 34−37.

The complex [W(η²−i-PrTeC≡CPh)(CO)₂Tp*][BF₄] containing the strongly π-donating alkyltelluro substituent displays near coincident alkyne resonances, consistent with the equality of the two W–C separations found in the crystal structure and in agreement with a large contribution to the ground state structure from resonance form B (Figure 4.9). The phenyl up rotamer of the salt [W(η²−i-PrOC≡CPh)(CO)₂Tp*][BF₄], 34', similarly shows near equivalent chemical shifts for the alkyne carbons (δC1−C2: 2.2 ppm) and close W–C(alkyne) separations.

Charge-transfer from the oxygen atom to the triple bond in alkoxyalkynes has been previously demonstrated and spectroscopic data for the phenyl down isomer of [W(η²−i-PrOC≡CPh)(CO)₂Tp*][BF₄] (δPh–C≡C 187.6 vs C≡C–O 237.8) are consistent with the highly polarised triple bond that would result from such a positive mesomeric effect (as shown in Figure 4.14). For the phenyl up isomer 34', however, the oxygen lone pairs are involved in a constructive interaction with the syn carbonyl ligands, which perhaps compromises conjugation with the triple bond, and thus the intramolecular polarisation of the π-system is reduced.

\[
\text{Ph} \overbrace{\text{C} \equiv \text{C}}^{\text{O}} \overline{\text{i-Pr}} \leftrightarrow \text{Ph} \overbrace{\text{C} \equiv \text{C}}^{\text{O}} \overline{\text{i-Pr}}
\]

Figure 4.14. Mesomeric charge transfer from alkoxy substituent to C≡C bond.

Replacement of one carbonyl ligand in [W(η²−i-PrSeC≡CPh)(CO)₂Tp*][BF₄] (36) with chloride to give [W(η²−i-PrSeC≡CPh)Cl(CO)₂Tp*] (38 and 38') eliminates the symmetry plane of the molecule and has a dramatic impact on dπ orbital combinations and orientational preferences (Figure 4.12 cf. Figure 4.6). Two isomeric forms are present due to the two alkyne rotamers, i.e., phenyl up and phenyl down (ca. 51:49 ratio). These rotamers may be separated by solvent-
dependent recrystallisation, (conditions: diethyl ether–pentane, 38; low temperature dichloromethane–pentane, 38') exploiting the highly ordered nature of the solid state. The recrystallisation selectively traps one isomer and is an effective draining of the equilibrium, leading to the isolation of the pure rotamers 38 and 38'. Re-equilibration of the isomer distribution slowly occurs in solution at ambient temperature, suggesting that there is no ligand property sufficiently dominant to create a substantial alkyne preference between the available orientations. A similar phenomenon has recently been exploited by Harman, whereby selective crystallisation of an η²-arene complex [W(η²-anisole)(NO)(PMe₃)Tp] afforded one rotamer, with subsequent dissolution in the presence of a reagent that reacted more rapidly than the isomer equilibration affording stereoselectivity of reaction products.³³

Both ¹H and ¹³C{¹H} NMR spectra obtained from dichloromethane-δ₂ solution of the mixture of [W(η²-i-PrSeC≡CPh)Cl(CO)Tp*] show pair-wise signals of near equal intensities for the two isomeric forms. The three non-equivalent pyrazolyl rings of [W(η²-i-PrSeC≡CPh)Cl(CO)Tp*] give rise to a 1:1:1 intensity pattern in both ¹³C{¹H} and ¹H NMR spectra for each conformer, consistent with the chirality of the molecule. The methyl groups of the isopropyl substituent are diastereotopic, appearing as a pair of doublets for each rotamer, and the methine CH resonances are substantially deshielded compared with the salt [W(η²-i-PrSeC≡CPh)(CO)₂Tp*][BF₄⁻] (36) (δ: 4.52, 38, and 3.16, 38, vs 2.65, 36). Resonances for the isopropyl substituent in the ¹H NMR spectra display the expected shielding pattern with respect to proximity to the pyrazolyl rings.⁷

The average chemical shift for each of the alkynyl carbon nuclei in [W(η²-i-PrSeC≡CPh)Cl(CO)Tp*] is upfield of that found for the cationic complex, consistent with decreased π⁻ donation in the neutral case.³ The solitary metal carbonyl in [W(η²-i-PrSeC≡CPh)Cl(CO)Tp*] gives rise to a low-field signal (ca. δ: 240) in the ¹³C{¹H} NMR spectrum, somewhat lower than observed in the dicarbonyl analogue [W(η²-i-PrSeC≡CPh)(CO)₂Tp*][BF₄⁻] (δ: 217) and consistent with the more electron-rich tungsten centre. The position of this resonance is in close agreement with that reported for the metal carbonyl in Templeton’s iodide-complexes [W(η²-RC≡CR’I)(CO)Tp*] (R = R’ = Me; R = Ph, R’ = H, Me) (δ: 233)³ and the related hydride complexes [W(η²-PhC≡CMe)H(CO)Tp*] and [W(η²-MeC≡CMe)H(CO)Tp*] (δ: 244).⁵¹ The isomeric pair gave rise to a coincident carbonyl absorption in the infrared spectrum at 1907 cm⁻¹.
4.5.1 Dynamic processes

Dynamic processes of the salts \([W(\eta^2-i-PrEC=CPh)(CO)_2Tp^*][BF_4] (E = O, S, Se, Te)\)

In a phase-sensitive \(^1\)H NOESY study, distinction between cross peaks originating from the nuclear Overhauser effect (nOe) and those originating from chemical or conformational exchange is possible by the phase of the peak, i.e., with the diagonal signal phased positively, off-diagonal contours for nOes are phased negatively and those for chemical exchange are phased positively.

The room temperature \(^1\)H NOESY spectrum of \([W(\eta^2-i-PrOC=CPh)(CO)_2Tp^*][BF_4]\) was dominated by intense, positive cross peaks originating from conformational exchange between the independent sites of the two alkyne rotamers, \(34\) and \(34'\). The aromatic region of the COSY spectrum (a, Figure 4.15) revealed a series of proton–proton coupling connections allowing determination of the phenyl protons belonging to the intact aromatic rings of each isomer. The NOESY spectrum of the same region (b, Figure 4.15) exhibits cross peaks between these independent phenyl groups, consistent with conformational exchange due to alkyne rotation. A similar exchange phenomenon attributed to interconverting geometric isomers was observed in the \(^1\)H NOESY experiment for \([W(\eta^2-PhC=CMe)H(CO)Tp^*]\).\(^{54}\)

An estimate of the free energy of activation for alkyne rotation (\(\Delta G^2\)) in \([W(\eta^2-i-PrOC=CPh)(CO)_2Tp^*][BF_4]\) was obtained through a variable-temperature NMR study. As the sample temperature was raised, increased alkyne rotation and subsequent reduction of the lifetime of each substituent in the independent shielding zones led to broadening of the NMR signals. A coalescence temperature (\(T_c\)) of 373 K was observed and from this an energy barrier for alkyne rotation of 70.5 kJ mol\(^{-1}\) was calculated according to the modified Gutowsky equation (Equation 3.1).\(^{55}\)

The high \(\Delta G^2\) for alkyne rotation estimated for \([W(\eta^2-i-PrOC=CPh)(CO)_2Tp^*]^+\) approaches that found for related \([W(\eta^2-RC=CR)(L)(CO)Tp^*]\) complexes in which \(L\) is a strong \(\pi\)-donor ligand. In \(d^4\) metal alkyne complexes, the two \(d\pi\) orbitals directed toward the alkyne are differentiated by their interactions with the \(cis\) ligands, \(L\) and \(L'.\)\(^{1}\) Accordingly, a large barrier to alkyne rotation is anticipated for systems in which the \(\pi\)-acid/\(\pi\)-base properties of these \(cis\) ligands differ markedly, e.g., \([W(\eta^2-HC=CH)I(CO)Tp^*]\) \(\Delta G^2 = 79.5\) kJ mol\(^{-1}\) and small barriers for systems in which these ligands are similar or the same. The unusually high alkyne rotation barrier found for \([W(\eta^2-i-PrOC=CPh)(CO)_2Tp^*]\) \((L = L' = CO)\), is attributed to the complimentary interaction of the oxyalkyne ligand with a single carbonyl, as identified in the
crystallographic study, which greatly decreases its relative $\pi$-acid character and leads to a greater distinction between the two $d\pi$ orbitals directs towards the alkyne.

Figure 4.15. Red = 34, Blue = 34'. a) Aromatic region of the COSY spectrum of $[W(\eta^2-i-PrOC=\text{CPh})(\text{CO})_2\text{Tp}^*[\text{BF}_4]]$ in $\text{CD}_2\text{Cl}_2$ at 25 °C showing cross peaks arising due to proton–proton couplings; b) aromatic region of the NOESY spectrum of $[W(\eta^2-i-PrOC=\text{CPh})(\text{CO})_2\text{Tp}^*[\text{BF}_4]]$ in $\text{CD}_2\text{Cl}_2$ at 25 °C showing cross peaks arising due to chemical exchange of the two geometric isomers.

For the salt $[W(\eta^2-i-PrSC=\text{CPh})(\text{CO})_2\text{Tp}^*[\text{BF}_4]]$ (35), broadness of the alkyne associated resonances in the room temperature $^1\text{H}$ NMR spectrum hints at a lower energy fluxional process, which was confirmed by the observation of a coalescence temperature of 291 K. [NB: The coincident chemical shift of the conformers (500 MHz instrument) prevented an estimation of $\Delta G^\ddagger$.] A similar fluxionality was identified for the compounds 36 and 37, with $T_c$'s of 251 K and 183 K, respectively, corresponding to lower energy barriers to interconversion.

The fluxional behaviour for the salts 35–37 may be ascribed to facile alkyne rotation, in agreement with the generally decreased resistance to this process expected for systems in which the $cis$ ligands have similar $\pi$-acidities. In light of the multiple bond character identified for the C(alkyne)–E linkages and associated hindered rotation around the C–E bond, the fluxionality may also arise from differing relative orientations of the alkyl substituent and free lone-pair of the chalcogenolate, i.e., towards (Z) and away (E) from the W–C(alkyne) bond. Indeed, a similar fluxional behaviour involving hindered rotation of the diethylamino group was identified for Fillipou's aminoalkyne complex, $[W(\eta^2-\text{PhC}=\text{CNe}t_2)\text{Br}_2(\text{CN}=\text{Bu})_3]$, in which the spectroscopic data indicated substantial bond delocalisation in the 1-aminoalkyne ligand ($\Delta G^\ddagger = 61.4$ kJ mol$^{-1}$). The $^1\text{H}$ NOESY evidence for complexes 35–37 was, however, consistent with facile alkyne rotation on the NMR time-scale rather than the presence of a singly
populated isomer, revealing NOE interactions between each of the alkyne substituents and the pyrazolyl-methyl groups.

Dynamic processes of the neutral complex $[\text{W}(\eta^2-i\text{-PrSeC}=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^\ast]$  

A variable-temperature $^1$H NMR spectroscopic study of the isomeric mixture of $[\text{W}(\eta^2-i\text{-PrSeC}=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^\ast]$ revealed no coalescence up to 378 K, suggesting that the barrier to alkyne rotation is high as is expected for complexes of this type. The large alkyne rotation barrier indicates strong and specific $\pi$-interactions among the tungsten and the alkyne ligand and is a reflection of the disparity between the $\pi$-bonding characteristics of the adjacent cis ligands, i.e., CO = strong $\pi$-acid; Cl = strong $\pi$-base.

The salt $[\text{W}(\eta^2-i\text{-PrSeC}=\text{CPh})(\text{CO})\text{Tp}^\ast][\text{BF}_4]$ (36) and both geometric isomers of $[\text{W}(\eta^2-i\text{-PrSeC}=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^\ast]$ (38 and 38') each display distinctly shielded phenyl resonances, thus the formation of the neutral complex from 36 and [Bu₄N]Cl could be assayed via $^1$H NMR spectroscopy, despite dominance of the high-field portion of the spectrum by the tetrabutylammonium signals. Complex 36 and 2.5 equivalents of tetrabutylammonium chloride were combined in dichloromethane-$d_2$ in a sealed NMR tube at 25 °C and a $^1$H NMR spectrum obtained within fifteen minutes ($t = 0$ h in Figure 4.16) and every hour thereafter for 48 hours, after which time no further changes were apparent. The spectrum was found to be devoid of almost all peaks due to the cationic complex 36 after five hours, indicating that chloride for carbonyl replacement in the cis-$\text{W}(\text{CO})_2$ species is rapid ($t_{1/2} = 2$ h). The phenyl up isomer, 38', is the kinetically favoured reaction product, present in appreciable quantities within fifteen minutes of reagent combination, but the concentration of this species is depleted by slow isomerisation to give an equilibrium mixture of both the phenyl down (38) and phenyl up (38') isomers ($K_{eq}[38']/[38] = 1.08$ at 25 °C based on peak intensities at this time).

Initial preference for the phenyl up conformation of $[\text{W}(\eta^2-i\text{-PrSeC}=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^\ast]$ may reflect an alliance between the constructive interactions involving the chalcogen lone pair and parallel carbonyl ligand and the weakly attractive $\pi$-interactions of the aromatic rings of the pyrazolyl and alkyne ligands. The thermodynamic preference for this isomer is, however, very small, and it is suggested that the near equal stability of the phenyl down rotamer reflects the generally observed preference of the alkyne chalcogen complexes for placing the chalcogen fragment in the pocket created by the cis-pyrazolyl arms, as was observed crystallographically for the cis-dicarbonyl cationic complexes 35–37.
Figure 4.16. Aromatic region from an arrayed $^1$H NMR experiment monitoring the formation of 38 and 38' from 36 with [Bu$_4$N]Cl in CD$_2$Cl$_2$ at 25 °C. Green asterisk denotes 36, red asterisk denotes 38, blue asterisk denotes 38'.
4.6 Electronic spectra

Visible and ultraviolet spectra are associated with the transitions between electronic energy levels, typically between a bonding or occupied non-bonding orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength of absorption is thus a measure of the separation of the energy levels of the orbitals concerned. The electronic transitions of the alkynes, \( i\text{-PrEC}=C\text{Ph} (E = O, S, Se, Te) \), and those of their metal complexes should thus allow for a direct assessment of the role of the heteroatom in the \( \pi \)-framework.

| Table 4.6. Electronic absorption data for the free alkynes* |
|-----------------|-----------------|
| Alkyne          | \( \lambda_{\text{max}} \) nm (\( \varepsilon \), M\(^{-1}\) cm\(^{-1}\)) |
| \( i\text{-PrOC}=C\text{Ph} \) | 249 (11 930) |
| \( i\text{-PrSC}=C\text{Ph} \) | 242 (13 140), 264 (10 280) |
| \( i\text{-PrSeC}=C\text{Ph} \) | 250 (10 850), 263 (8 820) |
| \( i\text{-PrTeC}=C\text{Ph} \) | 255 (12 570), 269 (10 760), 291 (8 855), 350 (10 930) |

* Data are reported from CH\(_2\)Cl\(_2\). Approximate [conc.]: 4 \times 10\(^{-3}\) M.

The UV-visible absorption spectra of all compounds were recorded in dichloromethane in the range 240–800 nm. The free alkynylchalcoethers all absorb strongly in the UV region (Table 4.6) and exhibit closely similar absorption maxima with weakly-structured bands. The spectra are characterised by intense, Laporte-allowed \( \pi-\pi^* \) transitions near 250 nm, with shoulders near 260 nm, and tails extending to 400 nm. As the basicity of the chalcogen atom increases, the finer structure in the absorptions becomes more apparent, with the greatest band separation and the longest wavelength of absorption at 350 nm observed for 37.

The energy level calculations in Section 4.2 predict that the incorporation of more \( \pi \)-basic chalcogen atoms into the alkyne framework leads to attenuation of the HOMO/LUMO energy gap and the experimental results agree well with this prediction. The introduction of increasingly strong electron donor groups ER (\( E = O < S < Se < Te \)) results in a bathochromic shift of all observed transitions, which can be directly correlated to an extension of the conjugation of the \( \pi \)-system attributable to the auxochrome nature of the chalcogen atoms, i.e., the interaction of a lone pair of electrons with the \( \pi \)-orbital system of the triple bond.

The heteroalkyne complexes \([W(\eta^2-i\text{-PrEC}=C\text{Ph})(CO)_2Tp^*][\text{BF}_4] (E = O, S, Se, Te)\) are vividly coloured, as is typical of \([W(\eta^2-RC=CR)(L)(CO)Tp^*]\) compounds. The oxygen-, sulfur-, and selenium-containing salts are the typical bright green colour but a dramatic colour change to orange occurs upon coordination of the alkynyltelluroether. The absorption maxima that produce the brilliant visible green colours range from 14 900 to 15 500 cm\(^{-1}\) (\( \lambda_{\text{max}} \) av 657 nm) with \( \varepsilon \) between 135 and 185 M\(^{-1}\) cm\(^{-1}\) (Table 4.7, Figure 4.17 a) (NB: the colour of the tellurium
analogue is dictated by the strong absorption near 480 nm with $\varepsilon$ 8200 M$^{-1}$ cm$^{-1}$, as discussed below). A similar absorption near 700 nm is observed for a variety of $[W(\eta^2-R\text{C}=\text{CR})(L)(CO)Tp^*]$ compounds.$^{5,6}$ The low extinction coefficient and insensitivity of the energy of this transition to the nature of the alkyne is consistent with its assignment as the HOMO to LUMO transition localised in the $d\pi$ manifold of the $d^4$ tungsten centre, i.e., a symmetry-forbidden $d-d$ transition involving orbitals not directly involved in metal–alkyne bonding.

**Table 4.7.** Electronic absorption data for the alkyne complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda$, nm</th>
<th>$\varepsilon$, M$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_1$</td>
<td></td>
</tr>
<tr>
<td>(34/34')</td>
<td>646 (152)</td>
<td>368 (18 100)</td>
</tr>
<tr>
<td>(35)</td>
<td>650 (135)</td>
<td>401 (14 410)</td>
</tr>
<tr>
<td>(36)</td>
<td>661 (138)</td>
<td>422 (11 960)</td>
</tr>
<tr>
<td>(37)</td>
<td>674 (183)</td>
<td>481 (8290)</td>
</tr>
<tr>
<td>(38/38')</td>
<td>694 (144)</td>
<td>345 (8040)</td>
</tr>
</tbody>
</table>

$^a$ Data are reported from CH$_2$Cl$_2$, approximate [conc]: $^b$ 4 x 10$^{-5}$ M; $^c$ 7.5 x 10$^{-5}$ M.

**Figure 4.17.** UV-visible spectra of the salts $[W(\eta^2-J\text{PrEC}=\text{CPh})(CO)Tp^*][\text{BF}_4]$ (E = O --; S --; Se --; Te --) recorded in CH$_2$Cl$_2$. **a**) $d-d$ transitions; **b**) LMCT transitions.

In addition to the Laporte-forbidden $d-d$ transition, each of the complexes possesses intense, unresolved absorptions in the UV region of the spectrum near 250 nm ($\varepsilon > 20 000$ M$^{-1}$ cm$^{-1}$) as well as a second, less intense absorption between 350 and 500 nm ($\varepsilon_{av} 1400$ M$^{-1}$ cm$^{-1}$). The latter
absorption shifts towards lower energy upon descending Group 16 as displayed in Figure 4.17b. The trend in this second $\lambda_{\text{max}}$ with alkyne substituents suggests that the electronic transition is highly responsive to substituent factors mediated by $\pi_\perp$, favouring its assignment as Laporte-allowed ligand-to-metal-charge-transfer (LMCT) in origin, i.e., involving electron transfer from the filled $\pi_\perp$ orbital of the alkyne to the vacant metal d$\pi$ orbital. In the case of the tellurium auxochromes, extensive conjugation results in the LMCT absorption stretching strongly into the visible region of the spectrum ($\lambda_{\text{max}} = 481$ nm, $\varepsilon = 820$ M$^{-1}$ cm$^{-1}$), which accounts for the observed orange colouration of $[\text{W}(\eta^2-\text{i-PrTeC}C\text{Ph})(\text{CO})_2\text{Tp}^*][\text{BF}_4]$.

A plot of the observed energies for the two $\lambda_{\text{max}}$ (d–d and LMCT) of the salts 34–37 vs the calculated HOMO/LUMO energy gap in Figure 4.18 reveals the expected monotonic decrease in transition energy.

![Graph](image)

*Figure 4.18.* Energy of electronic transition vs HOMO/LUMO energy gap for $[\text{W}(\eta^2-\text{i-PrEC}C\text{Ph})(\text{CO})_2\text{Tp}^*]$ (— d–d; — LMCT).

Conversion of the cis-$\text{W}($CO$)_2$ cationic species 36 to the neutral complex $[\text{W}(\eta^2-\text{i-PrSeC}C\text{Ph})\text{Cl}($CO$)_2\text{Tp}^*]$ is accompanied by a red-shift for the forbidden d–d transition from 661 nm ($\varepsilon = 138$ M$^{-1}$ cm$^{-1}$) to 695 nm ($\varepsilon = 135$ M$^{-1}$ cm$^{-1}$). The lowered energy of this transition can be attributed to the altered d$\pi$ splitting pattern. Both filled d$\pi$ levels are stabilised by $\pi$-acceptor carbonyl ligands in the cationic 36, but in $[\text{W}(\eta^2-\text{i-PrSeC}C\text{Ph})\text{Cl}($CO$)_2\text{Tp}^*]$, the number of $\pi$-acid ligands is reduced and the HOMO consequently destabilised. The vacant d$\pi$-metal acceptor orbital is similarly driven to higher energy by the increased electron density at the metal centre resulting in a reduction in $\pi_\perp$-to-d$\pi$ donation. The absorption band at 343 nm has tentatively been assigned as the LMCT band for this complex and, as expected, has undergone a blue-shift compared with that of the starting cationic dicarbonyl reagent.
4.7 Summary and conclusions

Systematic variation of the π-system of the alkyne, by the inclusion of substituents of increasing π-donor strength that augment π-conjugation, contributes to an understanding of the influence upon π-bonding properties of this class of compounds. The geometric and spectroscopic data for the series of alkyne complexes \( [W(\eta^2-i-PrEC=\text{CPh})(\text{CO})_2\text{Tp}^*][\text{BF}_4] \) (E = O, S, Se, Te, 34–37), differing only in the identity of the chalcogen atom, provide a firm basis for interpreting the π-donor contribution to bonding in these complexes.

Calculations suggest that the strength of tungsten–alkyne bonding should increase as the heavier chalcogens are incorporated into the ligand. Whilst the π-basicity of the alkyne increases upon successive incorporation of stronger π-donor chalcogens, the π-acid capacity of the alkyne ligand is also increased. Nevertheless, the opposing interactions do not entirely cancel one another. Positive augmentation of the π↓ interaction is the dominant effect and leads to a net increase in the basicity of the alkyne ligands (increasing in the order E = O < S < Se < Te) as evident in the lowering in energy of the \( \nu_{\text{CO}} \) absorptions across the series 34–37.

UV-visible analyses show that the LMCT transition is highly responsive to substituent factors mediated by π↑, decreasing in energy as the π-basicity of the incorporated chalcogen atom increases.

Few trends are apparent in the geometric parameters for the series of salts \( [W(\eta^2-i-PrEC=\text{CPh})(\text{CO})_2\text{Tp}^*][\text{BF}_4] \) (E = O, S, Se, Te, 34–37), with the inter- and intra-molecular stacking of aromatic moieties dictating many of the geometric properties. There is, however, a slight C–C bond contraction noted upon descending Group 16, and a more obvious contraction upon formation of the neutral complex \( [W(\eta^2-i-PrSeC=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^*] \) from 36.

The most commonly found solid state orientation preferentially positions the chalcoether fragment in the pocket created by the cis-pyrazolyl rings. Nevertheless, isolable phenyl up isomers of \( [W(\eta^2-i-PrOC=\text{CPh})(\text{CO})_2\text{Tp}^*][\text{BF}_4] \) and \( [W(\eta^2-i-PrSeC=\text{CPh})\text{Cl}(\text{CO})\text{Tp}^*] \) are present in equal quantities due to stabilisation of this orientation by a constructive, through-space interaction of the lone pair on the chalcogen atom and the \( \pi^* \) orbital of the proximal carbonyl ligand. The orientation of the phenyl up isomers is akin to the situation found for ketenyl complexes containing a competing π-acid ligand in which bonding interactions maximise π-overlap when the chalcogen is proximal to a carbonyl ligand.\(^57\) Available data suggest that the complexes with the phenyl up orientation may experience a decreased
chalcogen contribution to the C–C–E π-system, with the chalcogen atom instead exerting its influence via through-space interactions with the π-system of the proximal carbonyl ligand.
REFERENCES

34. A. C. Filippou, C. Voelkl, W. Gruenleitner, P. Kiprof, Zeitschrift fuer Naturforschung, B: Chemical Sciences 1990, 45, 351.
CHAPTER FIVE

ALKYLIDYNE—ALKYNYL CHALCOETHER COUPLING REACTIONS
5.1 Introduction

Herein are described the reactions that occur between unsaturated alkylidyne bridged iron–molybdenum complexes of the type $[\text{MoFe(µ-CR)}(\text{CO})_2\text{Tp}]$ ($R = \text{C}_4\text{H}_8\text{S}-2, \text{Ph, 31}$) and the alkynyl chalcoethers $R^1\text{EC-}CR^2$ ($R^1 = i\text{-Pr, } R^2 = \text{Ph, } E = \text{S, Se, or Te}$). These were shown to proceed via coupling of the heteroalkyne with the µ-alkylidyne ligand to afford a chromatographically separable mixture of products that includes the compounds $[\text{MoFe}(µ-\text{C}CR^3\text{E})(\text{CO})_4\text{Tp}]$, $[\text{MoFe}(µ-\text{C}CR^3\text{E})(\text{CO})_4\text{Tp}]$, and $[\text{MoFe}(µ-\text{C}CC(\text{R})\text{C(O)})(\text{CO})_4\text{Tp}]$. The latter is especially noteworthy in that its formation involves cleavage of the C(alkyne)–E bond and intramolecular migration of the chalcogenolato Group 16 atom.

The molecular structures of several examples of these novel compounds have been established by X-ray diffraction studies and spectroscopic data for the new complexes are reported and discussed. A mechanistic manifold is presented to account for the variety of products. It is however instructive to begin with an albeit superficial and selective overview of the chemistry of µ-alkylidyne complexes, with particular emphasis on previous relevant work involving their reactions with alkynes.

5.1.1 Chemistry of polynuclear metal complexes with bridging carbyne ligands

The synthetic potential of alkylidyne complexes $[\text{M(=CR)}(\text{CO})_2\text{L}]$ ($M = \text{Mo or W, } R = \text{alkyl or aryl, } L = \text{Cp, Cp* or Tp}$) for the stepwise preparation of di-, tri- and polynuclear transition metal complexes has been impressively demonstrated by Stone (Scheme 5.1). The approach exploits the isobal analogy between the $M=C$ bond of alkylidyne species and the $C=C$ bond of organic alkynes. From this perspective, the unsaturated $M=C$ linkage is considered capable of acting as a ligand towards a vast array of low-valent metal–ligand fragments to afford compounds containing mixed metal–metal bonds (as was discussed for the pyrazolyliborate coligated Group 6 alkylidyne complexes in Chapter 1, Section 1.4.6). In the resultant complexes the $C_1 (µ-\text{CR})$ fragment is simultaneously bound to two or more different transition metals, each possessing their own unique bonding properties, which often results in unusual behaviour towards substrate molecules.

\[ \text{L}_n\text{M}≡\text{C} \rightarrow (i) \text{L}_n\text{M}≡\text{C} \rightarrow (ii) \text{L}_n\text{M}≡\text{C} \]

\[ \text{Scheme 5.1. General addition of a coordinatively unsaturated metal complex to } \left[\text{L}_n\text{M(=CR)}\right] (M = \text{Mo or W, } L_n = (\text{CO})_2\text{Cp, (CO)}_2\text{Cp* or (CO)}_2\text{Tp, } R = \text{aryl or alkyl}). \text{Reagents: (i) ML}_2; \text{(ii) ML}_3. \]

\[ ^\dagger \text{In an effort to aid clarity and understanding of this Chapter, substituents have been denoted by } R^1 \text{ and } R^2 \text{ throughout, rather than the } R' \text{ and } R'' \text{ abbreviations that have been typically employed elsewhere in this thesis.} \]
5.1.2 Alkylidyne–alkyne coupling reactions

Carbon–carbon bond formation via the coupling of alkynes with the bridging alkylidyne unit of polynuclear metal complexes has been an area of particular interest.\textsuperscript{12,15,18-27} The most common product is the dimetalla-allyl ligand (Scheme 5.2), which may bridge two or three metal atoms in the $\sigma,\sigma^\prime + \pi$ bonding mode. An archetypal example is the reaction that occurs between the alkylidyne-bridged heterobimetallic compounds (‘dimetallacycloprenes’) \( [L_xM'W(\mu-C-C_6H_4Me-4)(CO)_2Cp] \) \( (L_xM' = \text{Rh}^\text{η^5-C_5H_5}) \) or \( \text{CoCp}^* \) with disubstituted alkynes \( R^1\text{C}≡\text{CR}^2 \), affording the \( C_3 \) bridged species \( [L_xM'W(\mu-C(C_6H_4Me-4)C(R^1)C(R^2))(CO)_2Cp] \), which can be envisaged as a 14-electron metal fragment $\eta^4$-bound to a tungstacyclobutadiene ring (Scheme 5.2).\textsuperscript{19,23} The structurally related tungsten–iron complexes \( (\text{ML}_x = \text{Fe}(\text{CO})_3) \) may be similarly prepared from the $\mu_3$-CR trimetal clusters \( [\text{Fe}_2W(\mu_3-C_6H_4Me-4)(\mu-CO)(\text{CO})_8Cp] \) via displacement of a carbonyl iron fragment.\textsuperscript{19,28}

![Scheme 5.2](image)

The bridging \( C_3 \) ligand of these complexes can also be found in the related bimetallic compounds \( [\text{CoW}(\mu-C(C_6H_4Me-4)C(R^1)C(R^2))(\text{CO})_7] \), similarly obtained as a result of alkene–alkylidyne coupling, although the dimetal precursors in these syntheses contain terminal alkylidyne ligands, i.e., \( [\text{CoW}(\equiv\text{CR})(\text{CO})_8] \) \( (R = \text{C}_6\text{H}_4\text{Me}-4, \text{Ph} \text{ or } \text{Me}) \) (Scheme 5.2).\textsuperscript{21,29}

The \( C_1 \) group of the alkylidyne-bridged heteronuclear dimetal complexes provides an exceptionally reactive centre and the variety of insertion, coupling and migration processes that have been documented by Stone upon treatment with alkynes amply confirms the possibility of observing novel ligand transformations for this group.\textsuperscript{15,25,26} The reaction of heterobimetallic $\mu$-CR complexes with asymmetrically substituted alkynes \( R^1\text{C}≡\text{CR}^2, R^1 \neq R^2 \) often results in a mixture of complexes with isomeric $\mu$-C(R)C(R$^1$)C(R$^2$) and $\mu$-C(R)C(R$^2$)C(R$^1$) bridges.
Furthermore, in addition to the simple C₃ dimetallaallyl, a number of organic ligands incorporating carbonyl units into the bridging moiety arise from the coupling of μ-CR, C≡C and CO fragments at mixed-metal centres (Scheme 5.3).²⁶,²⁷ A specific example that showcases the remarkable reactivity of these systems is the reaction between the bimetallic species [MoFe(μ-CR)(CO)₅(PMe₃)Cp] and the somewhat nucleophilic alkyne MeC≡CMe, which affords a number of novel complexes arising from alkyne splitting and isomerisation processes together with the incorporation of additional alkyne or CO ligands into the growing organic fragment.²⁵,²⁷

\[
\begin{align*}
\mu\text{-}C\text{R} + R^1\text{C}≡\text{C}R^2 & \rightarrow \mu\text{-}C\text{R}C\text{R}^2C\text{R}^2 \text{ or } \mu\text{-}C\text{R}C\text{R}^2C\text{R}^2 \\
& \rightarrow \mu\text{-}C\text{R}C\text{R}^2C\text{R}^2 \text{ or } \mu\text{-}C\text{R}C\text{R}^2C\text{R}^2 \\
\end{align*}
\]

Scheme 5.3. Representative organic bridging ligands obtained from coupling of μ-CR, alkynes and CO at dimetal centres. (i) + CO; (ii) − CO.

### 5.1.3 Cluster chemistry of alkylnyl chalcoethers

The synthetic versatility of alkylnyl thioethers in cluster chemistry has been convincingly demonstrated. With iron carbonyl fragments the reactivity of the symmetrical alkyne MeSC≡CSMe is dominated by the triple bond;³⁰,³¹ treatment with either [Fe₂(CO)₉] or [Fe₂(CO)₁₂] results in coupling of two MeSC≡CSMe units and concomitant incorporation of a CO ligand to afford the cyclopentadienone-containing complex [Fe(CO)₂₅O≡CC₄(SMe)₄].³₀ In a similar manner, Raubenheimer and co-workers reported the formation of the ferrole complex [Fe₂(CO)₆₅C₄(SMe)₄] from the reaction of [Fe(CO)₅] and MeSC≡CSMe under irradiation.³¹

Jeannin and co-workers have explored the reactions of the asymmetric alkylnyl thioethers EtSC≡CR (R = alkyl or aryl) with iron and ruthenium carbonyls. In each case, both alkyne coupling processes and facile rupture of the S–C(alkyne) (S–Cₚ) bond were observed, the latter generating several polynuclear complexes containing (SEt) and (C≡CR) ligands.³²,³⁵ For example, the complex [Fe₂(μ-SEt)(μ-C≡CR)(CO)₅] could be isolated from the reaction of [Fe₂(CO)₅] and EtSC≡CR and this bimetallic species was found to undergo further reactions with electron-rich molecules. Of most relevance to this work is the reaction between [Fe₂(μ-SEt)(μ-C≡CR)(CO)₅] and the alkynes PhC≡CPh and EtSC≡CPh, each of which proceeded via the formation of two C–C bonds to the incoming alkyne, one with the Cₐ acetylide carbon and one with a carbonyl group, and concomitant migration of the μ-SEt group.
from a bridging site to the C₈ position of the acetylide ligand (Scheme 5.4). In contrast, the aminoalkyne CH₃C≡CNEt₂ afforded a complex best described as a ferracyclopentadienyl fragment that was ligated to a second iron atom by a Fe–Fe bond and an allylic linkage.

Scheme 5.4. Synthesis of [Fe₂(µ-SEt)(µ-C≡CR)(CO)]₆ and reactivity with electron-rich alkynes. R = Me or Ph. [Fe] = Fe(CO)₅. (i) R¹ = R² = Ph; (ii) R¹ = SEt, R² = Ph; R¹ = Ph, R² = SEt; (iii) R¹ = Me, R² = NEt₂.

More recently, Delgado and co-workers have reported trinuclear ruthenium complexes of the type [Ru₃(CO)₁₂(µ-η²-SC≡CR¹)(µ-η²-C≡CR²)] (R¹ = SiMe₃, R² = Si(i-Pr); R¹ = Si(i-Pr), R² = SiMe₃; R¹ = Si(i-Pr), R² = H; R¹ = H, R² = Si(i-Pr)₃), obtained by cleavage of one of the two S–Cₛₛ bonds of the precursor bis(alkynyl) thioether R¹C≡CSC≡CR² in the presence of [Ru₃(CO)₁₂]. These compounds have been used as precursors for a number of clusters of either higher or lower nuclearity from cleavage of the remaining S–Cₛₛ bond and C–C coupling reactions.

In view of the established reactivity of the µ-CR ligand of heterobimetallic complexes towards alkynes (vide supra) and the rich cluster chemistry of sulfur-substituted alkynes, the latter often being characterised by cleavage of the S–C(alkyne) bond, explorations into the reactivity of the alkynyl chalcocethers R¹EC≡CR² (R¹ = i-Pr, R² = Ph, E = S, Se, or Te; R¹ = Ph, R² = SiMe₃ – see Chapter 4) towards bridging alkylidyne complexes of the type [MoFe(µ-CR)(CO)₅Tp] were undertaken with the expectation of obtaining novel products in which rupture of the E–C(alkyne) bond might be induced, in addition to the more conventional alkyn−alkylidyne coupling reactions.
5.2 Reaction between [MoFe(μ-CC₄H₃S-2)(CO)₅Tp] and i-PrEC=CPH (E = S, Se, Te)

In dichloromethane at room temperature, the reaction between the coordinatively unsaturated molybdenum–iron complex [MoFe(μ-CC₄H₃S-2)(CO)₅Tp] (31) with the asymmetrically substituted alkynyl chalcocether i-PrSeC=CPH slowly (4 days) affords a complex mixture of alkylidyne–alkyne coupled products from which highly coloured golden-yellow (40), golden-brown (41) and maroon (42) compounds may be isolated in modest yields following careful cryostatic chromatography (silica gel, −33 °C) (Scheme 5.5). Compound 31 reacts with i-PrSC=CPH under similar conditions to yield a mixture of the related species 43, 44 and 45. In contrast, the reaction between 31 and i-PrTeC=CPH yields the maroon complex 46 as the major isolable product.

\[
\begin{array}{c}
Tₚ(CO)₂Mo≡C−R \quad \xrightarrow{\text{(i)}} \quad Tₚ(CO)₂Mo\overset{\text{Fe(CO)}}{=}C−R \quad \xrightarrow{\text{(ii)}} \quad Tₚ(CO)₂Mo\overset{\text{Fe(CO)}}{=}C\overset{\text{E}}{=}C−R
\\
\end{array}
\]

Scheme 5.5. Principal products obtained from reaction of [MoFe(μ-CR)(CO)₅Tp] (R = C₄H₃S-2) with alkynyl chalcocethers. Reagents and conditions: (i) [Fe₂(CO)₉], diethyl ether (ii) R¹E=CR² (E = S, Se, or Te; R¹ = i-Pr; R² = Ph), CH₂Cl₂.

The distribution and identity of products obtained from the reaction between the heterobimetallic μ-alkylidyne species and the alkynyl chalcocethers is sensitive to both the reaction temperature and duration. Attempts to accelerate the transformations by heating were generally unsuccessful, resulting in a reduction of product selectivity to afford only trace quantities of the principal products (Scheme 5.5) together with a large number of uncharacterised compounds. Prolonged reaction times similarly appear to impact significantly upon both the composition and number of products formed, though substantial formation of 42, 45 and 46 was a recurrent feature (thin layer chromatography, up to 2 months). In dichloromethane solution, meticulous monitoring of the reaction progress allows for the
identification of 7 days as the point at which the formation and recovery of the three key compounds is optimised and it is at this point that the coupling reactions were halted.

Variations of the ligand properties of the alkynyl chalcoethers i-PrEC=CPH (E = S, Se or Te) upon chalcogen substitution were discussed in Chapter 4 and by employing the sulfur, selenium and tellurium containing alkyne derivatives it is in principle possible to further demonstrate differences between the reactivity and structural chemistry of the resulting complexes arising from the comparative strengths of the carbon–chalcogen bonds. Indeed, the product distribution for the alkynyl telluroether, having the weakest E–C bond, is notably different from those of the related thio- and seleno- derivatives which exhibit essentially identical reaction courses.

5.2.1 Carbon–carbon bond formation and chalcogenolate migration

The gold-coloured complexes

The formulation of the golden-yellow (40) and golden-orange (43) complexes as the alkylidyne–alkyne coupled products of the type [MoFe{µ-C(C₆H₄Me-4)C(Ph)C(Ph)}(CO)₃Cₚ] (E = Se, 40 or S, 43) followed from spectroscopic data (Tables 5.1 and 5.2) that are remarkably consistent with one another. In the case of 40 the formulation was confirmed by a crystallographic study (vide infra). The solution infrared spectrum of each compound features two strong and two weak absorptions (2049s, 1980s(br), 1863w, 1825w cm⁻¹ for 40 and 2049s, 1980s(br), 1865w, 1826w cm⁻¹ for 43), which are resolved into the expected five \( \nu_{\text{CO}} \) bands in the solid state spectrum. These data mirror the infrared intensity profile observed for the related purely hydrocarbon C₃-bridged heteronuclear complexes [MoFe{µ-C(C₆H₄Me-4)C(Ph)C(Ph)}(CO)₃Cₚ] (\( \nu_{\text{CO}} \) 2051s, 1992s, 1966w, 1940w cm⁻¹) and [WFe{µ-C(C₆H₄Me-4)C(Me)C(Me)}(CO)₃Cₚ] (\( \nu_{\text{CO}} \) 2041s, 1981s, 1961w, 1925w cm⁻¹). While in the latter complexes all carbonyl ligands are terminal, as was confirmed by an X-ray crystallographic study of [WFe{µ-C(C₆H₄Me-4)C(Me)C(Me)}(CO)₃Cₚ], the low frequency \( \nu_{\text{CO}} \) absorption for 40 and 43 (ca. 1825 cm⁻¹) is clearly indicative of a semi-bridging \( \mu\)-CO ligand.

Examination of the \(^1\)H NMR and \(^{13}\)C{\(^1\)H} NMR spectroscopic data for 40 and 43 reveal the diastereotopic nature of the isopropyl methyl groups (\( \delta \) 2.81(septet), 1.11(d), 0.88(d) for 40 and 2.83(septet), 1.02(d) and 0.73(d) for 43 for i-PrCH and i-PrCH\(_3\), respectively), consistent with the lack of symmetry in the molecules. The \( \mu\)-C nuclei of the newly formed C₃ fragment resonate, for each complex, at \( \delta \) 144.3, 120.7 and 114.2 (40) and 143.6, 123.7 and 114.3 (43) [\( \mu\)-C(Ph)C(Ei-Pr)C(C₆H₄S-2)]. The modest shielding noted for the central carbon of 40 relative to 43 is as might be expected for the carbon carrying the more electron rich selenium atom.
Assignments for the \( \mu\)-C nuclei were substantiated by two-dimensional HMBC experiments. Thus for 40, the \( \mu\)-C resonance at \( \delta_C 114.2 \) is strongly correlated to the \( ^1H \) NMR thienyl resonance at \( \delta_H 7.20 \) and that at \( \delta_C 120.7 \) weakly correlated to that for the i-PrCH proton of the isopropyl substituent (\( \delta_H 2.81 \)).

A comparison of these data with those for the C\(_3\) nuclei of Stone’s related complex [MoFe\{\( \mu\)-C(C\(_6\)H\(_4\)Me-4)C(Et)C(Et)\}]\((\mu\)-CO\)\)_\(5\)Cp] (\( \delta_C 125.2, 129.0, 115.8 \),\(^{26}\) in which the ligand spanning the Mo–Fe bond is \( \eta^3\)-coordinated to iron, suggests that the manner in which the organic chain traverses the metal–metal bond in 40 and 43 departs from that typically observed for such complexes (Scheme 5.6 and Scheme 5.2, vide supra). Indeed, data for 40 and 43 are more consistent with those of the complex [MoFe\{\( \mu\)-C(C\(_6\)H\(_4\)Me-4)C(Et)C(Et)\}]\((\mu\)-CO\)\)_\(5\)Cp] (\( \delta_C 157.9, 130.2, 106.8, 226.3 \))\(^{8}\) that arises from carbonylation of the former compound. The insertion of a CO ligand into an Fe–C bond is accompanied by a change in the nature of the C(R)C(Et)C(Et) fragment from \( \eta^1\)-coordination to iron to \( \eta^3\)-coordination to molybdenum (Scheme 5.6).\(^{26}\)

![Scheme 5.6. Carbonylation of the complex [MoFe{\( \mu\)-C(R)C(Et)C(Et)\}]\((\mu\)-CO\)\)_\(5\)Cp] (R = C\(_6\)H\(_4\)Me-4).](image)

Three carbonyl resonances are evident in the \( ^{13}\)C\{\( ^1\)H\} NMR spectra for 40 and 43, two of which may be assigned to the molybdenum carbonyls (\( \delta_C 238.9 \) and 231.1 for 40 and 240.9 and 231.6 for 43). The remaining broad resonance is attributable to the Fe(CO)_\(3\) moiety, which experiences rapid carbonyl site exchange on the \( ^{13}\)C\{\( ^1\)H\} NMR time-scale (ambient temperature).

The X-ray structural analysis of 40 unambiguously established its identity as [MoFe\{\( \mu\)-C(C\(_4\)H\(_3\)S-2)C(Si-Pr)C(Ph)\}]\((\mu\)-CO\)\)_\(5\)Tp] (Figure 5.1) and immediately confirms the most interesting feature of the structure, i.e., the nature of coordination of the C\(_3\) fragment arising from alkylidyne–alkynylselenoether coupling. As was suspected on the basis of spectroscopic data, the bridging carbon chain is best described as being \( \eta^3\)-bound to the

---

\(^{8}\) Multi-dimensional NMR spectroscopy was not routinely available at the time of this report complicating unequivocal assignments for these resonances. On the basis of evidence obtained in this work, it is likely that the resonances actually correspond to [\( \mu\)-C(Et)C(Et)C(C\(_6\)H\(_4\)Me-4)C(O)\]. The comparative chemical shifts of these nuclei nevertheless remain diagnostic of structural similarity, irrespective of the specific assignments.
molybdenum (Mo–C(1) 2.328(2), Mo–C(2) 2.389(2), Mo–C(3) 2.377(2) Å) and linked to the Fe by two σ bonds (Fe–C(1) 2.022(2), Fe–C(3) 1.987(2) Å). As a consequence of the bonding behaviour, a strongly semi-bridging carbonyl is present in 40 (Mo–C(20)–O(20) 159.2(2)°, Fe–C(20) 2.376(3) Å), which serves to alleviate the electron-rich iron centre.

