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**A Homologous Series of Alkynyl Chalcoether Complexes:  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  ( $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ;  $\text{Tp}^* =$  hydrotris(dimethylpyrazol-1-yl)borate).<sup>†</sup>**

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The first complete set of homologous alkynyl chalcoether complexes, isolated as the structurally characterised salts  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  ( $\text{A} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ;  $\text{Tp}^* =$  hydrotris(dimethylpyrazolyl)borate), result from the reactions of the free alkynes  $^i\text{PrEC}\equiv\text{CPh}$  with  $[\text{W}(\text{CO})_3(\text{Tp}^*)]$  in the presence of  $\text{AgBF}_4$ . The neutral complex  $[\text{W}(\eta^2\text{-}^i\text{PrSeC}\equiv\text{CPh})\text{Cl}(\text{CO})(\text{Tp}^*)]$  is obtained from the reaction of  $[\text{W}(\eta^2\text{-}^i\text{PrSeC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  with  $[\text{t}^n\text{Bu}_4\text{N}]\text{Cl}$  and co-exists in two forms in solution as a result of slow rotational isomerism of the alkyne. Depending on the choice of solvent, either pure rotamer may be crystallised.

Keywords: alkyne, chalcogen chalcoether, tungsten, complex

## Introduction

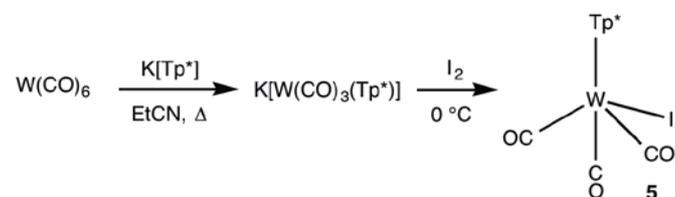
Alkynes are ubiquitous in organometallic chemistry, though the chemistry of hetero-atom substituted alkynes has received somewhat less attention. In the case of chalcogen substituted alkynes (alkynylchalcogenoethers,  $\text{RAC}\equiv\text{CR}'$ ,  $\text{A} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) the majority of reports concern the simple formation of  $\pi$ -complexes, though in some cases subsequent rearrangements have been observed involving C–A bond cleavage and bond formation processes.<sup>1</sup> Furthermore, classical alkyne coupling reactions have also been extended to alkynes bearing chalcogenolate substituents.<sup>2</sup> A characteristic feature of alkyne complexes in which the metal centre has a comparatively low d-occupancy, most commonly  $d^4$ , is the possibility that  $\text{MC}_2$  in-plane bonding, adequately described within the Dewar-Chatt-Duncanson paradigm, is supplemented by  $\pi$ -donation from the occupied  $\pi$ -bond orthogonal to this plane – so-called 4-electron interactions.<sup>3</sup> It might reasonably be anticipated that inclusion of positively mesomeric alkyne substituents such as chalcogenolates might perturb such interactions.

Although there is now a substantial, albeit sporadic, amount of spectroscopic and structural data available for alkynylchalcogenoether complexes, none relate to a single complete homologous series that vary in the identity of the chalcogen alone. We therefore considered that it would be useful to provide a benchmark for assessing variations in the nature of alkyne binding as a function of chalcogen with reference to a single series of complexes, all else being equal. All available structural data for mononuclear alkynyl telluroether complexes are limited to those for tungsten ( $d^2$ ) complexes<sup>4a-c</sup> and data for alkynylselenoether complexes are similarly sparse<sup>4c-e</sup> but include further W(IV) examples in addition to  $[\text{W}(\eta^2\text{-MeSeCCTol})(\text{CO})(\text{PPh}_3)(\text{Tp})]\text{I}$ , although this complex arises not from coordination of the free alkyne, but via *Se*-alkylation of the related selenoketenyl complex.<sup>4f</sup> In a similar manner, alkoxyalkyne complexes, though comparatively numerous, almost exclusively are derived from the coupling of CO at a metal centre with a carbonyl, carbyne or isonitrile ligand followed by electrophilic attack at oxygen. Herein we report the first example of a complete series, including full structural and spectroscopic data.