Figure 5.1. a) Molecular structure of 40 and b) depiction of the inner coordination sphere with thienyl, phenyl and pyrazolyl aromatic rings omitted, in addition to the carbonyl ligands of the molybdenum centre. 30% displacement ellipsoids are drawn and hydrogen atoms have been omitted. Selected distances (Å): Mo–Fe 2.7208(4), Mo–C(1) 2.328(2), Mo–C(2) 2.389(2), Mo–C(3) 2.377(2), Mo–N(21) 2.234(2), Mo–N(31) 2.230(2), Mo–N(41) 2.216(2), Mo–C(20) 1.975(3), Mo–C(30) 1.983(3), Fe–C(1) 2.022(2), Fe–C(3) 1.987(2), Fe–C(20) 2.376(3), Fe–C(40) 1.810(3), Fe–C(50) 1.822(3), Fe–C(60) 1.778(3), C(1)–C(2) 1.428(3), C(2)–C(3) 1.400(3), C(3)–C(4) 1.473(3), Se–C(2) 1.937(2), Se–C(61) 1.983(3). Selected angles (°): Mo–C(1)–Fe 77.07(8), Mo–C(2)–Fe 67.06(6), Mo–C(3)–Fe 76.56(8), Mo–C(1)–C(11) 136.1(2), Fe–C(1)–C(11) 130.0(2), Mo–C(2)–Se 128.8(1), Fe–C(2)–Se 164.1(1), Mo–C(3)–C(4) 130.0(2), Fe–C(3)–C(4) 133.9(2), C(2)–C(3)–C(4) 126.1(2), C(1)–Mo–C(2) 35.2(8), C(2)–Mo–C(3) 34.17(8), C(1)–Fe–C(3) 67.2(1), Fe–C(1)–C(2) 92.8(2), C(1)–C(2)–C(3) 103.4(2), C(2)–C(3)–Fe 95.1(2), C(2)–C(1)–C(11) 127.0(2), C(1)–C(2)–Se 128.6(2), C(3)–C(2)–Se 127.2(2), C(2)–Se–C(61) 96.8(1), OC–Mo–CO 86.2(1), N(21)–Mo–N(31) 86.61(8), N(21)–Mo–N(41) 77.08(8), N(31)–Mo–N(41) 78.24(8), Mo–C(20)–O(20) 159.2(2), Mo–C(30)–O(30) 173.7(2).
A number of complexes bearing metal–metal bonds bridged by C$_3$ fragments formed from μ-CR and C=C couplings have been structurally characterised, including [MoFe{μ-C(C$_6$H$_4$Me-4)C(OMe)CH}(CO)$_5$Cp],$^{16}$ [WFe{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_5$Cp],$^{23}$ [WRh{μ-C(C$_6$H$_4$Me-4)C(Ph)C(Ph)}(CO)$_2$Cp(η$^5$-C$_6$H$_5$)]$^{28}$ and [MoFe{μ-C(C$_6$H$_4$Me-4)C(=O)Me}C(Ph)C(Ph)}(CO)$_5$Cp].$^{26}$ Geometric parameters for the central core are similar for each, and those of 40 agree well with the established precedent, e.g., for the related complex [MoFe{μ-C(C$_6$H$_4$Me-4)C(Me)C{C(=O)Me}}(CO)$_5$Cp] the Mo–Fe separation (2.722(1) Å) is statistically equivalent to that of 40 (2.7208(4) Å). The internal ‘allyl’ C–C–C angle is similarly in close agreement (101.5(3)$^\circ$ vs 103.4(2)$^\circ$ for 40).$^{26}$ However, for each documented case the arrangement of the C$_3$ fragment is such that it is attached to the Group 6 metal by the two terminal carbon atoms (Scheme 5.7).

\[
\text{(a) } \text{MoFe(CO)}_5\{\mu-CR\} \quad \text{FeC(CO)}_5\text{Mo} \\
\text{(b) } \text{MoFe(CO)}_5\{\mu-CR\} \quad \text{FeC(CO)}_5\text{Mo} \\
\text{(c) } \text{Fe(CO)}_5\{\mu-CR\} \quad \text{FeC(CO)}_5\text{Mo} \\
\text{(d) } \text{Fe(CO)}_5\{\mu-CR\} \quad \text{FeC(CO)}_5\text{Mo}
\]

Scheme 5.7 Iron and molybdenum sites on the polyhedral cores of various binuclear complexes. The ‘allylic’ component is indicated in bold (R = C$_6$H$_4$Me-4). The alkylidyne and alkyne components are depicted in blue and red, respectively. (a) [MoFe{μ-CR}CMeC{C(=O)Me}](CO)$_5$Cp; (b) [MoFe{μ-CR}CMeC{C(=O)Me}](CO)$_5$Cp; (c) Compound 40; (d) Compound 41.

Given the isolobal relationship between Fe(CO)$_5$ and [CH]$,^4$ the central core of 40 may be envisaged as a ferracyclobutadiene ring η$^4$-bound to the ‘Mo(CO)$_5$’ group, however, due to the metal–metal bond which is necessarily longer than the molybdenum–carbon distances in the C$_3$ bridge, the C(1)–C(2)–C(3)–Fe ring is not planar (mean deviation 0.06 Å). The C(2)–C(3) bond length (1.400(3) Å), is 9 σ shorter than the corresponding C(1)–C(2) separation (1.438(3) Å). Typically, C–C separations for the C$_3$ bridges spanning heteronuclear metal–metal bonds exhibit comparable bond lengths, e.g., [MoFe{μ-C(C$_6$H$_4$Me-4)C(OMe)CH}(CO)$_5$Cp] (1.427(5) Å)$^{26}$ and [WFe{μ-C(C$_6$H$_4$Me-4)C(OMe)CH}(CO)$_5$Cp] (1.440(8) and 1.435(8) Å),$^{23}$ and data for 40 indicate the retention of considerable multiple bond character for the (former) alkyne unit.

The brown-coloured complexes

Alternative examples of alkylnyl chalcogen/thioalkylidyne coupling products could also be isolated from the reaction between 31 and i-PrSe=CPh or i-PrSC=CPh following elution of the chromatography columns with tetrahydrofuran–hexane eluant (Scheme 5.5). The golden-brown
complexes thus attained were formulated as the $\mu$-CR/C=C/CO coupled products [MoFe{µ-C(Ei-Pr)C(Ph)C(C,H$_3$S-2)C(=O)}(CO)$_4$Tp] (E = S, 44, or Se, 41), corresponding to the reverse orientation of the unsymmetrically substituted alkyne during C–C/Mo–C coupling attended by the insertion of a CO ligand.

Spectroscopic data for the seleno- and thio- derivatives, 41 and 44, (Table 5.1 and 5.2) are again highly consistent with one another. The solution infrared spectrum of each closely resembles those of 40 and 43 (vide supra) (2046s, 1983m, 1882w for 41 and 2047s, 1983m, 1884w cm$^{-1}$ for 44), however, these absorptions are not resolved into five separate bands in the solid state spectrum (KBr). $^1$H NMR spectroscopy for each of the complexes revealed the diastereotopic nature of the isopropyl methyl groups, however, the i-PrCH resonances are distinctly shifted upfield of those for 40 and 43 ($\delta$ 2.40 vs 2.81 for E = Se 41; 2.41 vs 2.83 for E = S 44).

Mass spectral data for 41 included a molecular ion consistent with the formulation as the suspected complex [MoFe{µ-C(Ph)C(Sei-Pr)C(C,H$_3$S-2)C(=O)}(CO)$_5$Tp]. The strongest daughter ion corresponded to [M – 4CO – i-Pr]$^+$, with no evidence for the loss of the final carbonyl ligand – presumably that involved in the ketone metallacycle. In the $^{13}$C{$^1$H} NMR spectrum of 41, in addition to the ipso carbons of the thiophenyl and phenyl rings, quaternary carbon resonances were identified at $\delta$ 238.1, 234.5, 218.5, 128.6, 111.2 and 87.2. The resonance at $\delta$ 218.7 was readily attributed to the carbonyls of an Fe(CO)$_3$ unit and the more downfield resonances ($\delta$ 238.1 and 234.5) were consistent with inequivalent molybdenum terminal and acyl carbonyl groups, the low-field position being somewhat characteristic of a semi-bridging functionality, e.g., the $\mu$-CO carbon for the complex [MoFe{µ-C(C$_6$H$_4$Me-4)C(Et)C(Et)(=O)}(µ-CO)(CO)$_4$Cp] resonates at $\delta$ 240.26 Two-dimensional HMBC experiments allowed for the identification of the resonances at $\delta$ 111.2 and 87.2 as the $\mu$-CPh and $\mu$-CC$_4$H$_3$S-2 carbons, respectively. The remaining resonance ($\delta$ 128.6) was thus attributed to $\mu$-CSe.
Table 5.1. Selected infrared data for molybdenum–iron complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>ν_{CO}, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(31) [MoFe(μ-CR³)(CO)₃Tp]</td>
<td>black</td>
<td>2048s, 1897m, 1965m, 1925w, 1860w</td>
</tr>
<tr>
<td>(39) [MoFe(μ-CR₃)(CO)₃Tp]</td>
<td>purple</td>
<td>2049s, 1888s, 1965s, 1925m, 1861w</td>
</tr>
<tr>
<td>(47) [MoFe(μ-CR₃)(η²-R²SeC=CR²)(CO)₃Tp]</td>
<td>brown</td>
<td>2027s, 2000s, 1991s, 1964m, 1940m</td>
</tr>
<tr>
<td>(43) [MoFe{μ-C(R³)(SR³)(R²)}(μ-CO)(CO)₄Tp]</td>
<td>orange</td>
<td>2049s, 1980s, 1865w, 1826w</td>
</tr>
<tr>
<td>(40) [MoFe{μ-C(R³)(SeR³)(R²)}(μ-CO)(CO)₄Tp]</td>
<td>yellow</td>
<td>2049s, 1891s, 1863w, 1825w</td>
</tr>
<tr>
<td>(48) [MoFe{μ-C(R³)(SeR³)(R²)}(μ-CO)(CO)₄Tp]</td>
<td>orange</td>
<td>2048s, 1983s, 1862w, 1826w</td>
</tr>
<tr>
<td>(44) [MoFe{μ-C(R³)(SR³)(R²)(CO)}(CO)₃Tp]</td>
<td>brown</td>
<td>2047s, 1983m, 1848w</td>
</tr>
<tr>
<td>(41) [MoFe{μ-C(SeR³)(R³)(R²)(CO)}(CO)₄Tp]</td>
<td>brown</td>
<td>2046s, 1983m, 1832w</td>
</tr>
<tr>
<td>(45) [MoFe{μ-C(R³)(C(R³)(SR³)}(CO)₄Tp]</td>
<td>maroon</td>
<td>1992s, 1952s, 1929m, 1834w</td>
</tr>
<tr>
<td>(42) [MoFe{μ-C(R³)(C(R³)(SeR³)}(CO)₄Tp]</td>
<td>maroon</td>
<td>1991s, 1952s, 1927m, 1834w</td>
</tr>
<tr>
<td>(46) [MoFe{μ-C(R³)(C(R³)(TeR³)}(CO)₄Tp]</td>
<td>maroon</td>
<td>1988s, 1950s, 1927m, 1833w</td>
</tr>
<tr>
<td>(49) [MoFe{μ-C(R³)(CC(R³)(SeR³)}(CO)₄Tp]</td>
<td>maroon</td>
<td>1989s, 1948s, 1926s, 1832w</td>
</tr>
</tbody>
</table>

Infrared data measured in CH₂Cl₂ solution. R¹ = C₄H₉S-2; R² = Ph; R³ = i-Pr.

Table 5.2. Selected \(^{13}\)C{\(^{1}\)H} NMR data for molybdenum–iron complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ_C, ppm</th>
<th>δ_MoCO</th>
<th>δ_FeCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(31) [MoFe(μ-CR³)(CO)₃Tp]</td>
<td>392.1</td>
<td>230.4</td>
<td>213.5</td>
</tr>
<tr>
<td>(39) [MoFe(μ-CR₃)(CO)₃Tp]</td>
<td>422.3</td>
<td>231.0</td>
<td>213.2</td>
</tr>
<tr>
<td>(47) [MoFe(μ-CR₃)(η²-R²SeC=CR²)(CO)₃Tp]</td>
<td>323.9</td>
<td>228.7</td>
<td>213.7, 216.6, 210.1</td>
</tr>
<tr>
<td>(43) [MoFe{μ-C(R³)(SR³)(R²)}(μ-CO)(CO)₄Tp]</td>
<td>143.6, 123.7, 114.3</td>
<td>240.9, 209.2</td>
<td></td>
</tr>
<tr>
<td>(40) [MoFe{μ-C(R³)(SeR³)(R²)}(μ-CO)(CO)₄Tp]</td>
<td>144.3, 120.7, 114.2</td>
<td>238.9, 209.7</td>
<td></td>
</tr>
<tr>
<td>(48) [MoFe{μ-C(R³)(SeR³)(R²)(μ-CO)(CO)₄Tp]</td>
<td>130.0, 129.4</td>
<td>233.3, 210.9</td>
<td></td>
</tr>
<tr>
<td>(41) [MoFe{μ-C(SeR³)(C(R³)(R²)(CO)}(CO)₄Tp]</td>
<td>238.1, 187.2, 111.2, 128.6</td>
<td>234.5, 218.7</td>
<td></td>
</tr>
<tr>
<td>(45) [MoFe{μ-C(R³)(CC(R³)(SR³)}(CO)₄Tp]</td>
<td>118.9, 89.9, 111.6</td>
<td>236.8, 221.6</td>
<td></td>
</tr>
<tr>
<td>(42) [MoFe{μ-C(R³)(CC(R³)(SeR³)}(CO)₄Tp]</td>
<td>118.9, 80.3, 115.0</td>
<td>236.5, 221.8</td>
<td></td>
</tr>
<tr>
<td>(46) [MoFe{μ-C(R³)(CC(R³)(TeR³)}(CO)₄Tp]</td>
<td>118.9, 86.8, 114.5</td>
<td>235.5, 221.7</td>
<td></td>
</tr>
<tr>
<td>(49) [MoFe{μ-C(R³)(CC(R³)(SeR³)}(CO)₄Tp]</td>
<td>123.9, 221.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{13}\)C{\(^{1}\)H} NMR spectra measured in CD₂Cl₂ solution. R¹ = C₄H₉S-2; R² = Ph; R³ = i-Pr. "Due to the proximity of these resonances, the μ-CPh and μ-CSe carbons could not be unambiguously distinguished from 2D experiments, though the more shielded resonance has been tentatively attributed to μ-CSe, see text."

The precise nature of the products 41 and 44 was not unequivocally deduced from the spectroscopic data and hence a single crystal diffraction study of 44 was undertaken, the results
of which are summarised in Figure 5.2. The molecular geometry of 44 revealed a structure based on a molybdacyclopentadienone fragment (see also Scheme 5.7d) that is bound to the Fe(CO)$_3$ unit by a Mo–Fe bond and three adjacent carbon atoms. The latter comprise a pseudo-allylic linkage, which is reminiscent of the geometry of the diiron cluster [Fe$_2$(µ-[C(O)SEt]C(Ph)C(Me)C(NEt$_2$))(CO)$_6$] described by Jeannin and co-workers (Scheme 5.4).$^{35}$

![Figure 5.2](image_url)

Figure 5.2. a) Molecular geometry of [MoFe{µ-[Si-Pr]C(Ph)C(C$_4$H$_3$S-2)C(O)}(CO)$_4$Tp] (44) in a crystal of 44•CH$_2$Cl$_2$ and b) depiction of the inner coordination sphere with thienyl, phenyl and pyrazolyl aromatic rings and the molybdenum carbonyl omitted. Selected distances (Å): Mo–Fe 2.9095(5), Mo–S 2.5362(7), Mo–C(3) 2.011(3), Mo–C(20) 2.038(4), Mo–C(30) 2.240(3), Mo–N(21) 2.237(2), Mo–N(31) 2.236(2), Mo–N(41) 2.198(2), Fe–C(1) 2.143(3), Fe–C(2) 2.087(3), Fe–C(3) 2.026(3), Fe–C(40) 1.805(4), Fe–C(50) 1.814(4), Fe–C(60) 1.779(4), C(30)–C(1) 1.503(4), C(1)–C(2) 1.447(4), C(2)–C(3) 1.398(4), C(3)–S 1.740(3), S–C(61) 1.849(3), O(20)–C(20) 1.053(4), O(30)–C(30) 1.222(3). Selected angles (°): Mo–C(3)–Fe 92.2(1), Mo–C(3)–S 84.7(2), Mo–C(3)–C(2) 132.5(2), Mo–C(30)–C(1) 115.6(2), Mo–C(20)–O(20) 171.8(3), Mo–C(30)–O(30) 125.3(2), Fe–C(3)–S 124.7(2), Fe–C(2)–C(4) 130.5(2), C(40)–Fe–C(50) 122.7(2), C(1)–Fe–C(2) 40.9(1), C(2)–Fe–C(3) 39.7(1), C(3)–C(2)–C(3) 106.6(2), C(30)–C(1)–C(2) 112.8(2), S–Mo–C(3) 43.09(8), C(3)–S–C(61) 107.6(1), N(21)–Mo–N(31) 82.50(9), N(21)–Mo–N(41) 78.04(9), N(31)–Mo–N(41) 83.29(9), C(40)–Fe–C(50) 102.8(2), C(40)–Fe–C(60) 89.9(2), C(50)–Fe–C(60) 96.4(2).
The \( \mu\text{-}C(\text{Si-Pr})\text{C(Ph)C(C}_3\text{H}_5\text{-}2\text{)}\text{C}(=\text{O}) \) chain that spans the considerably elongated Mo–Fe bond (2.9095(5) \( \text{Å} \) for 40) arises from the coupling of one molecule of the alkylene with the bridging alkylidyne group and subsequent insertion of a CO ligand into the molybdenum–carbon framework. The molybdenum centre is attached to the bridging chain by two \( \sigma \) bonds to carbon (Mo–C(30) 2.240(3) \( \text{Å} \) and Mo–C(3) 2.011(3) \( \text{Å} \)) and a dative bond from the pendant thioether (2.5362(7) \( \text{Å} \)). The iron atom formally receives four electrons from the molybdenacycloketone, with the \( \eta^3 \)-coordination by the atoms C(1), C(2) and C(3) being characterised by progressively stronger Fe–C bonds (2.143(3), 2.087(3) and 2.026(3) \( \text{Å} \), respectively). As was found for 40, the C(1)–C(2) and C(2)–C(3) bond separations (1.447(4) and 1.398(4) \( \text{Å} \), respectively) within the allyl unit are indicative of residual multiple bonding for the (former) alkylene C–C bond.

As mentioned in Section 5.1.2, the combination of \( \mu\text{-}CR \), \( C\equiv C \) and CO ligands during the treatment of heterobimetallic \( \mu \)-alkylidyynes with alkynes is not unusual and this result is similar to the many such examples described by Stone and co-workers.\(^{20,27}\) However, the regioselectivity of the CO insertion for 44 is of note, being consistent with the insertion event following alkylene–alkylidyne coupling, as documented for the preparation of complexes such as

\[
\text{[MoFe} \{\mu\text{-}C(\text{C}_3\text{H}_5\text{Me}-4\text{)}\text{C(}\text{Et})\text{C(}\text{Et})\text{C}(=\text{O})\}\{\mu\text{-}\text{CO}\}(\text{CO})_2\text{Cp}\] (Scheme 5.6).\(^{26}\) In general, the isomeric side-products formed by CO insertion prior to alkylene–alkylidyne coupling reactions contain the \( \mu\text{-}C(R)\text{C}(O)\text{C}(R^1)\text{C}(R^2) \) fragment.\(^{24,26}\) Thus CO may in principle insert into either Mo–C bond (Mo–C(Thienyl) vs Mo–C(Si-Pr) of the presumed intermediate iron-complexes molybdcyclobutadiene. Assuming mechanistic parallels between the formation of

\[
\text{[MoFe} \{\mu\text{-}C(\text{C}_3\text{H}_5\text{Me}-4\text{)}\text{C(}\text{Et})\text{C(}\text{Et})\text{C}(=\text{O})\}\{\mu\text{-}\text{CO}\}(\text{CO})_2\text{Cp}\] and 41 and 44, it may therefore be inferred that the propensity for CO to insert into these bonds is dependent on the substituent, increasing in the order Si-Pr ≈ Sei-Pr < aryl < alkyl.

**Chalcogenolate migration: the maroon-coloured complexes**

The maroon complexes \([\text{MoFe} \{\mu\text{-}C(\text{C}_3\text{H}_5\text{S}-2\text{)}\text{C(}\text{Et})\text{Pr})\} \text{(CO)}_2\text{Cp}\] \((E = S, 45, \text{Se, 42})\) can be isolated from the treatment of 31 with each of the alkynyl chalcoethers \( \text{i-PrEC} = \text{CPh} \) \((E = S \text{ or Se})\), in addition to the complexes of the type \([\text{MoFe} \{\mu\text{-}C(\text{C}_3\text{H}_5\text{S}-2\text{)}\text{C(}\text{Et})\text{Pr})\text{C(Ph)}\}\{\mu\text{-}\text{CO}\}(\text{CO})_2\text{Cp}\) and \([\text{MoFe} \{\mu\text{-}C(\text{Et})\text{Pr})\text{C(Ph)C(C}_3\text{H}_5\text{S}-2\text{)}\text{C}(=\text{O})\}\{\mu\text{-}\text{CO}\}(\text{CO})_2\text{Cp}\) (vide supra) (Scheme 5.5). The complexes 45 and 42 correspond to products in which, in addition to the expected alkylene–alkylidyne coupling, the anticipated migration of the chalcogenolate fragment between carbon centres has occurred; a process coupled with release of a CO ligand from the iron centre. Notably, for the reaction of this same substrate with \( \text{i-PrTeC} = \text{CPh} \), the analogous compound \([\text{MoFe} \{\mu\text{-}C(\text{C}_3\text{H}_5\text{S}-2\text{)}\text{C(}\text{Et})\text{Pr})\} \text{(CO)}_2\text{Cp}\] \((46)\) represents
CHAPTER 5. ALKYLIDyne–ALKYNYL CHALCOETHER COUPLING REACTIONS

244

the major isolable species, consistent with the characteristic facility of C–Te single bond rupture, i.e., the migratory aptitude in general increases down a main group as the bond dissociation enthalpy for the C–Element bond decreases. The migratory aptitude of the tellurolate group should thus result in kinetically easier access to the lowest energy product. The dominance of this product vs products analogous to 40 and 41 for i-PrTeC≡CPh suggests that the maroon complexes, bearing direct iron–chalcogen bonds, represent the most thermodynamically favoured outcome under these (remarkably mild) conditions.

The new complexes 42, 45 and 46 have been characterised crystallographically and results will be discussed in detail below. Spectroscopic data for the series of complexes 42, 45 and 46 (Tables 5.1 and 5.2), are closely similar and, where possible, will be discussed in terms of global trends. The infrared spectrum for each complex features four carbonyl absorptions that are indicative of the presence of both terminal (ca. 1990, 1950, and 1928 cm\(^{-1}\)) and semi-bridging (1834 cm\(^{-1}\)) carbonyl ligands, with a modest shift towards lower frequency noted upon successive substitution of the incorporated chalcogen atom, i.e., in moving from 45 (S) to 42 (Se) to 46 (Te).

At ambient temperature, \(^1\)H NMR spectroscopic investigations of the complexes 42, 45 and 46 reveal the operation of a low energy fluxional process. The \(^1\)H NMR spectra obtained at room temperature for 42 and 46 each exhibit broadened resonances (more pronounced in the case of 46), while the ambient temperature spectrum of 45 comprises resonances which are, in contrast, sharp. The increase in energy barrier observed for this fluxional behaviour upon descending Group 16 is consistent with an inversion process at the coordinated chalcogen atom, giving rise to a pair of diastereomers, though chalcoether dissociation and recoordination cannot be excluded. In the case of 46, a variable temperature \(^1\)H NMR study revealed a coalescence temperature \((T_c)\) of 25 \(^\circ\)C, but over the range measured (−50 to 90 \(^\circ\)C) the limiting structures (fast exchange or static arrangement) were not observed. At the highest measured temperature, although the fast exchange regime for 46 had yet to be reached, resonances had generally begun to develop significant structure, collapsing to a single environment for the isopropyl CH and each of the diastereotopic methyl groups.

An additional feature of the \(^1\)H NMR spectroscopic data for 42 and 45 are the pair-wise nature of resonances (independent of the fluxional processes), which is consistent with the presence of two isomeric compounds (ca. 0.3:1 by integrated peak intensity). This is most clearly evident from the doubling of resonances for the isopropyl unit (\(\delta_h\) 2.63 and 2.82 for 42 and 2.43 and 2.63 for 45 for i-PrCH of the major and minor isomers, respectively). Neither chromatographic nor fractional recrystallisation techniques were successful in achieving separation of the two
isomers. Furthermore, interconversion was not apparent over the temperature range studied (−75 to 55 °C). Interestingly, broadening of the spectrum of 45, comprising sharp resonances for each isomer at 25 °C (rapid sulfur inversion), at temperatures below 0 °C reveal that the two isomers are energetically different, with the methine resonance for the minor isomer (δH 2.63) showing a greater extent of decoalescence at −50 °C relative to that of the major isomer. Results for 42 are similar, with the minor isomer displaying some decoalescence of the methine resonance (δH 2.63) into two chemically inequivalent environments at −75 °C. In view of these results, the two compounds present for 42 and 45 are attributed to geometric isomers.

Notably, upon further standing, solutions of 40 and 43 undergo carbonyl dissociation and migration of the chalcogenolate fragment to afford 42 and 45 in near to spectroscopically quantitative yield. Complex 40 could not, however, be regenerated upon treatment of a solution of 42 with carbon monoxide. Thus, the gold-coloured complexes 40 and 43 are precursors in the formation of 42 and 45. Accordingly, with reference to Figure 5.3 displaying the core geometry of 40, it is proposed that migration of the chalcogenolate group from the central carbon [C(2)] to either C(1) or C(3) should be energetically similar, given the pseudo-mirror symmetry evident for the internal core of the pseudo-allylic linkage. It therefore follows that the geometric isomers evident for products 42 and 45 may be due to the occurrence of both migration events. Thus, migration of the chalcogenolate fragment from the central carbon [C(2)] to the carbon bearing the former alkyne substituent [C(3)] would afford geometric isomer A (Chart 5.1). Alternatively, migration onto the alkylidene-derived carbon [C(1)] would yield isomer B. On the basis of the 1H NMR spectra one migratory route is clearly favoured but the available spectroscopic data do not allow a distinction to be made. Due to the severe overlap of phenyl and thienyl resonances in the aromatic region of both 42 and 45, interrogation of a 1H NOESY spectrum for ‘off-diagonal’ responses between the resonances for the isopropyl unit and the thienyl or phenyl protons were ambiguous, but attention is again drawn to the comparatively short C(2)–C(3) bond length (C(1)–C(2) 1.428(3) Å vs C(2)–C(3) 1.400(3) Å) that was noted in the molecular structure determination of 40 (vide supra), which may exert an influence upon the favoured migratory route.
Figure 5.3. Core molecular structure of the $C_3$ bridge of [MoFe$_2$(µ-C(C$_4$H$_3$S-2)CC(Sei-Pr)(Ph))(µ-CO)$(CO)_4$Tp] (40) viewed along the Mo–Fe axis. Carbonyl and pyrazolylborate ligands excluded. 30% displacement ellipsoids are drawn. Hydrogen atoms have been omitted.

A similar isomeric distribution was not evident from the spectroscopic data of the tellurium analogue (46), with only single environments apparent for the proton resonances at the highest temperature studied (90°C), when tellurium inversion is rapid. It is suggested that the greater migratory aptitude of tellurium–carbon bonds may allow for complex 46 to attain the energetically most favourable orientation.

The chiral nature of the complexes 42 and 45 are clearly evident in the $^{13}$C{$^1$H} NMR spectroscopic data, which includes four resonances attributable to the metal carbonyls (δC 236.8, 231.2, 221.6, and 211.8 for 45 and 236.5, 231.5, 221.8, 212.2 for 42), corresponding to the semi-bridging and terminal molybdenum carbonyls and the two iron carbonyl ligands, respectively. The carbon nuclei of the three-carbon fragment resonate, for each complex, at δC 118.9, 81.9, 111.6 (45) and 118.9, 80.3, 115.0 (42) [C(C$_4$H$_3$S-2)CC(Ph)(Ei-Pr)], with a modest deshielding noted for the terminal carbon carrying the chalcogenolate donor in 42 relative to that of 45. Assignments for these quaternary nuclei were aided by 2D HMBC experiments, which in the case of 45 revealed a strong correlation for the resonance at δC 111.6 to both the methine and phenyl protons, allowing this resonance to be attributed to the terminal carbon atom of the allenyl chain [µ-C(Ei-Pr)(Ph)]. The assignment for the µ-CC$_4$H$_3$S resonance
(\(\Delta \approx 118.9\)), while not unambiguously indicated by the 2D NMR, follows from comparative data for the related complex 43 (\(\Delta \approx 114.3\)), in which the \(\mu\)-CC\(_3\)H\(_2\)S similarly spans a Mo–Fe bond (vide supra). The remaining resonance, which exhibits the lowest intensity, is presumably due to the central carbon atom of the organic ligand.

The thio- (45), seleno- (42) and telluroether (46) migration products [MoFe\{\(\mu\)-C(C\(_3\)H\(_2\)S-2)CC(Ph)(Et-Pr)\}(CO)\(_4\)Tp] (\(E = S, Se\) or \(Te\)) are isostructural and isomorphous and the molecular structures, illustrated in Figures 5.4, 5.5 and 5.6, will be discussed together in general terms, with their geometric parameters presented in Table 5.3. The structures may be compared with each other and to that of the iron complex [Fe\(_2\)(CO)\(_3\)\{\(\mu\)-EtSC(Me)CC(Ph)C(Ph)C(O)\}] (vide supra, Scheme 5.4).\(^3\)

The compounds 45, 42 and 46 each have a dimetallatetrahedrane core with a Mo–Fe bond that is transversely \(C_2\)-bridged by the first two atoms of a \(\mu\)-allenyl unit, the latter comprising \(C_\alpha\) and one of the alkynyl selenoether carbons. The Mo–\(\mu\)C separations (av. 2.15 Å) are intermediate between formal Mo–C double and single bonds and are only marginally longer than the corresponding Fe–\(\mu\)C distances (av. 2.03 Å), which is consistent with the symmetric nature in which the \(C_2\) unit bridges the metal–metal bond. Dimensions within the bridging moiety are comparable for each species (Mo–Fe\(_{av}\) 2.834(4) Å, C–C\(_{av}\) 1.38 Å), with a central geometry similar to that observed for the complex [MoW(\(\mu\)-RCCR)(CO)\(_4\)Cp(\(\eta^5\)-C\(_6\)H\(_6\)(COMe))] (\(R = \text{C}_6\text{H}_4\text{Me-4}, \text{Mo–W} 2.976(1), \text{C–C} 1.371(7) \text{Å}\).\(^3\)

Interest within the structures focuses on the geometry of the \(C_3\)E ligand chain that arises from chalcogenolate migration. Distances between the carbon atoms along the C(1)–C(2)–C(3)–E spine are closely similar for 45, 42 and 46, (av. 1.39 Å), though the specific properties of the terminal chalcogen atom are manifest in the progressive expansion of the FeC(3)E chelate, i.e., elongation of both the C(3)–E and Fe–E bond distances (1.793(2), 1.96(1), 2.155(4) and 2.2816(6), 2.403(2), 2.5394(6) Å for 45, 42 and 46, respectively).

The terminal chalcogen atom formally donates two electrons to the iron centre in a dative interaction and each metal centre is ligated by two carbonyl groups, one of which [C(20)O(20)] perceptibly semi-bridges the metal–metal bond (Mo–C(20)–O(20)\(_{av}\) 165°).
Figure 5.4. a) Molecular geometry of \([\text{MoFe}(\mu-C_{2}H_{5}S-2)CC(\text{Ph})(\text{Sei-Pr})(\text{CO})_{4}\text{Tp}] \) (42) and b) depiction of the inner coordination sphere with thienyl, phenyl and pyrazolyl aromatic rings and the non-bridging molybdenum carbonyl omitted. 30\% displacement ellipsoids shown.
Table 5.3. Summary of geometric parameters for \[\text{MoFe}\{\mu-\text{C}(R)\text{CC}(R^1)\text{ER}^1\}\text{(CO)}_4\text{Tp}\]^\(\text{a}\)

<table>
<thead>
<tr>
<th>Bond Lengths, Å</th>
<th>45</th>
<th>42</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Fe</td>
<td>2.8366(3)</td>
<td>2.833(2)</td>
<td>2.8324(6)</td>
</tr>
<tr>
<td>Mo-C(1)</td>
<td>2.158(2)</td>
<td>2.143(9)</td>
<td>2.160(3)</td>
</tr>
<tr>
<td>Mo-C(2)</td>
<td>2.141(2)</td>
<td>2.16(1)</td>
<td>2.139(3)</td>
</tr>
<tr>
<td>Mo-N(21)</td>
<td>2.244(2)</td>
<td>2.239(7)</td>
<td>2.245(2)</td>
</tr>
<tr>
<td>Mo-N(31)</td>
<td>2.219(2)</td>
<td>2.211(7)</td>
<td>2.219(2)</td>
</tr>
<tr>
<td>Mo-N(41)</td>
<td>2.230(2)</td>
<td>2.219(7)</td>
<td>2.226(2)</td>
</tr>
<tr>
<td>Fe-C(1)</td>
<td>2.050(2)</td>
<td>2.050(9)</td>
<td>2.039(4)</td>
</tr>
<tr>
<td>Fe-C(2)</td>
<td>2.017(2)</td>
<td>2.01(1)</td>
<td>2.021(4)</td>
</tr>
<tr>
<td>Fe-C(3)</td>
<td>2.049(2)</td>
<td>2.051(1)</td>
<td>2.087(4)</td>
</tr>
<tr>
<td>Fe-E</td>
<td>2.2816(6)</td>
<td>2.403(2)</td>
<td>2.5394(6)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.374(3)</td>
<td>1.40(1)</td>
<td>1.373(5)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.405(3)</td>
<td>1.36(2)</td>
<td>1.391(5)</td>
</tr>
<tr>
<td>E-C(3)</td>
<td>1.793(2)</td>
<td>1.96(1)</td>
<td>2.155(4)</td>
</tr>
<tr>
<td>E-(i-Pr)</td>
<td>1.836(2)</td>
<td>1.98(1)</td>
<td>2.170(4)</td>
</tr>
<tr>
<td>Mo-C_{\text{CO}}(20, 30)</td>
<td>1.993(2), 1.976(2)</td>
<td>2.01(1), 1.98(1)</td>
<td>1.991(4), 1.982(4)</td>
</tr>
<tr>
<td>Fe-C_{\text{CO}}(40, 50)</td>
<td>1.781(2), 1.781(2)</td>
<td>1.78(1), 1.77(1)</td>
<td>1.774(4), 1.785(4)</td>
</tr>
<tr>
<td>Fe-C(20)</td>
<td>2.617(2)</td>
<td>2.60(1)</td>
<td>2.602(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles, °</th>
<th>45</th>
<th>42</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-C(1)-Fe</td>
<td>84.75(7)</td>
<td>85.0(3)</td>
<td>84.8(1)</td>
</tr>
<tr>
<td>Mo-C(2)-Fe</td>
<td>85.98(7)</td>
<td>85.5(4)</td>
<td>85.8(1)</td>
</tr>
<tr>
<td>Mo-C(1)-C(11)</td>
<td>137.6(2)</td>
<td>139.3(4)</td>
<td>136.8(3)</td>
</tr>
<tr>
<td>Fe-C(1)-C(11)</td>
<td>131.6(2)</td>
<td>130.6(4)</td>
<td>133.0(3)</td>
</tr>
<tr>
<td>C(1)-Mo-C(2)</td>
<td>37.29(7)</td>
<td>38.0(4)</td>
<td>37.3(1)</td>
</tr>
<tr>
<td>C(1)-Fe-C(2)</td>
<td>39.49(8)</td>
<td>40.3(4)</td>
<td>39.5(1)</td>
</tr>
<tr>
<td>C(2)-Fe-C(3)</td>
<td>40.42(8)</td>
<td>39.0(4)</td>
<td>39.6(1)</td>
</tr>
<tr>
<td>C(3)-Fe-E</td>
<td>48.54(6)</td>
<td>51.6(3)</td>
<td>54.5(1)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(11)</td>
<td>135.72(2)</td>
<td>133.9(7)</td>
<td>134.5(3)</td>
</tr>
<tr>
<td>C(1)-C(2)-C(3)</td>
<td>129.72(2)</td>
<td>131(1)</td>
<td>129.6(3)</td>
</tr>
<tr>
<td>C(2)-C(3)-E</td>
<td>108.5(1)</td>
<td>108.7(9)</td>
<td>109.0(3)</td>
</tr>
<tr>
<td>C(3)-E-(i-Pr)</td>
<td>104.7(1)</td>
<td>101.9(5)</td>
<td>98.0(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
<td>125.7(2)</td>
<td>127(1)</td>
<td>127.3(3)</td>
</tr>
<tr>
<td>E-C(3)-C(4)</td>
<td>124.3(1)</td>
<td>122.0(8)</td>
<td>122.4(2)</td>
</tr>
<tr>
<td>OC-Mo-CO</td>
<td>90.70(9)</td>
<td>91.5(5)</td>
<td>91.3(2)</td>
</tr>
<tr>
<td>N(21)-Mo-N(31)</td>
<td>83.72(6)</td>
<td>83.9(3)</td>
<td>83.24(9)</td>
</tr>
<tr>
<td>N(21)-Mo-N(41)</td>
<td>77.696(6)</td>
<td>77.9(3)</td>
<td>78.43(9)</td>
</tr>
<tr>
<td>N(31)-Mo-N(41)</td>
<td>81.56(6)</td>
<td>82.1(3)</td>
<td>81.27(9)</td>
</tr>
<tr>
<td>Mo-C-O(20, 30)</td>
<td>164.8(2), 175.2(2)</td>
<td>164(1), 175(1)</td>
<td>164.9(3), 175.3(3)</td>
</tr>
<tr>
<td>Fe-C-O(40, 50)</td>
<td>175.7(2), 176.8(2)</td>
<td>176(1), 177(1)</td>
<td>175.4(4), 176.3(4)</td>
</tr>
<tr>
<td>OC-Fe-CO</td>
<td>96.6(1)</td>
<td>96.6(6)</td>
<td>97.2(2)</td>
</tr>
</tbody>
</table>

\(^{a}\) \(R = \text{C}_4\text{H}_3\text{S}-2, \text{R}^1 = \text{i-Pr}, \text{R}^2 = \text{Ph}; \text{E} = \text{S (45), Se (42) or Te (46).}\)
Figure 5.5. Molecular structure of 45 with 30% displacement ellipsoids shown. Hydrogen atoms have been omitted. Only the major orientation of the disordered thiophene group is displayed.

Figure 5.6. Molecular structure of 46 with 30% displacement ellipsoids shown. Hydrogen atoms have been omitted.
5.3 Mechanism of C–C bond formation and chalcogenolate migration

The mode of formation of the maroon complexes \[ \text{MoFe}\{\mu-C(R)CC(Ph)(Ei-Pr)\}(\mu-CO)\text{Tp} \] (E = S, 45, Se, 42 or Te, 46) via the rupture of one E–C(sp³) bond and the building of another is not without precedent. Jeannin and co-workers have demonstrated cleavage and reformation of the C–S bond of the thioalkynes EtSC=CR (R = Me or Ph) in a number of reactions with both iron and ruthenium carbonyls (vide supra). The intramolecular migration of a single SMe group of the alkynyl dithioether MeSC=CSMe documented by Angelici and co-workers provides an additional example. In this case, gentle heating of the S-bound alkyne complex \[ \text{Ru}\{S(Me)C-CSMe\}(\mu-CO)\text{Cp} \] (a, Scheme 5.8) led to formation of the corresponding thiolatovinylidene \[ \text{Ru}\{\mu-C(\mu-\text{Sei-Pr})\mu-\text{Ph}\}(\mu-CO)\text{Cp} \] (b). In a similar manner, the selenolatovinylidene complexes \[ \text{Ru}\{\mu-C(\mu-\text{Sei-Pr})\mu-\text{Ph}\}(\mu-CO)\text{Cp} \] were prepared by the treatment of \[ \text{Ru}\{\mu-C(\mu-\text{Sei-Pr})\mu-\text{Ph}\}(\mu-CO)\text{Cp} \] with i-PrSeC=CPh. This rearrangement was also proposed to proceed via initial selenoether coordination and subsequent isomerisation to an \[ \mu^2-\text{i-PrSeC=CPh} \] intermediate that underwent alkyne/vinylidene isomerisation, though no such intermediates were detected.

\[ \text{[RuCl(PMe\text{\textsubscript{3}})\text{Cp}] + MeSC=CSMe \rightarrow [Ru]+ \text{MeS-C=CSMe} } \]

Scheme 5.8. S-bound alkynyl thioether/vinylidene interconversion. [Ru] = Ru(PMe\text{\textsubscript{3}})\text{Cp}.

In the cases described herein, analogous processes involving initial coordination and migration of the chalcogenolate fragment between carbon centres prior to carbon–carbon bond formation can be excluded in view of the established intermediacy of complexes of the type \[ \text{MoFe}\{\mu-C(C_4H_3S-2)C(\mu-\text{CO})\text{C(Ph)}\}(\mu-CO)\text{Tp} \] (E = S, 43, or Se, 40) en route to the corresponding chalcogenolate migration products (42, 45 and 46).

A possible pathway by which the compounds 40–46 may be formed is shown in Scheme 5.9 and is discussed in terms of the products obtained from the reaction with \[ \text{i-PrSeC=CPh} \].
**Scheme 5.9.** \([\text{Mo}] = \text{Mo(CO)}_{n-1} \text{or } 2 \text{Tp}; \) \(n = 1\) for \(C, D, E, 40\) and \(41.\) For all other species \(n = 2.\) \(E = \text{Se}, \) \(R = \text{C}_2\text{H}_5\text{S-2}, \) \(R^1 = \text{i-Pr}, \) \(R^2 = \text{Ph}.\) (NB: Due to the variable number of valence electrons provided by both the alkyne and \(\mu\)-alkylidyne ligands the coordination number of the iron centre may vary. Thus, the number of carbonyl ligands indicated for intermediates \(A-E\) may vary from what is represented).
The initial mechanistic step likely involves ready reversion of the Mo=C bond of 31 from a four- to a two-electron donor in the presence of the alkyne to afford intermediate A, in line with the characteristic reactivity pattern of variable coordination exhibited by the M=C groups in complexes of the type [MFe(µ-CR)(CO)₅Tp]. Rapid rearrangement of the coordinated chalcoether A to the more stable η²-geometry would then afford the π-bound alkyne species B and B', which differ in the relative orientation of the unsymmetrical alkyne unit with respect to the bridging alkyldyne ligand. Precedent for the formation of an initial chalcoether complex prior to rearrangement to afford the corresponding η²-alkyne species is provided by Angelici's studies involving the sulfur-bound alkyne complex [Ru{S(Me)C=CMe}(PMe₃)₂Cp]₄⁰ above (Scheme 5.8).

Provided alkyne rotation is facile, the η²-alkyne complexes B and B' provide a common intermediate from which two mechanistically divergent routes can be envisaged, each of which ultimately leads to an alkyldyne–alkyne coupling product comprising a direct metal–chalcogen bond. Loss of a molecule of carbon monoxide from B and B' to give rise to the unsaturated intermediates C and D, respectively, is the next step proposed by analogy with the preferred mechanism suggested by Stone for related alkyldyne–alkyne coupling reactions involving MeC=CMe and R=C=CEt (R = H, Me, or Et) with [MoFe(µ-CC₆H₄Me-4)(CO)₅Cp]₂⁵,²⁶ The re-addition of a molecule of carbon monoxide to the reactive species C would then afford 40. The subsequent step affording 42, which involves loss of a carbonyl ligand and intramolecular migration of the chalcogenolate fragment from the central to a terminal carbon of the bridging C₃ chain has been experimentally established (vide supra).

For the reactive complex D, relating to the alternate alkyne orientation, facile insertion of a carbonyl ligand into the molybdenum–carbon framework could afford the acyl complex E, which, due to its unsaturated nature, re-captures a molecule of carbon monoxide to provide 41. If these ideas are valid it would suggest that the Mo-µC bond of intermediate D is more reactive than the corresponding group in C, and this may perhaps be due to stabilisation conferred to the latter by donation of electron density from the proximal chalcogen atom.
 CHAPTER 5. ALKYLIDYNE–ALKYNYL CHALCOETHER COUPLING REACTIONS

5.4 Reactions between [MoFe(µ-CPh)(CO)₅] and alkynyl chalcoethers

The sequence of reactions that occurs between complexes of the type [MoFe(µ-CR)(CO)₅Tp] and the unsymmetrical alkynyl chalcoethers i-Pr=CR₂ (E = S, Se, Te; R ≠ R₂) presents a complicated reaction manifold due to the formation of isomers depending on the mutual disposition of i-PrE, R and R₂ groups. The situation can, however, be somewhat simplified through employing reagents of the type [MoFe(µ-CR)(CO)₅Tp] (R = R₂), which serve to increase the symmetry of the system. Thus the new bimetallic complex [MoFe(µ-CPh)(CO)₅Tp] was required.

5.4.1 Preparation and characterisation of [MoFe(µ-CPh)(CO)₅] (39)

Preparation of the µ-alkylidyne species [MoFe(µ-CPh)(CO)₅Tp] (39) from the corresponding mononuclear carbyne precursor [Mo(=CPh)(CO)₂Tp] (50) is readily achieved upon treatment with [Fe₂(CO)₉] and spectroscopic features for 39 (Tables 5.1 and 5.2) are entirely comparable to those for 31 (Chapter 3). The infrared profile includes the characteristic five carbonyl absorptions (2049s, 1988s, 1965s, 1925m, 1861w cm⁻¹) and the µ-C carbon resonates at a downfield position (δC 422.3) diagnostic of the 4e⁻ donor functionality of the Mo=C bond, being considerably more deshielded than the corresponding resonance for the parent alkylidyne 50 (δC 293.2). Notably, this µ-C resonance is 30 ppm to lower field than was observed for 31 (δC 392.1), which perhaps suggests a more strongly electron-donating role for the Mo=C bond of 39.

The molecular structure of 39, illustrated in Figure 5.7, requires little comment. The core geometry comprises an asymmetrically bridging µ-benzylidyne group with the plane defined by the phenyl ring being twisted 14° outside of that defined by the dimetallacyclop propane ring. Geometric parameters within the dimetallacyclop propane unit are essentially unperturbed by the variation in the bridging substituent, being entirely comparable to those of 31 (Mo–C(1) 2.0207(19), Fe–C(1) 1.819(2), Mo–Fe 2.5919(3) for 39 vs Mo–C(1) 2.019(9), Fe–C(1) 1.815(9) and Mo–Fe 2.603(2) Å for 31).
5.4.2 Reaction between [MoFe(\(\mu\)-CPh)(CO)\(_5\)Tp] and i-PrSeC=CPh

In manner similar to that described for 31 (Scheme 5.5), the treatment of [MoFe(\(\mu\)-CPh)(CO)\(_5\)Tp] (39) with i-PrSeC=CPh affords the orange and maroon complexes [MoFe(\(\mu\)-C(Ph)C(Sei-Pr)C(Ph))(\(\mu\)-CO)(CO)\(_4\)Tp] (48) and [MoFe(\(\mu\)-C(Ph)CC(Ph)(Sei-Pr))(CO)\(_4\)Tp] (49), respectively.

The formulation of the orange complex 48 as the symmetrically substituted intermediate [MoFe(\(\mu\)-C(Ph)C(Sei-Pr)C(Ph))(\(\mu\)-CO)(CO)\(_4\)Tp] that arises from coupling of the alkyne selenoether with the \(\mu\)-alkylidyne follows from spectroscopic data (Tables 5.1 and 5.2). The infrared spectrum includes four carbonyl associated absorptions (2048s, 1983s(br), 1862w, 1826w cm\(^{-1}\)), with energies and intensities that are essentially equivalent to those observed for the structurally characterised 40 (2049s, 1981s(br), 1863w, 1825w cm\(^{-1}\)).

In the \(^1\)H NMR spectrum, the methyl units of the isopropyl substituent give rise to a single resonance with doublet multiplicity (\(\delta_r 0.85\)), suggesting that there is a plane of symmetry that includes the bond joining the isopropyl moiety to the rest of the molecule. Both the \(^1\)H and \(^{13}\)C{\(^1\)H} NMR data for 48 reveal a 2:1 intensity pattern for the arms of the Tp ligand and data for the phenyl rings are consistent with the equivalence of the two units attached to the terminal...
atoms of the C₃-bridge. In contrast to 40 in which three carbonyl resonances were present at δC 238.9, 231.1, and 209.7, attributed to µ-CO, Mo(CO) and Fe(CO)₃, respectively, the ¹³C {¹H} NMR spectrum of 48 features only two carbonyl resonances. The more downfield signal (δC 233.3) is attributed to the Mo(CO)₂ unit and that at δC 210.9 to the Fe(CO)₃ group. Furthermore, while the anticipated two resonances due to the C₃ allyl bridge were evident at δC 130 and 129.4, these resonances were weak, with the resonance to higher field exhibiting significant broadening. These data are consistent with either a static structure in which the two molybdenum carbonyls symmetrically straddle the Mo–Fe vector or a dynamic process that chemically equilibrates the two carbonyl ligands. Two processes could be considered: (i) pairwise exchange of terminal and semi-bridging sites or (ii) rotation of the entire ‘TpMo(CO)₂’ fragment (with two terminal CO ligands) about an axis normal to the FeC₃ ‘plane’. The former process would appear more likely both in terms of the modest energy requirements and the chemical shift of the carbonyl resonance, which is intermediate between those typical of terminal and semi-bridging CO ligands in similar Mo–Fe compounds (Table 5.2).

Formulation of the maroon complex as the chalcogenolate migration product [MoFe{µ-C(Ph)-CC(Ph)(Sei-Pr)}(CO)₄Tp] (49) followed unambiguously from spectroscopic data and was confirmed by a crystallographic study (Figure 5.8). The infrared spectrum included four carbonyl absorptions (1989s, 1948s, 1832 cm⁻¹), consistent with the emerging trend for the series of complexes [MoFe{µ-C(R¹)CC(R²)(ER³)}(CO)₄Tp].

The 'H NMR spectrum of 49 revealed the presence of only a single geometric isomer, with resonances for the isopropyl substituent reflecting the diastereotopicity of the methyl groups (δH 2.64(septet), 1.32(d) and 0.95(d) for i-PrCH and i-PrCH₃, respectively). The absence of geometric isomers for [MoFe{µ-C(Ph)CC(Ph)(Sei-Pr)}(CO)₄Tp] (49) is as anticipated due to the symmetric nature of the precursor 48 and substantiates the earlier hypothesis that in the case of the 2-thienyl system the reaction manifold was complicated by the availability of two energetically similar but inequivalent migration routes. The resonances again display broadening due to inversion of the coordinated selenoether.

An examination of the ¹³C {¹H} NMR data reveals that these are entirely comparable to those of 42, including two molybdenum and two iron carbonyl resonances (δC 235.5, 232.9 and 221.7, 212.2, respectively) and resonances for the µ-allenyl ligand spine (δC 118.8, 86.8 and 114.5 cf. 118.9, 80.3 and 115.0 for 42), the most notable distinction being an approximate 7 ppm up-field shift for the central carbon atom of the C₃Se ligand chain.
A single crystal X-ray diffraction study of the maroon migration complex [MoFe{µ-C(Ph)CC(Ph)(Sei-Pr)}(CO)₅Tp] (49) was performed and results are summarised in Figure 5.8. The central dimetallatetrahedrane core is essentially identical to those of the structurally characterised analogues, 42, 45 and 46 (vide supra) with an Mo–Fe bond that is transversely bridged by two carbon atoms of a µ-allenyl unit (Mo–Fe 2.8191(3), C(1)–C(2) 1.365(3) Å) and one linear and one bent (Mo–C=O 165.1(2)°) carbonyl ligand.

**Figure 5.8.** Molecular structure of 49 30% displacement ellipsoids shown. Hydrogen atoms have been omitted. Selected bond distances (Å): Mo–Fe 2.8191(3), Mo–C(1) 2.171(2), Mo–C(2) 2.138(2), Mo–N(21) 2.243(2), Mo–N(31) 2.212(2), Mo–N(41) 2.229(2), Fe–C(1) 2.044(2), Fe–C(2) 2.023(2), Fe–C(3) 2.065(2), Fe–Se 2.4326 (3), C(1)–C(2) 1.365(3), C(2)–C(3) 1.402(3), Se–C(3) 1.958(2), Se–C(61) 1.984(2), Mo–C(20) 1.993(2), Mo–C(30) 2.000(2), Fe–C(40) 1.773(2), Fe–C(50) 1.784(2), Fe–C(20) 2.569(2). Selected bond angles (°): Mo–C(1)–Fe 83.91(7), Mo–C(2)–Fe 85.23(7), Mo–C(1)–C(11) 135.0(1), Fe–C(1)–C(11) 133.3(1), C(1)–Mo–C(2) 36.92(7), C(1)–Fe–C(2) 39.21(7), C(2)–Fe–C(3) 40.10(7), C(3)–Fe–Se 50.80(5), C(2)–C(1)–C(11) 138.0(2), C(1)–C(2)–C(3) 129.0(2), C(2)–C(3)–Se 108.7(1), C(3)–Se–C(61) 101.73(8), C(2)–C(3)–C(4) 127.1(2), Se–C(3)–C(4) 121.4(1), OC–Mo–CO 87.23(9), N(21)–Mo–N(31) 83.33(6), N(21)–Mo–N(41) 79.13(6), N(31)–Mo–N(41) 80.83(6), Mo–C(20)–O(20) 165.1(2), Mo–C(30)–O(30) 175.5(2), Fe–C(40)–O(40) 179.0(2), Fe–C(50)–O(50) 176.4(2), OC–Fe–CO 95.8(1).

**Isolation of the π-bound intermediate:** [MoFe{µ-C(Ph)}(η²-i-PrSeC≡CPh)(CO)₅Tp] (47)

Monitoring of the reaction progress between [MoFe{µ-C(Ph)(CO)₅Tp}] (39) and i-PrSeC≡CPh by thin layer chromatography revealed behaviour somewhat inconsistent with that observed for 31. Within nine hours, the reaction had proceeded via complete consumption of (39) to, amongst
other products, a major brown compound 47 (indicated by thin layer chromatography). At first glance it would appear that the reaction pathway for 39 differs from that of 31, however, upon prolonged reaction times the subsequent depletion of this compound could be observed, affording the expected products 48 and 49. Thus, this compound 47 corresponded to an earlier intermediate along the reaction course. By halting the reaction progress at an early stage, rapid low-temperature chromatographic purification (silica gel, –33 °C) and immediate solvent removal afforded intermediate 47 as a brown solid in high yield (77%). Evidently, the phenyl for thienyl substitution in the bridging alkylidyne ligand of [MoFe(µ-CPh)(CO)₅Tp] results in a greater stabilisation and prolonged lifetime of this particular intermediate (Scheme 5.8). This increased longevity might be attributed to either (i) the greater donor property of the Mo=C bond of [MoFe(µ-CPh)(CO)₅Tp] to iron 39 relative to [MoFe(µ-CC₃H₅S-2)(CO)₅Tp] (31) inferred from ¹³C{¹H} NMR data (vide supra) or (ii) the modest increase in steric pressures that result from replacing the 5-membered 2-thienyl group with the 6-membered phenyl substituent.

Although the complex exhibits limited stability, undergoing further reaction to afford 48 and 49, the spectroscopic data that could be obtained support the formulation of 47 as the initially formed π-bound alkyne complex [MoFe(µ-CPh)(η²-i-PrSeC≡CPh)(CO)₅Tp] (47) and serve to effectively exclude the alternative formulation as a σ-Se alkynyl selenoether complex [MoFe(µ-CPh){Se(i-Pr)C≡CPh}{(CO)₅Tp}].

The infrared spectrum of 47 features five broad carbonyl absorptions at 2027s, 2000s, 1991s, 1964m, 1940m cm⁻¹ and in the solid state, a medium strength absorption at 1718 cm⁻¹ is evident, the latter being attributed to νC≡C of a π-bound alkyne. No evidence for νC≡C of a non-coordinated alkyne was discernable in the higher frequency region of the spectrum which would be consistent with the alternative chalcogen-bound alkyne complex, e.g., [Ru{S(Me)=CMe}{PMe₃}₂Cp][BF₄] with νC≡C of 2203 cm⁻¹.⁴⁰

The ¹H NMR spectrum of 47 reveals the diastereotopic nature of the isopropyl methyl groups (δH 3.14(septet), 1.31(d) and 1.19(d) for i-PrCH and i-PrCH₃, respectively) and unique environments for the two inequivalent phenyl rings. The ¹³C{¹H} NMR data include a downfield resonance for µ-C at δC 323.9, being some 100 ppm shielded relative to the parent bimetallic species (δC 422.3), which is consistent with reversion of the bridging alkylidyne unit to a two electron donor functionality (to iron) upon formation of the saturated 34 valence electron complex.⁴ The alkynyl nuclei of 47 resonate at δC 92.9 and 80.9, being assigned to SeC=CPh and SeC≡CPh, respectively (substantiated by 2D HMBC studies in which the more shielded resonance showed a correlation with aromatic phenyl resonances), and may be
compared with the corresponding values of δ 102 and 71 for the free alkyne.\textsuperscript{42} The movement of these resonances towards one another cf. their corresponding positions in the parent alkyne is informative and an analogy can be drawn from the related salts [Ru{S(Me)C≡CMe}(PMe\(_3\))\(_2\)Cp][BF\(_4\)] and [Ru(η\(^2\)-MeSC=CMe)(PMe\(_3\))\(_2\)Cp][BF\(_4\)] in which data is available for the alkynyl nuclei of both the sulfur-bound (δ 92.4 and 88.6) and η\(^2\)-bound alkyne complexes (δ 82.9 and 70.1).\textsuperscript{40} A comparison of the data for each of these complexes with the corresponding resonances for the free alkyne MeSC=CMe (δ 88.6 and 68.9) reveals that for the η\(^2\)-bound complex, the chemical shift of the alkynyl nuclei have moved towards one another, whereas for the S-bound version each resonance has experienced a downfield shift. Moreover, in the case of 47 the relatively shielded positions of the alkynyl resonances are consistent with the alkyne acting as a two rather than four electron donor cf. [W(η\(^2\)-i-PrSeC=CPPh)(CO)(CITp\(^*-\))] (38) (δ 199.7, 193.2, Chapter 4), in which the alkyne is a formal four electron donor.
5.5 Summary and Conclusions

The first study of the reactions of hetero-atom substituted alkynes (specifically, i-PrEC≡CPh, E = S, Se, Te) with dinuclear alkylidyne complexes of the type [MoFe(µ-CR)(CO)₅Tp] (R = C₄H₃S-2, 31, Ph, 39) is reported. The reactions were shown to proceed via coupling of the heteroalkyne with the µ-alkylidyne ligand to afford a chromatographically separable mixture of products that was dominated by the compounds [MoFe{µ-C(R)C(Ei-Pr)C(Ph)}(µ-CO)(CO)₄Tp] (R = C₄H₃S-2, E = S, 43, Se, 40; R = Ph, E = Se, 48), [MoFe{µ-C(Ei-Pr)C(Ph)C(R)C(O)}(µ-CO)(CO)₄Tp] (E = S, 44, Se, 41) and [MoFe{µ-C(R)CC(Ph)(Ei-Pr)}(CO)₄Tp] (R = C₄H₃S-2, E = S, 45, Se, 42, Te, 46; R = Ph, E = Se, 49). Thus, in addition to the conventional alkyne–alkylidyne coupling reactions, rupture of the E–C(alkyne) bond and intramolecular chalcogenolate migration events were also observed.

Similar results were obtained for i-PrSC≡CPh to those obtained for i-PrSeC≡CPh. The first product, [MoFe{µ-C(R)C(Ei-Pr)C(Ph)}(µ-CO)(CO)₄Tp] (R = C₄H₃S-2, E = S, 43, Se, 40), involved the formation of a 3-carbon bridge in which the chalcogenolate group was bound to the carbon opposite the molybdenum centre. However, with time these derivatives evolved via chalcogenolate migration (attended by loss of a carbonyl ligand) into a pair of isomeric µ-allenyl complexes [MoFe{µ-C(R)CC(Ph)(Ei-Pr)}(CO)₄Tp] and [MoFe{µ-C(Ph)CC(R)(Ei-Pr)}(CO)₄Tp] (R = C₄H₃S-2, E = S, 45, Se, 42) that differed according to which Mo–Ca atom (CR or CPh) of the former molybdocycle the chalcogenolate group migrated to. The third major component corresponded to the complex [Mo{µ-C(Ei-Pr)C(Ph)C(R)C(O)}(CO)₄Tp] (E = S, 44, Se, 41), in which the Mo–Fe vector was bridged by a 4-carbon chain comprising a carbonyl ligand coupled with the alkylidyne and alkyne. For i-PrTeC≡CPh, the only tractable product obtained was the tellurolate migration product [MoFe{µ-C(R)CC(Ph)(Tei-Pr)}(CO)₄Tp] (46), attesting perhaps to the greater migratory aptitude of the Tei-Pr group.

In the reaction of [MoFe(µ-CPh)(CO)₅Tp] with i-PrSeC≡CPh, an early intermediate could be isolated corresponding to the simple alkyne π-adduct [MoFe(µ-CPh)(η²-i-PrSeC≡CPh)(CO)₅Tp] (47), which converted over time to a mixture of alkyne–alkylidyne coupled products 48 and 49.
REFERENCES

CHAPTER SIX

TRIS(3,5-DIMETHYLpyrazolyl)BORATO LIGATED ALKYNYLSELENOMETHYLIDYNE COMPLEXES OF MOLYBDENUM
6.1 Introduction

This Chapter reports the synthesis and structural characterisation of the first examples of alkynylselenomethylidyne complexes, \([\text{Mo}(\equiv\text{S}\equiv\text{C})(\text{CO})_2\text{Tp}^*](R = \text{t-Bu}, \text{51}, \text{C}_6\text{H}_4\text{Me}-4, \text{52}, \text{SiMe}_3, \text{53}).\) The presence of two contrasting triple bonds (C\equivC and Mo\equivC) linked by a selenium atom provide the potential to lend these complexes a rich coordination chemistry. Accordingly, the metal-ligating properties of \text{51} towards [Co\textsubscript{2}(\text{CO})\textsubscript{8}] and [Pt(PPh\textsubscript{3})\textsubscript{2}(\text{C}_2\text{H}_4)] are described.

6.1.1 Heteroatom-substituted methylidyne

Since the very first synthesis of an alkylidyne complex containing a tris(pyrazolyl)borate ligand was achieved by Angelici through S-alkylation of a thiocarbonyl group,\textsuperscript{1} the incorporation of a wide array of heteroatom-substituents into the carbyne architecture of such compounds has been documented. As detailed in Chapter 1, Lalor’s haloalkylidyne complexes [M(\equiv\text{Cl})(\text{CO})_2\text{Tp}^*] (M = Mo, W)\textsuperscript{2} have proven to be particularly powerful tools in this field. Nucleophilic displacement of the terminal chloride atom of this haloalkylidyne precursor provides a convenient entry into a variety of heteroatom-substituted molybdenum and tungsten alkylidyne species, with phosphonio-,\textsuperscript{3} aryloxy-,\textsuperscript{3} chalcogeno-\textsuperscript{4} and μ-carbido\textsuperscript{5} alkylidyne derivatives all available from this route (Scheme 6.1). The neutral PR\textsubscript{3} group of the cationic phosphoniocarbynes [W(\equiv\text{CPR}\textsubscript{3})(\text{CO})_2\text{Tp}^*]\textsuperscript{+} and the SMe substituent of the methylthiomethylidyne complex [W(\equiv\text{CSMe})(\text{CO})_2\text{Tp}^*] furthermore provide good leaving groups for methylidyne/methylidyne interconversions, though have been far less exploited.\textsuperscript{6,7}

![Scheme 6.1. Selected routes to Group 6 heteroatom substituted alkylidyne complexes.](image-url)
Methylthio-, seleno- and tellurocarbyne complexes are also accessible by treating [M(=CCl)(CO)₂Tp*] with Li₂S, Li₂Se, or Na₂Te and subsequent alkylation of the resulting chalcocarbonyl metallates [M(CO)₂(CE)Tp*]₁⁻ (E = S, Se, Te).⁴

6.1.2 Alkynylmethylidyne complexes

E.O. Fischer described the preparation of the first (thermally unstable) alkynylcarbyne ('propargylidyne') derivatives [W(=CC=CPh)X(CO)₄] (X = Cl, Br, I) through alkoxide abstraction from the alkoxycarbene precursor [W{=C(OEt)C=CPh}(CO)₅] within one year of his initial, ground-breaking construction of a metal–carbon triple bond (Scheme 6.2).⁸

![Scheme 6.2. Synthesis of [W(=CC=CPh)X(CO)₄] (X = Cl, Br, I).](image)

The 'one-pot' oxide-abstraction route developed by Mayr (Chapter 1, Scheme 1.9)⁹ (and adaptations thereof) subsequently allowed for the preparation of a series of propargylidyne complexes of molybdenum and tungsten containing various tri- and bidentate ligands (tmeda, bipy, Cp, Tp, Tp*, Tm), which exhibited enhanced thermal stability over Fischer's tetracarbonyl derivatives (Scheme 6.3).¹⁰⁻¹⁴

![Scheme 6.3. One-pot synthesis of [M(=CR)(CO)₂L] (M = Mo, W; L₀ = (O₂CCF₃)(CO)₂(L₂); L₂ = bipy, tmeda etc.; (CO)₂(L₃); L₃ = Cp, Tp, Tp*, Tm etc.; R = =CMeₓ, Ph, C₆H₄Me-4, t-Bu).](image)

Stone and co-workers demonstrated ligand properties towards low-valent unsaturated metal–ligand fragments for both the M=C and C=C triple bonds in the alkynylcarbyne complexes [M(=CC=Ct-Bu)(CO)₂L] (L = Cp, Tp, M = Mo, W; L = Tp*, M = Mo). The site of reactivity was influenced by the steric properties of the tripodal ligand with the bulky hydrotris(pyrazolyl)borato ligands reducing the reactivity of the alkylidyne M=C bond towards [Co₂(CO)₈] and [Mo₂(CO)₆Cp₂] (Scheme 6.4).¹²
Scheme 6.4. Reactions of alkynylcarbynes with low-valent metal fragments (M = Mo, W; L = Cp, Tp; M'Ln = Mo(CO)₂Cp, Co(CO)₃).

**Spectroscopy**

Table 6.1. ¹³C{¹H} NMR and IR data for a range of alkynyl-substituted carbynes

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹³C{¹H} NMR, ppm</th>
<th>IR, cm⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>δCα, δ(CO), δCβ, δCγ</td>
<td>νC≡C, νCO</td>
<td></td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>252.3, 223.3, 90.4, 75.9</td>
<td>NR</td>
<td>2007, 1923</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>274.9, 229.4, 93.9, 84.8</td>
<td>NR</td>
<td>2006, 1940</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>259.8, 226.0, 91.7, 78.5</td>
<td>NR</td>
<td>2002, 1919</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>256.7, 226.6, 91.8, 78.3</td>
<td>NR</td>
<td>1993, 1908</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>255.4, 227.4, 113.5, 75.3</td>
<td>2045</td>
<td>1995, 1915</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>247.8, 225.3, 98.1, 81.7</td>
<td>2133</td>
<td>1993, 1910</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>266.7, 221.5, 100.1, 88.9</td>
<td>NR</td>
<td>1988, 1929</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>250.1, 224.7, 97.3, 87.0</td>
<td>2127</td>
<td>1975, 1885</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>220.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>230.5, 191.0, 105.6, 72.1</td>
<td>2130</td>
<td>2096</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>244.6, 225.3, 118.9, 68.9</td>
<td>2091</td>
<td>1995, 1914</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>246.3, 225.0, 120.7, 76.6</td>
<td>2052</td>
<td>2000, 1918</td>
</tr>
<tr>
<td>[Mo≡CC≡CFC]</td>
<td>247.3, 226.1, 120.4, 79.5</td>
<td>2052</td>
<td>1982, 1896</td>
</tr>
</tbody>
</table>

Abbreviations: L¹ = O₂CCF₃; ²¹³C NMR data were determined in CDCl₃ and IR data were determined in CH₂Cl₂ solution unless otherwise indicated as follows: ° dichloromethane-d₂; ° light petroleum; ⁴ tetrahydrofuran; ° acetone-d₆

Selected ¹³C{¹H} NMR chemical shifts and infrared data for a range of propargylidynes are collected in Table 6.1 and reveal that all of the cis-dicarbonyl complexes of the type [LₙM≡CC≡CR(CO)₃] surveyed exhibit resonances for Cα in the range 245–275 ppm that are sensitive to the nature of the co-ligands. (NB: for Fischer’s tetracarbonyl species bearing four π-acid co-ligands, the Cα resonance for the alkynylcarbyne is shifted substantially upfield). Selected deshielding of the alkynyl carbon atom directly bound to the metal–carbon triple bond, Cβ, relative to that containing the terminal capping group, Cγ, is evident. It is also notable that electronic effects are transmitted along the conjugated M≡CC≡C chain such that Cα, Cβ and
Cγ are all affected by variations in the donor ligand set, however, the differences became less marked upon progressing along the carbon spine.

In addition to carbonyl-associated absorptions, infrared data for the alkynylearbynes include a weak C≡C vibration in the region typical for free alkynes, though this is not always discernible. The recently reported X-ray crystallographic study of the mononuclear complex [W(≡CC≡CSiMe3)(CO)2Tp*]10 revealed localised alkylidyne and alkynyl bonding along the W≡CC≡CSiMe3 chain, with W−Cα, Cα−Cβ and Cβ−Cγ separations of 1.844(6), 1.366(8) and 1.236(9) Å, characteristic of W−C triple, C−C single and C−C triple bonds, respectively, and angles at Cα (176.4(5)°) and Cβ (178.6(7)°), which were essentially linear.15
6.2 Synthesis and characterisation of alkynylselenomethylidyne complexes

Combining the well-established, convenient routes to heteroatom-substituted methylidyne complexes and the synthetic versatility of alkynylselenolithiums in organometallic chemistry, the novel alkynylselenomethylidyne dicarbonyl complexes were prepared by the reaction sequence shown in Scheme 6.5. A solution of Li[SeC=CR] (R = t-Bu, C₆H₄Me-4, SiMe₃) was prepared by first deprotonating the corresponding alkyne with n-butyllithium, followed by treatment with elemental selenium. Treating separate diethyl ether suspensions of [Mo(≡C=CCl)(CO)₂Tp*] with these solutions led to the precipitation of LiCl and a slow colour change from yellow to orange for the reaction mixture, from which the nucleophilic displacement products [Mo(≡CSeC=CR)(CO)₂Tp*] (R = t-Bu, 51, C₆H₄Me-4, 52, SiMe₃, 53) could be isolated following chromatographic separation from unreacted [Mo(≡CCl)(CO)₂Tp*].

![Scheme 6.5. Preparation of alkynylselenomethylidyne complexes.](image)

The new compounds are moderately stable in the solid state but show signs of decomposition over a period of weeks, a process that is accelerated in solution or with exposure to light and/or air. When two equivalents of Li[SeC=CSiMe₃] were employed in the synthesis of 53, the Se-free analogue [Mo(≡CC≡CSiMe₃)(CO)₂Tp*] (54) could be isolated in low yield (4%). Spectroscopic data for 54 were comparable to those recently reported for this compound (δ: 255.4 Cα, 113.3 Cβ, 74.9 Cγ, 227.4 CO, cf. literature data δ: 255.4 Cα, 113.5 Cβ, 75.3 Cγ, 227.4 CO), though in this case the alkynylcarbyne was prepared in 30% yield from the substitution of the labile ligands of the complex [Mo(≡CC≡CSiMe₃)(O₂CCF₃)(CO)₂(tmeda)] by treatment with K[Tp*]. The Se-free analogues are also suspected to be present amongst the alkynylselenomethylidyne decomposition products mentioned above. The isolation of the alkynylselenomethylidyne complexes and the corresponding Se-free compounds via this route (Scheme 6.5) raises questions about the low reported reactivity of the haloalkylidyne towards phenyllithium and their alleged inertness towards Li[C≡CSiMe₃]. However, the isolation of 54 appears to be a result of selenium extrusion from an initially formed alkynylselenomethylidyne complex, rather than direct attack of the haloalkylidyne by Li[C≡CSiMe₃]. Under anaerobic conditions, a solution of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tₜp*] in tetrahydrofuran at ambient temperature was shown to partially extrude selenium, affording the selenium free complex [Mo(≡CC≡Ct-Bu)(CO)₂Tₜp*] in appreciable quantities (ca. 20%) along with other minor
decomposition products (as determined by thin layer chromatography) over a one week period. The transformation of acetylenic selenides into vinlyc selenides or mono- and disubstituted acetylenes free of selenium has been previously demonstrated.\textsuperscript{19-22}

The compounds $51-53$ were characterised by their spectroscopic properties (Table 6.2). In the infrared spectra there are, as expected, two strong CO stretching bands that have not been substantially perturbed by the replacement of the chloride atom in $[\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*]^2$ [IR (CH$_2$Cl$_2$): 2002, 1915 (\nu CO) cm$^{-1}$, $k_{CO}$ 15.49 N m$^{-1}$] with the alkynyl selenolate substituent -SeC=CR ($k_{CO}$ = 15.49–15.51 N m$^{-1}$). The Cotton–Kraihanzel force constants, $k_{CO}$,\textsuperscript{23} for $51-53$ reveal a sensitivity towards the donor ability of the alkylidyne capping groups, which increase in the order $R = \text{SiMe}_3 < \text{C}_8\text{H}_8\text{Me}-4 < \text{t-Bu} (= \text{Cl})$. The high frequency of the CO absorptions for $51-53$ relative to the related chalcogeno complex $[\text{Mo}(=\text{CSePh})(\text{CO})_2\text{Tp}^*]$(cyclohexane: \nu CO 1988, 1914 cm$^{-1}$) indicate a more electron-deficient metal centre for $51-53$. This suggests that the basicity of the chalcogen substituent with respect to the metal–carbon triple bond in the alkynylselenomethylidyne complexes is positively augmented by interaction with the \text{C}=\text{C} \pi\text{-orbitals, as was documented in Chapter 4. The complex } [\text{Mo}(=\text{CSeC}(\text{SiMe}_3)\text{CCl})(\text{CO})_2\text{Tp}^*] \text{exhibited an additional weak absorption due to the \text{C}=\text{C} stretch at 2092 cm}^{-1} \text{, which is comparable to that reported for the Se-free version } [\text{Mo}(=\text{CC}(\text{SiMe}_3)(\text{CO})_2\text{Tp}^*](\text{THF: } \nu_{\text{C=C}} 2045 \text{ cm}^{-1})\text{.}\text{\textsuperscript{14}}$ For $51$ and $52$ this absorption is presumably too weak to be observed.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
Complex & $\delta C_{\alpha}$ & $\delta CO$ & $\delta C_{\beta}$ & $\delta C_{\gamma}$ & \textbf{v}_{\text{CAS}} & \textbf{v}_{\text{CO}} & \textbf{v}_{\text{C=C}} & \textbf{v}_{\text{C=Se}} & \textbf{v}_{\text{C=Cl}} & $k_{CO}$ \\
\hline
\textbf{(51)} & 245.0 & 225.1 & 52.0 & 114.7 & \text{n.d.} & 2000, 1916 & 15.49 & \text{c.f.} & \text{245.5} & \text{for } [\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*] \text{.}\text{\textsuperscript{2}} & \\
\textbf{(52)} & 246.6 & 225.0 & 63.8 & 119.9 & \text{n.d.} & 2000, 1918 & 15.50 & \text{c.f.} & \text{245.5} & \text{for } [\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*] \text{.}\text{\textsuperscript{2}} & \\
\textbf{(53)} & 244.8 & 224.8 & 78.7 & 113.8 & 2092 & 2002, 1919 & 15.51 & \text{c.f.} & \text{245.5} & \text{for } [\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*] \text{.}\text{\textsuperscript{2}} & \\
\hline
\end{tabular}
\caption{Selected infrared and $^{13}\text{C}\{\text{H}\}$ NMR data for alkynylselenomethylidyne complexes\textsuperscript{a}}
\end{table}

As with the infrared data, the $^{13}\text{C}\{\text{H}\}$ NMR spectra of $51-53$ reveal resonances for the carbonyl ligands in the range $225 \pm 0.2$ ppm that are essentially unperturbed from the $\delta C_{\alpha}$ 224.0 observed for the haloalkylidyne precursor.\textsuperscript{2} However, there is a pronounced deshielding of the resonances for the alkylidyne carbon nuclei ($\delta C_{\alpha}$ 245.5 $\pm$ 1 cf. 208.7 for $[\text{Mo}(=\text{CCl})(\text{CO})_2\text{Tp}^*])$.\textsuperscript{2}
Furthermore, the presence of the -SeC=CR substituent on C\textsubscript{a} evidently results in an increase in the shielding of these nuclei compared with those for metal complexes containing either chalcogeno (-SeR) or alkynyl (-C=CR) carbyne substituents such as [Mo(=CSePh)(CO)\textsubscript{2}Tp*] (\textv{\textdelta} \textsubscript{C} 261.8)\textsuperscript{4} and [Mo(=CC=Cr-Bu)(CO)\textsubscript{2}Tp*] (\textv{\textdelta} 256.7).\textsuperscript{12}

The most interesting spectroscopic features for complexes of the type [Mo(=CSeC=CR)(CO)\textsubscript{2}Tp*] (R = t-Bu, 51, C\textsubscript{6}H\textsubscript{4}Me-4, 52, SiMe\textsubscript{3}, 53) involves the \textsuperscript{13}C {\text{\text{\textv{\text{\text{1}}}}}H}^\text{NMR data associated with the alkynyl carbon nuclei. In all cases, the C=CR unit of the selenoalkyne is sheltered from the influence of the metal-carbon triple bond by the selenium atom. Thus, for 51–53 there is a reversal of the aforementioned shielding trend (Table 6.1), with the alkynyl nuclei directly bound to the selenium atom (C\textsubscript{B}) resonating substantially upfield of C\textsubscript{a}. Such a relative shielding pattern for the SeC=CR unit has been previously noted for the complex [Ir(SeC=CC\textsubscript{6}H\textsubscript{4}Me-4)(CO)(PPh\textsubscript{3})\textsubscript{2}] (CDCl\textsubscript{3}: \textv{\textdelta} \text{CR} 94.9, \textv{\textdelta} \text{Se} 68.0)\textsuperscript{18} and is consistent with that of free selenoalkynes, e.g., PhSeC=CC\textsubscript{6}H\textsubscript{4}Me-4 (CDCl\textsubscript{3}: \textv{\textdelta} \text{CR} 103.2, \textv{\textdelta} \text{Se} 68.2).\textsuperscript{24}

Assignments for the alkynyl carbon nuclei of 51–53 were confirmed by two-dimensional HMBC experiments, which in the case of 51 revealed a three-bond interaction between the alkynyl carbon resonance at \textv{\textdelta} \text{C} 114.7 and the singlet proton resonance associated with the methyl groups of the t-butyl substituent (\textv{\textdelta} \text{H} 1.23). A weaker, four-bond interaction is apparent for the Se-substituted alkynyl carbon, C\textsubscript{B} (\textv{\textdelta} \text{C} 52.0), to this same proton signal. The variable extent of shielding observed for the C\textsubscript{B} resonances for 51–53 is presumably an expression of the relative donor capacities of the alkyne capping groups, which are transmitted along the carbon chain.

On the basis of this spectroscopic evidence, three mesomeric structures may be drawn to provide a full description of the bonding situation in complexes of the type [Mo(=CSeC=CR)(CO)\textsubscript{2}Tp*] (Figure 6.1).

![Figure 6.1. Resonance contributions to ground state bonding for alkynyleisenomethylidyne complexes [Mo(=CSeC=CR)(CO)\textsubscript{2}Tp*] [Mo] = Mo(CO)\textsubscript{2}Tp*; R = t-Bu, C\textsubscript{6}H\textsubscript{4}Me-4, SiMe\textsubscript{3}.]
One example of the above complexes was characterised crystallographically and the molecular structure is illustrated in Figure 6.2 with pertinent bond lengths and angles in the caption. The geometry of the alkynylselenomethylidyne complex \([\text{Mo}(=\text{CSeC}═\text{CSiMe}_{3})(\text{CO})_{2}\text{Tp}^*]\) (53) may be described as distorted octahedral, with the typically acute N–Mo–N angles (ca. 80°) characteristic of Tp* chelate coordination. The anticipated trans influence of the alkylidyne relative to the carbonyl ligands is manifest in the lengthening of the Mo–N(21) bond (2.312(8) Å). The structural features of most interest, however, are associated with the alkynylselenomethylidyne ligand.

![Figure 6.2](image)

**Figure 6.2.** Molecular structure of 53 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Mo–C(1) 1.805(12), C(1)–Se 1.887(12), Se–C(2) 1.874(14), C(2)–C(3) 1.175(17), C(3)–Si 1.838(15), Si–CMc 1.834(9), Mo–N(21) 2.312(8), Mo–N(31) 2.222(8), Mo–N(41) 2.227(8), Mo–C(20) 1.970(12), Mo–C(30) 1.999(14), C(20)–O(20) 1.135(13), C(30)–O(30) 1.190(14), Mo–C(1)–Se 162.4(8), C(1)–Se–C(2) 93.4(6), Se–C(2)–C(3) 171.6(15), C(2)–C(3)–Si 166.8(11), N(21)–Mo–N(31) 81.6(3), N(21)–Mo–N(41) 80.8(3), N(31)–Mo–N(41) 83.3(3), N(21)–Mo–C(1) 177.8(5), N(31)–Mo–C(1) 100.2(4), N(41)–Mo–C(1) 100.7(5), C(1)–Mo–C(20) 84.7(5), C(1)–Mo–C(30) 83.7(5), C(20)–Mo–C(30) 83.1(5), Mo–C(20)–O(20) 172.7(13), Mo–C(30)–O(30) 172.9(10).

The Mo–C(1) triple bond length, 1.805(12) Å, is comparable to those found for \([\text{Mo}(=\text{CC}_{6}\text{H}_{4}\text{Me}-4)(\text{CO})_{2}\text{Tp}^*])\) (1.804(4) Å)\(^{25}\) and the related complex \([\text{Mo}(=\text{CSeC}_{6}\text{H}_{4})_{3}(\text{CO})_{2}\text{Tp}^*]\) (1.801(4) Å).\(^{4}\) The Mo–C(1)–Se angle (162.4(8)°) shows a considerable departure from linearity, however, a comparable angle was observed for \([\text{Mo}(=\text{CSeC}_{6}\text{H}_{4}\text{Me}-4)(\text{CO})_{2}\text{Tp}^*]\) (163.1(3)°),\(^{25}\) suggesting that this parameter does not indicate a reduction of the Mo–C bond order. The bonds between the two coordinate selenium atom and carbon atoms C\(_a\) [C(1)] and C(alkyne) [C(2)] may be considered to be of statistically equal length, varying by less than 1 σ (1.887(12) and 1.874(14) Å) and are intermediate of carbon–selenium single and double bonds. The equality of the chalcogen–carbon bond lengths in 53 is distinct from the situation observed for the related complex \([\text{Mo}(=\text{CSeC}_{6}\text{H}_{4}\text{NO}_{2}-4)(\text{CO})_{2}\text{Tp}^*]\), in which the C\(_a\)–S bond was significantly (> 12 σ) shortened relative to the S–C(aryl) bond (1.712(4) vs
1.768(5) Å. The comparable C–Se bond lengths for 53 may be attributed to the interaction of the selenium lone pairs with each of the π-systems of the M–C and C–C triple bonds, i.e., contribution to the ground state from valence bond descriptions A and C, Figure 6.1.

A plane is defined by the chain of atoms of the alkynylselenomethylidyne ligand (CSeC₂Si) with the angle subtended by the two triple bonds at the selenium being 93.4(6)°. For substantial C–Se contributions to the ground state an angle closer to 120° would be expected. The bond lengths and angles within the linear -C≡CSiMe₃ moiety are unremarkable. The C–C separation (1.175(17) Å) is fully consistent with a triple bond and shorter than that found for the related complex [Mo(=CC≡CSiMe₃)(CO)₂Tp] (1.258(11) Å), in which some limited delocalisation of electron density was suggested.¹⁴ Angles at C(2) and C(3) are 171.6(15) and 166.8(11)°, respectively. The Si–C(alkyne) (1.838(15) Å) and Si–C(methyl) (1.834(9) Å) separations for 53 are not exceptional.
6.3 Reaction of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] with [Co₂(CO)₈]

As mentioned in Chapters 1 and 3 and discussed in detail in Chapter 5, the metal–carbon triple bond of alkylidyne complexes presents a reactive centre for the attachment of a variety of metal fragments. The metal-ligating properties of M=C bonds in the species [M(≡CR)(CO)₂L] (M = Cr, Mo, W; R = aryl or alkyl; L = Cp, Cp*, Tp) have been extensively studied and were reviewed by Stone in 1984, though the field concerning the construction of polymetallic assemblies containing μ₂- and μ₃-carbyne ligands has experienced continued growth since that time. Several cluster compounds containing μ₂- or μ₃-thiocarbyne ligands have been reported to arise from the treatment of Angelici’s thiomethylidyne complex [W(≡CSMe)(CO)₂Tp] with a number of metal complexes containing labile ligands (Scheme 6.6). The resultant complexes were found to be essentially analogous to those obtained from the related alkyl and aryl carbynes [W(≡CR)(CO)₂Tp] (R = Me, C₆H₄Me-4), i.e., the SMe group plays only a spectator role.

Investigations into the reactivity of the alkynylcarbyne complexes [M(≡CC≡Ct-Bu)(CO)₂L] (M = Mo, W; L = Cp, Tp, Tp*) towards low-valent metal fragments [L₉M(CO)₄] (L₉M = Mo(CO)₃Cp, Co(CO)₃) revealed that the site of ligation could be varied by altering the nature of the tridentate co-ligand, occurring through the C–C triple bond with the pyrazolylborate co-ligands (L = Tp, Tp*) and the M–C triple bond for the cyclopentadienide complexes (L = Cp), thus affording polymetallic assemblies containing homo- and heteronuclear metal–metal bonds, respectively (vide infra, Scheme 6.4).

In view of the rich cluster chemistry of Angelici’s thiocarbyne and the possibility of M=C or C=C coordination observed by Stone for alkynylcarbyne complexes, the reactivity of the
alkynylselenocarbynes described herein (comprising two independent units of unsaturation in addition to a selenoether donor) towards cluster formation was thus of interest.

Treatment of [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] (51) with one equivalent of [Co₂(CO)₈] in diethyl ether at room temperature proceeded with vigorous evolution of carbon monoxide to afford, in 81% yield, a brown complex formulated as [Co₂{µ-t-BuC=C=Mo(CO)₂Tp*} (CO)₆] (55) in which the dicobalt unit traverses the carbon–carbon triple bond distal to the molybdenum, as might be expected on steric grounds (Scheme 6.7). The infrared spectrum of 55 comprises the characteristic fingerprints of CO absorbances attributable to ‘Mo(CO)₃’ and ‘C₂=Co(CO)₆’ fragments (IR (hexane): 2091 m, 2055 vs, 2034 s, 2024 s, 1999 m, 1921 s (v CO) cm⁻¹). On the basis of comparative data for the dicobaltatetrahedrane complex [Co₂(µ-PhC≡CPh)(CO)₆] (IR: 2089 m, 2056 vs, 2027 s, 1985 vw), in which all infrared absorptions are due to the ‘Co₂(CO)₆’ unit, the pair of v CO absorptions at lowest frequency in the infrared spectrum of 55, 1999 and 1921 cm⁻¹, may be attributed to the ‘Mo(CO)₃’ unit. The intensity profile of the infrared spectrum for 55 resembles that of the related, selenium-free complex [Co₂{µ-t-BuC≡C=Mo(CO)₂Tp*}] (CO)₈. However, in the latter case the absorptions associated with the molybdenum carbonyls are at lower energy (1975 and 1898 cm⁻¹), reflecting the trend observed for the free carbyne complexes, i.e., [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] with v CO 2000 and 1916 cm⁻¹ vs [Mo(≡CEC≡Ct-Bu)(CO)₂Tp*] with v CO 1993 and 1908 cm⁻¹. An absorption attributable to the C–C stretch of the η²-alkyne at approximately 1700 cm⁻¹, expected to be very weak, was not observed.

Scheme 6.7. Formation of dimetallatetrahedrane 55 from treatment of 51 with dicobalt octacarbonyl.

The retention of the intact terminal alkylidyne group upon coordination of the dicobalt unit is confirmed by the characteristic low-field ¹³C{'H} NMR signal, δ 261.7 (Mo≡C), which is deshielded relative to the corresponding resonance for the precursor 51 (δ 245.0). A downfield shift was also noted for the molybdenum carbonyls upon formation of the dimetallatetrahedrane

---

8 For clarity, line formulae for binuclear complexes in this Chapter will take this form rather than that which is recommended by IUPAC in order to reflect the emerging behaviour of the Mo(CO)₃Tp* group as an effectively innocent substituent.
55 ($\delta$ 227.2 vs 225.1 for 51). In addition, the appearance of a singlet resonance attributable to the CO ligands of the ‘$\text{Co}_2(\text{CO})_6$’ moiety ($\delta$ 199.9) was observed, which displays the characteristic broadening due to the quadrupolar cobalt nuclei.

The bridging alkyne carbon nuclei of $[\text{Co}_2\{\mu-t\text{-BuCSe}=\text{Mo}(\text{CO})_2\text{Tp}^*\}_2(\text{CO})_6]$ resonate at $\delta$ 113.7 ($t$-BuC=CSe) and 85.6 ($t$-BuC=CSe), near the 85–106 ppm range reported by Lang for those in the related alkyne selenoether-derived dicobaltatetrahedranes $[\text{Co}_2(\mu-R'C_2\text{SeR})(\text{CO})_6]$ ($R = \text{Ph}, R' = \text{Ph}, \text{SiMe}_3$; $R = \text{C}_6\text{H}_4\text{Me}_2-2,4,6, R' = \text{Ph}, \text{SiMe}_3$; $R = \text{C}_6\text{H}_4\text{OMe}-4, R' = \text{Ph}$).$^{28}$ Furthermore, the corresponding data for the $\eta^2$-coordinated alkyne carbon atoms in Stone’s analogous complex $[\text{Co}_2\{\mu-t\text{-BuCSe}=\text{Mo}(\text{CO})_2\text{Tp}^*\}_2(\text{CO})_6]$, $\delta$ 113.0 ($t$-BuC=C) and 92.5 ($t$-BuC=C),$^{12}$ are in close agreement with those for 55, though the resonance for the selenium substituted carbon atom appears at a typically shielded position relative to the hydrocarbon derivative. Moreover, the significant deshielding noted for the resonances associated with $t$-butyl substituted alkyne carbon centres upon coordination through the C=C bond ($\delta$ 113.7, $t$-BuC=CSe, 36.8, $C(\text{CH}_3)_2$ and 32.2, $C(\text{CH}_3)_3$ cf. 52.0, 30.7, and 29.3, respectively, for 51) resembles the situation found for the selenium-free complex $[\text{Co}_2\{\mu-t\text{-BuCSe}=\text{Mo}(\text{CO})_2\text{Tp}^*\}_2(\text{CO})_6]$ ($\delta$: 113.0, $t$-BuC=C, 37.6, $C(\text{CH}_3)_3$ cf. 33.3 $C(\text{CH}_3)_3$ cf. 78.3, 30.7, 28.0, respectively, for $[\text{Mo}(\equiv\text{CC}=\text{Ct-Bu})(\text{CO})_2\text{Tp}^*]$).$^{12}$

The reaction of 55 with bis(diphenylphosphino)methane

The reaction between 55 and bis(diphenylphosphino)methane (dpmm) was conducted under dichloromethane reflux for three and a half hours after which time thin layer chromatography revealed that all of the starting material had been consumed. Subsequent solvent removal and cryostatic chromatographic separation (~33 °C) afforded two new complexes. The more rapidly eluted brown-orange band corresponded to the major reaction product and contained a compound formulated as the desired species $[\text{Co}_2\{\mu-t\text{-BuC}=\text{Mo}(\text{CO})_2\text{Tp}^*\}_2(\mu\text{-dpmm})(\text{CO})_6]$ (56), in which the dpmm ligand has displaced a carbonyl ligand from each cobalt centre. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 56 revealed the presence of a single broad resonance at $\delta$ 38.2, consistent with the dpmm ligand bridging the two cobalt atoms.$^{12}$ In the $^1\text{H}$ NMR spectrum, the dpmm CH$_2$ group gives rise to two multiplets at $\delta$ 3.35 and 3.25, and though in principle a characteristic ABXX' splitting pattern should be observed for the diastereotopic CH$_2$ protons, the significant overlap of these two resonances precluded the resolution of accurate $J_{\text{ph}}$ couplings. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 56, the methylene carbon of the dpmm ligand resonates at $\delta$ 35.2 and has triplet multiplicity due to coupling to the two $^{31}\text{P}$ nuclei. Corresponding resonances in the tungsten diynyl complex $[\text{Co}_2\{\mu-\text{PhC}=\text{C}-\text{W}(\text{CO})_3\text{Cp}\}_2(\mu\text{-dpmm})(\text{CO})_4]$, in which the dpmm ligand similarly bridges a ‘$\text{Co}_2\text{C}_2$’ unit, appear
at $\delta_\parallel$ 3.15, 3.78 and $\delta_\perp$ 34.82.$^{29}$ Two broad, down-field resonances are attributed to the cobalt-bound carbonyl ligands ($\delta_c$ 207.1, 202.5) (the dppm ligand prevents the fluxional exchange of the carbonyl sites that is observed for the precursor) and the $\mu$-alkyne carbons resonate at $\delta$ 119.2 ($t$-BuC=CSe) and 83.9 ($t$-BuC=CSe) with triplet multiplicity, though the unsatisfactory signal-to-noise ratio again prevented the determination of accurate $J_{PC}$ or $J_{sec}$ values.