## Results

Templeton<sup>5</sup> and Connelly<sup>6</sup> have investigated in detail the synthesis, properties and reactivity of alkyne complexes of the form  $[\text{M}(\eta^2\text{-RC}\equiv\text{CR}')(\text{CO})_2(\text{Tp}^*)]^+$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Tp}^* =$  hydrotris(dimethylpyrazolyl)borate). Accordingly, the coordination of alkynes to the cationic ' $d^4\text{-M}(\text{CO})_2(\text{Tp}^*)^+$ ' fragment is well understood and fully consistent with the 4-electron ( $\sigma+\pi$ )-donor/ $\pi$ -acceptor bonding description.<sup>3</sup> Furthermore, structural data are available not only for complexes of conventional alkynes,  $[\text{W}(\eta^2\text{-MeC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]^+$ <sup>5</sup> and  $[\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]^{n+}$  ( $n = 0, 1$ ),<sup>6</sup> but also for the bis(thiolato)alkyne salts  $[\text{W}(\eta^2\text{-RSC}\equiv\text{CSR})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  ( $\text{R} = \text{CH}_2\text{Ph}$ ,<sup>1h</sup>  $\text{C}_2\text{H}_4\text{SiMe}_3$ <sup>1j</sup>). Accordingly, synthetic routes to the new salts  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  ( $\text{E} = \text{O}$  **[1]BF<sub>4</sub>**,  $\text{S}$  **[2]BF<sub>4</sub>**,  $\text{Se}$  **[3]BF<sub>4</sub>**,  $\text{Te}$  **[4]BF<sub>4</sub>**) were explored. Two comparatively general approaches to the syntheses of alkyne complexes  $[\text{M}(\text{alkyne})(\text{CO})_2(\text{Tp}^*)]^+$  have been described previously;<sup>4b</sup> (i) The oxidation of  $[\text{W}(\text{CO})_3(\text{Tp}^*)]^+$  by ferrocenium salts in the presence of alkyne or (ii) Halide

abstraction by silver salts from  $[\text{W}(\text{CO})_3(\text{Tp}^*)]$  (**5**) in the presence of alkyne. We have employed the latter approach due to the ready availability of **5**, the synthesis of which we have refined such that it is now conveniently available in 'one pot' in *ca* 80% yield from  $[\text{W}(\text{CO})_6]$  (Scheme 1; see Experimental Section). Thus heating  $[\text{W}(\text{CO})_6]$  and  $\text{K}[\text{Tp}^*]$  in propionitrile followed by cooling to 0°C and treating with iodine results in precipitation of **5** (*ca* 80% yield) in sufficient purity for subsequent synthetic applications.



Scheme 1 One pot synthesis of  $[\text{W}(\text{CO})_3(\text{Tp}^*)]$  **5**.

The results of a crystallographic study of **5** are summarized in Figure 1 and call for little comment other than to note that the molecular geometry in the solid state is, as would be inferred from infrared and low-temperature <sup>1</sup>H NMR data (-80°C), an octahedron in which a  $\text{C}, \text{C}', \text{I}$  face is capped by one carbonyl ligand. The pyrazolyl group that is *pseudo-trans* to iodide has a marginally shorter (6-9 e.s.d.) W–N bond length (2.207(3)Å) relative to those that are *pseudo-trans* to carbonyl ligands (2.225(3), 2.235(3)Å). This low-symmetry ( $C_s$ ) geometry is not maintained in solution under ambient conditions, with <sup>1</sup>H and <sup>13</sup>C NMR data<sup>5b</sup> indicating single pyrazolyl and carbonyl environments, *i.e.*, either a static  $\text{C}_{3v} 3.3.1$  arrangement in which the  $\text{C}, \text{C}', \text{C}''$ -tricarbonyl face is capped by an iodide ligand, or more likely, the operation of a facile fluxional process.

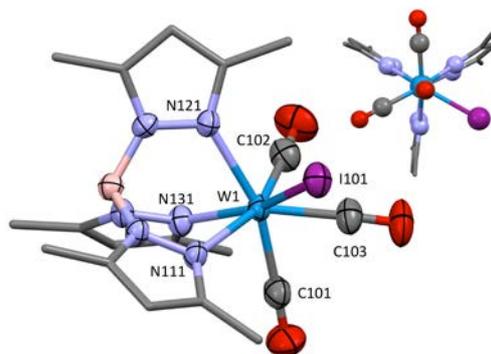
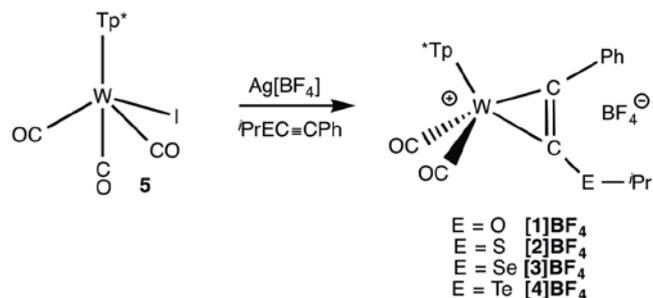


Fig. 1 Molecular structure of **5** in a crystal of  $5_3\cdot\text{EtCN}$  with 60% probability displacement ellipsoids and hydrogen atoms omitted. One of three crystallographically independent molecules shown. Inset: View along W–B vector. Selected bond lengths (Å): W101–I101 2.8695(3), W101–N111 2.225(3), W101–N121 2.235(3), W101–N131 2.207(3), W101–C101 2.003(5), W101–C102 1.992(5), W101–C103 1.985(5).