A minor product was isolated from the second, narrower green band and was formulated as the selenium-free complex $[\text{Co}_2(\mu-\text{t-BuC_2C}=\text{Mo(CO)}_2\text{Tp}^*)(\mu\text{-dppm})(\text{CO})_4]$ (57), which was obtained in 2% isolated yield and presumably results from minor decomposition of the starting alkynylselenomethylidyne complex under these reaction conditions. Infrared and $^{13}$C{¹H} NMR spectroscopic data for 57 are consistent with those reported by Stone and co-workers for the analogous tungsten compound $[\text{Co}_2(\mu-\text{t-BuC_2C}=\text{W(CO)}_2\text{Tp}^*)(\mu\text{-dppm})(\text{CO})_4]$. Complex 57 displayed a broad singlet resonance in the $^{31}$P{¹H} NMR spectrum ($\delta_p$ 33.5), which was approximately 5 ppm upfield of that observed for 56. Differences in the proton spectra for 56 and 57 suggest that the relative position adopted by the $\mu$-dppm ligand with respect to the remaining ligands of the complex differs for each of these compounds. In 56, the two $^1$H NMR resonances for the $\text{CH}_2$ group are near coincident whereas in 57 the chemical shifts for the diastereotopic dppm methylene protons differ appreciably ($\delta_\parallel$ 3.65, 3.45).

Both 56 and 57 were crystallographically characterised and results of these studies are summarised in Figures 6.3, 6.4, 6.5 and Table 6.3. Systematic errors in the crystal data for 57 precluded a full refinement but the identity of the complex was nevertheless unambiguously confirmed.

The molecular structure of $[\text{Co}_2(\mu-\text{t-BuC_2CSeC}=\text{Mo(CO)}_2\text{Tp}^*)(\mu\text{-dppm})(\text{CO})_4]$ (56) revealed the expected disruption of the C-C=tBu chain that is induced by $\pi$-bonding, with the familiar bending back of the substituents attached to the alkynyl unit, $\text{C}=$C-Se 142.8(4)$^0$ and $\text{C}=$C=tBu 141.6(4)$^0$. This is comparable to the approximately 40$^0$ distortions that were observed for the selenoalkyne ligand in the structurally characterised salt $[\text{W}(\eta^2\text{-t-PrSeC}=\text{CPh})(\text{CO})_2\text{Tp}^*)]^+$ (58) (Chapter 4). The C-C bond length of 1.338(7) Å, which as expected has experienced a significant lengthening (83 σ) upon $\pi$-coordination (cf. 1.175(17) Å for 53), is identical to that observed for the coordinated C$_2$ unit of the selenoalkyne in the complex cation $[\text{W}(\eta^2\text{-t-PrSeC}=\text{CPh})(\text{CO})_2\text{Tp}^*)]^+$ (1.338(7) Å) and also in the structurally characterised simple alkynyl adduct $[\text{Co}_2(\mu-\text{PhC_2SePh})(\text{CO})_4]$ (1.338(7) Å),$^{28}$ offering support to the suggested independence of this unit from the $\text{M}=$C bond in the alkynylselenomethylidyne complexes 51–53.
CHAPTER 6. Tp* Ligated Alkynylselenomethylidyne Complexes of Molybdenum

Figure 6.3. Molecular structure of 56 with 30% probability ellipsoids and hydrogen atoms omitted.

Table 6.3. Selected bond distances (Å) and angles (°) for 56

<table>
<thead>
<tr>
<th>Bond Distances, Å</th>
<th>Bond Angles, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo–C(1)</td>
<td>1.823(5)</td>
</tr>
<tr>
<td>C(1)–Se</td>
<td>1.857(5)</td>
</tr>
<tr>
<td>Se–C(2)</td>
<td>1.903(5)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.338(7)</td>
</tr>
<tr>
<td>C(3)–(4)</td>
<td>1.504(7)</td>
</tr>
<tr>
<td>Co(1)–Co(2)</td>
<td>2.459(1)</td>
</tr>
<tr>
<td>Co(1)–C(40, 50)</td>
<td>1.795(6), 1.779(6)</td>
</tr>
<tr>
<td>Co(2)–C(60, 70)</td>
<td>1.755(6), 1.775(6)</td>
</tr>
<tr>
<td>Mo–C(1)–Se</td>
<td>152.3(3)</td>
</tr>
<tr>
<td>C(1)–Se–C(2)</td>
<td>109.0(2)</td>
</tr>
<tr>
<td>Se–C(2)–C(3)</td>
<td>142.8(4)</td>
</tr>
<tr>
<td>C(2)–C(3)–C(4)</td>
<td>141.6(5)</td>
</tr>
<tr>
<td>P(1)–C(10)–P(2)</td>
<td>111.7(3)</td>
</tr>
<tr>
<td>Co(1)–C(2)–Co(2)</td>
<td>78.1(2)</td>
</tr>
<tr>
<td>Co(1)–C(3)–Co(2)</td>
<td>75.5(2)</td>
</tr>
<tr>
<td>Co(1)–Co(2)–C(2)</td>
<td>51.1(2)</td>
</tr>
<tr>
<td>Co(1)–Co(2)–C(3)</td>
<td>51.6(2)</td>
</tr>
<tr>
<td>Co(2)–Co(1)–C(2)</td>
<td>50.8(2)</td>
</tr>
<tr>
<td>Co(1)–C–O (40, 50)</td>
<td>177.2(5), 178.4(6)</td>
</tr>
<tr>
<td>Co(2)–C–O (60, 70)</td>
<td>177.3(6), 177.8(6)</td>
</tr>
<tr>
<td>C(2)–Co(1)–C(40, 50)</td>
<td>144.5(3), 101.1(2)</td>
</tr>
<tr>
<td>C(2)–Co(2)–C(60, 70)</td>
<td>110.3(3), 140.2(3)</td>
</tr>
</tbody>
</table>
Of greater interest are the changes that occur in the alkylidyne portion of the molecule upon \( \eta^2 \)-coordination of what has been suggested to be an independent triple bond. The Mo–C(1) distance, 1.823 (5) Å, while remaining consistent with a molybdenum–carbon triple bond separation, is longer than the corresponding bond length measured for the free alkynylselenomethylidyne complex 53 \( (1.805(12) \text{ Å}) \). Moreover, the valence angle across C\(_\alpha\) is distinctly non-linear \( (152.3(3)^\circ) \) and represents the largest distortion observed amongst reported data for Group 6 alkylidyne complexes with pyrazolylborate co-ligands, which typically fall within the range 161–180° (see Appendix A.2, Table 1.2). This distortion may be attributed to the unfavourable interactions that arise from the nestling of the \( \tau \)-butyl group within the cleft provided by the pyrazolyl groups based on N31 and N41.

Calculations for the free alkyynes MeEC=CMMe (E = O, S, Se, Te), which were discussed in Chapter 4 (Section 4.2), suggest that upon chalcalkyne \( \pi \)-coordination the C–E bond should be positively augmented at the expense of the alkynyl C–C linkage. However, experimental data for 56 do not follow this prediction, with the Se–C(alkyne) separation \( (1.903(5) \text{ Å}) \) being substantially elongated upon coordination and best described as having a bond order close to unity. Conversely, the Se–C\(_\alpha\) bond is contracted \( (1.857(5) \text{ Å}) \) relative to the average selenium–carbon separation \( (1.881(13) \text{ Å}) \) that was observed for the alkynylselenomethylidyne ligand in 53. Moreover, the angle across the central selenium atom has been substantially \( (39^\sigma) \) expanded \( (109.0(2)^\circ) \) for 56 cf. \( 93.4(6)^\circ \) for 53), which implies an increase in s-character in the hybridisation of this central atom. In the related selenoalkyne complex \( [\text{Co}_2(\mu-\text{PhC}_2\text{SePh})(\text{CO})_6] \) the Se–C(Ph) and Se–C(alkyne) separations \( (1.896(4) \text{ and } 1.878(5) \text{ Å}, \) respectively) remain comparable to one another, differing by less than \( 4^\sigma \). It should be noted that for the alkynylselenomethylidyne complexes described herein the situation is complicated by the availability of a second \( \pi \)-system belonging to the M–C triple bond. Accordingly, it is suggested that the data for 56 are consistent with a significant contribution to the ground state structure from the heteroallenic resonance form A (Figure 6.1). Above all, however, the steric clutter of the structure should not be discounted as a contributing factor to these geometric features.

Structural dimensions of the Co\(_2\)C\(_2\) tetrahedrane of 56 (Figure 6.4) are extremely close to those found for the related complex \( [\text{Co}_2(\mu-\text{PhC}_2\text{SePh})(\text{CO})_6] \),\(^{28}\) despite the replacement of an aryl selenium substituent with a selenoalkylidyne unit. Bond lengths and angles between the \( \eta^2 \)-alkyne and the cobalt centres are consistent with the Co–C(alkyne) atoms forming the vertices of two isosceles triangles. The dppm ligand has replaced an axial carbonyl from each cobalt centre and the remaining terminal carbonyl ligands emanate from the Co\(_2\)C(2) plane in the direction away from the phosphine. The Co–Co separation, 2.4586(10) Å, is shorter than
that observed for the related complexes \([\text{Co}_2\{\mu-\text{PhC}_2\text{CC}=\text{CW}(\text{CO})_3\text{Cp}\}(\mu-\text{dppm})(\text{CO})_4]\) (2.470(2) Å)\(^2\) and \([\text{Co}_2\text{W}(\mu_3-\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_8\text{Cp}]\) (2.488(1) Å)\(^3\) but is comparable to the corresponding separation for the simple selenoalkyne-cobalt adduct \([\text{Co}_2(\mu-\text{PhC}_2\text{SePh})(\text{CO})_6]\) (2.46(4) Å).\(^2\) The similarity of structural parameters for 56 and this simple adduct is in line with the alkyne and alkylidyne bonds having no direct impact upon one another in the alkynylselenomethylidyne complexes. However, it appears that effects may be mediated in a ‘push/pull’ manner via the selenium atom, i.e., a weakening of the interaction of one triple bond with the selenium allows for a strengthening of the interaction with the other π-system.

\[\text{Figure 6.4. Dicobaltatetrahedrane core of 56 with 30\% probability ellipsoids shown. Alkyne substituents, phenyl arms of dppm ligand and hydrogen atoms have been omitted for clarity.}\]

Geometric parameters associated with the dicobaltatetrahedrane in the selenium-free complex \([\text{Co}_2\{\mu-t-\text{BuC}_2\text{C}=\text{Mo}(\text{CO})_3\text{Tp}\}](\mu-\text{dppm})(\text{CO})_4]\) (57) are in good general agreement with those of 56. An in depth analysis of the possible significance of structural dimensions for 57 would not be justified in view of the low quality of the crystal data but several salient features nevertheless warrant mentioning. As assumed on the basis of spectroscopic data, the dppm ligand adopts a different relative orientation in each of these complexes. In 56 the bridging phosphine ligand, though distal to the molybdenum centre, may be described as being syn with respect to the carbonyl ligands of the molybdenum atom, whereas in 57 the relative orientation of the dppm ligand and the t-butyl moiety is reversed such that the dppm ligand is oriented anti to the molybdenum carbonyls. The preference for an anti disposition of the dppm ligand in the solid state conformation of 57 can be rationalised on the basis of an attractive π–π stacking interaction between the aromatic moieties of the pyrazolyl ligand and one dppm phenyl arm, which is possible due to the closer approach of these two units in 57, i.e., one rather than two atoms separate the alkyne unit, and hence the ‘Co₂(CO)₆(μ-dppm)’ cluster, from the molybdenum centre.
Variations to the molecular geometry of the alkynylcarbyne ligand upon formation of the μ-alkyne-dicobalt complex are as expected in the absence of the π-donating selenium atom, which appeared to amplify the structural changes for 56 through enhanced interaction with the metal–carbon triple bond upon coordination of the alkyne unit. The C(2)–C(3) bond length of 57 (1.34(3) Å) is consistent with the anticipated elongation of the C–C alkyne bond (cf. 1.258(11) Å for [Mo(≡CC≡SiMe₃)(CO)₂Tp])¹⁴ that occurs upon μ-coordination across the Co–Co bond and, together with the carbon–carbon single bond separation between the two triple bonds (1.45(3) Å), is consistent with a reduction in the conjugation along the carbon spine. Moreover, the alkylidyne Mo–C(1) separation (1.85(2) Å) and the Mo–C(1)–C(2) angle (174.1(8)°) both vary little from those recently reported for [Mo(≡CC≡SiMe₃)(CO)₂Tp] (1.833(7) Å and 176.8 (8)°, respectively),¹⁴ suggesting that the impact of η²-alkyne coordination upon the carbyne end of the molecule is minimal.
6.4 Reaction of [Mo(≡CSe≡Ct-Bu)(CO)₂Tp*] with [Mo(CO)₃Cp]₂

Somewhat surprisingly, analogous polynuclear assemblies were not formed upon treating 51 with synthetic equivalents of [Mo(CO)₃Cp]₂. Heating the complex [Mo(≡CSe≡Ct-Bu)(CO)₂Tp*] with [Mo(CO)₃Cp]₂ in toluene (110 °C) led to complete decomposition of the alkynylselenomethylidyne complex (as determined by thin layer chromatography). In contrast, Stone and co-workers described the isolation of µ-alkyne trimetal complexes \([\text{Mo}_2\{\mu-t\text{-BuC}_2\equiv\text{C}W(\text{CO})_2\text{Tp}\}_2(\text{CO})_4\text{Cp}_2]\) from a parallel reaction with the related, selenium-free tungsten propargyldiyne \([W(≡\text{CC≡Ct-Bu})(\text{CO})_2\text{Tp}]^{12}\) bearing the sterically less bulky Tp ligand.

Similarly, no productive reaction was observed when the highly reactive triply bound dimer \([\text{Mo(CO)}_2\text{Cp}]_2\) (derived by heating \([\text{Mo(CO)}_2\text{Cp}]_2\) to fusion (215–217 °C) under vacuum)\(^{31}\) was employed in tetrahydrofuran solution, with regeneration of the singly bound dimer \([\text{Mo(CO)}_3\text{Cp}]_2\) from the tetracarbonyl molybdenum derivative being instead observed.

Evidently, the dimolybdenum species \([\text{Mo(CO)}_2\text{Cp}]_2\) is not as well behaved as the more reactive \([\text{Co}_2(\text{CO})_8]\) towards µ-coordination across the metal–metal bond, but the reasons for this reticence remain unclear.
6.5 Reaction of \([\text{Mo(=CSeC=Cl-Bu)(CO)}_2\text{Tp}^*]\) with \([\text{Pt(PPh}_3)_2\text{(C}_2\text{H}_4)]\)

A characteristic and general reaction occurs between low-valent platinum complexes of the type \([\text{Pt(PR}_3)_2\text{(C}_2\text{H}_4)]\) and transition metal carbyne complexes \([\text{L}_n\text{M(=CR)}]\), which involves displacement of the alkene by the metal–carbon triple bond to afford complexes of the general formula \([\text{PtM(=CR)(PR}_3)_2\text{L}_n]\) (a, Scheme 6.8).\(^{20,27,32,33}\) By employing the zero-valent metal–alkene complexes \([\text{Pt(alkene)}_n]\) \((n = 3\) or \(4;\) alkene = ethylene or ½ cod) in a 2:1 ratio, the trimetallic complexes \([\text{M}_2\text{Pt(=CR)}_2\text{(L)}_n]\) may be obtained, comprising the typical bis(alkylidyne) ‘bowtie’ structure (b, Scheme 6.8).\(^{26,27,34}\)

![Scheme 6.8](image)

Scheme 6.8. Characteristic products arising from the addition of low-valent platinum species to \(M=\text{C}\) bonds (\(M = \text{Mo or W};\) \(R = \text{alkyl or aryl}, n = 3\) or \(4;\) alkene = ethylene or ½ cod).

Several examples of platinum complexes containing \(\eta^2\)-alkyne ligands are also known, with Chatt and co-workers describing the isolation of a series of stable examples of the form \([\text{Pt}(\eta^2\text{-RC=CR})(\text{PPh}_3)_2]\) \((R = R' = \text{H, alkyl, aryl}; R = \text{H, R'} = \text{alkyl, aryl})\) as early as 1957.\(^{35}\) Monomeric platinum complexes involving 2,4-hexadiyne ligands were later described\(^6\) and in 1978, Stone described the reaction of \([\text{Pt}(\text{L})_2\text{(C}_2\text{H}_4)]\) \((\text{L} = \text{PPh}_3\) or \(\text{PMePh}_2)\) with 1,4-diphenylbuta-1,3-diyne to give, successively, both mono- and diplatinum compounds \([\text{Pt}(\eta^2\text{-PhC=CPh})(\text{PPh}_3)_2]\) and \([\text{Pt}_2(\eta^2\text{-PhC=CPh})(\text{PPh}_3)_4]\).\(^{37}\)

It was thus of interest to establish whether ‘\(\text{Pt}(\text{PPh}_3)_2\)’ fragments would bond preferentially with the \(\text{C=C}\) or \(\text{M=C}\) group in the alkynylselenomethylidyne complexes 51–53. Interestingly, however, the treatment of 51 with \([\text{Pt}(\text{PPh}_3)_2\text{(C}_2\text{H}_4)]\) in tetrahydrofuran at room temperature ultimately provided an air-stable, yellow solid in which the bis(phosphine)platinum species was not ligated by either distinct triple bond of the alkynylselenomethylidyne precursor.

Elemental microanalytical data for the isolated material were consistent with the expected 1:1 combination of the complex \([\text{Mo(=CSeC=Cl-Bu)(CO)}_2\text{Tp}^*]\) and a ‘\(\text{Pt}(\text{PPh}_3)_2\)’ fragment, but the remaining spectroscopic data were at odds with a structure involving simple \(\eta^2\)-\(\text{M,}\) \(\text{C}\) or \(\text{C,}\) \(\text{C}\) coordination to the platinum unit. Instead, the spectroscopic data were consistent with formulation as \(\text{trans-[Pt}\{\text{SeC=Mo(CO)}_2\text{Tp}^*\}(\text{C=C} \text{-Bu})(\text{PPh}_3)_2]\) (59), in which oxidative addition of the Se–C(alkynyl) bond to the platinum centre had occurred, resulting in terminal alkynyl and ‘selenolate’ ligands (Scheme 6.9), though initial \(\pi\)-coordination of the ‘\(\text{Pt}(\text{PPh}_3)_2\)’ unit is likely a preliminary mechanistic step. The C–Se bond cleavage of selenophenes by
transition-metal complexes and the oxidative addition of a C-Se bond of Ph₂Se to [Pt(PE₃)₃] to produce trans-[PtPh(SePh)(PE₃)₂] have been previously reported.\(^{45}\)

![Scheme 6.9. Treatment of 51 with [Pt(PPh₃)₂(C₂H₄)] to provide the Pt-insertion product 59.](image)

The formulation of 59 as resulting from insertion of the ‘Pt(PPh₃)₂’ unit into the Se-C(alkynyl) bond of the alkynylselenomethylidyne ligand was supported by the \(^{31}\)P{\(^{1}\)H} NMR spectrum (Figure 6.6), which featured a singlet resonance (δ₂ 21.1) with Pt satellites (\(^{1}\)J\(^{pp}\) = 2695 Hz). The position of this resonance and magnitude of the coupling are similar to those observed for the related platinum alkynyl complex trans-[Pt(C₆H₄Me-4)(C≡CC≡CH)(PPh₃)₂] (CDCl₃; δ₂ 21.3, \(^{1}\)J\(^{pp}\) = 2959 Hz)\(^{46}\) and confirm the trans stereochemistry of the phosphine ligands. The virtual coupling pattern of the phenyl carbons in the \(^{13}\)C{\(^{1}\)H} NMR spectrum and the triplet multiplicity of the resonances for the alkynyl nuclei, δ₂ 120.2 (PtC≡Ct-Bu) and 74.5 (PtC≡Ct-Bu), with a \(^{3}\)J\(^{PC}\) coupling of 16 Hz resolvable for the latter, were also consistent with the trans-(PPh₃) geometry.

![Figure 6.6. \(^{31}\)P{\(^{1}\)H} NMR spectrum of 59 in CD₂Cl₂ at 25 °C.](image)

The solution infrared spectrum of 59 revealed two carbonyl absorptions at low frequency (1952 and 1868 cm\(^{-1}\)), reflecting an increase in electron density at the molybdenum centre upon replacing the alkyne substituent of 51 (2000, 1916 cm\(^{-1}\)) with a ‘Pt(PPh₃)₂’ unit. In Angelici’s bridging thiomethylidyne complex [WPt(µ-CSMe)(CO)₂(PMe₃)₂Tp], in which the M≡C bond
behave as a ligand towards the platinum species, the infrared spectrum revealed carbonyl-associated absorptions that were at substantially lower frequencies than those observed for 59 (1866, 1784 cm\(^{-1}\), though one of these assumes semi-bridging character.\(^{27}\)

A strong daughter ion in the mass spectrum was consistent with the bis(triphenylphosphine)platinum alkyne fragment [Pt(PPh\(_3\))\(_2\)(C≡Ct-Bu)]\(^+\) (m/z: 800.2, 100%), and indicative of C-Se cleavage having occurred via the C\(_\beta\)-Se vs the C\(_\alpha\)-Se bond. The regioselectivity of the oxidative addition was furthermore confirmed by the \(^{13}\)C\(\{^1\)H\} NMR spectrum, which exhibited a singlet resonance characteristic of a metal carbyne at \(\delta_{\alpha}\) 302.5 (cf. [Mo=[CMe(CO)]\(_2\)Tp\(*\)] \(\delta_{\alpha}\) 304).\(^{47}\) A significantly more deshielded signal would be expected for the complex arising from C\(_\alpha\)-Se cleavage, i.e., [Mo=[Cp]Pt(PPh\(_3\))\(_2\)(SeC≡Ct-Bu)(CO)]\(_2\)Tp\(*\)]. Indeed, in Templeton’s related metal carbide [Mo=[CFe(CO)]\(_2\)Cp\(_2\)](CO\(_2\))Tp\(*\)], the bridging carbon resonates at \(\delta_{\alpha}\) 381, which is near the range expected for vinylidene C\(_\alpha\) chemical shifts and far below those of metal carbynes.\(^5\) Furthermore, the carbido complex [Ru=[CpCl\(_2\)SMe\(_2\)]\(_2\)Cl\(_2\)](PCy\(_3\))\(_2\)], in which the carbido coordinates to square planar palladium, also has a \(\delta_{\alpha}\) resonance at 381.\(^{48}\) Thus one may, with considerable confidence, expect a similar chemical shift for the putative carbide isomer [Mo=[Cp]Pt(PPh\(_3\))\(_2\)(SeC≡Ct-Bu)(CO)]\(_2\)Tp\(*\)]. Presumably, the regiospecificity of the C-Se cleavage is a consequence of the steric congestion, which would exist if insertion had occurred at the C\(_\alpha\)-Se bond, or indeed operate en route to the alternative transition state.

A single crystal X-ray analysis provided unambiguous confirmation of the identity of 59 as trans-[Pt{SeC≡Mn(CO)]\(_2\)Tp\(*\)}(C≡Ct-Bu)(PPh\(_3\))\(_2\}] and the results of this study are summarised in Figure 6.9. The molecular structure of the complex revealed the expected octahedral coordination at the molybdenum centre, with three facial positions occupied by the nitrogen atoms of the tripodal ligand and the customary elongation of the Mo–N separation trans to the alkylidyne unit (2.306(3) Å).

The bimetallic species 59 represents the first example of a structurally characterised complex bearing an end-to-end \(\mu:\sigma(C)\cdot\sigma(Se)\) bridging selenocarbonyl unit. While the bend across the alkylidyne moiety (163.1(2)°) is minimally distorted from that observed for the intact alkynylselenomethyldyne ligand of complex 53, an examination of the Mo–C separation reveals (although within 6 \(\sigma\) due to the poor bond precision in 53) a relative elongation for this parameter (1.834(4) cf. 1.805(12) Å for 53), with that of 59 being towards the longer end of observed M≡C bonds in molybdenum carbyne complexes.\(^{49}\) Additionally, the contraction of the C\(_\alpha\)-Se distance (1.828(12) Å) and expansion of the angle across the central selenium atom (104.9(1)°) compared with the corresponding data for the uninterrupted
alkynylselenomethylidyne ligand of \([\text{Mo}(\equiv\text{CSeC}≡\text{CSiMe}_3)\text{(CO)}_2\text{Tp}^*])\) (1.887(12) Å, and 93.4(6)° respectively) together imply a significant contribution to the ground state structure of 59 from the heteroallenic resonance form A in Figure 6.7.

Figure 6.7. Resonance contributions to ground state bonding for 59.

An analogous end-to-end bridging mode for the related thiocarbonyl ligand has been previously observed and bond lengths and angles within the bridging selenocarbonyl ligand may be compared to those of the structurally characterised complex \([\text{Mo}_2(\mu-\text{CS})\{\text{N}(\text{R})\text{Ar}\}_4]\) (R = C(CD₃)₂CH₃, Ar = C₆H₃Me₂-3,5) ((i) Figure 6.8), prepared by treating \([\text{Mo}\{\text{N}(\text{R})\text{Ar}\}_3]\) with carbon disulfide.⁵⁰ In this complex, the bridging CS unit clearly comprises M–C triple and C–S single bonds (Mo–C₉ 1.751(12) Å, Mo–C–S 162.7(8)°, and C–S–Mo 130.5(5)°). Treatment of the complex \([\text{W(CO)(CS)(dppe)}_2]\) with the reactive acetone species \([\text{W(CO)}_5(\text{OCMe}_2)]\) similarly affords a sulfur-bonded thiocarbonyl adduct \([\text{W}_2(\mu-\text{CS})(\text{CO})_6(\text{dppe})_2]\) ((ii), Figure 6.8).⁵¹ Notably, the \(\mu_2,\eta^2-\text{C}_4\text{S}\) bridging mode observed for the above complexes contrasts with the semibridging⁵² and side-on bridging⁵³ modes exhibited by the thiocarbonyl ligand in pyrazolylborate co-ligated systems, which are of relevance to this work. In fact, the W–Au bond in the complex \([\text{W} \equiv \text{Au}(\text{CO})_2(\text{CS})(\text{PR}_3)\text{Tp}]\) ((iii), Figure 6.8) is semi-bridged by both a CO and CS ligand, with a stronger interaction noted for the thiocarbonyl group.⁵² In the neutral W–Mo bonded dimer \([\text{MoW}(\mu-\text{CS})(\text{CO})_4(\eta^5-\text{C}_9\text{H}_7)\text{Tp}]\), the thiocarbonyl ligand exhibits a four electron side-on bridging mode, thereby allowing each of the two metals to reach coordinative saturation ((iv), Figure 6.8).⁵³

Figure 6.8. Selected bridging thiocarbonyl complexes (i)⁵⁰ (R = C(CD₃)₂CH₃, Ar = C₆H₃Me₂-3,5), (ii)⁵¹, (iii)⁵² (PR₃ = PPh₃, PMe₃), (iv)⁵³ (In = \(\eta^1-\text{C}_9\text{H}_7\)).
A near idealised square planar geometry is evident for the platinum centre of 59, with only minimal distortions from linearity noted for the trans inter-ligand angles (Se–Pt–C 177.04(12)° and P–Pt–P 170.17(3)°). The selenium–platinum bond length (2.4914(4) Å) is appropriate for the separation between platinum and an organic selenolate ligand and is similar to that reported for the complex cis-[Pt{CH=CPh(SeC_6H_4Cl-4)}(SeC_6H_4Cl-4)(PPh_3)_2] (2.488 Å).\(^{54}\) The phosphorus–platinum bond lengths (2.3080(10) and 2.3175(9) Å) fall within the normal range expected for four-coordinate, tertiary phosphine platinum complexes, e.g., the structurally characterised bis(alkynyl) compound trans-[Pt(C≡CSiMe_3)_2(PPh_3)_2] (Pt–P 2.3113(8) Å).\(^{46}\)

Figure 6.9. Molecular structure of 59 with 30% probability ellipsoids shown. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Mo–C(1) 1.834(4), C(1)–Se 1.828(4), Se–Pt 2.4914(4), Pt–C(2) 1.992(4), C(2)–C(3) 1.176(5), C(3)–C(4) 1.487(6), Pt–P(1) 2.3080(10), Pt–P(2) 2.3175(9), Mo–N(2) 2.306(3), Mo–N(3) 2.253(3), Mo–N(4) 2.233(3), Mo–C(20) 1.987(5), Mo–C(30) 1.999(5), Mo–C(1)–Se 163.1(2), C(1)–Se–Pt 104.86(12), Se–Pt–C(2) 177.04(12), P(1)–Pt–P(2) 170.17(3), Pt–C(2)–C(3) 178.2(3), C(2)–C(3)–C(4) 177.6(5).

Bond lengths and angles within the σ-alkynyl ligand (C(2)–C(3) 1.176(5) Å, C(2)–C(3)–C(4) 177.6(5)°) are strikingly similar to the independent C≡C bond of the crystallographically characterised alkynylselenomethylidyne complex [Mo=C≡C≡CSiMe_3](CO)_2Tp*] (C≡C 1.175(17) Å and Se–C(2)–C(3) 171.6(15)° for 53). The π-basic organic chalcogenolate ligand results in a slight shortening of the trans-disposed Pt–σ-alkynyl separation (1.992(4) Å)
relative to that reported for the related complex \( \text{trans-}[\text{Pt}(C=\text{CSiMe}_3)(\text{PPh}_3)_2] \) (2.004(3) Å), in which the \( \text{trans} \) ligand is a \( \pi \)-acidic \( \sigma \)-alkynyl.\(^{45}\)

### 6.5.1 Mechanism of Pt-insertion into the C–Se bond of 51

The reaction between \([\text{Pt}(\text{PPh}_3)_2(C_2H_4)]\) and \([\text{Mo}=\text{CSeC}≡\text{Ct-Bu})(\text{CO})_2\text{Tp}^*\]) to provide the \( \text{trans-(PPh}_3)\) \( \text{species 59 was very slow, taking seven days to reach completion. In situ monitoring of the reaction mixture, however, revealed that all of the starting material had been consumed much earlier than this, with the carbonyl absorptions for [Mo(=CSeC≡Ct-Bu)(CO)_2Tp^*] in the infrared spectrum being replaced by a cluster of absorbances near 1970 and 1880 cm\(^{-1}\). Furthermore, several \( \text{cis-(PPh}_3)\) \( \text{species were evident during the reaction course (as determined by } ^{31}\text{P}(\text{H}) \text{NMR spectroscopy). This pattern of reactivity is consistent with a complex mechanism that ultimately leads to insertion of the ‘Pt(PPh}_3)' unit into the Se–C(alkyne) bond. Indeed, by halting the reaction progress at an early stage, several intermediates could be isolated and characterised to varying extents, depending on their solution stability.}

![Scheme 6.10. Sequence of events observed during the reaction of alkynylselenomethylidyne with \([\text{Pt}(\text{PPh}_3)_2(C_2H_4)] ([\text{Mo}]=\text{Mo}(\text{CO})_2\text{Tp}^*).]

The proposed reaction sequence is outlined in Scheme 6.10 and involves initial and rapid \( \pi \)-coordination of the alkynyl C–C bond prior to the oxidative addition of the C\(_6\)-Se linkage. Isomerisation of the kinetically produced \( \text{cis-(PPh}_3)\) \( \text{species to the more stable } \text{trans-(PPh}_3)\) \( \text{arrangement subsequently affords the crystallographically characterised complex 59. A similar mechanistic pathway has been recently proposed for the oxidative addition of the acyclic vinyl selenide PhHC=CH(SeC_6H_4Cl-4) to the Pt(0) complex, furnishing the cis vinyl complex cis-[Pt\{CH=\text{CPh(SeC}_6H_4\text{Cl-4)}\}(\text{SeC}_6\text{H}_4\text{Cl-4})(\text{PPh}_3)_2], which was found to slowly isomerise to the \( \text{trans} \) complex in solution.\(^{54}\)
Within two hours of reagent combination, infrared spectroscopy of the reaction mixture revealed the complete consumption of the starting material, with two new peaks evident at lower frequency (1980 and 1897 cm\(^{-1}\)), suggesting an increase in the \(\sigma\)-donor/\(\pi\)-acceptor role of the organic chalcogenide ligand but not consistent with coordination of platinum to the Mo=C bond (vide supra). Solvent removal afforded an orange solid identified as the \(\pi\)-alkyne complex \([\text{Pt}\{\eta^2-\text{t-BuC}_2\text{SeC≡Mo(CO)}_2\text{Tp}^*\}(\text{PPh}_3)_2]\) (60) in spectroscopically quantitative yield. Analytically pure 60 could not be obtained due to its solution instability but the formulation as the \(\eta^2\)-C,C'-adduct is strongly supported by the available spectroscopic data. The two carbonyl absorptions in the infrared spectrum appear at frequencies intermediate of those observed for the insertion product 59 and the free alkynylselenomethyldiyne complex 51. Moreover, a weak absorption at 1722 cm\(^{-1}\) in the solid state infrared spectrum can be assigned to the vibration of the coordinated C=C bond, which is comparable to that observed for the 1,4-diphenylbuta-1,3-diyne complex \([\text{Pt}(\eta^2-\text{PhC}_2\text{C≡CPh})(\text{PPh}_3)_2]\) (1731 cm\(^{-1}\)).\(^{37,55}\) The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the crude orange solid is displayed in Figure 6.10, revealing two doublet resonances (\(\delta_1\) 26.2 and 25.4) with \(^{2}J_{pp}\) coupling of 20 Hz, which is consistent with the expected cis-(PPh\(_3\))\(_2\) geometry. The anticipated \(^{195}\text{Pt}\) satellites were not observed due to poor signal-to-noise ratio and the pair of resonances at lower field (marked by a red asterisk in Figure 6.10) remain unassigned. The position and multiplicity of the \(^{31}\text{P}\{^1\text{H}\}\) resonances for the complex formulated as \([\text{Pt}(\eta^2-\text{t-BuC}_2\text{SeC≡Mo(CO)}_2\text{Tp}^*\}(\text{PPh}_3)_2]\) are, however, comparable to corresponding data for the \(\pi\)-bound diyne complex \([\text{Pt}(\eta^2-\text{PhC}_2\text{C≡CPh})(\text{PPh}_3)_2]\), which displays two doublet phosphorus signals at \(\delta_2\) 23.9 and 23.6 having \(^{2}J_{pp}\) coupling of 24.7 Hz and attendant Pt-satellites for each resonance with \(^{1}J_{pp}\) of 3598 and 3378 Hz, respectively.\(^{37,55}\)

![Figure 6.10. \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of crude 60 in CD\(_2\)Cl\(_2\) at 25 °C (signals denoted by a red asterisk remain unidentified).](image)
The non-linearity of coordinated alkyne units causes the alkyne π-orbitals to acquire substantial s character, thus reducing the π-bond order relative to a linear R–C≡C–R arrangement and increasing the localisation of electrons at the alkyne carbon atoms. It is perhaps not surprising then that the kinetically formed π-adduct 60 proved unstable in solution, undergoing Se–C(alkyne) bond cleavage within 24 hours to produce the oxidative addition product cis-[Pt{SeC=Mo(CO)₂Tp*}(C≡Ct-Bu)(PPh₃)] (61), which contains adjacent organic selenolate and σ-alkynyl ligands. Chromatographic separation from the trans-isomer 59 furnished the cis complex, 61, in the pure form.

The infrared spectrum of 61 displays two carbonyl associated absorptions at frequencies comparable to those observed for the trans complex (1957 and 1875 for 61 vs 1952 and 1868 cm⁻¹ for 59). The ¹H NMR aromatic resonances of the triphenylphosphate ligands for 61 are at a somewhat shielded position compared to the corresponding pattern of signals that were evident for 59, whereas signals for the Tp* ligand, exhibiting a 2:1 intensity pattern, are to lower field, suggesting that the Tp* ligand is acting as a stronger net donor in 61. Furthermore, the slight upfield shift of the ³¹C{¹H} NMR resonance for the alkylidyne carbon (Δδ 297.2 for 61 cf. Δδ 302.5 for 59) is indicative of greater electron density at the molybdenum centre. Most notable amongst the ³¹C{¹H} NMR data, however, is the doublet multiplicity of the arylphosphine carbons and the resonances for the alkynyl nuclei, the latter of which appear at Δδ 122.5 (PtC≡Ct-Bu) and 83.0 (PtC≡Ct-Bu), being modestly deshielded relative to corresponding data for the trans isomer (Δδ 120.2 and 75.4, respectively).

The most diagnostic spectroscopic indicators of the differing geometries of 59 and 61 are the characteristic splitting patterns of the resonances associated with the triphenylphosphate ligands in the ³¹P{¹H} NMR spectrum, which is reproduced for 61 in Figure 6.11. The two inequivalent phosphorus nuclei of the cis-(PPh₃)₂ product give rise to two doublet resonances, Δδ 19.59 and 14.23, with ²J_Pₚ of 16.5 Hz. The differing magnitudes of the couplings measured for the attendant platinum satellites (³J_Pₚ of 2411 and 3071 Hz, respectively) are an expression of the relative trans influences of the organic selenolate and σ-alkynyl ligands. On this premise, the resonance at Δδ 14.23 with the larger ³J_Pₚ coupling has been attributed to the nucleus lying trans to the Se ligand. The ³¹P{¹H} NMR spectroscopic data for 61 are clearly distinct from those of 59 in which a single resonance was observed for the trans phosphorus ligands. Data for 61 are instead comparable to those observed for the related complex cis-[Pt{CH=CSiMe₃(SeC₆H₄Cl-4)}(SeC₆H₄Cl-4)(PPh₃)]₂, which revealed a pair of doublets centered at Δδ 18.7 and 14.4, each having a ²J_Pₚ value of 17 Hz and ³J_Pₚ values of 3395 and 1781 Hz, respectively. In solution, the cis-oxidative addition product 61 isomerises to the trans isomer 59 upon further standing.
The molecular structure of cis-[Pt\{Se\equiv\text{Mo}(CO)\text{$_{3}$}Tp*\}(\text{C\equivCl-Bu})(\text{PPh$_{3}$})\text{$_{2}$}\} (61) was determined by an X-ray diffraction study and the results are summarised in Figure 6.12. Structural dimensions within the bridging selenocarbonyl ligand are identical to those of 59 within 6 \sigma and will not be discussed in detail. In the case of 61 two adjacent coordination sites of the square planar platinum are occupied by the ligands arising from alkynylselenomethylidyne cleavage, which impacts on the structural parameters pertaining to the remainder of the molecule. Indeed, the disparity of the platinum–phosphorus bond lengths in the molecular structure of 61 is a reflection of the pronounced trans influence of the \sigma-alkynyl ligand relative to that of the organic selenolate, with Pt–P(1) (2.3334(8) Å) being significantly elongated (90 \sigma) relative to the distance noted for the remaining phosphorus atom (2.2617(8) Å). The trans inter-ligand angles (Se–Pt–P(2) 176.06(2)° and P(1)–Pt–C(2) 171.10(9)°) display the same pattern of systematic distortions that were observed for the trans isomer 59 (Se–Pt–C 177.04(12)° and P–Pt–P 170.17(3)°), with the greater bend observed for the ligand pair perpendicular to the selenomethylidyne unit in the direction away from the Tp* ligand being driven by the relief of steric strain. Perhaps the most interesting structural feature of the molecule is associated with the \sigma-alkynyl ligand, exhibiting a 6 \sigma elongation of the C–C bond, 1.206(4) Å, relative to that observed for 59 (1.176(5) Å).
Figure 6.12. Molecular structure of 61 with 30% probability ellipsoids shown. Hydrogen atoms and solvent molecules have been omitted. Selected bond distances (Å) and angles (°): Mo–C(1) 1.832(3), C(1)–Se 1.836(3), Pt–C(2) 1.997(3), C(2)–C(3) 1.206(4), C(3)–C(4) 1.487(5), Pt–P(1) 2.3334(8), Pt–P(2) 2.2617(8), Mo–N(2) 2.306(3), Mo–N(3) 2.214(3), Mo–N(4) 2.249(3), Mo–C(20) 1.966(4), Mo–C(30) 1.991(4), Mo–C(1)–Se 166.5(2), C(1)–Se–Pt 105.36(10), Se–Pt–P(2) 176.06(2), P(1)–Pt–C(2) 171.10(9), P(1)–Pt–P(2) 97.71(3), Pt–C(2)–C(3) 174.7(3), C(3)–C(3)–C(4) 175.7(3).

Preferential cleavage of the Cβ–Se vs Cα–Se bond, whilst undoubtedly reflecting the steric properties of the system, might also be rationalised in terms of the changes that were noted along the C–Se–C backbone of 51 upon π-coordination, as revealed in the structural determination of 56; namely a weakening of the Cβ–Se bond and concomitant strengthening of the Cα–Se bond (vide supra). The ‘remote’ activation of thiophene rings in coordinated benzothiophenes has been documented, with the C–S bonds becoming more susceptible to cleavage upon coordination of a number of electrophilic ML₄ moieties (Mn(CO)₅⁺, FeCp⁺, RuCp⁺, Ru(C₂Me₅)₂²⁺ and Cr(CO)₆⁺). In this case, steric effects would appear to disfavour such an initial activation of the Se–C linkage of 51. An alternative mode of coordinative activation may, however, be entertained when one considers that even diphenylselenide may oxidatively add to zero-valent platinum (vide supra), i.e., a reagent devoid of vinylic or alkylnyl groups for prior coordination. Thus one might envisage that, whilst not spectroscopically observed, an alternative isomer involving selenoether coordination arises en route to C–Se activation. In addition to the simple σ-donation of the selenoether, retrodonation from the π-basic platinum centre could occur into the σ*(C–Se) orbital, leading to a weakening and eventual rupture of this bond. This remains mechanistic conjecture at this stage, but might account in part for the facility of this (and related) oxidative addition.
6.6 Summary and conclusions

Nucleophilic displacement of the chloride substituent of the chlorocarbyne complex [Mo(≡CCl)(CO)₂Tp*] with the alkynyl selenolates Li[SeC≡CR] (R = t-Bu, C₆H₄Me-4, SiMe₃) affords alkynylselenomethylidyne complexes [Mo≡CSeC≡CR)(CO)₂Tp*]. An X-ray diffraction analysis for 53 revealed that the compounds contain unconjugated M≡C and C≡C triple bonds. Each of these units of unsaturation may interact independently with the lone pairs of the linking selenium atom, as suggested by spectroscopic observations. Thus resonance forms A and C (Figure 6.1) may also contribute to the overall bonding description.

The reaction of 51 with [Co₂(CO)₈] proceeds with the expected steric control over attachment of the dimetal fragment to the C–C triple bond rather than the Mo–C bond, i.e., distal to the bulky Tp* ligand. The resulting μ-alkyne dicobalt complex reacts with dpmm with concomitant loss of a carbonyl ligand from each cobalt centre to produce the crystallographically characterised complex [Co₂(μ-t-BuC₅SeC≡Mo(CO)₂Tp*)(μ-dpmm)](CO)₄ 56. Structural data for this π-alkyne adduct were consistent with a ‘push/pull’ role for the selenium lone pairs upon the two independent π-systems rather than serving to extend the electron delocalisation along the entire alkynylselenomethylidyne ligand backbone.

Similarly, the reaction between 51 and the Group 10 metal complex [Pt(PPh₃)₂(C₂H₄)] proceeds via initial π-coordination to the alkynyl C–C bond. The kinetically formed π-adduct displays only limited stability; with subsequent oxidative addition of the alkynylselenomethylidyne ligand to the Pt center via regiospecific cleavage of the C₇–Se bond to furnish the first example of a binuclear complex bearing a bridging selenocarbonyl ligand. The activation of the C–Se bond by transition-metals has been a recurrent phenomenon throughout this thesis. The kinetic product of oxidative addition comprises cis-disposed σ-alkynyl and organic selenolate ligands arising from the cleaved alkynylselenomethylidyne ligand. Upon standing in solution, however, isomerisation to the thermodynamically favoured trans isomer occurs. Both the cis- and trans-[PPh₃]₃ isomers have been crystallographically characterised.

The novel alkynylselenomethylidyne complexes described herein [Mo≡CSeC≡CR)(CO)₂Tp*] (R = t-Bu, 51, C₆H₄Me-4, 52, SiMe₃, 53) represent a new class of highly-functionalised carbyne compounds. Initial studies into their use for the formation of polymetallic assemblies indicates that the Tp* ligand confers a degree of steric protection to the M≡C bond, as was reported for Stone’s related alkynylcarbyne complexes.¹² In the current situation, the presence of an interceding π-donating selenium atom confers fragility to the alkylidyne ligand that is not observed for the alkynylcarbynes, providing an extraordinary potential for the isolation of novel cluster compounds not possible with the more traditional alkylidyne complexes.
CHAPTER 6. Tp* LIGATED ALKYNYLSELENOMETHYLIDYNE COMPLEXES OF MOLYBDENUM

REFERENCES

15. R. D. Dewhurst, A. F. Hill, A. C. Willis, Chemical Communications (Cambridge, United Kingdom) 2004, 2826.
7.1 General procedures

All manipulations, unless otherwise stated, were carried out under an atmosphere of pre-purified and dried N₂ using conventional Schlenk and glove-box techniques. Dichloromethane (CH₂Cl₂) and acetonitrile were dried over CaH₂ and distilled under N₂. Diethyl ether, hexane, toluene and tetrahydrofuran (THF) were distilled from Na/benzophenone under N₂. Reactions were carried out at room temperature unless stated otherwise. ¹H, ³¹P{¹H}, ⁷⁷Se{¹H}, and ¹³C{¹H} NMR spectra were recorded on Varian INOVA 300 or GEMINI 300 spectrometers (¹H 300.075 MHz, ³¹P{¹H} 121.419 MHz, ¹³C{¹H} 75.421 MHz, ⁷⁷Se{¹H} 57.204 MHz). ¹H and ¹³C{¹H} NMR chemical shifts (δ) are reported relative to residual solvent signals. ³¹P{¹H} NMR chemical shifts are reported relative to an external 85% H₃PO₄ reference. ⁷⁷Se{¹H} NMR chemical shifts are reported relative to an external Ph₂Se₂ reference in CDCl₃ (δ 463). Coupling constants (J) are given in Hz. All NMR spectra were recorded at 25°C unless otherwise stated. Elemental microanalytical data were obtained from the Research School of Chemistry microanalytical service. Electrospray (ESI) and electron impact (EI) mass spectrometry were performed by the Research School of Chemistry mass spectrometry service. UV-vis spectra (dichloromethane solutions, 1 cm quartz cuvette) were recorded on a Shimadzu UV-2450 UV-visible spectrophotometer. IR spectra were recorded in the solid state (Nujol mulls, KBr disks) and in solution. Data for X-ray crystallography were collected by the Research School of Chemistry crystallography service with a Nonius Kappa CCD diffractometer. Structures were solved by direct methods and refined using a full-matrix least-squares procedure against F or F². Solution and refinement for most crystals were performed by Dr Anthony C. Willis, with some additional structural models solved and refined by Dr Matthew K. Smith and Dr Jörg Wagler. Non-routine structural refinement was performed by Professor A. David Rae.