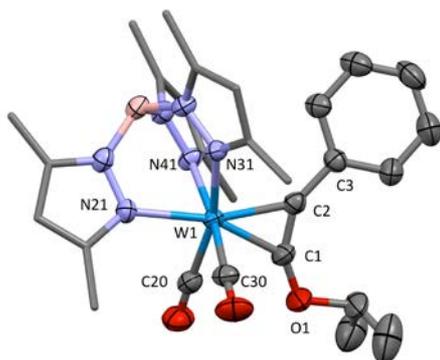
Treating a dichloromethane solution of **5** and the appropriate alkyne in the dark at 0°C with  $\text{AgBF}_4$  resulted in deposition of  $\text{AgI}$  and formation a green ( $\text{A} = \text{O}, \text{S}, \text{Se}$ ) or orange ( $\text{A} = \text{Te}$ ) solution. Filtration followed by concentration and then dilution with diethyl ether provided the desired salts  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  ( $\text{E} = \text{O}$  **1.BF<sub>4</sub>**,  $\text{S}$  **2.BF<sub>4</sub>**,  $\text{Se}$  **3.BF<sub>4</sub>**,  $\text{Te}$  **4.BF<sub>4</sub>**) in 31-65% yield following recrystallisation from dichloromethane/diethyl ether (Scheme 2). In the case of **[1]BF<sub>4</sub>**

an additional cryostatic (-33 °C) chromatographic purification step was required.

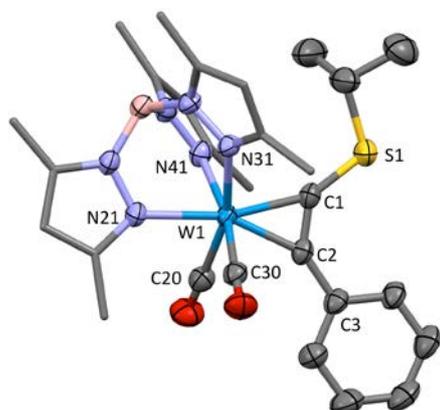


**Scheme 2** Synthesis of the salts  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]\text{BF}_4$  (E = O, S, Se, Te).

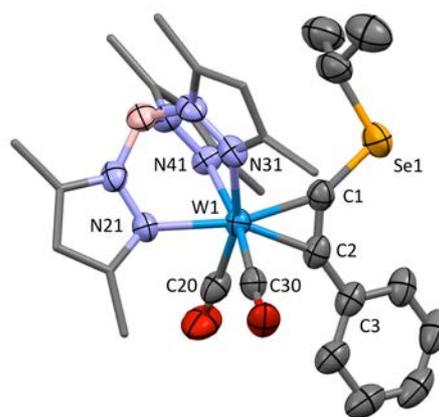
In contrast to the thioether complex  $[\text{Ru}\{\sigma\text{-S}(\text{C}\equiv\text{CSMe})\text{Me}\}(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$  observed by Angelici<sup>1a</sup> *en route* to the alkyne complex  $[\text{Ru}(\eta^2\text{-MeSC}\equiv\text{CSMe})(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$  there is no evidence for initial coordination *via* the chalcogen although this would seem most likely, followed by rapid rearrangement. In the case of Angelici's complex, the alkyne coordination would be destabilized due to a repulsive interaction between the alkyne  $\pi$ -donor orbital (orthogonal to the  $\text{RuC}_2$  plane) and the full ( $d^6$ ) set of  $t_{2g}$ -type orbitals. This most likely contributes not only to the barrier to  $\sigma\text{-S}/\eta^2\text{-C,C'}$  isomerization but also to the remarkable subsequent chemistry that the coordinatively activated alkyne undergoes.



**Fig. 2** Molecular structure of  $[\mathbf{1}]^+$  in a crystal of  $[\mathbf{1}]\text{BF}_4$  with 60% probability displacement ellipsoids and hydrogen atoms omitted.



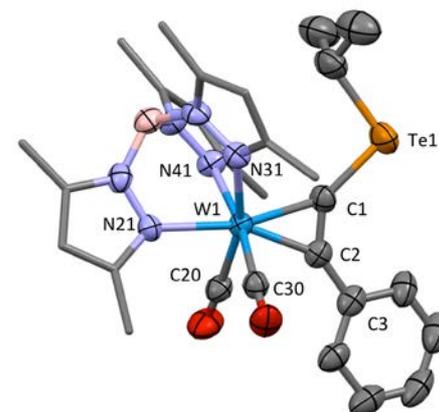
**Fig. 3** Molecular structure of  $[\mathbf{2}]^+$  in a crystal of  $[\mathbf{2}]\text{BF}_4$  with 60% probability displacement ellipsoids and hydrogen atoms omitted.



**Fig. 4** Molecular structure of  $[\mathbf{3}]^+$  in a crystal of  $[\mathbf{3}]\text{BF}_4$  with 60% probability displacement ellipsoids and hydrogen atoms omitted.