Multiplicity of NMR resonances is reported using the following abbreviations: br (broad), s (singlet), d (doublet), t (triplet), vt (virtual triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets) etc. Solvent of crystallisation, as suggested by microanalytical data, when present, was confirmed by integration of ¹H NMR spectra where possible. Mass spectrometry data are reported as follows: mass (percentage height cf. base peak) [assignment]ʰ⁻¹ in = charge. For salts, ‘M’ refers to the complex ion of interest. Assignments were substantiated by simulation of isotopic distribution.
Cryostatic chromatography was performed using jacketed columns loaded with degassed silica gel which were cooled by an alcohol recirculating cryostat using the apparatus and set up in Figure 7.1.

The known compounds \([\text{RuHCl(CO)}(\text{PPh}_3)_3]\), \([\text{RuH(CO)}_2(\text{NCMe})(\text{PPh}_3)_2][\text{BF}_4]\), \([\text{Ru(CO)}_3(\text{PPh}_3)_3]\), \([\text{Ru(CO)}_2(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]\), \([\text{K}[\text{Tp}]]\), \([\text{K}[\text{Tp}^*]]\), \([\text{i-PrEC}=\text{CPh} \text{ (E = Se)}]\), \([\text{K}[\text{Tp}^*]]\), \([\text{WI}[\text{CO)}_3(\text{Tp}^*)]\), \([\text{Mo}(=\text{CCl})(\text{CO})_2(\text{Tp})]\), \([\text{Mo}(=\text{CCl})(\text{CO})_2(\text{Tp})^*] \), \([\text{Mo}(=\text{CCl})(\text{CO})_2(\text{Tp}^*)]\) and \([\text{Mo}(=\text{CCl})(\text{CO})_2(\text{Tp}^*)]\) were prepared according to previously described procedures. The compound \([\text{Ru(CO)}(\text{CNMe})(\text{PPh}_3)_3]\) was prepared as previously detailed for \([\text{Ru(CO)}(\text{CNR})(\text{PPh}_3)_3]\) \(\text{R = t-Bu, C}_6\text{H}_4\text{Me-4, C}_6\text{H}_3\text{Me-2,6).}\) The sample of \([\text{Os}(\text{n}^2-\text{TeCPh})\text{Cl(CO)}(\text{PPh}_3)_3]\) was obtained from Professor A. F. Hill and prepared as previously described for \([\text{Os}(\text{n}^2-\text{TeCC},\text{H}_4\text{Me-4})\text{Cl(CO)}(\text{PPh}_3)_3]\) \(14,15\) The compounds \([\text{Pt(PPh}_3)_2(\text{C}_2\text{H}_4)]\) \(16\) and \([\text{i-PrOC}={\text{CPh}}]\) \(17\) were prepared by Mr H. Neumann according to the indicated published procedures. All other chemicals were used as received from commercial sources.

Safety note. Selenium and isocyanides have been identified as hazardous (according to the criteria of the NOHSC and the ADG code) and care should be taken to avoid inhalation and skin
contact. The hazards of isoselenocyanates are, as yet, unknown and appropriate safety precautions should be taken when handling these potentially toxic compounds.

7.2 Chemistry of organyl isoselenocyanates

Preparation of mesityl formamide (2)

Acetic formic anhydride was prepared in situ by heating acetic anhydride (20.4 mL, 0.22 mol) and formic acid (99%, 8.5 mL, 0.22 mol) for two hours at 50–60 °C in a flask equipped with a magnetic stirrer and a drying tube. The solution was cooled to 5 °C in an ice bath and 2,4,6-trimethylaniline (15.2 mL, 0.10 mol) was added drop-wise over a 15 minute period so that the temperature did not rise above 25 °C. The resulting yellow suspension was allowed to warm to room temperature before the addition of diethyl ether (25 mL). The suspension was stirred for a further hour before the product was collected by vacuum filtration, rinsing thoroughly with diethyl ether to yield the formamide as a white crystalline solid. Both \(^1\)H and \(^13\)C{\(^1\)H} NMR data revealed the presence of two rotational isomers and data relates to the mixture. Yield 14.3 g (81%). 

\(^1\)H NMR (CDCl\(_3\), 25 °C, 300.075 MHz): \(\delta \) 8.33 (d, 1 H, \(J_{HH, cis} = 1.5\), CHO), 7.05 (br, NH), 6.88 (s, 2 H, C\(_6\)H\(_2\)), 2.25, 2.19 (s \(\times 2\), 3:6 H, CH\(_3\)). \(^13\)C{\(^1\)H} NMR (CDCl\(_3\), 25 °C, 75.421 MHz): \(\delta \) 159.7 (CHO), 137.4 [C\(^4\)(C\(_6\)H\(_2\))], 134.9 [C\(^5\),C\(_6\)H\(_2\))], 128.9 [C\(^3\),C\(_6\)H\(_2\))], 129.7 [C\(^1\)(C\(_6\)H\(_2\))], 20.9, 18.4 (1:2, CH\(_3\)). 

Isomer 2: \(^1\)H NMR (CDCl\(_3\), 25 °C, 300.075 MHz): \(\delta \) 8.04 (d, \(J_{HH, trans} = 12.0\), 1 H, CHO), 7.24 (d(br), NH), 6.92 (s, 2 H, C\(_6\)H\(_2\)), 2.89, 2.25 (s \(\times 2\), 3:6 H, CH\(_3\)). 

\(^13\)C{\(^1\)H} NMR (CDCl\(_3\), 25 °C, 75.421 MHz): \(\delta \) 165.2 (CHO), 137.5 [C\(^6\)(C\(_6\)H\(_2\))], 135.1 [C\(^2\),C\(_6\)H\(_2\))], 130.4 [C\(^1\)(C\(_6\)H\(_2\))], 129.3 [C\(^3\),C\(_6\)H\(_2\))], 20.9, 18.5 (1:2, CH\(_3\)). MS (EI): m/z 163.1 (100) [M\(^+\)], 146.1 (75) [M – OH\(^+\)], 135.1 (83) [M – CO\(^+\)], 134.1 (98) [M – COH\(^+\)], 120.1 (90) [M – NOH\(^+\)]. Anal. Found: C, 73.64; H, 8.24; N, 8.45%. C\(_{10}\)H\(_{13}\)NO: C, 73.59; H, 8.03; N, 8.58%.

Preparation of mesityl isocyanide (3)

To a suspension of mesityl formamide (2.00 g, 12.3 mmol) in dichloromethane (15 mL) and diisopropylamine (4.64 mL, 33.1 mmol) at 0 °C was added phosphoryl chloride (1.3 mL, 13.5 mmol) drop-wise with stirring. Stirring was continued at room temperature overnight. Sodium carbonate (2.40 g, 22.6 mmol) in water (15 mL) was slowly added to the resulting pale orange suspension (maintaining the temperature below 30 °C) and the suspension then stirred for a further hour. Water (15 mL) and dichloromethane (10 mL) were added and the organic layer was collected, washed with water (3 \(\times\) 10 mL) and dried with anhydrous sodium sulphate. Evaporation of the resulting yellow solution provided the crude isocyanide which was purified.
by sublimation (50 ºC, 0.1 mm) to provide a white, malodorous solid. Yield 1.27 g (72%). Mp:
37–40 ºC. IR (Nujol): 2112 (vNC) cm⁻¹. IR (CH₂Cl₂): 2120 (vNC) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 ºC,
300.075 MHz): δ 6.91 (s, 2 H, C₆H₂), 2.36, 2.29 (s × 2, 6:3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂,
25 ºC, 75.421 MHz): δ 168.1 (t, 1JCN = 5.8, N≡C), 139.3 [C¹(C₆H₂)], 134.9 [C²,₃(C₆H₂)], 128.8
[C²,₅(C₆H₂)], 124.6 [t, 1JCN = 12.7, C¹(C₆H₂)], 21.3, 18.9 (1:2, CH₃). MS (EI): m/z (%): 145.1
(61) [M]⁺, 130.1 (100) [M – CH₃]⁺. Anal. Found: C, 82.40; H, 7.93; N, 9.41%. Caled. for
C₁₀H₁₁N: C, 82.72; H, 7.64; N, 9.65%. Crystal data for C₁₀H₁₁N, Mᵣ = 145.20, orthorhombic,
Pnma, a = 15.7158(5), b = 6.8883(2), c = 8.2512(3) Å, V = 893.23(5) Å³, Z = 4, ρcalc = 1.080 Mg m⁻³, μ(Mo Kα) = 0.063 mm⁻¹, T = 200(2) K, colourless plate, 1100
independent measured reflections (θ ≤ 54º), R₁ = 0.0387, wR = 0.0481 for 707 independent
observed absorption-corrected reflections (I > 3σ(I)), 86 parameters. The crystallographic
asymmetric unit consists of one half of a C₁₀H₁₁N molecule, the other half of which is generated
by a crystallographic mirror plane.

Isolation of O-methyl-N-mesityl selenocarbamate (4) and preparation of mesityl
isoselenocyanate (I)

Isolation of O-methyl-N-mesityl selenocarbamate (4)

Mesityl isocyanide (1.00 g, 6.89 mmol), grey selenium (0.60 g, 7.60 mmol) and DBU (1.13 mL,
7.55 mmol) were combined in tetrahydrofuran (100 mL) and heated to reflux. The reaction was
monitored by thin layer chromatography and, once no more changes were apparent, excess selenium
was removed by filtration through Celite. Solvent was removed and an unsuccessful
recrystallisation from warm methanol was attempted. Subsequent chromatography (silica gel,
hexane) provided a major yellow eluate. Recovery of this eluate, solvent removal, and
recrystallisation from hexane gave pure 4 as a pale white-pink solid. Yield 0.32 g (18%). Mp:
112–114 ºC. IR (Nujol): 1642 (vCN) cm⁻¹. IR (CH₂Cl₂): 1609 (vCN) cm⁻¹. The compound exists
as two rotational isomers (ca. 2:3:1 ratio) and data relates to the mixture. Minor isomer:
¹H NMR (CD₂Cl₂, 25 ºC, 300.075 MHz): δ 8.10 (s(br), 1 H, NH), 6.94 (s, 2 H, C₆H₂), 4.16 (s,
3 H, OCH₃), 2.28, 2.21, (s × 2, 3:6 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 ºC, 75.421 MHz):
δ 196.5 (C=Se), 138.6 [C⁴(C₆H₂)], 136.4 [C²,₃(C₆H₂)], 133.1 [C¹(C₆H₂)], 129.3, [C²,₅(C₆H₂)],
60.9 (OCH₃), 21.1, 18.3 (1:2, CH₃). ⁷⁷Se{¹H} NMR (CD₂Cl₂, 25 ºC, 57.204 MHz): δ 228.3.
Major isomer: ¹H NMR (CD₂Cl₂, 25 ºC, 300.075 MHz): δ 8.98 (s(br), 1 H, NH), 6.91 (s, 2 H,
C₆H₂), 4.08 (s, 3 H, OCH₃), 2.27, 2.19 (s × 2, 3:6 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 ºC,
75.421 MHz): δ 193.9 (C=Se), 138.5 [C⁴(C₆H₂)], 135.3 [C²,₃(C₆H₂)], 132.5 [C¹(C₆H₂)], 129.1
[C²,₅(C₆H₂)], 62.4 (OCH₃), 21.0, 18.3 (1:2, CH₃). ⁷⁷Se{¹H} NMR (CD₂Cl₂, 25 ºC, 57.204 MHz):
δ 216.4. MS (EI): m/z (%): 257.0 (95) [M]⁺, 242.0 (23) [M – CH₃]⁺, 225.0 (23) [M – OCH₃]⁺,
176.1 (72) [M – SeH]⁺, 161.1 (100) [M – SeH₂]⁺. Anal. Found: C, 51.53; H, 5.98; N, 5.41%.
Calcd. for C₁₁H₁₃NOSe: C, 51.57; H, 5.90; N, 5.47%. Crystal data for C₁₁H₁₂NOSe, \( M_r = 256.21 \), monoclinic, \( P2_1/a \), \( a = 7.4032(1) \), \( b = 20.6361(3) \), \( c = 8.1946(1) \) Å, \( \beta = 111.4576(6)^\circ \), \( V = 1165.14(3) \) Å³, \( Z = 4 \), \( \rho_{\text{calc}} = 1.460 \) Mg m⁻³, \( \mu(\text{Mo } K\alpha) = 3.192 \) mm⁻¹, \( T = 200(2) \) K, colourless plate, 2635 independent measured reflections (2\( \theta \leq 54^\circ \)), \( R_1 = 0.0236 \), \( wR = 0.0289 \) for 2049 independent observed absorption-corrected reflections (\( I > 3\sigma(I) \)), 172 parameters.

**Preparation of mesityl isoselenocyanate (1)**

Mesityl isocyanide (3.00 g, 20.7 mmol) and grey selenium (1.79 g, 22.7 mmol) and DBU (3.39 mL, 22.7 mmol) were combined in tetrahydrofuran (300 mL) and heated to reflux under an atmosphere of nitrogen. The reaction was monitored by thin layer chromatography and, once no more changes were apparent, excess selenium was removed by filtration through Celite. The volume of the filtrate was reduced to ca. 10 mL and the mixture flushed through a short silica gel column with tetrahydrofuran. Removal of the solvent in vacuo yielded the crude isoselenocyanate as a cream solid, which could be recrystallised from ethanol to yield pure mesityl isoselenocyanate as a white, microcrystalline solid. Yield 2.93 g (63%). Mp: 68–72 °C. IR (Nujol): 2098 s(br) (vSeCN), 2019 sh (vSeCN) cm⁻¹. IR (CH₂Cl₂): 2122 s(br) (vSeCN), 2018 (sh) (vSeCN) cm⁻¹. \(^1\)H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): \( \delta \) 6.88 (s, 2 H, C₆H₂), 2.34, 2.27 (s x 2, 6.3 H, CH₃). \(^{13}\)C{\(^1\)H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): \( \delta \) 138.3 [\( C^4(\text{C}_6\text{H}_2) \)], 135.4 [\( C^{2,6}(\text{C}_6\text{H}_2) \)], 130.26 (br, SeCN), 128.8 [\( C^{2,5}(\text{C}_6\text{H}_2) \)], 126.4 [br, \( C^1(\text{C}_6\text{H}_2) \)], 21.2, 18.6 (1:2, CH₃). MS (EI): m/z (%) 225.0 (100) [\( ^{80}\)Se] [M]+, 145.1 (60) [MH – Se]⁺, 144.1 (60) [M – Se]⁻, 130.1 (38) [M – SeCH₃]⁻. Anal. Found: C, 53.85; H, 5.20; N, 6.03%. Calcd. for C₁₀H₁₁NSe: C, 53.58; H, 4.95; N, 6.25%. Crystal data for C₁₀H₁₁NSe, \( M_r = 224.16 \), triclinic, \( P \overline{1} \), \( a = 8.2407(2) \), \( b = 8.2497(2) \), \( c = 8.9423(3) \) Å, \( \alpha = 92.966(1) \), \( \beta = 104.613(1) \), \( \gamma = 119.849(1) \)°, \( V = 498.71(3) \) Å³, \( Z = 2 \), \( \rho_{\text{calc}} = 1.493 \) Mg m⁻³, \( \mu(\text{Mo } K\alpha) = 3.710 \) mm⁻¹, \( T = 200(2) \) K, colourless prism, 2276 independent measured reflections (2\( \theta \leq 54^\circ \)), \( R_1 = 0.0313 \), \( wR = 0.0338 \) for 1810 independent observed absorption-corrected reflections (\( I > 3\sigma(I) \)), 152 parameters.

**Stability assay of 1 in solution**

*Thermodynamic stability*

Mesityl isoselenocyanate (0.060 g, 0.27 mmol) was dissolved in 1,1,2,2-tetrachloroethane-\( d_2 \) in a sealed NMR tube under argon. The solution was heated at 70 °C for 48 days in the absence of light and spectral changes were monitored by the acquisition of \(^{13}\)C{\(^1\)H} NMR spectra at regular intervals. No decomposition was detected after this time. \(^{13}\)C{\(^1\)H} NMR (Cl₂CDCl₂, 25 °C, 75.421 MHz): \( \delta \) 138.3 [\( C^4(\text{C}_6\text{H}_2) \)], 135.4 [\( C^{2,6}(\text{C}_6\text{H}_2) \)], 129.9 (br, SeCN), 128.9 [\( C^{2,5}(\text{C}_6\text{H}_2) \)], 126.1 [br, \( C^1(\text{C}_6\text{H}_2) \)], 21.4, 18.7 (1:2, CH₃).
Photolytic stability
Mesityl isoselenocyanate (0.060 g, 0.27 mmol) was dissolved in 1,1,2,2-tetrachloroethane-$d_2$ in a sealed NMR tube under argon. The solution was allowed to stand in sunlight for 2 days after which time traces of elemental selenium had been extruded from the sample. $^{13}$C $\{^1$H$\}$ NMR spectroscopy of the resultant solution was, however, consistent with bulk SeCNMes composition. $^{13}$C $\{^1$H$\}$ NMR (CD$_2$CDCl$_4$, 25 °C, 75.421 MHz): $\delta$ 138.3 [C$^4$(C$_6$H$_2$)], 135.4 [C$^{2,6}$(C$_6$H$_2$)], 129.9 (br, SeCN), 128.9 [C$^{3,5}$(C$_6$H$_2$)], 126.1 [br, C$^1$(C$_6$H$_2$)], 21.4, 18.7 (1:2, CH$_3$).

Kinetic assay of reaction of I with PPh$_3$
Mesityl isoselenocyanate (0.030 g, 0.133 mmol) and one equivalent of triphenylphosphine (0.035 g, 0.133 mmol) were combined in a sealed NMR tube under argon. A $^{31}$P $\{^1$H$\}$ NMR spectrum was obtained within 15 minutes of combining reagents and every hour after that for 48 h. An immediate 11% conversion of Ph$_3$P to Ph$_3$PSe was observed but no further changes occurred over the time period. Estimated $K_{eq}$ = 1.7 × 10$^{-2}$. $^{31}$P $\{^1$H$\}$ NMR (CD$_6$D$_6$, 25 °C, 121.419 MHz): $\delta$ 35.96 ($^1$J$_{Se}$ = 756, Ph$_3$PSe), −4.76 (PPh$_3$).

Preparation of [Pt(n$_2$-SeCNMes)(PPh$_3$)$_2$] (5)
[Pt(PPh$_3$)$_2$]$_2$ (C$_2$H$_4$) (0.400 g, 0.535 mmol) and mesityl isoselenocyanate (0.119 g, 0.531 mmol) were combined in a flask equipped with a magnetic stirrer. Hexane (50 mL) was added and the initially buttk-coloured suspension was stirred at room temperature for 90 minutes, during which time the colour changed to pale orange. The bone-coloured product was collected by vacuum filtration, rinsing thoroughly with hexane. Yield 0.491 g (98%). IR (KBr): 1672 s (vCN) cm$^{-1}$. IR (CH$_2$Cl$_2$): 1670 (vCN) cm$^{-1}$.

1H NMR (CD$_6$D$_6$, 25 °C, 300.075 MHz): $\delta$ 7.67, 7.45 (m $\times$ 2, 10 H, C$_6$H$_5$), 6.87 (m, 20 H, C$_6$H$_5$, 2 H, C$_3$H$_2$), 2.34, 2.19 (s $\times$ 2, 6:3 H, CH$_3$). $^{13}$C $\{^1$H$\}$ NMR (CD$_2$Cl$_2$, −40 °C, 75.421 MHz): $\delta$ 187.0 (d, $^2$J$_{CP}$ trans = 114, CN), 153.6 [d, $^1$J$_{CP}$ trans = 11, C$^1$(C$_6$H$_2$)], 134−127 (C$_6$H$_5$, C$_3$H$_2$), 125.5 [C$^4$(C$_6$H$_2$)], 20.5, 18.2 (1:2, CH$_3$). $^{31}$P $\{^1$H$\}$ NMR (CD$_6$D$_6$, 25 °C, 121.419 MHz): $\delta$ 31.2 (d, $^2$J$_{PP}$ = 12.1, $^1$J$_{PP}$ = 4409, Ph$_3$P trans to Se); 25.1 (d, $^2$J$_{PP}$ = 12.2, $^1$J$_{PP}$ = 2694, Ph$_3$P trans to C=N). MS (ESI): m/z (%) 945.1 (100) [M$^+$]. Anal. Found: C, 58.75; H, 4.51; N, 1.21%. Calcd. for C$_{46}$H$_{41}$NP$_2$PtSeC$_6$H$_6$: C, 58.54; H, 4.38; N, 1.48%.

Crystal data for C$_{46}$H$_{41}$NP$_2$PtSeC$_6$H$_6$. $M_t$ = 1021.95, monoclinic, P2$_1$/n, $a = 9.3964(2)$, $b = 28.1491(7)$, $c = 17.1415(4)$ A, $\beta = 100.441(1)^\circ$, $V = 4458.9(2)$ A$^3$, $Z = 4$, $\rho_{calc}$ = 1.522 Mg m$^{-3}$, $\mu$(Mo K$\alpha$) = 4.071 mm$^{-1}$, $T = 200(2)$ K, pale brown needle, 10196 independent measured reflections ($2\theta \leq 54^\circ$), $R_1$ = 0.0235, $wR_2$ = 0.0253 for 6186 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 568 parameters. The benzene molecule was disordered such that two overlapping images were identified at a ratio of 0.519(8): 0.481.
Preparation of [Ru(CO)₂(CNMes)(PPh₃)] (6)

Mesityl isocyanide (0.024 g, 0.158 mmol) and [Ru(CO)₂(PPh₃)] (0.150 g, 0.159 mmol) were combined in benzene (10 mL) and stirred for 10 minutes. The solution was filtered through Celite and the volume of the yellow solution was reduced to 2 mL. Degassed methanol (50 mL) was added to precipitate the bright yellow product which was collected on a frit and rinsed thoroughly with ethanol and hexane. Yield 0.119 g (91%). IR (Nujol): 2031 (v CN), 1893, 1852 (v CO) cm⁻¹. IR (CH₂Cl₂): 2135 (v CN), 1954 (v CO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.45, 7.34 (m × 2, 12:18 H, C₆H₃), 6.62 (s, 2 H, C₆H₂), 2.16, 1.67 (s × 2, 3:6 H, CH₂). ¹³C {¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 213.1 (t, JPC = 16.3, RuCO), 127.6 (t, JPC = 18.6, CN), 138.0 [vt, JPC = 23.2, C¹(C₆H₃)], 136.6 [C¹(C₆H₂)], 134.3 [vt, JPC = 6.9, C²⁺(C₆H₃)], 134.6 [C²⁻(C₆H₂)], 129.9 [C¹(C₆H₃)], 128.2 [vt, JPC = 5.2, C³⁺(C₆H₂)], 128.1 [C³⁻(C₆H₃)], 127.5 [C¹(C₆H₂)], 21.0, 18.5 (1:2, CH₃). ³¹P {¹H} NMR (CD₆, 25 °C): δ 60.5. MS (ESI): m/z (%) 828.2 (100) [M + 2H⁺]. Anal. Found: C, 68.35; H, 5.25; N, 1.77%. Caled. for C₄₈H₄₁NO₃P₂Ru•H₂O: C, 68.24; H, 5.13; N, 1.66%.

Preparation of [RuHCl(CO)(CNMes)(PPh₃)] (10)

Method 1 Mesityl isocyanide (0.153 g, 1.05 mmol) and mer-[RuHCl(CO)(PPh₃)] (1.00 g, 1.05 mmol) were combined in dichloromethane (20 mL) and stirred for thirty minutes. The solution was filtered through Celite and the volume of the pale yellow solution was reduced to one third. Ethanol (10 mL) was added and the volume was further reduced. The dilution/volume reduction procedure was repeated until a cream-coloured microcrystalline precipitate was obtained. The product was collected by vacuum filtration and rinsed with ethanol/hexane. Yield 0.70 g (81%). IR (KBr): 2142 (v CN), 1953 (v CO) cm⁻¹. IR (CH₂Cl₂): 2129 (v CN), 1953 (v CO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.81, 7.33 (m × 2, 12:18 H, C₆H₃), 6.79 (s, 2 H, C₆H₂), 2.25, 1.97 (s × 2, 3:6 H, CH₃), −5.58 (t, JPH = 19.9, 1 H, RuH). ¹³C {¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 201.2 (t, JPC = 12.8, RuCO), 163.6 (t(br), CN), 138.3 [C¹(C₆H₂)], 135.6 [vt, JPC = 22.2, C¹(C₆H₃)], 134.6 [vt, JPC = 5.2, C²⁺(C₆H₃)], 134.6 [C²⁻(C₆H₂)], 129.9 [C¹(C₆H₃)], 128.5 [C³⁺(C₆H₂)], 128.2 [vt, JPC = 4.9, C³⁻(C₆H₃)], 125.5 [br, C¹(C₆H₂)], 21.2, 18.4 (1:2, CH₃). ³¹P {¹H} NMR (CD₆, 25 °C): δ 43.6. MS (ESI): m/z (%) 875.1 (20) [M + CH₃CN]⁺, 834.1 (10) [M – H⁺], 800.2 (15) [M – Cl]⁺. Anal. Found: C, 65.57; H, 5.17; N, 1.57%. Caled. for C₄₈H₄₁NClO₃P₂Ru·H₂O: C, 65.46; H, 5.26; N, 1.62%.

Method 2 Substitution of mesityl isocyanide with mesityl isoselenocyanate (0.236 g, 1.05 mmol) in the above procedure provided 10 as the only isolated species in a comparable yield.
Preparation of [Ru(CH=CHi-Pr)Cl(CO)(PPh₃)₂] (12)

To a solution of mer-[RuHCl(CO)(PPh₃)₃] (4.00 g, 4.19 mmol) in dichloromethane (50 mL) was added two equivalents of 3-methyl-1-butene (0.86 mL, 8.40 mmol). The resulting red solution was stirred for thirty minutes after which time the solvent volume was reduced to one third. Dilution with ethanol and further solvent volume reduction caused precipitation of a bright orange microcrystalline solid, which was collected by vacuum filtration and washed with ethanol and diethyl ether. Yield 2.97 g (93%). Mp (decomp): 156 °C. IR (Nujol): 1913 (ν(CO)) cm⁻¹. IR (CH₂Cl₂): 1928 (ν(CO)) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.83, 7.03 (m × 2, 30 H, C₆H₃), 7.46 (dt, 3JHHtrans = 12.3, 8 JHH = 1 H, RuCH=CHi-Pr), 5.00 (ddt, 3JHHtrans = 12.3, 8JHH = 6.9, 1 H, CH=CHi-Pr), 2.30 (m, 1 H, i-PrCH), 0.84 (d, 6 H, 3JHH = 6.6, i-PrCH₃). ¹³C [¹H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 203.0 (t, 2JPC = 13.6, RuCO), 143.3 (RuCH=CHi-Pr), 134.8 [vt, 2JPC = 6.0, C²(C₆H₃)], 134.4 (CH=CHi-Pr), 133.1 [vt, 1JPC = 21.1, C¹(C₆H₃)], 130.1 [C⁴(C₆H₃)], 128.5 [vt, 5JPC = 4.5, C³⁵(C₂H₅)], 35.2 (i-PrCH), 23.4 (i-PrCH₃). ³¹P [¹H] NMR (CD₂Cl₂, 25 °C, 121.419 MHz): δ 31.5. MS (ESI): m/z (%) 723.0 (10) [M–Cl]⁺, 645.9 (100) [M–Cl–vinyl]⁺. Anal. Found: C, 66.74; H, 5.25%. Calcd. for C₄₂H₃₅ClO₅P₂Ru: C, 66.53; H, 5.18%. Crystal data for C₄₂H₃₅ClO₅P₂Ru: Mₜ = 758.24, monoclinic, P2₁/a, α = 18.5960(2), b = 9.7975(1), c = 22.2758(3) Å, β = 114.3349(6)°, V = 3697.93(8) Å³, Z = 4, ρcalcd = 1.362 Mg m⁻³, μ(Mo Kα) = 0.614 mm⁻¹, T = 200(2) K, orange plate, 8485 independent measured reflections (2θ ≤ 54°), R₁ = 0.0240, wR₁ = 0.0190 for 5571 independent observed absorption-corrected reflections (I > 3σ(I)), 458 parameters. The carbonyl and chloride ligands were disordered with respect to one another.

Preparation of [Ru(CH=CHi-Pr)Cl(CO)(CNMes)(PPh₃)₂] (11)

Method 1 Mesityl isocyanide (0.098 g, 0.670 mmol) and [Ru(CH=CHi-Pr)Cl(CO)(PPh₃)₃] (0.507 g, 0.669 mmol) were combined in dichloromethane (20 mL) and stirred for thirty minutes. The volume of the solution was reduced to one third and ethanol (10 mL) was added before the volume was reduced again. This procedure was repeated until a bone-coloured microcrystalline precipitate was obtained. The product was collected by vacuum filtration and rinsed with ethanol/hexane and ethanol/diethyl ether. Yield 0.430 g (72%). IR (KBr): 2132 (v(CN)), 1958 (ν(CO)) cm⁻¹. IR (CH₂Cl₂): 2116 (v(CN)), 1957 (ν(CO)) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.81, 7.28 (m × 2, 12:18 H, C₆H₃), 6.80 (s, 2 H, C₆H₃), 6.76 (dt, 3JHHtrans = 17.4, 4JHH = 3.3, 1 H, RuCH=CHi-Pr), 4.90 (ddt, 3JHHtrans = 17.1, 8JHH = 6.3, 4JHH = 1.8, 1 H, CH=CHi-Pr), 2.26, 2.07 (s × 2, 3:6 H, CH₃), 1.93 (m, 1 H, i-PrCH), 0.59 (d, 3JHH = 6.6, 6 H, i-PrCH₃). ¹³C [¹H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 201.3 (t, 2JPC = 12.8, RuCO), 163.0 (br, N≡C), 147.5 (t, 2JPC = 14.0, RuCH=CHi-Pr), 145.4 (t, 3JPC = 4.7, 8JHH not resolved.)
CH=CH-i-Pr), 138.3 [C(6-C6H5)], 134.8 [vt, 5.2, C(5-C6H5)], 134.7 [vt, 1.0, C(6-C6H5)], 134.5 [C(6-C6H5)], 129.8 [C(6-C6H5)], 128.5 [C(5-C6H5)], 128.2 [vt, 4.7, C(6-C6H5)], 125.7 [C(6-C6H5)], 37.3 (t-PrCH), 22.4 (t-PrCH), 21.2, 18.6 (1.2, CH3). 31P{1H} NMR (CD2Cl2, 25 °C, 121.419 MHz): δ 25.9. MS (ESI): m/z (%) 909.3 (100) [M + CH3CN – Cl]⁺, 868.2 (26) [M – Cl]⁺. Anal. Found: C, 67.55; H, 5.48; N, 1.20%. Calcd. for C52H50CINOP2Ru•H2O: C, 67.78; H, 5.69; N, 1.52%. Crystal data for C52H50CINOP2Ru, Mᵣ = 903.45, triclinic, P ̅ 1, a = 9.8659(2), b = 11.6114(2), c = 21.1262(5) Å, α = 96.833(1), β = 100.704(1), γ = 115.072(1)°, V = 2260.27(8) Å³, Z = 2, ρcalc = 1.327 Mg m⁻³, μ(Mo Kα) = 0.515 mm⁻¹, T = 200(2) K, pale yellow plate, 10359 independent measured reflections (2θ ≤ 55°), R₁ = 0.0338, wR = 0.0281 for 6118 independent observed absorption-corrected reflections (I > 3σ(I)), 529 parameters.

Method 2 Substitution of mesityl isocyanide with mesityl isoselenocyanate (0.151 g, 0.670 mmol) in the above procedure provided 11 as the only isolated species in a comparable yield.

Preparation of [Ru(CO)₂(dppe)(PPh₃)] (9)
[RuH(CO)₂(NCMe)(PPh₃)][BF₄] (1.33 g, 1.64 mmol) and dppe (0.650 g, 1.63 mmol) were suspended in methanol (100 mL) and the mixture degassed with an N₂ purge for 15 minutes. Two pellets of KOH were added and the initially white suspension was heated at reflux for 15 minutes during which time it turned pale yellow. The suspension was allowed to cool and the impure yellow powder collected by filtration onto a glass frit, rinsing with ethanol/water and ethanol/hexane. Recrystallisation from toluene/hexane provided 9 as a pure, pale yellow powder. Yield 0.771 g (58%). IR (Nujol): 1930 m, 1853 s (vCO) cm⁻¹. 1H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.59, 7.05, 6.91 (m × 3, 35 H, C₆H₅), 2.06 (d, 3JPH = 18.8, 4 H, CH₂). 13C{1H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 215.8 (d, 3JCP = 17.5, RuCO), 138.9 [d, 1JCP = 33.8, C(5-PPh₃-C₆H₅)], 313.9 [vd(br), 1JCP = 40.1, 3JCP = 11.6, C(2-C₂H₆)], 313.7 [d, 3JCP = 11.6, C(2-C₂H₆)], 129.3 [br, C(2-C₂H₆)], 128.7 [br, C(2-C₂H₆)], 128.3 [d, 3JCP = 9.4, C(2-C₂H₆)], 127.8 [d, 3JCP = 9.4, C(2-C₂H₆)], 32.1 (vt, 1JCP = 24, CH₃). 31P{1H} NMR (CD₂Cl₂, 25 °C, 121.419 MHz): δ 69.1 (d, 3JPP = 83, dppe), 56.3 (t, 2JPP = 83, PPh₃). MS (ESI): m/z (%) 819.11 (100) [MH⁺]. Anal. Found: C, 66.10; H, 4.87%. Calcd. for C₅₅H₃₉O₂P₃Ru, Mᵣ = 817.81, orthorhombic, Pnca. a = 17.3779(4), b = 19.9195(5), c = 21.9812(7) Å, V = 7609.0(4) Å³, Z = 8, ρcalc = 1.428 Mg m⁻³, μ(Mo Kα) = 0.577 mm⁻¹, T = 200(2) K, yellow needle, 5648 independent measured reflections (2θ ≤ 48°), R₁ = 0.0305, wR = 0.0295 for 3333 independent observed absorption-corrected reflections (I > 1.5σ(I)), 469 parameters.
In situ NMR complexation studies with SeCNMe₃ (1) and CNMe₃ (3)

In situ NMR experiments were performed in 5 mm NMR tubes equipped with Teflon stopcocks under an atmosphere of argon in benzene-$d_6$ or dichloromethane-$d_2$ solvent. $^{31}$P{¹H} NMR spectra (25 °C, 121.419 MHz) were recorded within five minutes of reactant combination.

**Reaction of 3 with [Ru(CO)₂(PPh₃)₃]**

[Ru(CO)₂(PPh₃)₃] (30 mg, 32 µmol) and one equivalent of mesityl isocyanide (5 mg, 32 µmol) were combined in benzene-$d_6$. The $^{31}$P{¹H} NMR spectrum of the resultant yellow solution revealed the formation of [Ru(CO)₂(CNMe₃)(PPh₃)₂] and free PPh₃, along with minor products arising from ligand redistribution. $^{31}$P{¹H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)₂(CNMe₃)(PPh₃)₂], 58.0, 45.8 (m × 2) [RuH₂(CO)(PPh₃)₃], 56.3 [Ru(CO)₂(PPh₃)₃], −4.8 (free PPh₃). No changes were apparent after 24 h at ambient temperature.

**Reaction of 1 with [Ru(CO)₂(PPh₃)₃]**

[Ru(CO)₂(PPh₃)₃] (30 mg, 32 µmol) and one equivalent of mesityl isoselenocyanate (7 mg, 31 µmol) were combined in benzene-$d_6$. The $^{31}$P{¹H} NMR spectrum of the resultant orange solution revealed the formation of [Ru(CO)₂(CNMe₃)(PPh₃)₂] and Ph₃PSe as the major products, along with some free PPh₃ and minor products arising from ligand redistribution. A signal not seen in the reaction with CNMe₃ was attributed to a small quantity of the desired π-adduct. $^{31}$P{¹H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)₂(CNMe₃)(PPh₃)₂], 58.0, 45.8 (m × 2) [RuH₂(CO)(PPh₃)₃], 56.3 [Ru(CO)₂(PPh₃)₃], 45.4 [Ru(η⁻-SeCNMe₃)(CO)₂(PPh₃)₂], 35.9 ($^1$Jₚₛₑ = 756, P₃PSe), −4.8 (free PPh₃). No changes were apparent after 24 h at ambient temperature.

**Reaction of 3 with [Ru(CO)(CNMe₃)(PPh₃)₃]**

[Ru(CO)(CNMe₃)(PPh₃)₃] (30 mg, 28 µmol) and one equivalent of mesityl isocyanide (4 mg, 28 µmol) were combined in benzene-$d_6$. The $^{31}$P{¹H} NMR spectrum of the resultant orange solution revealed the formation of [Ru(CO)(CNMe₃)(PPh₃)₂] and free PPh₃, along with minor products arising from ligand redistribution. $^{31}$P{¹H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)(CNMe₃)(PPh₃)₂], 58.0, 45.8 (m × 2) [RuH₂(CO)(PPh₃)₃], 54.5 [Ru(CO)(CNMe₃)₂(PPh₃)₂], 43.5 (unassigned), −4.8 (free PPh₃). After 24 h at ambient temperature the resonance due to [Ru(CO)(CNMe₃)₂(PPh₃)₂] was no longer apparent.

$^8$ The formation of [RuH₂(CO)(PPh₃)₃] often accompanies the synthesis of [Ru(CO)₂(PPh₃)₃] and this presumably accounts for the unexpected presence of the dihydride complex throughout the following section.
Reaction of 1 with [Ru(CO)(CNMes)(PPh₃)₂] 
[Ru(CO)(CNMes)(PPh₃)₂] (30 mg, 32 μmol) and one equivalent of mesityl isoselenocyanate (6 mg, 27 μmol) were combined in benzene-δ₆. The 31P {1H} NMR spectrum of the resultant orange solution revealed the formation of a small amount of [Ru(CO)(CNMes)₂(PPh₃)₂] and the unassigned compound seen in the reaction with CNMes (δ 43.5). The major signals were due to [RuH₂(CO)(PPh₃)₃] (arising from ligand scrambling) and Ph₃PSe, along with several minor complex decomposition products. No free PPh₃ was observed. In addition, a small resonance at δ 45 was not seen with the CNMes reaction was observed. 31P {1H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)₂(CNMes)(PPh₃)₂], 58.0, 45.8 (m x 2) [RuH₂(CO)(PPh₃)₃], 54.5 [Ru(CO)(CNMes)₂(PPh₃)₂], 45.0 [Ru(η²-SeCNMes)(CO)(CNMes)(PPh₃)₂], 43.5 (unassigned), 35.9 (JPSe = 756, Ph₃PSe). After 24 h at ambient temperature [Ru(CO)(CNMes)₂(PPh₃)₂] was no longer present and signals due to Ph₃PSe and the unassigned compound at δ 45.5 had increased in intensity.

Reaction of 3 with [Ru(CO)₂(PPh₃)₂(C₂H₄)] 
[Ru(CO)₂(PPh₃)₂(C₂H₄)] (30 mg, 42 μmol) and one equivalent of mesityl isocyanide (6 mg, 41 μmol) were combined in benzene-δ₆. The 31P {1H} NMR spectrum of the resultant yellow solution revealed the formation of [Ru(CO)₂(CNMes)(PPh₃)₂]. 31P {1H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)₂(CNMes)(PPh₃)₂].

Reaction of 1 with [Ru(CO)₂(PPh₃)₂(C₂H₄)] 
[Ru(CO)₂(PPh₃)₂(C₂H₄)] (30 mg, 42 μmol) and one equivalent of mesityl isoselenocyanate (9 mg, 40 μmol) were combined in benzene-δ₆. The 31P {1H} NMR spectrum of the resultant reddish orange solution revealed the formation of [Ru(CO)₃(CNMes)(PPh₃)₃] as the major product, along with Ph₃PSe and minor products arising from ligand scrambling. In addition, a small resonance not seen with the CNMes reaction was observed. 31P {1H} NMR (C₆D₆, 25 °C, 121.419 MHz): δ 60.5 [Ru(CO)₂(CNMes)(PPh₃)₂], 56.3 [Ru(CO)₃(PPh₃)₃], 45.4 [Ru(η²-SeCNMes)(CO)(CNMes)(PPh₃)₂], 35.9 (JPSe = 756, Ph₃PSe). After 24 h at ambient temperature the resonance at δ 45.4 was no longer evident and that due to Ph₃PSe had increased in intensity.

Reaction of 3 with [RuHCl(CO)(PPh₃)₃] 
[RuHCl(CO)(PPh₃)₃] (30 mg, 31 μmol) and one equivalent of mesityl isocyanide (4 mg, 28 μmol) were combined in dichloromethane-δ₂. The 31P {1H} NMR spectrum of the resultant colourless solution revealed the formation of [RuHCl(CO)(CNMes)(PPh₃)₃] and free triphenylphosphine. 31P {1H} NMR (CD₂Cl₂, 25 °C, 121.419 MHz): δ 43.8 [RuHCl(CO)(CNMes)(PPh₃)₃], -4.46 (free PPh₃).
CHAPTER 7. EXPERIMENTAL

7.3 Molybdenum selenoaroyl complexes

Structural study of [Mo(α=CC₄H₄S-2)(CO)₂Tp] (14)

Single crystals suitable for X-ray analysis were grown from dichloromethane/hexane at -11 ºC.

Crystal data for C₁₄H₁₂BMoN₆O₂S, Mᵣ = 460.13, orthorhombic, P bcm, a = 11.8515(2), b = 14.6972(3), c = 13.0805(2) Å, V = 2278.41(7) Å³, Z = 4, ρcalcd = 1.341 Mg m⁻³, μ(Mo Kα) = 0.686 mm⁻¹, T = 200(2) K, orange needle, 2730 independent measured reflections (2θ ≤ 55º), R₁ = 0.0311, wR = 0.0242 for 1789 independent observed absorption-corrected reflections (I > 3σ(I)), 158 parameters. The molecule lies on a crystallographic mirror plane, with the thiophene unit equally disordered across this plane.
Structural study of [Mo(η^2-SCC_4H_3S-2)(CO)_2Tp] (16)

Single crystals suitable for X-ray analysis were grown from dichloromethane/hexane at −11 °C. Crystal data for C_{16}H_{28}MoN_6O_2S_2·CH_2Cl_2, M_r = 577.13, monoclinic, P2_1/c, a = 13.5866(2), b = 8.3741(1), c = 21.0109(3) Å, β = 107.1596(6)°, V = 2284.12(5) Å³, Z = 4, ρ_{calc} = 1.678 Mg m⁻³, μ(Mo Kα) = 1.018 mm⁻¹, T = 200(2) K, black block, 5233 independent measured reflections (2θ ≤ 54°), R_I = 0.0237, wR = 0.0254 for 3110 independent observed absorption-corrected reflections (I > 3σ(I)), 296 parameters. The thiophene group was unequally disordered, with the two orientations related by 180° rotation around the Cα=Cip(thiophene) bond (ratio 0.895(4):0.105).

Structural study of [Os(η^2-TeCPhCl(CO)(PPh_3)] (13)

Single crystals suitable for X-ray analysis were grown from slow diffusion of hexane into a dichloromethane solution of 13. Crystal data for (C_{44}H_{35}BrCl_{1-x}OOSp_2Te)_2, M_r = 2018.72, triclinic, P 1bar, α = 11.159(2), b = 14.276(3), c = 24.825(5) Å, α = 74.493(1), β = 87.58(3), γ = 81.98(3), V = 3773.5(13) Å³, Z = 2, ρ_{calc} = 1.777 Mg m⁻³, μ(Mo Kα) = 5.387 mm⁻¹, T = 200(2) K, green prism, 17308 independent measured reflections (2θ ≤ 54°), R_I = 0.0480, wR = 0.1095 for 11818 independent observed absorption-corrected reflections (I > 2σ(I)), 904 parameters. The crystallographic asymmetric unit consisted of two molecules of C_{44}H_{35}BrCl_{1-x}OOSp_2Te. The chloro and bromo complexes were disordered with 0.69:0.31 and 0.66:0.34 site occupation ratios for the two crystallographically independent molecular sites.

Preparation of [Mo(=CC_4H_3S-2)(CO)_2Tp] (15)

Molybdenum hexacarbonyl (3.00 g, 11.4 mmol) was suspended in diethyl ether (50 mL) and 2-thienyllithium (11.4 mL, 1.0 M solution, Aldrich, 11.4 mmol) was added drop-wise over a 15 min period. The solution was cooled in a dry ice/acetone bath (−78 °C) and then treated with trifluoroacetic anhydride (1.6 mL, 11.4 mmol), resulting in an immediate purple colouration. The cooling bath was removed and the mixture was warmed gradually. After the last traces of purple colouration had dissipated, K[Tp^*] (4.06 g, 12.1 mmol) was added in one portion with stirring. The evolution of CO was noted and the solution was stirred at room temperature for one hour at which time the dark brown mixture was filtered through a short column of silica with dichloromethane. The resultant orange filtrate was evaporated to dryness and the crude residue subjected to chromatographic purification (silica gel, 1:1 dichloromethane–hexane, −33 °C), collecting only the major red band. Solvent removal and recrystallisation from dichloromethane/hexane provided pure 15 as a microcrystalline orange solid. Yield 3.53 g

The bromide is assumed to originate from LiPh•LiBr used in the synthesis.
(57%). IR (Nujol): 1987, 1908, 1896 (sh) (vCO) cm⁻¹. IR (CH₂Cl₂): 1988, 1904 (vCO), cm⁻¹.