**Table 1. Structural data for cationic alkyne complexes  $[\text{W}(\eta^2\text{-}^i\text{PrEC}\equiv\text{CPh})(\text{CO})_2(\text{Tp}^*)]^+$**

E =	$[\mathbf{1}]^+$ O	$[\mathbf{2}]^+$ S	$[\mathbf{3}]^+$ Se	$[\mathbf{4}]^+$ Te
<i>Bond Lengths (Å)</i>				
W–N21	2.203(2)	2.205(2)	2.190(3)	2.197(3)
W–N31	2.213(2)	2.194(2)	2.195(3)	2.198(3)
W–N41	2.186(2)	2.175(2)	2.166(3)	2.175(3)
W–C20	2.015(3)	2.029(3)	2.010(4)	2.014(4)
W–C30	2.054(3)	2.042(3)	2.039(4)	2.041(4)
W–C1(E)	2.050(3)	2.048(4)	2.055(4)	2.052(4)
W–C2(Ph)	2.050(3)	2.058(4)	2.046(4)	2.057(4)
C1–C2	1.335(4)	1.342(4)	1.338(6)	1.332(5)
C2–C3	1.447(4)	1.457(4)	1.447(5)	1.456(5)
C1–E	1.290(4)	1.676(3)	1.823(4)	2.029(4)
<i>Bond Angles (°)</i>				
N31–W–C20	164.8(1)	164.3(1)	162.3(1)	162.9(1)
N41–W–C30	173.3(1)	168.6(1)	171.1(1)	171.6(1)
C20–W–C30	86.1(1)	89.0(1)	87.8(2)	87.0(2)
C2–W–C20	72.7(1)	77.2(1)	76.8(2)	77.3(2)
C2–W–C30	81.5(1)	81.0(1)	81.0(2)	80.3(1)
C1–C2–C3	144.5(3)	133.7(2)	141.7(4)	140.9(4)
C2–C1–E	149.3(3)	135.7(3)	135.7(3)	137.6(3)
C1–E–C( <i>i</i> -Pr)	119.9(3)	109.2(1)	102.7(2)	99.1(2)

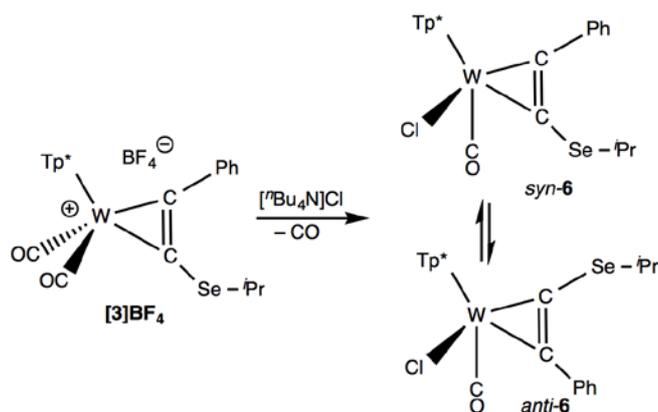


**Fig. 5** Molecular structure of  $[\mathbf{4}]^+$  in a crystal of  $[\mathbf{4}]\text{BF}_4$  with 60% probability displacement ellipsoids and hydrogen atoms omitted.

Table 1 summarizes key geometric features for the cationic complexes  $[\mathbf{1}]^+ - [\mathbf{4}]^+$  and the most immediately obvious point is that the ether complex  $[\mathbf{1}]^+$  is unique in having the O<sup>*i*</sup>Pr group proximal to the  $\text{W}(\text{CO})_2$  unit whilst the remaining examples have the E<sup>*i*</sup>Pr (E = S, Se, Te) group distal and nestled in the cleft provided by two pyrazolyl groups. We suggest that this is purely

a solid state effect since NMR studies (*vide infra*) indicate that both rotamers of **[1]**<sup>+</sup> co-exist in solution and have very comparable energies. Throughout the series, neither of the bond lengths between tungsten and the alkyne vary to any crystallographically significant extent. Indeed, essentially all geometric features are close to invariant with the exception of the increase in C–E bond lengths with increasing covalent radii of the chalcogen in addition to the commonly observed contraction in angles at the chalcogen towards 90° as the hybridization trends from *sp*<sup>3</sup> (E = O) to *p*<sup>3</sup> (E = Te).