¹H NMR (CDCl₃, 25 °C, 300.075 MHz): δ 7.30 (d, 3JHH = 3.3, 1 H, C₅H₅S), 7.15 (d, 3JHH = 4.9, 1 H, C₅H₅S), 6.90 [dd, 3JHH = 4.2, 3JHH = 3.9, 1 H, H²(C₅H₅S)₁], 5.85, 5.75 (s x 2, 2 H, Tp*H), 2.54, 2.39, 2.37, 2.34 (s x 4, 6:3:6:3 H, Tp*CH₃). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.421 MHz): δ 271.1 (Mo=C), 225.7 (Mo=CO), 151.2, 151.1, 144.9, 144.4 (1:2:1:2, Tp*CH₃), 106.3, 106.2 (1:2, Tp*CH), 169.1 [C¹(CH₅S)₅], 130.2, 126.6, 126.3 (C₅H₅S), 15.9, 14.6, 12.7, 12.6 (2:1:2:1, Tp*CH₃). MS (ESI): m/z (%) 571.8 (15) [M - 2CO + 2CH₃CN]⁺, 559.8 (17) [M - CO + CH₃CN]⁺, 546.8 (18) [M]⁺, 517.8 (94) [M - CO]⁺, 489.8 (100) [M - 2CO]⁺. Anal. Found: C, 48.60; H, 4.71; N, 15.19%. Calcd. for C₂₂H₂₅BMoN₆O₃S: C, 48.55; H, 4.63; N, 15.44%. Crystal data for C₂₂H₂₅BMoN₆O₃S·(CH₃)₂CO, Mᵣ = 602.38, triclinic, P ₁, a = 7.9656(2), b = 10.4781(3), c = 17.8776(6) Å, α = 90.963(2), β = 91.237(2), γ = 107.606(2)°, V = 1421.46(7) Å³, Z = 2, ρcalc = 1.407 Mg m⁻³, µ(Mo Kα) = 0.571 mm⁻¹, T = 200(2) K, orange needle, 5062 independent measured reflections (2θ ≤ 50°), R₁ = 0.0401, wR² = 0.0353 for 4099 independent observed absorption-corrected reflections (I > 3σ(I)), 381 parameters. The crystal was twinned and refined accordingly (final twin ratio 0.839(2):0.161). The thiophene group was unequally disordered with the two orientations related by 180° rotation around the C(carbyme)–Cₛₒ(thiophene) bond (ratio 0.710(5):0.290).

Preparation of [Mo(≡CC₅H₅S-2)(CO)(CNMes)Tp] (24)

[Mo(≡CC₅H₅S-2)(CO)₂Tp] (14) (0.200 g, 0.435 mmol) and mesityl isocyanide (3) (0.069 g, 0.475 mmol) were combined in hexane (15 mL) and the dark blood red solution heated at reflux for 7 h after which time the solution was dark brown. Solvent was removed in vacuo and the residue redissolved in minimal tetrahydrofuran and chromatographed (silica gel, −33 °C), eluting with dichloromethane–hexane (1:2). Orange and brown fractions were developed and solvent removal from the initial, orange eluate afforded 0.033 g of 14 (17% recovery). Similar treatment of the brown fraction afforded 24 as a pale brown solid. Yield 0.044 g (16%). IR (CH₂Cl₂): 2083 (vCN), 1899 (vCO), cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.97, 7.95, 7.72, 7.66 (d x 4, 1:1:2:2 H, TpH₃), 7.11 (dd, 3JHH = 3.6, 4JHH = 1.2, 1 H, C₅H₅S), 7.08 (dd, 3JHH = 5.1, 4JHH = 1.2, 1 H, C₅H₅S), 6.92 (s, 2 H, C₆H₂), 6.85 [dd, 3JHH = 5.1, 3.6, 1 H, H¹(CH₅S)₁], 6.25 (m, 2 H, TpCH₄), 6.17 (t, 1 H, TpCH₃), 2.35, 2.28 (s x 2, 6:3 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 271.8 (Mo=C), 237.9 (Mo=CO), 188.2 (Mo-CN), 150.5 [C¹(CH₅S)₁], 144.7, 144.0, 143.0, 135.7, 135.6 (1:1:1:1:2, TpCH), 137.7 [C¹(CH₅S)₁], 133.7 [C³(CH₅S)₁], 128.7 [C³(CH₅S)₁], 126.8 [C¹(CH₅S)₁], 128.1, 126.5, 125.6 (CH₅S), 105.6, 105.5, 105.3 (TpCH₃), 21.2, 19.0 (1:2 CH₃). Anal. Found: C, 52.35; H, 4.41; N, 16.13%. Calcd. for C₂₅H₂₅BMoN₆S: C, 52.01; H, 4.19; N, 16.98%.
Attempted preparation of \([\text{Mo}(\eta^2-\text{TeCC}_3\text{H}_5\text{S}-2)(\text{CO})_2\text{Tp}]\) from PEt\(_3\) / Te

\([\text{Mo}(=\text{CC}\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) (14) (0.20 g, 0.43 mmol) and tellurium powder (0.055 g, 0.43 mmol) were combined in hexane (30 mL). Triethylphosphine (0.100 g, 0.86 mmol) was added and the mixture heated at reflux. No reaction was apparent after 5 days (thin layer chromatography) and hexane solvent was removed prior to resuspension in toluene and heating at reflux for a further 12 h, over which time the colour of the solution changed from orange to a deep burgundy. Solvent was removed under vacuum and the red-brown residue transferred as a concentrated dichloromethane solution to a chromatography column (silica gel, −33 °C). Elution with dichloromethane–hexane (1:1) afforded a broad maroon fraction as the major reaction product. Continued elution with tetrahydrofuran freed a narrow brown-grey band from the baseline material. Solvent removal and recrystallisation of the maroon eluate afforded \([\text{Mo}(=\text{CC}\text{H}_3\text{S}-2)(\text{CO})(\text{PEt}_3)\text{Tp}]\) (30) as a pure burgundy solid. Yield 0.153 g (64%). IR (KBr): 2465 w (v\(_{\text{BH}}\)), 1867 s (v\(_{\text{CO}}\)), 1500 (v\(_{\text{CN}}\)) cm\(^{-1}\). IR (CH\(_2\)Cl\(_2\)): 1870 (v\(_{\text{CO}}\)) cm\(^{-1}\). ¹H NMR (CD\(_3\)Cl\(_2\), 25 °C, 300.075 MHz): δ 7.89, 7.76, 7.70, 7.62, 7.58 (d × 5, 2:1:1:1:1 H, TpH), 7.01 (m, 2 H, C\(_4\)H\(_3\)S), 6.83 (dd, ³J\(_{\text{HH}}\) = 5.1, 1 H, \(\text{H}^1(\text{C}_4\text{H}_3\text{S})\)), 6.26, 6.18, 6.16 (t × 3, 3 H, TpH\(^2\)), 1.80 (m, 6 H, CH\(_2\)), 0.82 (dt, ³J\(_{\text{PH}}\) = 14.4, ³J\(_{\text{HH}}\) = 7.8, 9 H, CH\(_3\)). ¹³C\(^{1}\H\) NMR (CD\(_3\)Cl\(_2\), 25 °C, 75.421 MHz): δ 264.2 (d, \(^2\)J\(_{\text{PC}}\) = 19.2, Mo\(\equiv\)C), 249.9 (d, \(^2\)J\(_{\text{PC}}\) = 9.6, MoCO), 150.9 [C\(^1\H\)] (C\(_4\)H\(_3\)S), 144.2, 142.9, 136.2, 135.9, 135.1 (2:1:1:1:1, TpCH), 126.9, 126.4, 124.0 (C\(_4\)H\(_3\)S), 105.4, 105.3 (1:2, TpCH\(^4\)), 20.5 (d, \(^2\)J\(_{\text{PC}}\) = 21.1, CH\(_2\)), 7.48 (CH\(_3\)). ³¹P\(^{1}\H\) NMR (CD\(_3\)Cl\(_2\), 25 °C, 121.419 MHz): δ 36.8. MS (ESI): m/z (%) 575.0 (3) [M + Na]\(^+\), 553.1 (3) [M]\(^+\), 521.1 (100) [M − CO]\(^+\), 496.0 (23) [M − 2Et]\(^+\), 432.0 (15) [M − PEt\(_3\)]\(^+\), 405.0 (15) [M − CO − PEt\(_3\)]\(^+\). Solvent removal from the second, brown-grey fraction afforded a light-sensitive compound identified as Et\(_3\)PTe. Yield 0.073 g (81%). ¹H NMR (CD\(_3\)Cl\(_2\), 25 °C, 300.075 MHz): δ 2.01 (dq, \(^2\)J\(_{\text{PH}}\) = 11.4, ³J\(_{\text{HH}}\) = 7.5, 6 H, CH\(_2\)), 1.10 (dt, \(^3\)J\(_{\text{PH}}\) = 20 Hz, ³J\(_{\text{HH}}\) = 7.5 Hz, 9 H, CH\(_3\)). ³¹P\(^{1}\H\) NMR (CD\(_3\)Cl\(_2\), 25 °C, 121.419 MHz): δ −0.37. Mp. 77−79 °C cf. literature data δ \(\text{p} \) 0.3\(^{18}\) andMp. 76−78 °C.

Preparation of \([\text{Mo}(=\text{CC}\text{H}_3\text{S}-2)(\text{CO})(\text{PEt}_3)\text{Tp}]\) (30)

Complex \([\text{Mo}(=\text{CC}\text{H}_3\text{S}-2)(\text{CO})(\text{PEt}_3)\text{Tp}]\) (30) could be prepared in the absence of tellurium (in a similar manner to that described above) employing triethylphosphine (0.051 g, 0.432 mmol) and \([\text{Mo}(=\text{CC}\text{H}_3\text{S}-2)(\text{CO})_2\text{Tp}]\) (14) (0.20 g, 0.434 mmol) in toluene (20 mL) at reflux for 12 h. Solvent removal and chromatographic purification (silica gel, 1:1 dichloromethane–hexane, −33 °C) of the residue afforded an initial orange eluate corresponding to 0.046 g (23%) of recovered 14 prior to elution of the major red-brown fraction containing 30. Yield 0.147 g (80% based on recovered starting material).
Reactions between alkylidyne complexes and SeCNMes

**Treatment of [Mo(≡CC₆H₅-S-2)(CO)₂Tp]** with 1

**Method 1** [Mo(≡CC₆H₅-S-2)(CO)₂Tp] (14) (1.00 g, 2.17 mmol) and mesityl isoselenocyanate (1) (0.487 g, 2.17 mmol) were suspended in hexane (40 mL) and the mixture heated at reflux for 4 h. The resulting dark solution was evaporated to dryness, redissolved in minimum dichloromethane (ca. 3 mL) and transferred to a chromatography column (silica gel, −33 °C).

Elution with dichloromethane–hexane (1:2) developed an initial orange band corresponding to recovered 14 (0.28 g, 28% recovery) (NB: the remaining yields are calculated on this basis) followed by narrow teal and broad royal blue bands. Continued elution of the chromatography column with neat dichloromethane afforded a final purple fraction. Solvent removal from the narrow teal eluate and recrystallisation from dichloromethane/hexane afforded dark blue microcrystals of [Mo(κ²-Se₂C₆H₅-S-2)(CO)₂Tp] (19). Yield 0.029 g (3% based on recovered 14). IR (Nujol): 1931, 1856 (Yeo), 1747, 1548 cm⁻¹. MS (ESI): \( m/z \) 513.8 (100) [M − 2CO].

**Crystal data for C₁₆H₂₃BMoN₆O₂Se₂:** C, 31.09; H, 2.12; N, 13.60%. Crystal data for C₁₆H₂₃BMoN₆O₂Se₂: Mₚ = 618.06, orthorhombic, Pben, \( a = 30.1864(6), b = 9.3031(2), c = 14.5289(2) \) Å, \( V = 4080.1(1) \) Å³, \( Z = 8 \), \( \rho_{\text{calc}} = 2.012 \) Mg m⁻³, \( \mu(\text{Mo Kα}) = 4.340 \) mm⁻¹, \( T = 200(2) \) K, black needle, 3599 independent measured reflections (\( 2θ \leq 50° \)), \( R₁ = 0.0594 \), \( wR = 0.0659 \) for 2194 independent observed absorption-corrected reflections \( (I > 3\sigma(I)) \), 247 parameters. The precision of the model was compromised by unresolved, systematic errors in the diffraction data, however the identity of the compound was unequivocally established.

Recovery of the royal blue eluate and solvent removal afforded blue microcrystals of [Mo(η²-Se₂C₆H₅-S-2)(CO)₂Tp] (16). Yield 0.269 g (32% based on recovered 14). IR (Nujol): 1976, 1897 cm⁻¹. IR (CH₂Cl₂): 1988, 1909 cm⁻¹. \( ^1H \) NMR (CD₂Cl₂, 25 °C, 300.075 MHz): \( \delta \) 7.89, (dd, \( 3J_{HH} = 5.1, 4J_{HH} = 1.2, 1 \) H, C₆H₅S), 7.86 (dd, \( 3J_{HH} = 3.9, 4J_{HH} = 0.9, 1 \) H, C₆H₅S), 7.30, (dd, \( 3J_{HH} = 5.1, 4J_{HH} = 3.9, 1 \) H, H(C₆H₅S)]. 7.81, 7.47, 6.26 (s(br) \times 3, 9 H, TpH).

**Crystal data for C₁₆H₁₃BMoN₆O₂Se₂:** C, 35.65; H, 2.43; N, 15.59%. Crystal data for C₁₆H₁₃BMoN₆O₂Se₂: C, 35.65; H, 2.43; N, 15.59%.
c = 21.0335(3) Å, β = 107.2505(6)°, V = 2309.05(4) Å³, Z = 4, \( \rho_{\text{calc}} = 1.795 \text{ Mg m}^{-3} \), 
\( \mu(\text{Mo}\ \alpha) = 2.493 \text{ mm}^{-1} \), T = 200(2) K, black needle, 5300 independent measured reflections
(2θ ≤ 54°), \( R_1 = 0.0257 \), \( wR = 0.0279 \) for 3672 independent observed absorption-corrected reflections
(I > 3σ(I)), 296 parameters. The thiophene group was unequally disordered, with the two orientations
related by 180° rotation around the C\( \alpha \)-C\( \psi \)
(thiophene) bond (ratio 0.873(4):0.127).

Similarly, solvent removal from the final purple fraction and recrystallisation from dichloromethane/hexane afforded purple microcrystals of
[Mo(\( \text{SeCC}_3\text{H}_5\text{S}-2\))(CO)(CNMes)Tp] (16). Yield 0.246 g (24% based on recovered 14).

IR (Nujol): 2103 (\( \nu_{\text{CN}} \)), 1890 (\( \nu_{\text{CO}} \)) cm\(^{-1} \). IR (CH\(_2\)Cl\(_2\)): 2099 (\( \nu_{\text{CN}} \)), 1885 (\( \nu_{\text{CO}} \)) cm\(^{-1} \). \(^1\)H NMR
(CD\(_2\)Cl\(_2\), 25 °C, 300.075 MHz): \( \delta = 7.95, 7.83, 7.79, 7.67, 7.39 \) (m(br) × 5, 1:1:2:1:1 \( H \)), TpH\(^3\),
7.67 (m(br), 2 \( H \), C\( \text{H}_2\)), 7.13 [dd, \( \delta = 4.8 \) and 3.6, 1 \( H \), H\(^4\)(C\( \text{H}_5\text{S}\))]. 6.80 (s, 2 \( H \), C\( \text{H}_2\)),
6.32, 6.27, 6.22 (s × 3, 3 \( H \), TpH\(^1\)), 2.22, 1.93 (s × 2, 3 \( H \), CH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\),
25 °C, 75.421 MHz): \( \delta = 267.6 \) (SeC), 239.5 (CO), 186.3 (CN), 155.6 [C\(^1\)(C\( \text{H}_5\text{S}\))], 146.6, 145.0,
143.1, 136.3, 135.7 (1:1:1:1:2, TpCH\(^3\)), 138.6 [C\(^4\)(C\( \text{H}_2\))], 134.0 [C\(^2\)(C\( \text{H}_2\))], 133.9, 133.7
(C\( \text{H}_5\text{S}\)), 128.8 [C\(^3\)(C\( \text{H}_2\))], 128.6 [C\(^4\)(C\( \text{H}_5\text{S}\))], 125.8 [C\(^1\)(C\( \text{H}_2\))], 106.1, 166.0, 105.97
(TpCH\(^4\)), 21.1, 18.4 (1:2, CH\(_3\)). MS (ESI): m/z (%): 680.0 (40) [M + Na\(^+\)], 656 (10) [M\(^+\)], 629
(85) [M - CO\(^+\)], 485 (15) [M - CO - CNMes\(^+\)]. Anal. Found: C, 43.63; H, 3.51; N, 13.89%.

Calcd. for C\(_{35}\)H\(_{24}\)BMoN\(_2\)OSSe•CH\(_2\)Cl\(_2\): C, 43.83; H, 3.61; N, 14.03%. Crystal data for
C\(_{35}\)H\(_{24}\)BMoN\(_2\)OSSe•CH\(_2\)Cl\(_2\), \( M_r = 741.22 \), triclinic, \( P \overline{1} \), \( a = 8.8257(1) \), \( b = 12.2737(2) \),
\( c = 14.3685(3) \) Å, \( \alpha = 82.1624(7) \), \( \beta = 84.5846(7) \), \( \gamma = 84.684(1)^\circ \), \( V = 1530.00(4) \text{ Å}^3 \), \( Z = 2 \),
\( \rho_{\text{calc}} = 1.609 \text{ Mg m}^{-3} \), \( \mu(\text{Mo}\ \alpha) = 1.894 \text{ mm}^{-1} \), T = 200(2) K, black rod, 7007 independent measured reflections
(2θ ≤ 54°), \( R_1 = 0.0312 \), \( wR = 0.0340 \) for 4192 independent observed absorption-corrected reflections
(I > 3σ(I)), 378 parameters. The thiophene group was unequally disordered, with the two orientations related by 180° rotation around the C\( \alpha \)-C\( \psi \)
(thiophene) bond (ratio 0.743(5):0.257).

Method 2 Using a similar procedure to that described above, [Mo(\( \text{SeCC}_3\text{H}_5\text{S}-2\))(CO)\(_2\)Tp]
(1.78 g, 3.87 mmol) and SeCNMes (0.870 g, 3.88 mmol) were suspended in hexane (80 mL)
and the mixture heated at reflux for 50 h. Chromatographic purification of the residue (silica gel, 1:2 dichloromethane–hexane, –17 °C) afforded an initial royal blue eluate corresponding to
0.502 g (24%) of 16. Increasing the dichloromethane content of the eluant solvent mix
developed the second, major purple band corresponding to 16 (1.026 g, 40%).

Method 3 A mixture of [Mo(\( \text{SeCC}_3\text{H}_5\text{S}-2\))(CO)\(_2\)Tp] (14) (1.00 g, 2.17 mmol) and SeCNMes (1)
(0.487 g, 2.17 mmol) in dichloromethane (20 mL) were stirred at room temperature with the
exclusion of light for 50 h. Solvent was removed from the brown solution and the residue
redissolved in the minimum dichloromethane before being transferred to a chromatography
column (silica gel, −17 °C). Elution with dichloromethane–hexane (1:1) developed a large orange band (0.446 g recovered 14, 44.6% recovery) (NB: the remaining yields are calculated on this basis), a broad blue band (16, 0.278 g, 43%), an intermediate narrow bright orange band, and a narrow purple band corresponding to 16 (0.043 g, 5%). Recovery of the orange eluate followed by removal of solvent in vacuo and recrystallisation from dichloromethane/hexane afforded orange microcrystals of \([\text{Mo}[\text{CN}(\text{Mes})C(=\text{N}\text{Mes})\text{SeC(=\text{N}\text{Mes})C}(_{3}\text{H}_{5}S-2)])[\text{CO}]_{2}\text{Tp}]\) (26). Yield 0.058 g (15%). IR (KBr): 2466 (v_{\text{BH}}), 1905 (v_{\text{CO}}), 1615, 1600 (v_{\text{CN}}) cm\(^{-1}\). 1H NMR (CD_{2}Cl_{2}, 25 °C, 300.075 MHz): \(\delta\) 9.35, 7.78, 7.70, 7.52 (d x 5, 5 H, TpH\(^{1,2}\)), 7.13, 7.06, 6.84, 6.75, 6.72, 6.69 (s (br) x 6, 6 H, C_{6}H_{2}), 6.80 (dd, \(^{3}J_{\text{HH}} = 3.3, \(^{4}J_{\text{HH}} = 1.5\), 1 H, C_{4}H_{2}S), 6.57 (m, 2 H, C_{4}H_{2}S), 6.27, 6.17, 5.79 (t x 3, 3 H, TpH\(^{1}\)), 2.66, 2.52, 2.37, 2.22, 2.17, 1.82, 1.69 (s x 8, 3.3:3:3:3:6:3:3:6 H, CH\(_{3}\)). 13C\(^{1}\)H NMR (CD_{2}Cl_{2}, 25 °C, 75.421 MHz): \(\delta\) 241.2 (Mo=C), 232.5, 228.9 (MoCO), 166.5 (SeCN\(_{2}\)), 153.9 [C\(^{1}\)(C\(_{4}\)H\(_{2}\)S)], 149.1, 144.9, 143.9, 136.1, 136.0, 135.0 (TpCH), 137.5 (SeCN\(_{2}\)), 148.6, 145.8, 141.4, 139.6, 138.0, 135.8, 134.4, 134.0, 130.0, 129.5, 129.3, 129.2, 129.1, 127.9, 127.1, 127.0, 126.6 (C\(_{4}\)H\(_{2}\)), 126.3, 125.4, 125.0 (C\(_{4}\)H\(_{2}\)S), 106.0, 105.3, 104.8 (TpCH\(^{1}\)), 37.3 (MoCC\(_{4}\)H\(_{2}\)S), 21.2, 20.8, 20.7, 19.7, 19.4, 19.0, 18.7, 18.1, 18.0 (CH\(_{3}\)). MS (ESI): m/z (%): 978.2 (10) [M]\(^{+}\), 948.3 (38) [M - CO]\(^{+}\), 920.2 (100) [M - 2CO]\(^{+}\), 775.23 (48) [M - C\(_{4}\)H\(_{2}\)S - C\(_{4}\)H\(_{1}\)]. Anal. Found: C, 56.22; H, 4.65; N, 12.42; S, 3.15%. Calcd. for C\(_{46}\)H\(_{46}\)BMoN\(_{6}\)O\(_{2}\)Se: C, 56.68; H, 4.76; N, 12.93; S 3.29%. Crystal data for C\(_{46}\)H\(_{46}\)BMoN\(_{6}\)O\(_{2}\)Se: \(M_{r} = 974.69\), triclinic, \(P\ 1\), \(a = 11.879(2), \ b = 13.366(3), c = 15.554(3) \AA, \ \alpha = 79.76(3), \ \beta = 73.06(3), \ \gamma = 89.64(3)^{\circ}, \ V = 2322.1(8) \AA^{3}, \ Z = 2, \rho_{\text{calc}} = 1.394 \text{ Mg m}^{-3}, \mu_{\text{Mo Ko}} = 1.158 \text{ mm}^{-1}, \ T = 200(2) \text{ K}, \) orange prism, 9433 independent measured reflections (2θ ≤ 50°), \(R_{1} = 0.0471, wR_{2} = 0.0943\) for 6771 independent observed absorption-corrected reflections (\(I > 2\sigma(I)\)), 562 parameters.

**Treatment of [Mo(≡C\(_{4}\)H\(_{1}\)Me-4)(CO)\(_{2}\)Tp] with 1**

Using a similar procedure described for the reaction of 14 with SeCN\(_{2}\) (1), a mixture of [Mo(≡C\(_{4}\)H\(_{1}\)Me-4)(CO)\(_{2}\)Tp] (20) (0.50 g, 1.06 mmol) and mesityl isoselenocyanate (0.263 g, 1.17 mmol) were heated in hexane (25 mL) at reflux for 4 h. The resulting dark solution was evaporated to dryness, redissolved in dichloromethane (minimum) and transferred to a chromatography column (silica gel, −17 °C). Elution with dichloromethane–hexane (1:1) developed an initial orange band containing recovered 20 (0.140 g, 30% recovered yield), a narrow intermediate light purple band that was not collected (presumed to be due to minor formation of [Mo(κ\(^{2}\)Se\(_{2}\)CC\(_{4}\)H\(_{1}\)Me-4)(CO)\(_{2}\)Tp]) and a broad blue-purple band. By increasing the dichloromethane content of the eluant solvent a final dark purple fraction could be obtained. Solvent removal from the blue-purple eluate and recrystallisation from dichloromethane/hexane...
afforded dark purple microcrystals of [Mo(η²-SeCC₆H₄Me-4)(CO)₂Tp] (21). Yield 0.035 g (6%). IR (CH₂Cl₂): 1988, 1905 (νCO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.86, 7.39 (d × 2, 3JHH = 8.1, 4 H, C₆H₄Me-4), 7.81, 7.46, 6.26 (s(br) × 3, 9 H, TpH), 2.47 (s, 3 H, Me-4). ¹³C[¹H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 288.2 (SeC), 230.8 (CO), 145.9 (C₁(C₆H₄Me-4)), 144.9(br), 136.0, 106.4 (TpCH), 142.6, (C₆H₄Me-4)), 135.6, 129.5 (2:2, C₆H₄Me-4), 21.8 (Me-4).

Similar treatment of the larger dark purple eluate afforded [Mo(η²-SeCC₆H₄Me-4)(CO)(CNMes)Tp] (23). Yield 0.180 g (25%). IR (Nujol): 2473 (νBH), 2105 (νCN), 1855 (νCO) cm⁻¹. IR (CH₂Cl₂): 2102 (νCN), 1879 (νCO), cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.82, 7.24 (d × 2, 3JHH = 7.8, 4 H, C₆H₄Me-4), 7.96, 7.80, 7.72, 7.35 (s(br) × 4, 1:3:1:1, 6 H, TpH) 6.73 (s, 2 H, C₆H₂), 6.31, 6.27, 6.21 (t(br) × 3, 3 H, TpH², 2.36 (Me-4), 2.19, 1.76 (s × 2, 3:6 H, CH₃). ¹³C[¹H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 292.4 (SeC), 240.3 (CO), 186.7 (CN), 144.9 (C₁(C₆H₄Me-4)), 146.7, 146.4, 142.5, 139.8, 138.3, 136.0 (TpCH), 135.6 [C⁴(C₆H₂)], 135.5 [C⁴(C₆H₄Me-4)], 133.7 [C²S(C₆H₂)], 133.8, 128.9 (2:2, C₆H₄Me-4), 128.5 [C³S(C₆H₂)], 125.5 [C¹(C₆H₂)], 106.0, 105.9, 105.8 (TpCH²), 21.4 (Me-4), 20.9, 18.0 (1:2, CH₃). MS (ESI): m/z (%) 687.9 (15) [M + Na]⁺, 659.8 (10) [M - CO + Na]⁺, 492.8 (35) [M - CO - CNMes]⁺. Anal. Found: C, 50.94; H, 4.29; N, 14.25%. Calcld. for C₂₈H₃₈BMoN₇O₇Se: C, 50.63; H, 4.25; N, 14.76%. Crystal data for C₂₈H₃₈BMoN₇SeO₇: M, 664.29, monoclinic, C2/c, a = 16.5485(3), b = 3.2092(2), c = 27.386(4) Å, β = 104.065(9)°, V = 5806.8(2) Å³, Z = 8, ρcalcd = 1.520 Mg m⁻³, μ(Mo Kα) = 1.739 mm⁻¹, T = 200(2) K, black plate, 6670 independent absorption-corrected reflections (2θ ≤ 54°), R₁ = 0.0251, wR₂ = 0.0264 for 4383 independent observed absorption-corrected reflections (I > 3σ(I)), 391 parameters.

Treatment of [Mo(η²-SeCC₆H₄S-2)(CO)₂Tp*] with 1
[Mo(η²-SeCC₆H₄S-2)(CO)₂Tp*] (15) (0.20 g, 0.367 mmol) and mesityl isoselenocyanate (1) (0.091 g, 0.405 mmol) were suspended in hexane (20 mL) and the mixture heated at reflux for 3 days. The resulting dark brown solution was allowed to stand for 24 h, whereupon dark blue crystals of [Mo(η²-SeCC₆H₄S-2)(CO)₂Tp*] (26) formed, which were isolated by filtration and washed with hexane. Yield 0.065 g (28%). IR (KBr): 2546 w (νBH), 1970 s, 1899 s (νCO), 1540 (νCN) cm⁻¹. IR (CH₂Cl₂): 1981, 1900 cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.85 (dd, 3JHH = 5.24, 4JHH = 1.05, 1 H, C₆H₄(S)), 7.76 (dd, 3JHH = 3.89, 4JHH = 0.89, 1 H, C₆H₄(S)), 7.30 [dd, 3JHH = 5.09, 3JHH = 3.89, 1 H, H₁(C₆H₄(S))], 5.95, 5.87 (1:2, Tp*CH), 2.51, 2.44, 2.41(br), 2.13 (3:6:3:6 Tp*CH₃). ¹³C[¹H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 258.5 (SeC), 229.0

The sample decomposed during overnight acquisition of ¹³C[¹H] NMR data however major resonances due to the desired compound were clearly distinguishable.
Reactions between alkylidyne complexes and elemental selenium

**Treatment of [Mo(≡CC₄H₅S-2)(CO)₂Tp] with elemental selenium**

**Method 1** [Mo(≡CC₄H₅S-2)(CO)₂Tp] (14) (0.200 g, 0.434 mmol) and grey selenium (0.172 g, 2.18 mmol) were suspended in hexane (10 mL) and the mixture heated at reflux for 10 days at which time all of 14 was consumed (thin layer chromatography). The resulting dark solution was filtered through Celite, evaporated to dryness, redissolved in minimal dichloromethane and subjected to chromatography (silica gel, −17 °C). Elution with dichloromethane–hexane (1:1) afforded an initial, broad teal band that was collected and concentrated under reduced pressure to furnish blue microcrystals of 19. Yield 0.120 g (44%). Continued elution allowed for the collection of a slightly narrower royal blue band that was concentrated in vacuo to afford blue microcrystals of 16. Yield 0.090 g (38%).

**Method 2** [Mo(≡CC₄H₅S-2)(CO)₂Tp] (14) (0.500 g, 1.08 mmol) and grey selenium (0.34 g, 4.35 mmol) were suspended in dichloromethane (20 mL) and the mixture stirred at room temperature for 3 days at which time all of 14 was consumed (thin layer chromatography). The dark blue solution was filtered through Celite and concentrated to ca. 3 mL prior to transferring to a chromatography column (silica gel, −33 °C). Elution with dichloromethane–hexane (1:1) developed a small orange band spectroscopically identified as 14 (IR). Continued elution afforded a minor teal band followed by a broad royal blue fraction. Recovery of the teal blue eluate followed by removal of solvent in vacuo yielded dark blue microcrystals of 19. Yield 0.080 g (12%). Similar treatment of the royal blue eluate yielded dark blue microcrystals of 16. Yield 0.412 g (70%).

**Treatment of [Mo(≡CC₄H₅S-2)(CO)₂Tp⁺]** with elemental selenium

[Mo(≡CC₄H₅S-2)(CO)₂Tp⁺] (15) (0.20 g, 0.367 mmol) and selenium powder (0.087 g, 1.10 mmol) were suspended in hexane (20 mL) and the mixture heated at reflux, reaching equilibrium after 2 days. The resulting dark brown solution was pumped dry, recrissolved in minimum tetrahydrofuran and transferred to a chromatography column. Elution with dichloromethane–hexane (1:1) afforded an initial orange band corresponding to recovered 15
(0.141 g, 70% recovery). A second, broad blue eluate was obtained and solvent removal and recrystallisation from dichloromethane/pentane afforded blue microcrystals of 26. Yield 0.053 g (23% yield).

**Conversion of [Mo(η²-SeCC₄H₅S-2)(CO)₂Tp] (16) to [Mo(κ⁻SeCC₄H₅S-2)(CO)₂Tp] (19)**

**Method 1** [Mo(η²-SeCC₄H₅S-2)(CO)₂Tp] (16) (0.100 g, 0.185 mmol) and elemental selenium (0.029 g, 0.367 mmol) were combined in dichloromethane (15 mL) and stirred at room temperature for 3 weeks, at which time complete consumption of 16 had occurred (thin layer chromatography). The blue solution was filtered through Celite, concentrated to ca. 3 mL and subjected to chromatographic purification (silica gel, -33 °C). Elution with dichloromethane–hexane (1:1) developed a broad teal band and solvent removal in vacuo and subsequent recrystallisation from dichloromethane/hexane afforded blue microcrystals of 19. Yield 0.056 g (50%).

**Method 2** [Mo(η²-SeCC₄H₅S-2)(CO)₂Tp] (16) (0.100 g, 0.185 mmol) and mesityl isoselenocyanate (I) (0.042 g, 0.187 mmol) were combined in dichloromethane (15 mL) and stirred at room temperature. After 1 week thin layer chromatography indicated the presence of both 16 and 19 in approximately equal proportions. A second equivalent of mesityl isoselenocyanate (0.042 g, 0.187 mmol) was added and the mixture stirred for a further two weeks, however, no apparent change in the product distribution was observed. The blue solution was filtered through Celite and the solvent volume reduced in vacuo prior to chromatographic separation of the mixture (silica gel, -33 °C). Elution with dichloromethane–hexane (1:1) developed a teal band followed by a royal blue band. Solvent removal from the teal blue eluate afforded blue microcrystals of 19. Yield 0.035 g (30%). Recovery of the royal blue eluate followed by removal of solvent in vacuo furnished blue microcrystals of 16. Yield 0.062 g (62% recovery).

**Method 3** To a suspension of elemental selenium (0.018 g, 0.228 mmol) in tetrahydrofuran (10 mL) was added Li[HBE₃] (0.185 mL) in a drop-wise fashion. The mixture was stirred for 1 h, affording a red solution of Li₂Se₂. [Mo(η²-SeCC₄H₅S-2)(CO)₂Tp] (16) (0.100 g, 0.185 mmol) in tetrahydrofuran (20 mL) was slowly added to the red solution, resulting in an immediate blue colouration. The mixture was stirred for a further hour before being filtered through a short pad of silica gel (dichloromethane) to remove excess selenium and Li₂Se₂. The solvent volume was reduced in vacuo and the residue subjected to chromatographic purification (silica gel, -33 °C). Elution with dichloromethane–hexane (1:1) developed a teal band followed by a broad royal blue fraction. Removal of the solvent from the initial teal eluate provided 0.07 g (6%) of 19. Solvent removal from the royal blue eluate provided recovered 16 (0.021 g, 21% recovery).
Preparation of \([\text{Mo}({\eta}^2-\text{MeSeCC}_4\text{H}_3\text{S}-2)\text{(CO)}\text{Tp}][\text{BF}_4]\) (27)

\([\text{Mo}({\eta}^2-\text{SeCC}_4\text{H}_3\text{S}-2)\text{(CO)}\text{Tp}]\) (16) (0.150 g, 0.278 mmol) and trimethylxionium tetrafluoroborate (0.049 g, 0.331 mmol) were combined in diethyl ether (10 mL) and the resulting suspension stirred vigorously for seven days during which time a slow colour change from blue to yellow-green occurred. The reaction liquor was decanted away from the yellow precipitate and the product washed with diethyl ether (2 × 10 mL). Recrystallisation from dichloromethane/hexane provided a bright mustard yellow powder. Yield 0.163 g (92%).

IR (Nujol): 2043, 1973 (v_CO) cm\(^{-1}\). IR (CH\(_2\)Cl\(_2\)): 2055, 1991 (v_CO) cm\(^{-1}\). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 °C, 300.075 MHz): \(\delta\) 8.23 (dd, \(^3J_{HH} = 4.95\), \(^4J_{HH} = 1.04\), 1 H, C\(_4\)H\(_3\)S), 8.13 (dd, \(^3J_{HH} = 4.04\), \(^4J_{HH} = 1.04\), 1 H, C\(_4\)H\(_3\)S), 7.96 (m, 3 H, TpH\(^{30\text{r}}\)), 7.56 (d(br), 1 H, TpH\(^{30\text{r}}\)), 7.51 (dd, \(^3J_{HH} = 4.95\), \(^3J_{HH} = 4.04\), 1 H, H\(^1\)(C\(_4\)H\(_3\)S)), 7.44 (d(br), 1 H, TpH\(^{30\text{r}}\)), 6.50, 6.46, 6.44 (4 × 3, 3 H, TpH\(^{1}\)), 2.39 (s, 3 H, SeMe). \(^13\)C\({}\text{H}\) NMR (CD\(_2\)Cl\(_2\), 25 °C, 75.421 MHz): \(\delta\) 243.8 (SeC), 217.8, 217.5 (MoCO), 152.2 [C\(^1\)(C\(_4\)H\(_3\)S)], 146.1, 144.6, 144.3, 138.7, 138.2, 138.0 (TpCH\(^{30\text{r}}\)), 141.6, 140.5 (C\(_4\)H\(_3\)S), 131.9 [C\(^4\)(C\(_4\)H\(_3\)S)], 108.1, 107.9, 107.7 (TpCH\(^{1}\)), 17.7 (SeMe). MS (ESI): m/z (%) 554.7 (38) [M\(^+\)], 539.8 (33) [M – CH\(_3\)\(^+\)], 526.8 (63) [M – CO\(^+\)], 498.8 (100) [M – 2CO\(^+\)]. Anal. Found: C, 31.31; H, 2.50; N, 12.68; S, 4.90%. Calcd. for C\(_{17}\)H\(_{16}\)BMoN\(_6\)O\(_2\)S\(_2\)Se: C, 31.86; H, 2.52; N, 13.11; S, 5.00%. Crystal data for C\(_{17}\)H\(_{16}\)BMoN\(_6\)O\(_2\)S\(_2\)Se\(_2\)BF\(_4\), \(M_r = 640.93\), monoclinic, \(P2_1/n\), \(a = 8.5790(1)\), \(b = 17.2143(4)\), \(c = 15.7532(4)\) Å, \(\beta = 92.430(2)^\circ\), \(V = 2324.36(8)\) Å\(^3\), \(Z = 4\), \(\rho_{\text{calc}} = 1.831\) Mg m\(^{-3}\), \(\mu\) (Mo K\(\alpha\)) = 2.280 mm\(^{-1}\), \(T = 200(2)\) K, green plate, 5320 independent measured reflections \((2\theta \leq 54^\circ)\), \(R_I = 0.0318\), \(wR = 0.0335\) for 3587 independent observed absorption-corrected reflections \((I > 3\sigma(I))\), 369 parameters. The thiophene group was unequivally disordered, with the two orientations related by 180° rotation around the C\(_\alpha\)–C\(_{\text{ipso}}\)(thiophene) bond (ratio 0.894(4):0.106). The anion was also disordered, giving rise to two superimposed images.

Preparation of \([\text{Mo}({\eta}^2-\text{MeSeCC}_4\text{H}_3\text{S}-2)\text{(CO)}\text{(CNMe)}\text{Tp}][\text{BF}_4]\) (28)

In a similar procedure to that described above, \([\text{Mo}({\eta}^2-\text{SeCC}_4\text{H}_3\text{S}-2)\text{(CO)}\text{(CNMe)Tp}]\) (16) (0.150 g, 0.229 mmol) and trimethylxionium tetrafluoroborate (0.049 g, 0.331 mmol) were combined in diethyl ether (10 mL) and the resulting suspension stirred vigorously for two days during which time a slow colour change from blue to yellow-green occurred. The reaction liquor was decanted away from the yellow precipitate and the product washed with diethyl ether (2 × 10 mL). Recrystallisation from dichloromethane/diethyl ether provided a mustard yellow powder. Yield 0.122 g (71%). IR (CH\(_2\)Cl\(_2\)): 2144 (v_CN), 1968 (v_CO) cm\(^{-1}\). Both \(^1\)H and \(^13\)C\({}\text{H}\) NMR data for 28 show two sets of resonances of differing intensities due to two inseparable isomers present in a 4:1 ratio and data relates to the mixture. Minor product: \(^1\)H NMR
Preparation of [Mo(η²-PhSeCC₆H₅S₂)-(CO)₂Tp][PF₆] (29)

A solution of phenylselenenyl chloride (0.499 g, 2.61 mmol) in dichloromethane (25 mL) at 0 °C was added in a drop-wise fashion to a red suspension of [Mo(η²CC₆H₅S₂)-(CO)₂Tp] (14) (1.20 g, 2.61 mmol) and a stoichiometric amount of silver hexafluorophosphate (0.659 g, 2.61 mmol) in dichloromethane (25 mL) at 0 °C. After stirring at room temperature for 30 min the solution was green with a grey precipitate. The solution was filtered through Celite and the volume of the filtrate reduced to ca. 3 mL. The addition of diethyl ether (150 mL) precipitated a lime-green powder that was isolated by filtration, washed with diethyl ether (2 × 10 mL) and dried in vacuo. Yield 1.982 g (99%). IR (Nujol): 2056, 1989 s (νCO) cm⁻¹. IR (CH₂Cl₂): 2056, 1994 (νCO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.86 (dd, 3JHH = 3.9, 4JHH = 0.89, 1 H, C₆H₅S), 7.35 (dd, 3JHH = 5.1, 4JHH = 3.9, 1 H, H' (C₆H₅S)), 6.96 (s(br), 2 H, C₆H₅), 6.41 (m, 3 H, TpH²), 2.16 (s, 3 H, SeMe), 2.30, 2.12 (s × 2, 3:6 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 244.6 (SeC), 228.7 (MoCO), 171.2 (MoCN) 152.7 [C¹(C₆H₅S)], 145.5, 145.3, 143.8, 137.9, 137.8 (TpCH²⁻⁵), 141.4 [C⁴(C₆H₅S)], 137.5, 137.2 (C₆H₅S), 135.1 [C²⁻⁵(C₆H₅S)], 130.3 [C⁴(C₆H₅S)], 129.4 [C⁵⁻⁵(C₆H₅S)], 124.0 [C¹(C₆H₅S)], 107.4, 107.3, 107.2 (TpCH⁴), 21.3, 18.7 (1:2, CH₃), 14.9 (SeMe). Major product: ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 8.52 (dd, 3JHH = 5.1, 4JHH = 0.89, 1 H, C₆H₅S), 7.97, 7.95, 7.93, 7.64, 7.49 (d × 5, 5 H, TpH), 7.51 (m, 1 H, C₆H₅S, 1 H, TpH), 7.38 (dd, 3JHH = 5.1, 4JHH = 3.9, 1 H, H' (C₆H₅S)), 6.90 (s(br), 2 H, C₆H₅), 6.41 (m, 3 H, TpH⁴), 2.29 (s, 3 H, SeMe), 2.28, 2.05 (s × 2, 3:6 H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 246.8 (SeC), 229.6 (MoCO), 170.7 (MoCN) 152.5 [C¹(C₆H₅S)], 145.6, 143.9, 143.8, 137.9, 137.7, 137.6 (TpCH²⁻⁵), 141.3 [C⁴(C₆H₅S)], 138.4, 137.6 (C₆H₅S), 135.0 [C²⁻⁵(C₆H₅S)], 130.8 [C⁴(C₆H₅S)], 129.3 [C⁵⁻⁵(C₆H₅S)], 124.0 [C¹(C₆H₅S)], 107.5, 107.4, 107.0 (TpCH⁴), 21.3, 18.5 (1:2, CH₃), 17.6 (SeMe). MS (ESI): m/z (%) 671.9 (20) [M⁺], 643.9 (100) [M – CO]⁺. Anal. Found: C, 40.69; H, 3.77; N, 12.88; S, 4.01%. Calcd. for C₆H₅₃B₃F₄Mn₂O₇S₆Se: C, 41.19; H, 3.59; N, 12.93; S, 4.23.

¹Remaining resonances were obscured by those of the major isomer.
Preparation of [MoFe(μ-CC4H3S-2)(CO)3Tp] (31)

[Mo(μ-CC4H3S-2)(CO)3Tp] (14) (2.00 g, 4.34 mmol) and [Fe2(CO)9] (3.16 g, 8.69 mmol) were stirred in diethyl ether (100 mL) for 6 h during which time the initially red suspension darkened to a deep brown. The solution was transferred via filter cannula into a second flask and the solvent was removed in vacuo. Recrystallisation of the dark residue from dichloromethane/hexane afforded a black microcrystalline solid. Yield 2.37 g (91%). IR (KBr): 2482 (νHH), 2039, 1973, 1945, 1922, 1875, 1855 (νCO) cm⁻¹. IR (CH2Cl2): 2048 s, 1987 m, 1965 m, 1925 w, 1860 w(br) cm⁻¹. 1H NMR (CD2Cl2, 25 °C, 300.075 MHz): δ 8.65, 7.88, 7.86 (d × 3, 1:1:2 H, TpH3^3), 7.91 (dd, JHH = 5.1, JHH = 0.9, 1 H, C4H3S), 7.08 [dd, JHH = 5.1, JHH = 3.9, 1 H, H^1(C4H3S)], 6.98 (dd, JHH = 3.6, JHH = 0.9, 1 H, C4H3S), 6.47, 6.05 (t × 2, 1:2 H, TpH^3), 6.31 (d, 2 H, TpH^2), 1.53 (1:2:1:2, TpCH3), 160.1 [1C^1(H4C4S)], 139.3, 134.5, 129.4 (C4H3S), MS (ESI): m/z (%): 611.9 (3) [M - CO + CH3CN], 573.9 (3) [M - CO], 482.1 (20) [FeTp^2], 269.1 (100) [FeTp]^+. Anal. Found: C, 38.36; H, 2.39; N, 14.09%. Calcd. for C15H13BFeMoO9S2: C, 38.03; H, 2.18; N, 14.01%. Crystal data for (C19H13BFeMoO9S2)·CH2Cl2, Mf = 1284.96, triclinic, P ̅1, a = 11.069(2), b = 13.258(2), c = 17.097(2) Å, α = 93.370(7), β = 98.641(6), γ = 94.259(9)°, V = 2467.4(6) Å³, Z = 2, ½ = 1.729 Mg m⁻³, μ(Mo Kα) = 1.333 mm⁻¹, T = 200(2) K, black plate, 6401 independent measured reflections (2θ ≤ 46°), R1 = 0.0683, wR = 0.0561 for 4144 independent observed absorption-corrected reflections (I > 3σ(I)), 617 parameters. The crystal was of low quality, with only 91% of the data being retained. However, despite the parameter/observation ratio being poorer than preferred (≥ 10) the identity of the compound was clearly established. The thiophene unit shows the typical disordering around the μC=Cipso(thiophene) bond (ratio 0.657(11):0.343 and 0.522(11):0.478 for each of the independent molecules) and the dichloromethane molecules of solvation were also disordered.
Preparation of [MoFe(μ-SeCC₄H₃S-2)(CO)₅Tp] (32)

Method 1 [MoFe(μ-CC₄H₃S-2)(CO)₅Tp] (31) (0.300 g, 0.499 mmol) and elemental selenium (0.158 g, 2.00 mmol) were stirred rapidly in diethyl ether (20 mL) for 24 h. The dark golden solution was filtered through Celite and the solvent removed under reduced pressure before the residue was redissolved in dichloromethane (ca. 2 mL) and chromatographed (silica gel, −33 °C). Elution with dichloromethane–hexane (1:1) developed a broad golden-brown band followed by a narrow blue fraction that corresponded to minor formation of the selenoaryl complex 16, which was identified spectroscopically and by a unit cell determination. Yield 16: 0.010 g (4%). Solvent removal from the initial golden-yellow eluate afforded a mixture of the alkylidyne 14 and the desired bimetallic selenoaryl species [MoFe(μ-SeCC₄H₃S-2)(CO)₅Tp] (32) (1H NMR). A second chromatographic purification of this fraction (silica gel, −33 °C) eluting with diethyl ether–hexane (1:1) afforded an initial orange band corresponding to 14 (IR) followed by a broad golden-yellow eluate. Solvent removal and recrystallisation from the second golden-yellow fraction afforded compound 32 as a pure powder. Yield 0.240 g (71%).