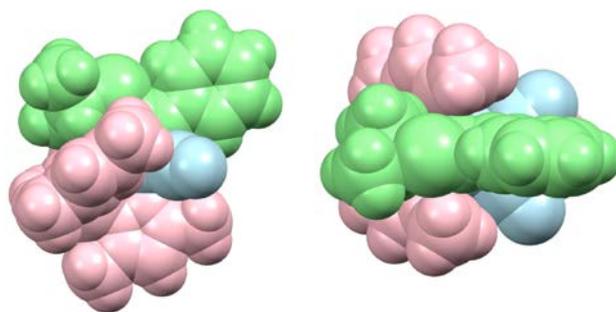
In addition to the salts **[1]BF**<sub>4</sub> – **[4]BF**<sub>4</sub>, the neutral complex  $[\text{W}(\eta^2\text{-}i\text{PrSeC}\equiv\text{CPh})\text{Cl}(\text{CO})(\text{Tp}^*)]$  (**6**) was synthesized cleanly by treatment of the salt **[3]BF**<sub>4</sub> with excess [<sup>n</sup>Bu<sub>4</sub>N]Cl in dichloromethane (Scheme 3).



**Scheme 3** Synthesis of the isomeric complexes  $[\text{W}(\eta^2\text{-}i\text{PrSeC}\equiv\text{CPh})(\text{CO})\text{Cl}(\text{Tp}^*)]$  (**6**)

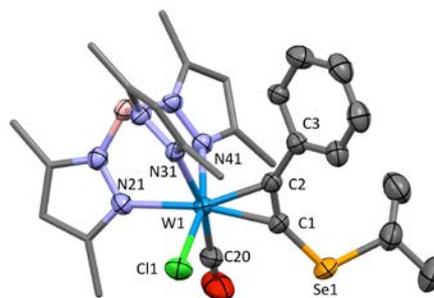
Attempts to similarly prepare the corresponding iodide analogue using [<sup>n</sup>Bu<sub>4</sub>N]I were however unsuccessful, and afforded only the chloro complex **6**, the chloride ligand being derived from the solvent. Incorporation of a solvent-derived chloride ligand similarly occurred during the reaction of  $[\text{W}(\text{S}_2\text{CNEt}_2)(\text{CO})_2(\text{Tp}^*)]$  with 2-butyne-1,4-diol in refluxing 1,2-dichloroethane to provide  $[\text{W}(\eta^2\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})(\text{CO})\text{Cl}(\text{Tp}^*)]$ .<sup>7</sup> Dichloromethane is a far less reactive solvent than 1,2-dichloroethane and furthermore Connelly has prepared related iodo or bromo complexes of simple hydrocarbon alkynes in dichloromethane without any indication of chloride incorporation.<sup>6</sup> The abstraction of chloride from dichloromethane by **[3]**<sup>+</sup> is therefore curious, though entirely reproducible. Attempts to synthesise  $[\text{W}(\eta^2\text{-}i\text{PrSeC}\equiv\text{CPh})\text{I}(\text{CO})(\text{Tp}^*)]$  by thermal decarbonylation of **5** in the presence of *i*PrSeC≡CPh were also unsuccessful, with a variety of products being evident (thin layer chromatography), although none was sufficiently predominant to allow isolation. In the case of diphenylacetylene, Templeton has suggested that unfavorable steric interactions between the alkyne and bulky Tp\* ligands might discourage the formation of  $[\text{W}(\eta^2\text{-PhC}\equiv\text{CPh})\text{I}(\text{CO})(\text{Tp}^*)]$ .<sup>5b</sup> Given the isolation of **[3]BF**<sub>4</sub> and both conformers of **6** from an alternative route, steric factors do not appear to ultimately preclude the formation of  $[\text{W}(\eta^2\text{-}i\text{PrSeC}\equiv\text{CPh})\text{I}(\text{CO})(\text{Tp}^*)]$ . Indeed a space-filling representation of **[3]**<sup>+</sup> (Figure 6) indicates that the Tp\*W unit presents an ideal cleft for accommodating alkyne coordination. We might therefore conclude that failure to obtain the iodide analogue reflects kinetic issues and that the plethora of complexes

observed from the thermal reaction possibly arises from C–Se bond cleavage under the forcing conditions required.

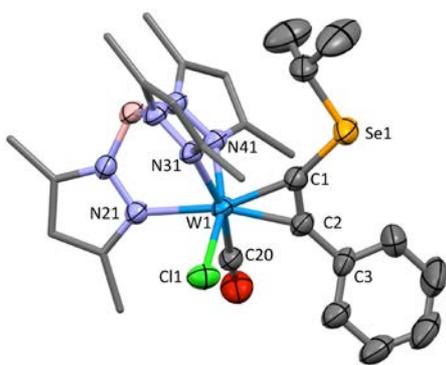


**Fig. 6** Coordination cleft (two views) for alkynes (green) presented by the '(Tp\*)W(CO)<sub>2</sub>' fragment (pink and blue)