IR (Nujol): 2482 w (νBH), 2044 s, 1976, 1960 sh, 1854 (νCO) cm⁻¹. IR (CH₂Cl₂): 2053 s, 1985, 1845 w (νCO) cm⁻¹. 1H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.85, 7.75, 7.73, 7.64 (d × 4, 2:1:1:1 H, TpH¹), 7.44 (s(br), 1 H, TpH⁵), 7.29, 7.12, 6.96 (s(br) × 3, 3 H, C₄H₃S), 6.37, 6.25, 6.14 (t × 3, 3 H, TpH¹), 13C¹H NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 231.6, 227.3 (MoCO), 211.0, 208.7 (FeCO), 154.9 [C(I₃)₃(C₄H₃S)], 145.4, 145.0, 144.2, 137.3, 136.4, 135.2 (TpCH²⁻), 139.3, 127.9, 127.7, 124.5 (C₄H₃S), 106.7, 106.5, 106.0 (TpCH³). MS (ESI): m/z (%): 701.1 (3) [M + Na]⁺, 679.9 (4) [M⁺, 659.0 (3) [M − CO]⁺, 568.9 (10) [M − Fe(CO)₅ + 2CH₃CN]⁺, 539.8 (20) [M − Fe(CO)₅]⁺, 482.1 (80) [FeTp⁺], 269.1 (40) [FeTp⁺]. Anal. Found: C, 33.30; H, 2.19; N, 11.92%. Calcd. for C₁₉H₁₃BFeMoN₀₆O₇Se: C, 33.61; H, 1.93; N, 12.38%. Crystal data for C₁₉H₁₃BFeMoN₀₆O₇Se, Mᵣ = 678.97, triclinic, P ̅₁, a = 9.6874(5), b = 11.0179(5), c = 11.9337(6) Å, α = 106.618(3), β = 101.917(2), γ = 98.138(3)°, V = 1166.6(1) Å³, Z = 2, ρcalcd = 1.933 Mg m⁻³, μ(Mo Kα) = 2.854 mm⁻¹, T = 200(2) K, brown block, 5397 independent measured reflections (2θ ≤ 54°), R₁ = 0.0214, wR₂ = 0.0209 for 4240 independent observed absorption-corrected reflections (l > 3σ(l)), 316 parameters.

Attempted Method 2 [Mo(η²-SeCC₄H₃S-2)(CO)₅Tp] (16) (0.150 g, 0.278 mmol) and [Fe₂(CO)₉] (0.011 g, 0.305 mmol) were combined in dichloromethane (15 mL) and the dark blue mixture stirred at room temperature (with monitoring via thin layer chromatography) for seven days, after which time all of 16 had reacted and a major maroon compound was evident in addition to minor orange and golden compounds. Solvent was removed from the dark brown

---

The resonance for the μ-CSe nucleus was not unequivocally identified, likely due to an insufficiently concentrated sample.
solution and the residue redissolved in dichloromethane and subjected to chromatography (silica gel, $-33 \, ^\circ$C). Elution with dichloromethane–hexane (1:2) afforded a major maroon fraction in addition to a minor orange band, the latter spectroscopically identified as 14 (0.040 g, 31%). Solvent removal from the maroon eluate and recrystallisation from dichloromethane/hexane gave 0.041 g (51%) of $[\text{Fe}_2\text{Se}_2(\text{CO})_3]$ (33), which was identified spectroscopically. IR (CH$_2$Cl$_2$): 2056, 2038, 2012 cm$^{-1}$. 20 Crystal data for $\text{Cs}_2\text{Fe}_2\text{Os}_2\text{Se}_2$, $M_r = 460.13$, $P \bar{1}$, $a = 6.7831(1)$, $b = 9.1868(2)$, $c = 13.0799(4)$ Å, $\alpha = 93.946(1)$, $\beta = 94.513(2)$, $\gamma = 110.674(2)^\circ$, $V = 756.14(3)$ Å$^3$, $T = 200(2)$ K, cf. literature data (i) at room temperature: $a = 6.83$, $b = 9.22$, $c = 13.12$ Å, $\alpha = 93.3$, $\beta = 94.20$, $\gamma = 110.40$, $V = 756.14(3)$ Å$^3$; and (ii) at 150 K: $a = 6.748(1)$, $b = 9.163(1)$, $c = 13.044(1)$ Å, $\alpha = 93.97(1)$, $\beta = 94.54(1)$, $\gamma = 110.75(1)^\circ$, $V = 747.75$ Å$^3$.

7.4 Tungsten–alkyne complexes

Preparation of $[\text{W}(\eta^2-i\text{PrSeC}=\text{CPh})(\text{CO})_2\text{Tp}^*][\text{BF}_4]$ (36)

In a representative synthesis, a dark brown dichloromethane solution (10 mL) containing $[\text{W}(\text{CO})_3\text{Tp}^*]$ (0.700 g, 1.01 mmol) and a slight excess of isopropyl(2-phenylethynyl)selane (0.271 g, 1.21 mmol) at 0 °C was added to a stoichiometric amount of AgBF$_4$ (0.197 g, 1.01 mmol) in dichloromethane (5 mL). After being stirred at room temperature for 2 h, the solution was green with a grey precipitate. The solution was filtered (filter cannula stick equipped with a Celite pad) into a separate flask, the volume reduced to ca. 3 mL and diethyl ether (150 mL) added to induce precipitation. The green powder that formed was isolated by filtration and washed with benzene (10 mL) and diethyl ether (10 mL). Recrystallisation from dichloromethane/diethyl ether yielded green microcrystals of 36. Yield 0.560 g (65%). IR (Nujol): 2562 w (v$_{BH}$), 2043 s, 1958 s (v$_{CO}$), 1715 w (v$_{CO}$), 1543 (v$_{CO}$) cm$^{-1}$. IR (CH$_2$Cl$_2$): 2047, 1974 (v$_{CO}$) cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.075 MHz): $\delta$8.24, 7.83 (m × 2, 5 H, C$_6$H$_3$), 6.15, 6.07 (s × 2, 1:2 H, Tp*H), 2.80, 2.60, 2.45, 1.66 (s × 4, 3:6:3:6 H, Tp*CH$_3$), 2.65 (septet, 1 H, i-PrCH), 1.09 (d, $^3$J$_{HH} = 7.2$, 6 H, i-PrCH$_3$). $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, 25 °C, 75.421 MHz): $\delta$219.1 (PhC=Cs), 216.5 (WCO), 199.4 (PhC=Cs), 155.7, 152.5, 150.5, 147.9 (1:2:1:2, Tp*CH$_3$), 134.7, 134.3, 133.4, 130.7 (C$_6$H$_5$), 110.1, 108.7 (1:2, Tp*CH), 42.8 (i-PrCH), 24.5 (i-PrCH$_3$), 16.8, 15.3, 13.4, 12.6 (1:2:1:2, Tp*CH$_3$). MS (ESI): $m/z$ (%) 761.2 (100) [M]$^+$, 733.2 (49) [M – CO]$^+$, 705.2 (18) [M – 2CO]$^+$. Anal. Found: C, 39.23; H, 4.15; N, 10.22%. Calcd. for C$_{28}$H$_{32}$B$_2$F$_2$N$_2$O$_2$SeW: C, 39.70; H, 4.05; N, 9.92%. UV–vis (CH$_2$Cl$_2$): $\lambda_{max}$ 422 nm (ε = 11 960 M$^{-1}$ cm$^{-1}$), 661 nm (ε = 138 M$^{-1}$ cm$^{-1}$). Crystal data for C$_{28}$H$_{32}$BN$_2$O$_2$SeW·BF$_4$, $M_r = 847.04$, monoclinic, C2/c, $a = 30.2338(5)$, $b = 14.2584(2)$, $c = 16.1047(2)$ Å, $\beta = 109.2096(7)^\circ$, $V = 6556.0(2)$ Å$^3$, $Z = 8$, $T = 200(2)$ K, cf. literature data (i) at room temperature: $a = 6.83$, $b = 9.22$, $c = 13.0799(4)$ Å, $\alpha = 93.946(1)$, $\beta = 94.513(2)$, $\gamma = 110.674(2)^\circ$, $V = 756.14(3)$ Å$^3$; and (ii) at 150 K: $a = 6.748(1)$, $b = 9.163(1)$, $c = 13.044(1)$ Å, $\alpha = 93.97(1)$, $\beta = 94.54(1)$, $\gamma = 110.75(1)^\circ$, $V = 747.75$ Å$^3$. 22
\( \rho_{\text{calc}} = 1.716 \text{ Mg m}^{-3}, \ \mu(\text{Mo } K\alpha) = 4.693 \text{ mm}^{-1}, \ T = 200(2) \text{ K}, \) green plate, 7533 independent measured reflections \( (2\theta \leq 54^\circ), \ R_1 = 0.0231, \ wR = 0.0257 \) for 5121 independent observed absorption-corrected reflections \( (I > 3\sigma(I)), 437 \) parameters. The anion was disordered, with there being two tetrahedral images, centred close to one another but differing as to the orientations of the F atoms.

**Preparation of [W(η²-i-PrSC≡CPh)(CO)₂Tp⁺][BF₄] (35)**

Compound 35 was prepared as a bright green powder following the procedure described for 36 from isopropyl(2-phenylethynyl)sulfane \( (0.061 \text{ g, } 0.35 \text{ mmol}), \ [\text{WI(CO)}_5\text{Tp}^+] \) \( (0.200 \text{ g, } 0.29 \text{ mmol}), \) and AgBF₄ \( (0.056 \text{ g, } 0.29 \text{ mmol}). \) Yield 0.091 g \( (40\%). \) IR (Nujol): 2575 w \( (\nu_{\text{BH}}), \) 2052 s, 1969 vs \( (\nu_{\text{CO}}), \) 1718 w \( (\nu_{\text{C=C}}), \) 1544 \( (\nu_{\text{C=O}}) \) cm\(^{-1}. \) IR (CH₂Cl₂): 2049, 1975 \( (\nu_{\text{CO}}) \) cm\(^{-1}. \)

\(^1\)H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): \( \delta 8.25, \ 7.81 \ (m \times 2, 5 \text{ H}, C_6H_5), \ 6.15, \ 5.07 \ (s \times 2, 1:2 \text{ H}, \text{Tp}^*)H), \ 2.82, \ 2.59, \ 2.45, \ 1.68 \ (s \times 4, 3:6:3:6 \text{ H}, \text{Tp}^*\text{CH}_3), \ 2.50 \ (\text{septet}, 1 \text{ H}, \text{i-PrCH}), \ 0.97 \ (d, \text{br}, 3J_{HH} = 6.0, \ 6 \text{ H}, \text{i-PrCH}_3). \)

\(^{13}\text{C}\{^1\text{H}\} \) NMR (CD₂Cl₂, 25 °C, 75.421 MHz): \( \delta 221.1 \) (PhC=CS), 215.5 \( (\text{PhC}=\text{CS}), \) 155.7, 152.5, 150.5, 147.9 \( (1:2:1:2, \text{Tp}^*\text{CH}_3), \) 134.7, 134.2, 133.1, 130.7 \( (C_6H_5), \) 110.1, 108.7 \( (1:2, \text{Tp}^*\text{CH}), \) 45.6 \( (\text{i-PrCH}), \) 23.4 \( (\text{i-PrCH}_3), \) 16.8, 15.2, 13.4, 12.7 \( (1:2:1:2, \text{Tp}^*\text{CH}_3). \) MS (ESI): \( m/z \) 713.2 \( (100) \) [M⁺], 685.2 \( (78) \) \( [\text{M} - \text{CO}]^+, \) 657.2 \( (29) \) \( [\text{M} - 2\text{CO}]^+. \) Anal. Found: C, 41.95; H, 4.25; N, 10.43; S, 4.07%. Calcd. for C₂₈H₄₂B₃F₄N₆O₇SW: C, 42.03. \( \text{(Yeo)}, \) 24.03; H, 4.28; N, 10.50; S, 4.01%. UV-vis \( \text{(CH₂Cl₂): } \lambda_{\text{max}} \text{ 401 nm(\varepsilon = 14410 M}^{-1} \text{ cm}^{-1}), \) 650 nm \( (\varepsilon = 135 \text{ M}^{-1} \text{ cm}^{-1}). \) Crystal data for C₂₈H₄₂B₃N₆O₇SW·BF₄:

\( M_r = 800.15, \) monoclinic, \( P2_1/n, \ a = 10.1686(1), \ b = 24.4955(2), \ c = 13.1753(1) \) Å, \( \beta = 103.1297(5)^\circ, \ V = 3195.98(5) \) Å\(^3, \) \( Z = 4, \ \rho_{\text{calc}} = 1.663 \) Mg m\(^{-3}, \) \( \mu(\text{Mo } K\alpha) = 3.739 \) mm\(^{-1}; \) \( T = 200(2) \) K, green plate, 7324 independent measured reflections \( (2\theta \leq 54^\circ), \ R = 0.0190, \ wR = 0.0218 \) for 5356 independent observed absorption-corrected reflections \( (I > 3\sigma(I)), 397 \) parameters.

**Preparation of [W(η²-i-PrTeC≡CPh)(CO)₂Tp⁺][BF₄] (37)**

Compound 37 was prepared as a brick-red powder following the procedure described for 36 from isopropyl(2-phenylethynyl)tellane \( (0.094 \text{ g, } 0.35 \text{ mmol}), \ [\text{WI(CO)}_5\text{Tp}^+] \) \( (0.200 \text{ g, } 0.29 \text{ mmol}), \) and AgBF₄ \( (0.056 \text{ g, } 0.29 \text{ mmol}). \) Yield 0.097 g \( (38\%). \) IR (Nujol): 2576 w \( (\nu_{\text{BH}}), \) 2044 s, 1961 s \( (\nu_{\text{CO}}), \) 1717 w \( (\nu_{\text{C=C}}), \) 1542 \( (\nu_{\text{C=O}}) \) cm\(^{-1}. \) IR (CH₂Cl₂): 2043, 1970 s \( (\nu_{\text{CO}}) \) cm\(^{-1}. \)

\(^1\)H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): \( \delta 8.19, \ 7.83 \ (m \times 2, 5 \text{ H}, C_6H_5), \ 6.15, \ 6.07 \ (s \times 2, 1:2 \text{ H}, \text{Tp}^*)H), \ 2.78, \ 2.61, \ 2.45, \ 1.65 \ (s \times 4, 3:6:3:6 \text{ H}, \text{Tp}^*\text{CH}_3), \ 2.65 \ (\text{septet}, 1 \text{ H}, \text{i-PrCH}), \ 1.31 \ (d, \ 3J_{HH} = 6.9, \ 6 \text{ H}, \text{i-PrCH}_3). \)

\(^{13}\text{C}\{^1\text{H}\} \) NMR (CD₂Cl₂, 25 °C, 75.421 MHz): \( \delta 217.8 \) (WCO), 201.4 \( (\text{PhC}\\text{=CTe}), \) 200.8 \( (\text{PhC}\\text{=CTe}), \) 155.9, 152.3, 150.6, 147.7 \( (1:2:1:2, \text{Tp}^*\text{CH}_3), \) 134.9, 134.6, 133.6, 130.7 \( (C_6H_5), \) 110.1, 108.9 \( (1:2, \text{Tp}^*\text{CH}), \) 27.5 \( (\text{i-PrCH}), \) 26.8 \( (\text{i-PrCH}_3), \) 16.8,
15.6, 13.4, 12.6 (1:2:1:2, Tp*CCCH). MS (ESI): m/z (%) 809.1 (100) [M]+, 781.1 (50) [M − CO]+, 753.1 (10) [M − 2CO]+. Anal. Found: C, 37.3; H, 4.01; N, 9.06%. Calcd. for C28H34B6N602TeW•BF4, M r = 996.68, monoclinic, C2/c, a = 30.5636(5), b = 14.4234(2), c = 15.9962(2) Å, \( \beta = 109.5840(7) \), \( V = 6643.7(2) \) Å\(^3\), \( Z = 8 \), \( \rho_{\text{calcd}} = 1.791 \) Mg m\(^{-3}\), \( \mu(\text{Mo K} \alpha) = 4.396 \) mm\(^{-1}\), \( T = 200(2) \) K, brown needle, 7624 independent measured reflections (2\( \theta \leq 54^\circ \)), \( R_1 = 0.0234 \), \( wR = 0.0277 \) for 5544 independent observed absorption-corrected reflections (\( I > 3\sigma(I) \)), 437 parameters. The anion was disordered, with there being two tetrahedral images, centred close to one another but differing as to the orientations of the F atoms.

Preparation of \([W(\eta^2-i-PrOC=CPH)(CO)_2Tp^*][BF_4](34/34')\)

The preparation of complex 34 as a bright green powder followed a procedure similar to those used for 35, 36 and 37 from isopropoxy(2-phenylethynyl)ether (0.261 g, 1.63 mmol), \([Wl(CO)_2Tp^*]\) (0.805 g, 1.16 mmol), and AgBF\(_4\) (0.227 g, 1.16 mmol). Due to low alkyne purity\(^3\) it was necessary to subject the crude residue to chromatographic purification (silica gel, 3:1 dichloromethane–acetonitrile, \(-33 ^\circ \)C), collecting only the major green band. Solvent removal and recrystallisation from dichloromethane/diethyl ether provided pure 34 as a mixture of the phenyl up (34') and phenyl down (34) isomers and data relates to the mixture. Yield 0.282 g (31%). IR (Nujol): 2564 w (v\(_{BH}\)), 2056 s, 1979 s (v\(_{CO}\)), 1681 w (br) (v\(_{CN}\)), 1541 (v\(_{CN}\)) cm\(^{-1}\). IR (CH\(_2\)Cl\(_2\)): 2054, 1978 (v\(_{CO}\)) cm\(^{-1}\). Isomer 34: \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 \(^\circ\)C, 300.075 MHz): \( \delta = 8.23, 7.77 (m \times 2, 5 H, C_6H_5)\), 6.13, 6.10, (s \times 2, 1:2 H, Tp*H), 3.96 (septet, \( J_{HH} = 6.2\), 1 H, i-PrCH), 2.82, 2.59, 2.43, 1.78 (s \times 4, 3:6:3:6 H, Tp*CH\(_3\)), 1.10 (d, \( J_{HH} = 6.3, 6 H, i-PrCH\(_3\)\)). \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 25 \(^\circ\)C, 75.421 MHz): \( \delta = 237.8 (\text{PhC}=\text{CO}), 215.1 (\text{WCO}), 187.6 (\text{PhC}=\text{CO}), 155.6, 152.2, 150.2, 148.2 (1:2:1:2, Tp*CH\(_3\)), 133.1 [C\(^1\) (C\(_6\)H\(_5\))], 134.7, 132.0, 130.5 (C\(_6\)H\(_5\)), 109.9, 108.7 (1:2, Tp*CH), 87.9 (i-PrCH), 22.9 (i-PrCH\(_3\)), 16.7, 16.0, 13.3, 12.8 (1:2:1:2, Tp*CH\(_3\)). Isomer 34': \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 \(^\circ\)C, 300.075 MHz): \( \delta = 7.56, 7.33, 6.90 (m \times 3, 5 H, C_6H_5), 6.10, 5.95 (s \times 2, 1:2 H, Tp*H), 5.53 (septet, \( J_{HH} = 6.14, 1 H, i-PrCH\)), 2.63, 2.62, 2.45, 1.48 (s \times 4, 3:6:3:6 H, Tp*CH\(_3\)), 1.69 (d, \( J_{HH} = 6.3, 6 H, i-PrCH\(_3\)\)). \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 25 \(^\circ\)C, 75.421 MHz): \( \delta = 216.1 (\text{WCO}), 213.2 (\text{PhC}=\text{CO}), 211.0 (\text{PhC}=\text{CO}), 155.4, 152.0, 150.2, 147.6 (1:2:1:2, Tp*CH\(_3\)), 135.1 [C\(^1\) (C\(_6\)H\(_5\))], 133.9, 131.6, 130.0 (C\(_6\)H\(_5\)), 109.7, 108.8 (1:2, Tp*CH), 88.9 (i-PrCH), 23.0 (i-PrCH\(_3\)), 16.4, 15.7, 13.3, 12.8 (1:2:1:2, Tp*CH\(_3\)). MS (ESI): m/z (%) 697.1 (47) [M]+, 626.1 (100) [M − CO − i-Pr]+, 598.1 (43) [M − CO − i-Pr]6+. Anal. Found: C, 42.24; H, 4.45; N, 10.63%. Calced for

---

\(^3\) The isopropyl(2-phenylethynyl)ether contained an inseparable iodosobenzene contaminant and was used in subsequent reactions without further purification.
CHAPTER 7. EXPERIMENTAL

C_{28}H_{34}B_{2}F_{4}N_{5}O_{3}W-H_2O: C, 41.93; H, 4.52; N, 10.48%. UV–vis (CH_2Cl_2): λ_{max} 368 nm (ε = 18 100 M^{-1} cm^{-1}), 646 nm (ε = 152 M^{-1} cm^{-1}). Crystal data for C_{28}H_{34}B_{2}N_{5}O_{3}W-BF_4 (34'). 

UV(\text{CH}_2\text{Cl}_2): ν_{\text{max}} 368 nm, 1 \text{M}^{-1} \text{cm}^{-1}, \lambda(\varepsilon) = 8040 \text{cm}^{-1}, 18.3646(3) \AA, a = 10.3774(3), b = 12.1348(2), c = 12.849(3) \AA, \alpha = 77.136(1), \beta = 88.384(1), \gamma = 82.709(1), V = 1564.77(6) \AA^3, Z = 2, \rho_{\text{calc}} = 1.664 \text{Mg m}^{-3}, \mu(\text{Mo Kα}) = 3.755 \text{mm}^{-1}, T = 200(2) \text{K}, \text{green plate}, 7188 \text{independent measured reflections (2θ ≤ 54°), } R_1 = 0.0232, \text{for 5958 independent observed absorption-corrected reflections (I > 2σ(I)), 437 parameters. The anion was disordered, with there being two tetrahedral images, centred close to one another but differing as to the orientations of the F atoms.}

Preparation of [W(η^2-\text{i-PrSeC-CPh})Cl(CO)Tp*] (38/38')

Method 1 A green dichloromethane solution (10 mL) containing [W(η^2-\text{i-PrSeC-CPh})(CO)Tp*][BF_4] (0.100 g, 0.118 mmol) and an excess of tetrabutylammonium chloride (0.139 g, 0.470 mmol) was stirred at room temperature for 2 days, with reaction progress monitored by thin layer chromatography. Solvent was removed in vacuo and the green residue extracted with diethyl ether. Dilution with pentane and concentration yielded an impure green solid that was subjected to chromatography (silica gel, 1:1 dichloromethane–hexane, −33 °C). Solvent removal from the bright green eluate afforded the pure product as a mixture of separable isomers. Yield 0.092 g (99%). IR (Nujol): 1902 s (ν_{CO}), 1715 w (ν_{CO}) cm^{-1}. IR (CH_2Cl_2): 1907 s (ν_{CO}) cm^{-1}. Low temperature recrystallisation from dichloromethane/pentane yielded isomer 38'; room temperature dichloromethane/pentane or diethyl ether/pentane recrystallisation yielded isomer 38'.

Isomer 38: \text{^1H NMR (CD}_2\text{Cl}_2, 25 ^\circ \text{C}, 300.075 MHz): } δ7.95, 7.61, 7.49 (m × 3, 5 H, C_{6}H_{5}), 6.01, 5.89, 5.83 (s × 3, 3 H, Tp*H), 3.16 (septet, \text{^3J}_{HH} = 6.8, 1 H, i-PrCH), 2.86, 2.53, 2.49, 2.36, 2.29, 1.58 (s × 6, 18 H, Tp*CH_2). 1.24, 0.72 (d × 2, 6 H, \text{^3J}_{HH} = 6.8, i-PrCH_3). \text{^13C}{{\text{\{1\}}}H} \text{NMR (CD}_2\text{Cl}_2, 25 ^\circ \text{C}, 75.421 MHz): } δ241.3 (\text{WCO}), 199.7 (\text{PhC}==\text{CSe}), 193.2 (\text{PhC}==\text{Se}), 154.7, 154.6, 150.4, 146.4, 145.4, 144.7 (Tp*CH), 139.1 ([\text{C}(\text{C}_{6}H_{5})], 130.8, 130.1, 129.0 (C_{6}H_{5}), 108.1, 108.0, 107.7 (Tp*CH), 35.5 (i-PrCH), 25.2, 23.3 (i-PrCH_3), 16.3, 16.2, 16.0, 12.9, 12.7, 12.6 (Tp*CH), UV–vis (CH_2Cl_2): λ_{max} 345 nm (ε = 8040 M^{-1} cm^{-1}), 694 nm (ε = 144 M^{-1} cm^{-1}). Crystal data for C_{28}H_{34}BCl_{2}N_{5}O_{3}SeW (38), M_t = 767.68, monoclinic, P2_1/n, a = 10.1041(1), b = 18.3646(3), c = 16.4175(2) \AA, β = 95.6786(8)^\circ, V = 3031.44(7) \AA^3, Z = 4, \rho_{\text{calc}} = 1.682 \text{Mg m}^{-3}, \mu(\text{Mo Kα}) = 5.130 \text{mm}^{-1}, T = 200(2) \text{K}, \text{green block}, 6949 \text{independent measured reflections (2θ ≤ 54°), } R_1 = 0.0186, wR = 0.0190 for 5105 independent observed absorption-corrected reflections (I > 3σ(I)), 343 parameters. Isomer 38': \text{^1H NMR (CD}_2\text{Cl}_2, 25 ^\circ \text{C}, 300.075 MHz): } δ7.16, 6.57 (m × 2, 5 H, C_{6}H_{5}), 5.88, 5.76, 5.72 (s × 3, 3 H, Tp*H), 4.52 (septet, \text{^3J}_{HH} = 6.9, 1 H, i-PrCH), 2.80, 2.53(br), 2.51(br), 2.36, 1.62, 1.59(br) (s × 6, 18 H, Tp*CH_2), 1.61, 1.48
(d × 2, 6 H, JHH = 6.9, i-PrCH3). 13C{1H} NMR (CD2Cl2, 25 °C, 75.421 MHz): δ 238.4 (WCO), 209.5 (PhC≡CSe), 188.6 (PhC≡CSe), 154.5, 153.8, 152.4, 146.4, 145.4, 144.2 (Tp*CCH3), 137.9 [C1(C6H5)], 128.9, 128.7, 128.2 (C6H5), 108.3, 108.0, 107.5 (Tp*CH), 35.9 (i-PrCH), 26.7, 23.0 (i-PrCH3), 16.8, 16.1, 15.0, 12.9, 12.8, 12.7 (Tp*CH3). (ESI): m/z (%) 791.2 (83) [M + Na]+, 769.3 (48) [M]+, 740.3 (63) [M – CO]+, 733.3 (100) [M – Cl]+, 705.3 (47) [M – Cl – CO]+. Anal. Found: C, 42.39; H, 4.55; N, 10.71%. Calcd. for C29H34BCIN6OSeW: C, 42.24; H, 4.46; N, 10.95%. Crystal data for C29H34BCIN6OSeW (38'). Mr = 767.68, monoclinic, P21/n, a = 10.8646(1), b = 19.5161(2), c = 14.7036(2) Å, β = 101.7898(7)°, V = 3051.90(6) Å3, Z = 4, ρcalcd = 1.671 Mg m−3, μ(Mo Kα) = 5.095 mm−1, T = 200(2) K, green plate, 6973 independent measured reflections (2θ ≤ 54°), R1 = 0.0179, wR = 0.0180 for 5340 independent observed absorption-corrected reflections (I > 3σ(I)), 343 parameters.

Method 2 Compound 38 could also be prepared in an analogous manner from excess [Bu4N]I (0.26 g, 0.70 mmol) and [W(η2-i-PrSe≡CPh)(CO)2Tp*][BF4] (0.107 g, 0.126 mmol) in dichloromethane (20 mL) over a period of 6 days.

Kinetic Study of the formation of 38 and 38'

[W(η2-i-PrSe≡CPh)(CO)2Tp*][BF4] (0.015 g, 0.018 mmol) and an excess of tetrabutylammonium chloride (2.5 equiv., 0.013 g, 0.044 mmol) were combined in dichloromethane-d2 in a sealed NMR tube under argon at 25 °C. A 1H NMR spectrum (CD2Cl2, 300.075 MHz, 25 °C) was obtained within 15 minutes of combining reagents and every hour thereafter for 48 h, at which time no further changes were apparent. At 25 °C

Keq [38']/38 = 1.08 (t1/2 = 2 h).

7.5 Alkylidyne–Alkynyl Chalcoether Coupling Reactions

Preparation of [Mo(≡CPh)(CO)2Tp] (50)

Compound 50 was prepared as an orange microcrystalline powder following the procedure described for 15 from molybdenum hexacarbonyl (9.00 g, 34.1 mmol), phenyllithium (prepared from Li and BrPh, 34.1 mL, 1.0 M, 34.1 mmol), trifluoroacetic anhydride (4.80 mL, 34.5 mmol) and K[Tp] (9.15 g, 36.2 mmol). Yield 6.20 g (40%). IR (Nujol): 1993, 1900 (νCO) cm−1. IR (CH2Cl2): 1996, 1911 s (νCO) cm−1. 1H NMR (CDCl3, 25 °C, 300.075 MHz): δ 7.93, 7.69, 7.66 (d × 3, 6 H, TpH35), 7.53, 7.33 (m × 2, 5 H, C6H5), 6.24, 6.12, (t × 2, 2:1 H, TpH). 13C{1H} NMR (CDCl3, 25 °C, 75.421 MHz): δ 293.2 (Mo=C), 225.7 (MoCO), 146.0 [C1(C6H5)], 144.2, 142.9, 135.3(br) (2:1:3, TpCH35), 129.0, 128.6, 128.0 (C6H5), 105.2 (TpCH3). MS (ESI): m/z (%) 497.8 (87) [M + CH3CN]+, 481.9 (100) [M – CO + 2CH3CN]+, 469.8 (42) [M – CO + CH3CN]+, 456.8 (73) [M]+, 428.9 (75) [M – CO]+, 400.9 (43)
Preparation of [MoFe(µ-CPh)(CO)₅Tp] (39)

[MoFe(µ-CPh)(CO)₅Tp] (39) was prepared in an analogous manner to that described for 31 from [Mo(≡CPh)(CO)₅Tp] (50) (1.00 g, 2.20 mmol) and [Fe₂(CO)₉] (1.60 g, 4.40 mmol) in diethyl ether (50 mL). After stirring for 12 h at room temperature the dark purple mixture was transferred by filter cannula into a separate flask and the solvent was removed in vacuo. The dark residue was redissolved in tetrahydrofuran (ca. 3 mL) and purified by chromatography (silica gel, -33 °C). Elution with diethyl ether–hexane (1:1) developed a broad purple fraction from which solvent removal afforded [MoFe(µ-CPh)(CO)₅Tp] (39) as a microcrystalline purple solid. Yield 1.05 g (80%). IR (KBr): 2475 w (vBH), 2045 s, 1986 s, 1960 (sh), 1917, 1867, 1853 m (vC=O), 1406 m (vCN) cm⁻¹. IR (CH₂Cl₂): 2049 s, 1988 s, 1965 s, 1925 m, 1861 m (vCO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 5.86, 7.87, 7.84, 6.46, 6.01 (d × 4, 1:1:2:2 H, TpH), 7.32 (s(br), 5 H, C₆H₅), 6.46, 6.01 (t × 2, 1:2 H, TpH). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 136.3, 136.0, 128.6, 130.1, 130.8, 136.6, 136.0, 107.4, 106.0 (1:2:1:2:1:2, TpCH), 155.0 (C₁(C₆H₅)), 103.0, 128.6 (C₆H₅). MS (ESI): m/z (%) 635.1 (10) [M + K⁺], 539.9 (20) [M – 2CO]⁺, 485.0 (60) [M – 4CO]⁺, 440.9 (88) [M – Fe(CO)₅ + CH₃CN]⁺, 399.9 (90) [M – Fe(CO)₅]⁺, 269.1 (100) [FeTp]⁺. Anal. Found: C, 43.02; H, 3.11; N, 13.61%. Calcd. for C₂₁H₁₅BFeMoN₆O₅: C, 42.46; H, 2.55; N, 14.15%.

Crystal data for C₂₁H₁₅BFeMoN₆O₅•0.5(C₆H₅O), Mₜ = 631.05, monoclinic, C2/c, a = 36.1404(5), b = 7.8040(1), c = 20.1497(2) Å, β = 107.1991(8)°, V = 5428.89(12) Å³, Z = 8, ρcalcd = 1.544 Mg m⁻³, μ(Mo Kα) = 1.042 mm⁻¹, T = 200(2) K, purple block, 6208 independent measured reflections (2θ ≤ 54°), R₁ = 0.0241, wR = 0.0283 for 4606 independent observed absorption-corrected reflections (I > 3σ(I)), 339 parameters.

Reactions between i-PrEC=CPH (E = S, Se, Te) and µ-alkylidynes

Treatment of [MoFe(µ-CC₄H₃S-2)(CO)₅Tp] with i-PrSeC=CPH

Method 1 Isopropyl(2-phenylethynyl)selane (0.364 g, 1.63 mmol) and [MoFe(µ-C₄H₃S-2)(CO)₅Tp] (31) (0.500 g, 0.833 mmol) were combined in dichloromethane (40 mL). The initially black mixture was stirred at room temperature for 4 days, after which time thin layer chromatography revealed that all of 31 had been consumed and major gold and maroon

---

8 Throughout the following section carbons of the bridging chain of alkylidyne–alkynyl chalcogeno coupling products are denoted by the prefix 'µ' when reported in the ¹³C{¹H} NMR data, irrespective of whether they are directly bound to one or two metal centres.
products were apparent, in addition to dark brown baseline material. The solvent volume was reduced and the brown residue subjected to chromatographic separation (silica gel, –33 °C). Elution with dichloromethane–hexane (1:2) developed initial pale yellow and pale orange bands corresponding to recovered alkyne (0.172 g, 47%) and the known alkylidyne species 14 (0.055 g, 15%), respectively. Continued elution of the chromatography column with this same solvent mixture afforded a broad golden-yellow fraction (40) and further elution with dichloromethane–hexane (2:1) as eluant afforded a maroon band (42) of comparable size. Finally, elution with tetrahydrofuran–hexane (1:1) mobilised a golden compound (41) from the baseline as an additional reaction product. Recovery of the golden-yellow eluate and solvent removal afforded yellow microcrystals of the alkyne/alkylidyne coupled product [MoFe(µ-C(C₄H₅S-2))C(Se-Pr)(C(Ph))(µ-CO)(CO)₅Tp] (40). Yield 0.123 g (18%). IR (KBr): 2488 w (νBH), 2048 s, 1992 s, 1984 s, 1956 s, 1810 m (νCO) cm⁻¹. IR (CH₂Cl₂): 2049 s, 1981 s(br), 1863 w(br), 1825 w(br) (νCO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 8.07, 7.85, 7.83, 7.65, 7.63 (d × 5, 5 H, TpH²⁻), 7.31 (dd, JHH = 5.1, JHH = 1.1, 1 H, C₄H₅S), 7.20 (m, 1 H C₄H₅S, 1 H TpH²⁻), 7.0 (m, 3 H C₅H₅, 1 H C₄H₅S), 6.68 (m, 2 H, C₅H₅), 6.27, 6.23, 5.81 (t × 3, 3 H, TpH), 2.81 (septet, JHH = 6.89, 1 H, i-PrCH), 1.11, 0.88 (d × 2, JHH = 6.89, 6 H, i-PrCH₃). ¹³C {¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 238.9, 231.1 (MoCO), 209.7 (FeCO), 147.5 [C(C₄H₅S)], 147.1 [C(C₄H₅S)], 144.3 (µ-CPH), 147.0, 145.9, 144.4, 137.4, 136.7, 136.5 (TpCH), 130.7, 127.2, 126.9 (C₅H₅), 130.5, 127.3, 126.7 (C₄H₅S), 120.7 (µ-CSe), 114.2, (µ-C₆), 106.2 (TpCH³⁻), 35.9 (i-PrCH), 25.7, 25.3 (i-PrCH₃). MS (ESI): m/z (%) 860.9 (5) [M + K]⁺, 683.0 (5) [M – 5CO]⁺, 641.9.0 (17) [M – 5CO – i-Pr]⁺, 563.0 (15) [M – 5CO – Se- Pr]⁺. Anal. Found: C, 43.74; H, 3.17; N, 10.04; S, 3.70%. Calcd. for C₃₀H₂₅BFeMoN₆O₅SSe: C, 43.77; H, 3.06; N, 10.21; S, 3.89%. Crystal data for C₃₀H₂₅BFeMoN₆O₅SSe, Mᵣ = 823.19, monoclinic, P2₁/a, a = 14.6525(2), b = 14.2222(2), c = 16.1523(2) Å, β = 106.5621(8)°, V = 3226.34(8) Å³, Z = 4, ρcalcd = 1.695 Mg m⁻³, μ(Mo Kα) = 2.080 mm⁻¹, T = 200(2) K, yellow plate, 7379 independent measured reflections (2θ ≤ 54⁰), R₁ = 0.0221, wR = 0.0255 for 4412 independent observed absorption-corrected reflections (I > 3σ(I)), 415 parameters.

The maroon fraction was concentrated and diluted with hexane and, following storage for 24 h at –11 °C, the complex [MoFe(µ-C(C₄H₅S-2))C(Se-Pr)(C(Ph))(µ-CO)(CO)₅Tp] (42) was isolated by filtration as a crystalline maroon solid and rinsed with ethanol. Yield 0.152 g (23%). IR (Nujol): 2480 cm⁻¹ (νBH), 1982, 1942, 1916, 1820 (νCO) cm⁻¹. IR (CH₂Cl₂) 1991 s, 1952 s, 1927 m, 1834 w(br) (νCO) cm⁻¹. The ¹H NMR spectrum revealed the presence of two isomeric forms (ratio 1:0.3) and data relates to the mixture. Minor isomer: ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.96, 7.92, 7.77, 7.72, 7.70, 7.57, 7.45, 7.22, 7.02, 6.85, 6.64 (m(br) × 11, TpH³⁻, C₅H₅, C₄H₅S), 6.26 (t, 2 H, TpH), 5.95 (t(br), 1 H, TpH³⁻), 2.82 (septet(br), 1 H, i-PrCH), 1.38,
1.07 (d(br) \times 2, i-PrCH₃). **Major isomer:** ^1H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.96, 7.92, 7.77, 7.72, 7.70, 7.57, 7.45, 7.22, 7.02, 6.85, 6.64 (m(br) \times 11, TpH^3), C₆H₅, C₅H₅), ^2 6.23 (t, 2 H, TpH^4), 6.01 (t(br) 1 H, TpH^4), 2.63 (septet(br) 1 H, i-PrCH), 1.35, 0.97 (d(br) \times 2, i-PrCH₃). ^13C[^1H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 236.5, 231.5 (MoCO), 221.8, 212.2 (FeCO), 144.8, 144.7, 142.8, 136.0, 135.9, 135.3, 106.0, 105.7, 105.5 (TpCH), 133.2(br), 129.5, 128.4 (C₆H₅). 144.1 [C₁(C₅H₅)], 127.9, 126.9, 124.4 (C₅H₅), 118.9 (µ-CC₅H₅), 115.0 (µ-CSe), 80.3 (µ-C), 42.5 (i-PrCH), 23.7, 23.4 (i-PrCH₃). The resonance due to C₁(C₅H₅) could not be unambiguously assigned. MS (ESI): m/z (%) 795.4 (4) [M]^+, 711.6 (9) [M - C₅H₅]^+, 685.2 (8) [M - Fe(CO)₅]^+, 640.7 (32) [M - Fe(CO)₂ - i-Pr]^+, 482.1 (100) [FeTp₂]^+. Crystal data for C₂₉H₂₅BF₆Mo₉O₄S₄Se, Mᵣ = 795.18, triclinic, P 1, a = 7.9894(2), b = 11.5084(4), c = 17.4959(7) Å, α = 76.662(1), β = 86.851(2), γ = 85.719(2), V = 1555.81(9) Å³, Z = 2, ρ_{calc} = 1.697 Mg m⁻³, µ(Mo Kα) = 2.151 mm⁻¹, T = 200(2) K, red needle, 5442 independent measured reflections (2θ ≤ 50°), R₁ = 0.063, wR = 0.103 for 3862 independent observed absorption-corrected reflections (I > 3σ(I)), 210 parameters. The crystal was twinned and the model refined as such. The thiophene group was disordered over two orientations which are coplanar but related by 180° rotation about the µC-C_{iso}(thiophene) bond (ratio 0.734(10):0.266).

Solvent removal from the final golden-brown fraction afforded a brown solid that was subjected to a further chromatographic purification (silica gel, 25 °C). Elution with dichloromethane removed a minor red impurity before the desired compound was mobilised with tetrahydrofuran. The brown eluate was diluted with hexane and subsequent solvent removal afforded a brown solid formulated as the alkyldyne/alkyne/carbonyl coupled compound [MoFe{µ-C}Sei-Pr)(C₅H₃S-2)C(O)(CO)](CO)₅(Tp) (48). Yield 0.044 g (16%). IR (KBr): 2482 w (vBH), 2039 s, 1977 s(br), 1878 w(br) (vCO) cm⁻¹. IR (CH₂Cl₂): 2046 s, 1983 m, 1882 w(br) (vCO) cm⁻¹. ^1H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 8.08, 7.81, 7.75, 7.69, (d x 4, 4 H, TpH), 7.87 (m, 2 H C₆H₅, 1 H TpH), 7.56 (m, 3 H, C₅H₅), 7.18 (m, 1 H C₅H₅, 1 H TpH), 6.75 (m, 2 H, C₅H₅), 6.38, 6.36, 6.05 (t x 3, 3 H, TpH^4), 2.50 (septet, J_{HH} = 7.19, 1 H, i-PrCH), 0.76, 0.19 (d x 2, J_{HH} = 7.19, 6 H, i-PrCH₃). ^13C[^1H] NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 238.1 [C(O)CC₅H₅], 234.5 (MoCO), 218.7 (FeCO), 148.0, 145.0, 143.3, 136.7, 136.69, 135.5 (TpCH), 132.7 [C₁(C₅H₅)], 130.2(2), 129.3(2), 129.2 (C₅H₅), 137.1 [C₁(C₅H₅)], 127.1, 126.5, 125.2 (C₅H₅), 106.2, 106.0, 105.7 (TpCH^4), 128.6 (µ-CSe), 111.2 (µ-CPh), 87.2 (µ-CC₅H₅), 41.0 (i-PrCH), 24.2, 21.5 (i-PrCH₃). MS (ESI): m/z (%) 863.2 (5) [M + K]^+, 847.1 (5) [M + Na]^+, 821.2 (7) [M]^+, 797.1 (10) [M - CO]^+, 769.2 (30)

---

^1 Due to significant overlap and broadening in this region, aromatic resonances due to each isomer could not be unambiguously distinguished.
[M - CO - 2CH$_3$]$^+$, 741.1 (22) [M - 2CO - 2CH$_3$]$^+$, 699.1 (10) [M - 3CO - i-Pr]$^+$, 671.0 (60) [M - 4CO - i-Pr]$^+$, 482.2 (55) [FeTp]$^+$, 269.1 (100) [FeTp]$^+$.

Method 2 Isopropyl(2-phenylethynyl)selane (0.096 g, 0.430 mmol) in tetrahydrofuran (5 mL) was added to a solution of [MoFe(µ-CC$_4$H$_3$S-2)(CO)$_5$Tp] (31) (0.200 g, 0.333 mmol) in tetrahydrofuran (25 mL) and the black mixture heated at reflux for 6 h. Multiple products were evident by thin layer chromatography, including several compounds not previously observed. Solvent was removed in vacuo and the brown residue redissolved in dichloromethane and chromatographed (silica gel, −33 °C). Elution with dichloromethane–hexane (1:1) developed several minor bands but only the identifiable maroon fraction was recovered after increasing the dichloromethane content of the eluant (2:1). Concentration of the maroon eluate and storage at −20 °C afforded maroon crystals of 42 that were isolated by filtration and rinsed with ethanol. Yield 0.035 g (13%).

Treatment of [MoFe(µ-CC$_4$H$_3$S-2)(CO)$_5$Tp] with i-PrSC=CPH

In a manner analogous to that described above for isopropyl(2-phenylethynyl)selane, isopropyl(2-phenylethynyl)sulfane (0.117 g, 0.66 mmol) and [MoFe(µ-CC$_4$H$_3$S-2)(CO)$_5$Tp] (0.200 g, 0.333 mmol) were combined in dichloromethane (50 mL) and the initially black mixture stirred at room temperature for 7 days after which time thin layer chromatography revealed major golden-orange and maroon products, in addition to a large amount of gold baseline material. The solvent volume was reduced and the residue chromatographically separated (silica gel, −33 °C). Elution with dichloromethane–hexane (1:2) developed an initial orange band corresponding to the known alkylidyne species 14 (0.020 g, 13%). Continued elution of the chromatography column with this same solvent mixture afforded a broad golden-orange band (43) and further elution with dichloromethane–hexane (2:1) as eluant afforded a maroon fraction (45) of comparable size. Elution with tetrahydrofuran–hexane (1:1) mobilised a golden compound (44) from the baseline as an additional reaction product. Recovery of the golden-orange eluate and solvent removal afforded a microcrystalline golden-orange solid formulated as [MoFe(µ-C(C$_4$H$_3$S-2)C(SiPr)C(Ph))(µ-CO)(CO)$_5$Tp] (43). Yield 0.075 g (30%).