The complex **6** exists as an approximately 1:1 mixture of isomers in solution that are related *via* alkyne rotation (*vide infra*) which may however be separated by solvent-dependent recrystallisation (conditions: room-temperature diethyl ether **syn**-**6** and (Figure 7); low temperature dichloromethane/pentane, *anti*-**6** (Figure 8)). Following Templeton, the terms *syn* and *anti* describe the disposition of the chalcogen alkyne substituent relative to the CO ligand(s). When either of these isomers is re-dissolved, re-equilibration of the isomer distribution slowly occurs in solution at ambient temperature, suggesting that there is no ligand property sufficiently dominant as to create a substantial alkyne preference between the available orientations. A related phenomenon has previously been exploited by Harman, whereby selective crystallisation of an η<sup>2</sup>-arene complex  $[\text{W}(\eta^2\text{-MeOPh})(\text{NO})(\text{PMe}_3)(\text{Tp})]$  (Tp = hydrotris-(pyrazolyl)borate) afforded one rotamer. Subsequent dissolution in the presence of a reagent that reacted more rapidly than the isomer equilibration provided stereoselectivity of reaction products.<sup>8</sup> However, to the best of our knowledge *syn* and *anti*-**6** represent the first example of a pair of structurally characterized alkyne complex rotamers. Considering the smallest alkyne, for which steric factors should be minimized, Templeton has estimated from NMR studies that the barrier to ethyne rotation in  $[\text{W}(\eta^2\text{-HCCH})(\text{CO})\text{I}(\text{Tp}^*)]$  is approximately 80 kJmol<sup>-1</sup>.<sup>9</sup>



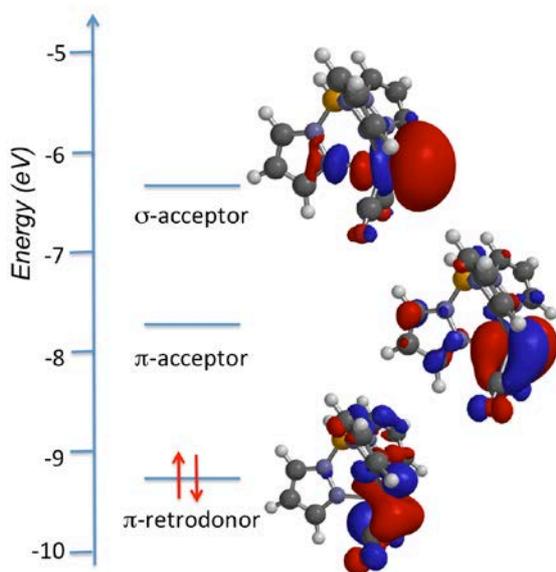
**Fig. 7** Molecular structure of *syn*-**6** in a crystal of *syn*-**6** with 60% probability displacement ellipsoids and hydrogen atoms omitted.



**Fig. 8** Molecular structure of *anti-6* in a crystal of *anti-6* with 60% probability displacement ellipsoids and hydrogen atoms omitted.

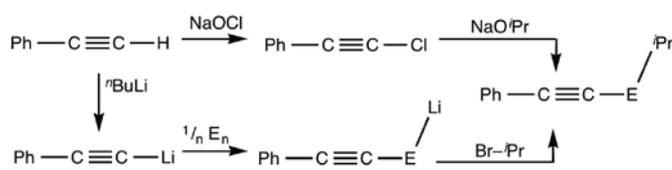
## Discussion

**The Metal Centre.** As noted above, a variety of alkyne complexes of the form  $[M(\eta^2\text{-RCCR})(\text{CO})_2(\text{Tp}^*)]^+$  ( $M = \text{Mo}, \text{W}$ ) are known and the  $d^4\text{-M}(\text{CO})_2(\text{Tp}^*)^+$  fragment has already provided a versatile and informative platform for investigating 4-electron alkyne coordination. For illustrative purposes, Figure 9 displays the topology of the frontier orbitals that this fragment presents to an alkyne ligand, derived from the coordinates for **[1]BF<sub>4</sub>** following removal of the alkyne, counteranion and the pyrazole methyl substituents. Thus the metal has acceptor orbitals of both  $\sigma$  and  $\pi$ -symmetry with respect to the metal-alkyne(centroid) vector in addition to an occupied orbital for retrodonation to the alkyne.



**Figure 9** Frontier orbitals of the hypothetical cationic  $(\text{Tp})\text{W}(\text{CO})_2^+$  fragment relevant to alkyne binding.

**The Free Alkynes.** The alkynes  ${}^i\text{PrEC}\equiv\text{CPh}$  ( $E = \text{O}, {}^{10}\text{S}, {}^{11}\text{Se}, {}^{1f}\text{Te}^{12}$ ) have been described previously. The ether is reported to form from phenylchloroacetylene and  $\text{NaO}^i\text{Pr}$ <sup>10</sup> however we were only able to isolate small amounts of impure material, even when  $[\text{Pt}(\text{PPh}_3)_4]$  was used as mediator. Reported procedures for the remaining heavier analogues were however found to be reliable and followed the general sequence of lithiating phenylacetylene with  ${}^n\text{BuLi}$  followed by treatment with elemental chalcogen and finally isopropyl bromide (Scheme 4).



**Scheme 4** Synthesis of alkynylchhalcoethers  $\text{PhC}\equiv\text{CE}^i\text{Pr}$  ( $E = \text{O}, \text{S}, \text{Se}, \text{Te}$ ).

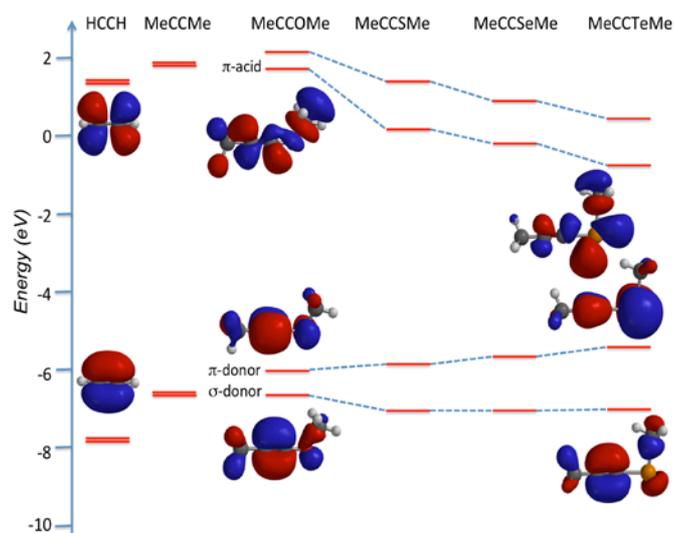
Each of the alkynes is a liquid and no structural data are available. Accordingly, the gas-phase structures were calculated (DFT: B3LYP-LACVP), revealing that variation in the chalcogen has negligible effect on the C–C bond length but does give rise to the expected progressive decrease in bond angle at the chalcogen on descending the group (Table 2).

**Table 2. Geometric properties calculated for the alkynyl chhalcoethers  $\text{PhC}\equiv\text{CE}^i\text{Pr}$ .**

E =	$r_{\text{C}\equiv\text{C}}/\text{\AA}$	C–E–C/ $^\circ$
O	1.216	117.60
S	1.221	100.75
Se	1.222	97.94
Te	1.225	95.54

Similar trends are observed for the simpler methylpropynyl chhalcoethers ( $\text{MeC}\equiv\text{CEMe}$ ,  $E = \text{O}, \text{S}, \text{Se}, \text{Te}$ ) and so for illustrative purposes, these are discussed in more detail. In the context of the Dewar-Chart-Duncanson description, adapted to include the possibility of the alkyne acting as a  $\pi$ -donor orthogonal to the  $\text{MC}_2$  plane, the valence frontier orbitals of interest correspond primarily to in-plane occupied  $\pi^b$  and empty  $\pi^*$  orbitals of the  $\text{C}\equiv\text{C}$  bond in addition to the occupied  $\pi^b$  orbital normal to the  $\text{MC}_2$  plane. Whilst the familiar orbitals of axially symmetric ethyne comprise degenerate  $\pi^b$  and  $\pi^*$  pairs, this degeneracy is lifted by conjugation with the chalcogen orbital(s). Figure 10 depicts the variation in energy (DFT: B3LYP-LACVP) on descending group 16 for the four frontier  $\pi$ -orbitals of interest in addition to illustrating the topology of these orbitals for the extreme congeners ( $E = \text{O}, \text{Te}$ ) of the series. From Figures 2–8 it is clear that in each case, the iso-propyl methine carbon lies in the  $\text{WC}_2$  coordination plane, such we may disregard the alkyne  $\pi^*$  orbital that would be orthogonal to the  $\text{WC}_2$  plane. Three trends relevant to alkyne coordination are immediately apparent. Firstly, the energy of the in-plane  $\sigma$ -donor orbital, apart from an initial drop in energy from O to S, is essentially invariant across the series and comprises very little chalcogen character. In contrast, the in-plane  $\pi^*$  orbital shows a consistent, progressive and significant drop in energy across the series with increasing contribution from the chalcogen atomic orbital(s) which may be expected to be manifest in steadily increasing  $\pi$ -acidity. Thus in a simple 2-electron alkyne coordination scenario, progressing from  $E = \text{O}$  to  $E = \text{Te}$ , the alkyne will be a more effective *net* acceptor. Within a 4-electron alkyne regime however an electroneutrality serving mechanism is provided by the gradually increasing energy of the orthogonal  $\pi$ -donor orbital and whilst this does not rise as rapidly as the energy of the  $\pi$ -acid orbital falls, it will to some extent off-set this increase in acceptor capacity. It should be stressed, however, that the relative contributions of these three bonding components will vary according to the respective energies (and occupancies) of the three metal orbitals involved.