IR (Nujol): 2049, 1993, 1985, 1955, 1808 (νCO) cm$^{-1}$. IR (CH$_2$Cl$_2$): 2049 s, 1980 s(br), 1865 w(sh), 1826 w (νCO) cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.075 MHz): δ 8.07, 7.87, 7.85, 7.63, 7.61 (d x 5, 5 H, TpH$^3$, 7.30 (dd, $^3$J$_{HH}$ = 5.1, $^4$J$_{HH}$ = 1.2, 1 H, C$_6$H$_5$S), 7.20 (dd, $^3$J$_{HH}$ = 3.9, $^4$J$_{HH}$ = 1.2, 1 H, C$_6$H$_5$S), 7.08 (d, 1 H, TpH$^3$); 7.06 (dd, $^3$J$_{HH}$ = 5.09, $^3$J$_{HH}$ = 3.59, 1H, H$^5$(C$_6$H$_5$S)) 6.99, 6.69 (m x 2, 5 H, C$_6$H$_5$), 6.29, 6.22, 5.7 (t x 3, 3 H, TpH$^4$), 2.83 (septet, $^3$J$_{HH}$ = 6.89, 1 H, i-PrCH), 1.02, 0.73 (d x 2, $^3$J$_{HH}$ = 6.59, 6 H, i-PrCH$_3$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 25 °C, 75.421 MHz): δ 240.9, 231.6 (MoCO), 209.2 (br (FeCO), 150.3 (C$_1$(C$_4$H$_3$S)), 146.6 (C$_1$(C$_4$H$_3$)), 143.6 (µ-CPh), 147.2, 145.5, 144.5, 137.6, 136.7, 136.3 (TpCH), 130.7, 127.2,
126.8 (C₈H₈), 130.9, 127.8, 126.7 (C₄H₇S), 123.7 (µ-CS), 114.3 (µ-C₆), 106.1, 106.0, 105.9 (TpCH⁴), 40.2 (i-PrCH), 24.7, 24.3 (i-PrCH₂). MS (ESI): m/z (%) 801.0 (5) [M + Na]⁺, 720.0 (10) [M – 2CO]⁺, 664.0 (10) [M – 4CO]⁺, 637.0 (28) [M – 5CO]⁺, 596.0 (60) [M – 5CO – i-Pr]⁺, 561.0 (30) [M – 5CO – Si–Pr]⁺. Anal. Found: C, 46.05; H, 3.90; N, 10.11%. Calcd. for C₅₀H₃₂BFeMoN₂O₅S₂: C, 46.42; H, 3.25; N, 10.83%.

Removal of solvent from the maroon eluate afforded a maroon solid formulated as [MoFe{µ-C(C₆H₅S-2)CC(Ph)(Si–Pr)}(CO)₄Tp] (45). Yield 0.023 g (9%). IR (Nujol): 2479 (vBH), 1982 s, 1942 s, 1918 s, 1818 s (vCO) cm⁻¹. IR (CH₂Cl₂) 1992 s, 1952 s, 1829 m, 1834 w(br) (vCO) cm⁻¹. The ¹H NMR revealed the presence of two isomeric forms (ratio 3:1) and data relates to the mixture. **Minor isomer:** ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.76, 7.67, 7.65, 7.55 (m(br) × 3, TpH⁴), 7.15, 6.99 (m(br) × 2, C₆H₅), 7.46, 7.04 (m(br) × 2, C₆H₅S), 6.22, 6.19, 5.99 (t × 3, 3 H, TpH⁴), 2.63 (septet, 3JHH = 7.19, 1 H, i-PrCH), 1.24, 0.99 (d × 2, 3JHH = 7.04, 6 H, i-PrCH₃). **Major isomer:** ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.92, 7.73, 7.69, 7.68, 7.58, 7.56 (dd(br) × 6, TpH⁴), 7.96, 7.48 (m(br) × 2, C₆H₅), 6.84 (dd, 3JHH = 5.1, 4JHH = 1.2, 1 H, C₆H₅S), 6.63 [dd, 3JHH = 5.1, 4JHH = 3.6, 1 H, H₄(C₆H₅S)], 6.58 (dd, 3JHH = 3.3, 4JHH = 0.9, 1 H, C₆H₅S), 6.25, 6.23, 6.02 (t × 3, 3 H, TpH⁴), 2.43 (septet, 3JHH = 6.6, 1 H, i-PrCH), 1.24, 0.90 (d × 2, 3JHH = 6.89, 6 H, i-PrCH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 236.8, 231.2 (MoCO), 221.6, 211.8 (FeCO), 144.8, 144.7, 142.9, 136.0, 135.9, 135.3, 106.0, 105.7, 105.5 (TpCH), 133.7(br), 129.8, 128.5 (C₆H₅), 144.7 [C¹(C₆H₅S)], 128.1, 126.7, 124.5 (C₆H₅S), 118.9 (µ-C₆H₅S), 111.6 (µ-CS), 81.9 (µ-C), 44.8 (i-PrCH), 23.1, 22.8 (i-PrCH₃). The resonance due to C¹(C₆H₅S) could not be unequivocally identified. MS (ESI): m/z (%) 771.1 (3) [M + Na]⁺, 677.0 (10) [M – 2CO – Me]⁺, 637.0 (50) [M – 4CO]⁺, 596.0 (100) [M – 4CO – i-Pr]⁺, 563.0 (40) [M – 4CO – Si–Pr]⁺. Anal. Found: C, 45.98; H, 3.70; N, 10.66%. Calcd. for C₅₀H₃₂BFeMoN₂O₅S₂: C, 46.55; H, 3.37; N, 11.23%. **Crystal data for C₅₀H₃₂BFeMoN₂O₅S₂.** M₀ = 748.29, triclinic, P ¯, a = 7.8989(1), b = 11.4958(2), c = 17.3711(3) Å, α = 78.3811(9), β = 86.544(1), γ = 84.708(1)°, V = 1537.23(4) Å³, Z = 2, ρcalcd = 1.617 Mg m⁻³, μ(Mo Kα) = 1.061 mm⁻¹, T = 200(2) K, dark red plate, 7038 independent measured reflections (2θ ≤ 50°), R₁ = 0.0251 wR = 0.0244 for 5321 independent observed absorption-corrected reflections (I > 3σ(I)), 437 parameters. The thiophene group was unequally disordered over two orientations which are coplanar but related by 180° rotation about the µC–Cipso(thiophene) bond (ratio 0.637(4):0.363).

Solvent removal from the final golden-brown fraction afforded a brown solid that was subject to a further chromatographic purification (silica gel, 25 °C). Elution with dichloromethane.

---

³ The remaining resonances were obscured by those of the major isomer and thus individual signals could not be unambiguously assigned at 300.075 MHz.
removed a minor red impurity before the desired compound was mobilised with tetrahydrofuran. The brown eluate was diluted with hexane and solvent removal afforded a golden-brown solid formulated as the alkylidyne/alkyne/carbonyl coupled complex \([\text{MoFe}\{\mu-C(Si-i-Pr)C(Ph)C(C_2H_5S-2)C(\text{O})\}]\) (44). Yield 0.080 g (30%). IR (KBr): 2480 w (\(\nu_{\text{BH}}\)), 2042 s, 1976 s(br), 1890 m(br) (\(\nu_{\text{CO}}\)) cm\(^{-1}\). IR (CH\(_2\)Cl\(_2\)): 2047 s, 1986 s, 1927 s, 1819 s (\(\nu_{\text{C}=\text{O}}\)) cm\(^{-1}\). H NMR (CD\(_2\)Cl\(_2\), 25 °C, 300.075 MHz): \(\delta\) 8.01, 7.89, 7.81, 7.76, 7.70 (d \(\times\) 5, 5 H, TpH), 7.85, 7.57 (m \(\times\) 2, 5 H, C\(_6\)H\(_5\)), 7.18 (dd, \(J_{\text{HH}} = 5.1\), \(J_{\text{HH}} = 1.2\), 1 H, C\(_4\)H\(_3\)S), 6.74 (m, 2 H, C\(_4\)H\(_3\)S), 6.39, 6.37, 6.05 (t \(\times\) 3, 3 H, TpH\(^+\)), 2.41 (septet, \(J_{\text{HH}} = 6.9\), 1 H, i-PrCH), 0.73, 0.74 (d \(\times\) 2, \(J_{\text{HH}} = 6.9\), 6 H, i-PrCH). Crystal data for \(\text{C}_{30}\text{H}_{25}\text{BF}_{6}\text{Mo}_{6}\text{Ni}_{4}\text{O}_{2}\text{S}_{2}\text{CH}_{2}\text{Cl}_{2}\), \(M_r = 861.23\), monoclinic, \(P_{2_1}/n\), \(a = 9.2350(2)\), \(b = 31.3856(6)\), \(c = 12.6399(2)\), \(\beta = 94.7914(8)^\circ\), \(V = 3650.82(12)\) \(\AA^3\), \(Z = 4\), \(\rho_{\text{calc}} = 1.567\) Mg \(\text{cm}^{-3}\), \(\mu(\text{Mo K\alpha}) = 1.049\) mm\(^{-1}\), \(T = 200(2)\) K, orange plate, 8362 independent observed absorption-corrected reflections (2\(\theta\) \(\leq\) 54°), \(R_{1} = 0.0277\), \(wR = 0.0318\) for 4859 independent observed absorption-corrected reflections (\(I > 3\sigma(I)\)), 460 parameters. Disorder was observed in the dichloromethane of solvation. The thiophene group was unequally disordered with the two orientations related by 180° rotation around the \(\mu\text{C}-\text{C}_{\text{iso}}\)(thiophene) bond (ratio 0.938(2):0.062)

**Treatment of [MoFe(μ-CC\(_2\)H\(_5\)S-2)(CO)\(_3\)Tp] with i-PrTeC≡CPh**

In a manner analogous to that described above for isopropyl(2-phenylethynyl)selane, isopropyl(2-phenylethynyl)tellane (0.181 g, 0.666 mmol) and [MoFe(μ-CC\(_4\)H\(_5\)S-2)(CO)\(_3\)Tp] (0.200 g, 0.333 mmol) were combined in dichloromethane (50 mL) and the initially black mixture stirred at ambient temperature for 7 days, after which time thin layer chromatography revealed a maroon complex as the major reaction product, in addition to minor brown and orange compounds. The solvent volume was reduced in vacuo and the brown residue purified by chromatography (silica gel, −33 °C). Initial elution with dichloromethane–hexane (1:2) removed the minor products and the dichloromethane content of the eluate was increased (2:1) to afford the maroon fraction (46). Concentration of the maroon solution, dilution with hexane and storage at −17 °C for 24 h afforded the complex [MoFe{μ-C(C\(_4\)H\(_5\)S-2)CC(Ph)(Te-i-Pr)}(CO)\(_3\)Tp] (46) as a crystalline maroon solid, which was collected by filtration and rinsed with ethanol. Yield 0.103 g (36%). IR (Nujol): 2478 (\(\nu_{\text{BH}}\)), 1979 s, 1940 s, 1915 s, 1819 s (\(\nu_{\text{CO}}\)) cm\(^{-1}\). IR (CH\(_2\)Cl\(_2\)) 1988 s, 1950 s, 1827 m, 1833 w(br) (\(\nu_{\text{CO}}\)) cm\(^{-1}\). H NMR (CD\(_2\)C\(_6\)D\(_4\)C\(_2\)Cl\(_2\), 80 °C, 300.075 MHz): \(\delta\) 8.36–8.10, 7.81 (m(br) \(\times\) 2, 11 H, TpH, C\(_6\)H\(_5\)), 7.59, 7.51, 7.33 (s(br) \(\times\) 3, 3 H, C\(_4\)H\(_3\)S), 6.89, 6.70, 6.56 (s(br) \(\times\) 3, 3 H, TpH\(^+\)), 2.88 (septet(br), 1 H i-PrCH), 2.07, 1.90 (d(br) \(\times\) 2, 6 H, i-PrCH). Useful \(^{13}\)C{\(^1\)H} NMR data were not obtained due to broadness at ambient temperature and decomposition of the complex upon prolonged data acquisition at higher temperatures (80 °C). MS (ESI): \(m/z\) (%) 869.0 (40) [M + Na]\(^+\), 715.0 (40)
[M – Tei-Pr]$^+$, 690.0 (100) [M – 4CO – i-Pr]$^+$. Anal. Found: C, 42.14; H, 3.51; N, 9.62%. Calcd. for C$_{29}$H$_{25}$BFeMo$_2$O$_4$S$_{Te}$: C, 41.28; H, 2.99; N, 9.96%. Crystal data for C$_{29}$H$_{25}$BFeMo$_2$O$_4$S$_{Te}$, $M_0 = 843.82$, triclinic, $P \bar{T}$, $a = 8.0528(1)$, $b = 11.6239(3)$, $c = 17.6070(5)$ Å, $\alpha = 75.3056(1)$, $\beta = 86.267(2)$, $\gamma = 85.787(2)^\circ$, $V = 1586.23(6)$ Å$^3$, $Z = 2$, $\rho_{calc} = 1.767$ Mg m$^{-3}$, $\mu$(Mo Kα) = 1.864 mm$^{-1}$, $T = 200(2)$ K, dark red needle, 7297 independent measured reflections ($2\theta \leq 50^\circ$), $R_1 = 0.0283$, $wR = 0.0250$ for 4452 independent observed absorption-corrected reflections ($I > 3\sigma(I)$), 397 parameters.

Treatment of [MoFe(µ-CPh)(CO)$_3$] with i-PrSeC=CPh

**Method 1** Isopropyl(2-phenylethynyl)selane (0.0976 g, 0.337 mmol) in dichloromethane (5 mL) was added to a solution of [MoFe(µ-CPh)(CO)$_3$] (39) (0.200 g, 0.337 mmol) in the same solvent (15 mL). The mixture was stirred at room temperature for 2.5 weeks with monitoring by thin layer chromatography. Solvent volume was reduced in vacuo (ca. 3 mL) and the concentrated solution transferred to a chromatography column (silica gel, −33 °C). After eluting initial faint yellow, orange and brown bands, elution with dichloromethane–hexane (1:2) afforded a red-orange fraction (48). Continued elution of the chromatography column with dichloromethane–hexane (2:1) eluant afforded a broad maroon band (49). Recovery of the orange eluate and solvent removal afforded a red-orange compound formulated as the alkyne/alkylidyne coupled product [MoFe{µ-C(Ph)C(Sei-Pr)C(Ph)}(µ-CO)(CO)$_3$] (49).

Yield 0.065 g (23%). IR (KBr): 2487 w (ν$_{BH}$), 2046 s, 1989 s, 1966 s, 1957 s, 1839 m (ν$_{CO}$) cm$^{-1}$. IR (CH$_2$Cl$_2$): 2048 s, 1833 s (br), 1862 w (br), 1826 w (br) (ν$_{CO}$) cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.075 MHz): $\delta$ 7.86, 7.77, 7.74, 7.73 (d × 4, 2:1:1:2, 6 H, TpH$^5$), 7.12, 6.91 (m × 2, 6.4 H, C$_6$H$_5$), 6.26, 6.05 (t × 2, 1:2 H, TpH$^3$), 2.47 (septet, $^3$J$_{HH}$ = 6.89, 1 H, i-PrCH), 0.85 (d, $^3$J$_{HH}$ = 6.9, 6 H, i-PrCH$_3$). $^{13}$C ($^1$H) NMR (CD$_2$Cl$_2$, 25 °C, 75.421 MHz): $\delta$ 233.3 (MoCO), 210.9 (FeCO), 146.6, 144.1, 136.9, 136.4 (2:1:1:2, TpCH$_3$), 145.2, [C($^1$C$_6$H$_5$)], 130.0, 129.4 (µ-C), 130.8, 127.6, 126.9 (C$_6$H$_5$), 106.3, 106.0 (1:2, TpCH$_3$), 54.4 (i-PrCH), 25.8 (i-PrCH$_3$). MS (ESI); m/z 763.0 (20) [M – 2CO]$^+$, 711.1 (10) [M – 3CO]$^+$, 664.9 (30) [M – 5CO – CH$_3$]$^+$, 583.10 (27) [M – 4CO – Sei-Pr]$^+$.

The maroon fraction was concentrated, diluted with hexane and allowed to stand for 24 h at −11 °C whereupon the complex [MoFe{µ-C(Ph)CC(Ph)(Sei-Pr)}(CO)$_3$] (49) was isolated as a crystalline maroon solid by filtration and rinsing with ethanol. Yield 0.128 g (48%). IR (KBr): 2489 (ν$_{BH}$), 1990 s, 1944 m, 1924 s, 1855 m (ν$_{CO}$) cm$^{-1}$. IR (CH$_2$Cl$_2$): 1989 s, 1948 s, 1826 w (br) (ν$_{CO}$) cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300.075 MHz): $\delta$ 7.86 (m, 1 H, TpH$_{3}^{10}$r), 2 H, C$_6$H$_5$), 7.73, 7.66, 7.50 (d × 3, 1:2:1 H, TpH), 7.40 (m, 1 H, TpH$_{3}^{10}$s), 3 H, C$_6$H$_5$), 7.22, 7.01 (m × 2, 5 H, C$_6$H$_5$), 6.23 (br), 6.21, 5.89 (br, t × 3, 3 H, TpH$_{3}$), 2.64 (septet, $^3$J$_{HH}$ = 6.89, 1 H, i-PrCH), 1.32, 0.95 (d × 2, $^3$J$_{HH}$ = 6.9, 6 H, i-PrCH$_3$). $^{13}$C ($^1$H) NMR
(CD$_3$Cl$_2$, 25 °C, 75.421 MHz): $\delta$ 235.5, 232.9 (Mo=CO), 211.7, 212.2 (Fe=CO), 144.8, 144.4, 142.7, 135.9, 135.8, 135.2, 105.9, 105.6, 105.2 (Tp=CH), 141.3, 131.1, 127.8, 126.5 (C$_6$H$_5$)$_2$, 133.0, 129.4, 128.4 (C$_6$H$_5$), 118.8 ($\mu$-CPh), 114.5 ($\mu$-CSe), 86.8 ($\mu$-C), 42.0 (i-PrCH), 23.6 (i-PrCH$_3$). MS (ESI): $m/z$ (%) 789.7 (4) [M]+, 734.0 (5) [M - 2CO]+, 677.9 (7) [M - Fe(CO)$_4$]$,^+$, 634.8 (12) [M - Fe(CO)$_2$ - i-Pr]+, 482.1 (100) [FeTp$_2$]+. Anal. Found: C, 47.27; H, 3.38; N, 10.32%. Calcd. for C$_3$H$_2$BFeMoN$_2$O$_2$: C, 47.18; H, 3.1%.

**Method 2** Isopropyl(2-phenylethynyl)selane (0.049 g, 0.219 mmol) in dichloromethane (5 mL) was added to a solution of [MoFe($\mu$-CPh)(CO)$_2$Tp] (39) (0.100 g, 0.168 mmol) in the same solvent (15 mL) and the mixture stirred at room temperature. After 8.5 h, thin layer chromatography revealed complete consumption of 39 and formation inter alia of a new brown compound (47). The solvent volume was decreased in vacuo and the residue transferred to a chromatography column (silica gel, –33 °C). Rapid elution with dichloromethane–hexane (1:2) afforded a major brown band from which solvent removal gave a brown microcrystalline product formulated as the π-bound alkyne complex [MoFe($\mu$-CPh)(η$^2$-i-PrSeC≡CPh)](CO)$_2$Tp (47). Yield 0.106 g (77%). IR (Nujol): 2042 m, 2027 m, 1984 s(br), 1966 m, 1940 m, 1868 w(br) (v CO), 1718 m (v CO, v CO). 1H NMR (CD$_2$Cl$_2$, 25 °C, 300.075 MHz): $^3$δ 8.14, 7.85, 7.73, 7.70, 7.31, 7.10 (d x 6, 6 H, TpH$^5$, 8.00, 7.97, 7.51, 7.35 (m x 4, 1:1:2:1 H, C$_6$H$_5$), 7.16, 6.75 (m x 2, 3:2 H, C$_6$H$_5$), 6.37, 6.11, 6.05 (t x 3, 3 H, TpH$^3$), 3.14 (septet, $^3$I$_{HH}$ = 7.19, 1 H, i-PrCH), 1.31, 1.19 (d x 2, 3$I_{HH}$ = 6.89, 6 H, i-PrCH$_3$). $^{13}$C{[1H]} NMR (CD$_2$Cl$_2$, 25 °C, 75.421 MHz): $\delta$ 323.9 ($\mu$-C), 228.7 (Mo=CO), 213.7, 211.6, 210.1 (br) (Fe=CO), 143.8, 143.5, 142.8, 136.4, 136.3, 135.7, (TpCH$^{3,5}$), 141.7 [$^{13}$C(C$_6$H$_5$)], 131.2, 128.5, 127.5 (C$_6$H$_5$), 153.9, [$^{13}$C(C$_6$H$_5$)], 128.2, 127.6, 124.3 (C$_6$H$_5$), 105.7, 105.9 (TpCH$_3$), 92.9 (SeC≡CPh), 80.9 (SeC≡CPh), 36.1 (i-PrCH), 25.9, 25.2 (i-PrCH$_3$). MS (ESI): $m/z$ (%) 817.2 (2) [M]$^+$, 763.2 (5) [M - 2CO]$^+$, 735.2 (5) [M - 3CO]$^+$, 705.2 (5) [M - 4CO]$^+$, 675.2 (6) [M - 5CO]$^+$, 665.1 (10) [M - 5CO - CH$_3$]$^+$, 636.1 (8) [M - 5(CO) - i-Pr]$^+$, 595.1 (12) [M - i-PrSeC≡CPh]$^+$, 482.1 (40) [FeTp$_2$]$^+$, 269.2 (100) [FeTp]$^+$.

Analytical data was not obtained due to solution instability (evolution into inter alia 48 and 49).

**Note** Upon storage of 47 (0.050 g, 0.061 mmol) as a dichloromethane–hexane solution (1:1) at –17 °C for 24 h pure compound 47 was transformed into a mixture containing compounds 48

---

4 $^4$H and $^{13}$C{[1H]} NMR resonances denoted by a prime (') are attributed to those of the $\mu$-CPh phenyl ring.
and 49. The new solution was chromatographed (silica gel, −33°C) and elution with dichloromethane–hexane solution (1:1) afforded recovered 47 (0.011 g, 22%) and compound 48 (0.014 g, 28%). Increasing to a 2:1 solvent mix afforded 49 (0.008 g, 16%).

Conversion of \([\text{MoFe}[\mu-C(\text{C}_3\text{H}_5\text{S}-2)\text{C}(\text{Sei-Pr})\text{C}(\text{Ph})](\mu-\text{CO})(\text{CO})_4\text{Tp}]\) (40) to \([\text{MoFe}[\mu-C(\text{C}_3\text{H}_5\text{S}-2)\text{CC}(\text{Sei-Pr})\text{C}(\text{Ph})](\mu-\text{CO})(\text{CO})_4\text{Tp}]\) (42)

**Method 1** \([\text{MoFe}[\mu-C(\text{C}_3\text{H}_5\text{S}-2)\text{C}(\text{Sei-Pr})\text{C}(\text{Ph})](\mu-\text{CO})(\text{CO})_4\text{Tp}]\) (40) (0.030 g, 0.036 mmol) was stirred in dichloromethane (10 mL) for 3 days at which time quantitative formation of 42 was evident (thin layer chromatography). The solvent volume was reduced and the maroon residue recrystallised from dichloromethane/ethanol to afford 42 as a maroon powder. Yield 0.024 g (84%).

**Method 2** \([\text{MoFe}[\mu-C(\text{C}_3\text{H}_5\text{S}-2)\text{C}(\text{Sei-Pr})\text{C}(\text{Ph})](\mu-\text{CO})(\text{CO})_4\text{Tp}]\) (40) (0.030 g, 0.036 mmol) and trimethylamine N-oxide dihydrate (0.004 g, 0.036 mmol) were combined in dichloromethane (10 mL) and the mixture stirred for 3 days at which time near quantitative formation of 42 was evident (thin layer chromatography, no further reaction occurred with 2 additional days of reaction). The solvent volume was reduced and the concentrated red solution subjected to flash chromatography (silica gel, 25 °C, air). Elution with dichloromethane–hexane (1:1) afforded a minor yellow band corresponding to 40 (Yield 0.003 g, 10% recovery). Continued elution with dichloromethane–hexane (2:1) afforded a maroon eluate from which solvent removal and recrystallisation from dichloromethane/ethanol afforded 42 as a maroon powder. Yield 0.018 g (70% based on recovered 40).

### 7.6 Tp* ligated alkyne/selenomethylidyne complexes of molybdenum

**Preparation of \([\text{Mo}(\equiv\text{CSeC≡Ct-Bu})(\text{CO})_2\text{Tp}^*]\) (51)**

In a representative synthesis, a solution of 3,3-dimethylbut-1-yne (0.495 mL, 4.03 mmol) in tetrahydrofuran (5 mL) at −78 °C was treated drop-wise (with stirring) with n-butyllithium (2.5 mL of a 1.6 M solution in hexane). The resultant pale yellow mixture was allowed to warm to ambient temperature and stirred for a further hour, after which time it was cooled to 0 °C and elemental selenium (0.317 g, 4.02 mmol) added. (NB: The mixture deepened in colour over approximately fifteen minutes as the selenium powder was consumed). The yellow reaction mixture was then cooled to −78 °C and transferred via a filter cannula into a separate flask containing a suspension of \([\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{Tp}^*]\) (2.00 g, 4.03 mmol) in diethyl ether (150 mL) at the same temperature. The cooling bath was removed and the resultant yellow mixture warmed to ambient temperature with stirring. After 24 h, the cloudy orange solution was filtered through Celite and solvent removed to afford a reddish-orange residue. The residue was redissolved in dichloromethane (3 mL) and transferred to a chromatography column (silica
CHAPTER 7. EXPERIMENTAL

with dichloromethane–hexane (1:5) afforded an initial yellow fraction, corresponding to recovered [Mo(≡CCl)(CO)₂Tp*] [IR (CH₂Cl₂): 2002, 1915 (v_CO) cm⁻¹ cf. literature data, IR(cyclohexane): 2005, 1921]¹⁰ (0.264 g, 13.2%), closely followed by a second broad orange band. Removal of solvent from the orange band and recrystallisation from chloroform/hexane afforded pure 51 as an orange powder. Yield 1.889 g (76%). IR (Nujol): 2545 w (v_BH), 1993 s, 1903 s (v_CO), 1544 vs, 1435 vs (Yeo), 1544 vs, 1325 s (Ye), 1230 s, 1147 s (Ye) cm⁻¹. IR(CH₂Cl₂): 1820 s, 1785 s, 1650 s (Yeo). NMR (CDCl₃, 25 °C, 200 MHz): δ 5.85, 5.73 (s x 2, 2:1 H, Tp*CH), 2.54, 2.37, 2.36, 2.32 (s x 4, 6:3:6:3 H, Tp*CH₃), 1.23 (s, 15H, t-Bu). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.4 MHz): δ 245.0 (Mo=O), 225.1 (Mo=CO), 151.5, 151.1, 145.1, 144.4 (1:2:1:2, Tp*CCH₃), 106.4, 106.2 (1:2, Tp*CH), 114.7 (t-BuC≡CSe), 52.0 (t-BuC≡CSe), 30.7 (t-BuCH₃), 29.3, [t-BuC(CH₃)₃], 16.0, 14.6, 12.6 (2:1:3, Tp*CCH₃). MS (ESI): m/z (%) 566.0 (100) [M – 2CO]⁺. Anal. Found: C, 45.14; H, 5.02; N, 13.00%. Calcd. for C₂₃H₃₁BMoN₆O₂SeSi: C, 45.09; H, 5.20; N, 13.15%.

Preparation of [Mo(≡CSe≡CSiMe₃)(CO)₂Tp*] (53)

Method 1 Compound 53 was prepared as an orange powder following the procedure described for 51 from ethynyltrimethylsilane (0.075 mL, 0.530 mmol) in tetrahydrofuran (10 mL), n-butyllithium (0.34 mL of a 1.6 M solution in hexane), elemental selenium (0.042 g, 0.532 mmol), and [Mo(≡CCl)(CO)₂Tp*] (0.264 g, 0.532 mmol) in diethyl ether (15 mL). Yield 0.128 g (61% based on recovered starting material). IR (Nujol): 2093 (v_C=C), 1996, 1910 (v_CO), 1543 (v_C=O) cm⁻¹. IR (CH₂Cl₂): 2092 (v_C=C), 2002, 1919 (v_CO) cm⁻¹. ¹H NMR (CDCl₃, 25 °C, 300.075 MHz): δ 5.85, 5.73 (s x 2, 2:1 H, Tp*H), 2.52, 2.36, 2.35, 2.31 (s x 4, 6:3:6:3 H, Tp*CH₃), 0.22 (s, 9H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.4 MHz): δ 244.8 (Mo=O), 224.8 (Mo=CO), 151.6, 151.2, 145.2, 144.5 (1:2:1:2, Tp*CCH₃), 106.5, 106.3 (1:2, Tp*CH), 113.8 (Me₃SiC≡CSe), 78.7 (Me₃SiC≡CSe), 16.0, 14.6, 12.6 (1:2:3, Tp*CCH₃), -0.25 (SiMe₃). MS (ESI): m/z (%) 582.9 (80) [M – 2CO]⁺, 484.9 (18) [M – 2CO – C≡CSiMe₃]⁺. Anal. Found: C, 43.40; H, 4.93; N, 12.96%. Calcd. for C₂₃H₃₁BMoN₆O₂SeSi: C, 43.34; H, 4.90; N, 13.19%.

Crystal data for C₂₃H₃₁BMoN₆O₂SeSi: Mr = 637.33, orthorhombic, P2₁2₁2₁, a = 8.0112(4), b = 17.7072(1), c = 20.381(1) Å, V = 2891.1(3) Å³, Z = 4, ρ_calcd = 1.464 Mg m⁻³, µ(Mo Kα) = 1.784 mm⁻¹, T = 200(2) K, brown needle, 5092 independent measured reflections (2θ ≤ 54°), R₁ = 0.062, wR₂ = 0.092 for 3124 independent observed absorption-corrected reflections (I > 3σ(I)), 239 parameters. The crystal was refined in terms of a 0.545(29):0.455 twin assuming a volume fraction of 0.518(4):0.482 of a P2₁2₁2₁ structure and a 1:1 disordered P mnb structure using reflections indexed for a smaller cell.

Method 2 Compound 53 was similarly prepared as an orange powder following the procedure described above from two equivalents of ethynyltrimethylsilane (0.569 mL, 4.03 mmol) in
tetrahydrofuran (20 mL), n-butyllithium (0.34 mL of a 1.6 M solution in hexane), elemental selenium (0.317 g, 4.015 mmol), and [Mo(=CCl)(CO)2Tp*] (1.00 g, 2.02 mmol) in diethyl ether (50 mL). In addition to unreacted [Mo(=CCl)(CO)2Tp*] (0.01 g, 10% recovery) and 53 (0.805 g, 63%), chromatography afforded an intermediate red fraction, corresponding to [Mo(=CC=CSiMe3)(CO)2Tp*] (54) Yield 0.045 (4%). IR (Nujol): 2048 (vCO), 2000 s, 1921 s (Y). IR (Nujol): 2000, 1917 cm−1. 1H NMR (CDCl3, 25 °C, 300.075 MHz): δ 5.85, 5.70 (s × 2, 2:1 H Tp* H), 2.54, 2.36, 2.35, 2.33, 2.30 (6:6:3:3, Tp*CH3), 0.18 (s, 9 H, SiMe3). 13C-1H NMR (CDCl3, 25 °C, 75.421 MHz): δ 255.4 (Mo=C), 227.4 (MoCO), 151.4, 151.1, 145.0, 144.4 (2:1:1:2, Tp*CH3), 106.3 (br, Tp*CH), 113.3, (Mo=CC=CSiMe3) 74.9 (Mo=CC=CSiMe3), 15.7, 14.6, 12.6 (1:2:3, Tp*CH3), −0.34 (SiMe3). MS (ESI): m/z (%) 586.21 (40) [M − 2CO + 2CH2CN]⁺, 573.18 (80) [M − CO + CH3CN]⁺, 560.15 (78) [M]⁺.

Preparation of [Mo(=CSeC≡CC6H4Me-4)(CO)2Tp*] (52)

Compound 52 was prepared as an orange residue following the procedure described for 51 from 4-ethynyl toluene (0.070 g, 0.603 mmol) in tetrahydrofuran (10 mL), n-butyllithium (0.38 mL of a 1.6 M solution in hexane), elemental selenium (0.048 g, 0.608 mmol), and [Mo(=CCl)(CO)2Tp*] (0.300 g, 0.604 mmol) in diethyl ether (100 mL). Yield 0.106 g (59% based on recovered starting material). IR (Nujol): 2000 s, 1920 s (vCO) cm−1. IR (CH2Cl2): 2001 s, 1918 s (vCO) cm−1. 1H NMR (CDCl3, 25 °C, 300.075 MHz): δ 7.36, 7.13 (d × 2, 2 H, C6H4Me-4), 5.84, 5.72 (s × 2, 2:1 H, Hpz*), 2.52, 2.36, 2.35, 2.31 (s × 4, 6:6:6:3 H, Tp*CH3, Me-4). 13C-1H NMR (CDCl3, 25 °C, 75.421 MHz): δ 246.6 (Mo=C), 225.0 (MoCO), 151.5, 151.2, 145.2, 144.5 (1:2:1:2, Tp*CH3), 138.7, 131.5, 129.0 (C6H4Me-4), 106.4, 106.3 (1:2, Tp*CH), 119.9 (CH3C6H4C≡CSe), 63.8 (CH3C6H4C≡CSe), 21.5 (CH3C6H4CH3), 15.9, 14.6, 12.6 (2:1:3, Tp*CH3). MS (ESI): m/z (%) 600.9 (19) [M − 2CO]⁺, 413.1 (90) [Tpt + C6H4Me]⁺, HR−MS (ESI): m/z (%) 656.07 (11) [M]⁺, 578.15 (45) [M−Se]⁺, 296.26 (100) [Tpt]⁺, 282.28 (95) [Tpt−CH3]⁺.

Treatment of [Mo(=CSeC≡Ct-Bu)(CO)2Tp*] with [Co2(CO)8]

[Mo(=CSeC≡Ct-Bu)(CO)2Tp*] (51) (0.200 g, 0.322 mmol) and [Co2(CO)8] (0.110 g, 0.322 mmol) were stirred together in diethyl ether (15 mL) for 1 h, during which time a period of CO evolution was observed. The dark brown mixture was transferred via filter cannula into a new flask and solvent was removed to give a brown solid comprising [Co2(µ-t-BuC5SeC≡Mo(CO)2Tp*)] (55). Yield 0.234 g (81%). IR (KBr): 2088 w, 2053 m, 2029 (sh), 2021 (sh), 2005 (sh), 1985 (sh), 1957 s, 1898 s (vCO) cm−1. IR (hexane): 2091 m, 2055 vs, 2034 s, 2024 s, 1999 m, 1921 s (vCO) cm−1. 1H NMR (CD2Cl2, 25 °C, 300.075 MHz): δ 5.90, 5.77 (s × 2, 2:1 H, Tp*H), 2.61, 2.37, 2.32, 2.30 (s × 4, 6:6:3:3 H, Tp*CH3), 1.30
(s, 9 H, t-BuCH₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 261.7 (Mo=Co), 227.2 (MoCO), 199.9 (br, CoCO), 152.0, 151.8, 146.2, 145.3 (2:1:1:2, Tp*CH₂), 106.7, 106.5 (1:2, Tp*CH), 113.7 (t-BuC≡CSe), 85.6 (t-BuC≡CSe), 36.8, [t-Bu-C(CH₃)] 32.2 (t-BuCH₃), 16.2, 14.6, 12.8 (2:1:3, Tp*CH₂). MS (ESI): m/z (%) 946.9 (1) [M + K]⁺, 850.2 (4) [M - t-Bu]⁺. Anal. Found: C, 39.00; H, 4.07; N, 8.34%. Calcd. for C₃₀H₃₁BCo₂Mo₆N₆O₆Se•1.5H₂O: C, 38.57; H, 3.67; N, 9.00%.

Reaction of [Co₂{µ-t-Bu₂SeC≡Mo(CO)₂Tp*}(CO)₄] with dpmm

[Co₂{µ-t-Bu₂SeC≡Mo(CO)₂Tp*}(CO)₄] (55) (0.216 g, 0.235 mmol) and dpmm (0.092 g, 0.239 mmol) were combined in dichloromethane (15 mL) and heated at reflux for 3.5 h after which time all of 55 was consumed (as determined by thin layer chromatography). The solvent volume was reduced to ca. 3 mL and the orange solution transferred to a chromatography column (silica gel, –33 °C). Elution with dichloromethane–hexane (1:1) afforded a major brown-orange fraction corresponding to [Co₂{µ-t-Bu₂SeC≡Mo(CO)₂Tp*}(µ-dppm)(CO)₄] (56) and a minor green band that was identified as the selenium-free analogue [Co₂{µ-t-Bu₂SeC≡Mo(CO)₂Tp*}(µ-dppm)(CO)₄] (57). Solvent removal from the brown fraction provided 56 as a brown solid: Yield 0.145 g (49%). IR (KBr): 2957, 2924, 2854 m (vCH), 1995 s (br), 1907 m, 1867 s, 1967 sh, 1542 (vCO) cm⁻¹. ¹H NMR (CDCl₃, 25 °C, 300.075 MHz): δ 7.44, 7.29, 7.20, 7.15, 7.02 (m x 5, 2H, C₆H₅), 5.77, 5.69 (s x 2, 2:1 H, Tp*H), 3.35, 3.25 (m x 2, 2H, Tp*CH), 1.40 (s, 9 H, t-Bu). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.421 MHz): δ 268.8 (Mo=Co), 226.8 (MoCO), 207.1, 202.5 (br, CoCO), 151.8, 151.0, 144.9, 144.1 (2:1:1:2, Tp*CH₂), 137.8 [vt, ¹J ═ 23.7, C¹(C₆H₅)], 134.6 [vt, ¹J = 16.6, C²(C₆H₅)], 132.6 [vt, ²J = 6.1, C²₅(C₆H₅)], 131.0 [vt, ²J = 5.7, C²₅(C₆H₅)], 129.6, 129.3 [C₄₃₋₄₄(C₆H₅)] 128.4, 127.9 (vt x 2, C₃₋₅(C₆H₅)) 110.6, 106.0 (1:2, Tp*CH), 119.2 (t(br), t-BuC≡CSe) 83.9 (t(br), t-BuC≡CSe), 37.2 [t-BuC(CH₃)₃], 35.2 (t, CH₃P), 32.5 (t-BuCH₃), 16.4, 14.6, 12.7 (2:1:3, Tp*CH₂). ³¹P{¹H} NMR (CDCl₃, 25 °C, 121.419 MHz): δ 38.25(br). MS (ESI): m/z (%) 1258.0 (5) [M + Na]⁺, 662.9 (63) [Co₂(C₂(CO)₂(dpmm) + Na]⁺, 439.1 (100) [Tp*Co₂C₃]⁺. Anal. Found: C, 52.94; H, 4.77; N, 6.72%. Calcd. for C₅₃H₃₅BCo₂Mo₆N₆O₆P₂Se•½C₆H₄: C, 52.60; H, 4.73; N, 6.57%. Crystal data for C₅₃H₃₅BCo₂Mo₆N₆O₆P₂Se, Mᵣ = 1235.57, triclinic, P ₁, a = 9.1891(2), b = 12.9671(4), c = 23.1494(6) Å, α = 87.108(1), β = 81.193(2), γ = 84.996(2)°, V = 2714.3(2) Å³, Z = 2, ρ calc = 1.512 Mg m⁻³, μ(Mo Kα) = 1.615 mm⁻¹, T = 200(2) K, brown needle, 9597 independent measured reflections (2θ ≤ 50°), R₁ = 0.0512, wR = 0.0527 for 6081 independent observed absorption-corrected reflections (I > 3σ(I)), 650 parameters. The crystal was twinned and refined accordingly (final twin ratio 0.589(6):0.411).
Solvent removal from the narrow green fraction provided 57 as a green solid: Yield 0.006 g (2%). IR (CH₂Cl₂): 2024 m, 1997 s(br), 1974 m, 1622 (sh), 1884 m(br) (ν_CO) cm⁻¹. ¹H NMR (CDCl₃, 25 °C, 300.075 MHz): δ 7.34, 7.12, 6.99 (m × 3, 20 H, C₆H₅), 5.70, 5.65 (s × 2, 2:1 H, Tp*H), 3.65, 3.45 (m × 2, 2 H, CH₂P), 2.39, 2.38, 2.29, 2.27, 2.27 (s × 4, 6:3:3:3:3 H, Tp*CH₃), 1.40 (s 9 H, t-Bu). ¹³C{¹H} NMR (CDCl₃, 25 °C, 75.421 MHz): δ 255.5 (Mo=C), ²¹Mo(CO) 230.2 (MoCO), 219.9, 195.0 (br, CoCO), ¹⁵NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.34, 7.12, 6.99 (m × 3, 20 H, C₆H₅), 5.70, 5.65 (s × 2, 2:1 H, Tp*H), 3.65, 3.45 (m × 2, 2 H, CH₂P), 2.39, 2.38, 2.29, 2.27, 2.27 (s × 4, 6:3:3:3:3 H, Tp*CH₃), 1.40 (s 9 H, t-Bu).

Reaction of [Mo≡CSe≡Ct-Bu](CO)₂Tp*] with [Pt(C₂H₅)(PPh₃)₂]

Method 1 [Mo≡CSe≡Ct-Bu](CO)₂Tp*] (51) (0.150 g, 0.241 mmol) and [Pt(PPh₃)₂(C₂H₅)] (0.180 g, 0.241 mmol) were combined in tetrahydrofuran (20 mL). The mixture was stirred at room temperature for 7 days, with monitoring via infrared spectroscopy until no further changes were apparent. Solvent removal gave a crude yield of 0.320 g (98%). The golden residue was dissolved in dichloromethane and transferred to chromatography column (silica gel, -33 °C). Elution with dichloromethane–hexane (1:2) afforded a major gold band. Solvent removal and recrystallisation from dichloromethane/ethanol afforded the isomer trans-[Pt{Se≡Mo(CO)₂Tp*}{C≡Ct-Bu}(PPh₃)₂] (58) as a pure yellow solid. Yield 0.298 g (91%). IR (KBr): 1947, 1864 s (ν_CO) cm⁻¹. IR (THF): 1952, 1868 (ν_CO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.77, 7.35, 7.22 (m × 3, 30 H, C₆H₅), 5.66, 5.65 (s × 2, 1:2 H, Tp*H), 2.39, 2.28, 2.26 (s × 3, 6:9:3 H, Tp*CH₃), 0.36 (s, 9 H, t-Bu). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 302.5 (Mo=C), 229.7 (MoCO), 152.2, 151.7, 145.0, 144.2 (2:1:1:2, Tp*CH₃), 135.6, 127.9 (νt × 2, C₂≡C₁≡C₃(CH₃)), 131.6 (νt, J_Pc = 29, C₁(CH₃)), 130.4 [C₂(CH₃)], 120.2 (t(br), Pt≡C≡Ct-Bu), 74.5 (t, J_Pc = 16, Pt≡C≡Ct-Bu), 106.1, 105.9 (2:1, Tp*CH), 30.8 (t-BuCH₃), 29.2, [t-BuC(CH₃)₂], 16.9, 14.6, 12.8, 12.6 (2:1:2:1, Tp*CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 121.419 MHz): δ 21.1 (J_Pp = 2695). MS (ESI): m/z (%) 1363.2 (1) [M + Na]⁺, 1342.4 (1)

Due to insufficient sample and poor signal-to-noise ratio denoted resonances have been assigned with low confidence.
Method 2 [Mo(≡CSeC≡Ct-Bu)(CO)₂Tp*] (51) (0.150 g, 0.241 mmol) and [Pt(PPh₃)₂(C₂H₄)] (0.180 g, 0.241 mmol) were combined in tetrahydrofuran (20 mL). Within 2 h infrared spectroscopic monitoring showed complete consumption of 51. Reaction was halted and solvent removal provided an orange solid formulated as the π-adduct [Pt{η²-t-BuC₂SeC≡Ct-Bu}Mo(CO)₂Tp*] (59) in spectroscopically quantitative yield. IR (KBr): 2524 (v₅) 1978 s, 1894 s, 1874 (sh) (vCO), 1722 w (vCC), 1542 w (vCN) cm⁻¹. IR (THF): 1980, 1897 (vCO) cm⁻¹.


Compound 51 was redissolved in tetrahydrofuran (20 mL) and reaction progress continued for a further 3 days at which time solvent was removed and the orange product transferred to a chromatography column (silica gel, -33 °C) using minimum dichloromethane. Elution with dichloromethane–hexane (1:1) afforded two major bands. The second, golden band corresponded to 0.178 g (58%) of 58, with data as described above. The first orange eluate, however, contained the isomeric complex cis-[Pt{SeC≡Ct-Bu}Mo(CO)₂Tp*] (58-A) (60).

Yield 0.085 g (26%). IR (KBr): 2524 (v₅) 1957 s, 1867 s, (vCO), 1542 w (vCN) cm⁻¹. IR (THF): 1957, 1875 (vCO) cm⁻¹. ¹H NMR (CD₂Cl₂, 25 °C, 300.075 MHz): δ 7.50, 7.41, 7.16 (m × 4, 30 H, C₆H₅), 5.79, 5.72 (s × 2, 2:1 H, Tp*H), 2.74, 2.35, 2.33, 2.29 (s × 4, 6:3:6:3 H, Tp*CH₃), 0.30 (s, 9 H, t-Bu). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C, 75.421 MHz): δ 297.2 (Mo=O), 228.9 (MoCO), 152.2, 151.5, 145.2, 144.3 (2:1:1:2, Tp*CH₃), 135.3, 134.9, 128.2, 127.9 [d × 4, C₂=O(C₆H₅)], 132.4, 130.8 [d × 2, C(C₆H₅)], 130.6, 130.3 [C(C₆H₅)], 122.5 (d, PtC≡Ct-Bu), 83.0 (d, PtC≡Ct-Bu), 106.1, 105.9 (2:1, Tp*CH), 30.7 (t-BuCH₃), 29.0, [t-BuC(CH₃)], 16.6, 14.7, 12.7, 12.6 (2:1:1:2, Tp*CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C, 121.419 MHz): δ 19.59 (d, Jpp = 16.5). MS (ESI): m/z (%) 1365.2 (46) [M + Na]⁺, 1341.2 (1) [M⁺], 1062.3 (27) [M – 2CO – PPh₃ + K]⁺, 841.3 (100) [M – 2PPh₃ + Na]⁺.

Anal. Found: C, 53.88; H, 4.68; N, 6.47%. C₆₀H₆₆BMoN₂O₂P₂PtSe: C, 53.74; H, 4.59; N, 6.27%. Crystal data for C₆₀H₆₆BMoN₂O₂P₂PtSe•1.55CH₂Cl₂•1.5H₂O•2EtOH: M_r = 1591.68, triclinic, P 1.
$a = 11.6097(1), \quad b = 14.8220(2), \quad c = 21.5820(3) \, \text{Å}, \quad \alpha = 80.746(1), \quad \beta = 82.351(1),
\gamma = 81.470(1)^\circ, \quad V = 3602.15(8) \, \text{Å}^3, \quad Z = 2, \quad \rho_{\text{calc}} = 1.467 \, \text{Mg m}^{-3}, \quad \mu(\text{Mo Kα}) = 2.828 \, \text{mm}^{-1},
T = 110(2) \, \text{K}, \quad \text{yellow block}, \quad 20,996 \quad \text{independent measured reflections} \ (2\theta \leq 60^\circ), \quad R_I = 0.0365, \quad wR_2 = 0.0895 \quad \text{for} \ 17,466 \quad \text{independent observed absorption-corrected reflections} \ (I > 2\sigma(I)), \quad 793 \quad \text{parameters}.\
REFERENCES