The infrared data for carbonyl co-ligands provides a convenient means of assessing the net acceptor ability of a ligand when all else is kept equal. Table 3 presents infrared data for the complexes **[1]<sup>+</sup>** - **[4]<sup>+</sup>** in addition to those for the corresponding ethyne and tolane complexes. Notably for the chalcogen complexes, a modest but monotonic decrease is seen in the  $\nu_{CO}$  frequencies and derived Cotton-Kraihanzel CO force constants ( $k_{CO}$ ). This would appear inconsistent with the above arguments for increasing net acidity descending group 16 and it must therefore be surmised that the  $\pi$ -donor component *more than compensates* for the increase in alkyne  $\pi$ -acidity, no doubt reflecting the cationic nature of this particular metal centre.



**Fig. 10** Frontier orbitals of relevance to alkyne coordination for ethyne, but-2-yne and the chalcogenes MeC≡CEMe (E = O, S, Se, Te).

**Table 3. Infrared Data<sup>a</sup> for Alkyne Complexes [W( $\eta^2$ -RC≡CPh)(CO)<sub>2</sub>(Tp\*)]<sup>+</sup>.**

R =	$\nu_{CO}/\text{cm}^{-1}$	$\nu_{CC}/\text{cm}^{-1}$	$k_{CO}/\text{Nm}^{-1}$
H <sup>ref</sup>	2062, 1987	-	16.56
Ph <sup>ref</sup>	2053, 1980	-	16.43
O <sup>Pr</sup>	2054, 1978	1681	16.42
S <sup>Pr</sup>	2049, 1975	1718	16.35
Se <sup>Pr</sup>	2047, 1974	1715	16.33
Te <sup>Pr</sup>	2043, 1970	1717	16.26

<sup>a</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup>Measured as a Nujol mull;  $k_{CO} = 2.0191 \times 10^{-6} \times \Sigma(\nu_{CO})^2$

Carbon-13 NMR data for the complexes **[1]<sup>+</sup>** - **[4]<sup>+</sup>** (Table 4) are generally unremarkable in that the carbonyl resonance is insensitive to variations in the chalcogen, showing only very a modest shift to low frequency. Two alkyne resonances are observed for each complex to comparatively low frequency, this being accepted as characteristic of 4-electron alkyne coordination.<sup>3</sup> One of these is comparatively invariant through the series (188 – 201 ppm) whilst the second spans almost 40 ppm and may therefore be attributed to that bearing the chalcogen substituent. Whilst **[1]BF<sub>4</sub>** crystallised as the rotamer contrary to **[2]BF<sub>4</sub>** – **[4]BF<sub>4</sub>**, NMR data indicate that both rotamers co-exist in solution. Thus the phase-sensitive <sup>1</sup>H NOESY spectrum obtained for **[1]BF<sub>4</sub>** at room temperature confirmed chemical exchange between the two isomers, whilst a

variable temperature NMR study revealed a coalescence temperature of 373 K and associated alkyne rotation barrier of 71 kJmol<sup>-1</sup>. A considerably lower coalescence temperature (183 K) was observed for **[2]BF<sub>4</sub>** however the coincident chemical shifts of the conformers (500 MHz instrument) prevented an estimation of  $\Delta G^\ddagger$ .

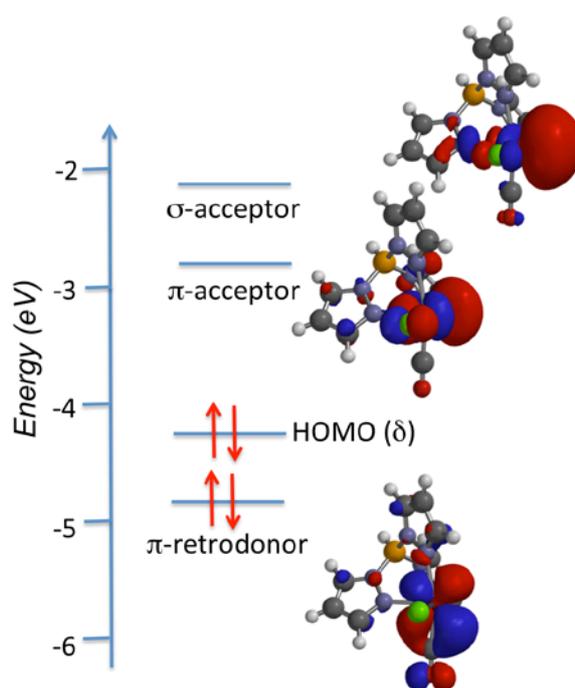
**Table 4 Selected NMR Data<sup>a</sup> for Alkyne Complexes**

**[W( $\eta^2$ -RC≡CPh)(CO)<sub>2</sub>(Tp\*)]<sup>+</sup>.**

R =	$\delta(\text{CO})$	$\delta(\text{CC})$	
H <sup>5b</sup>	215.7	197.1	224.6
Ph <sup>5b</sup>	217.7	200.0	226.4
O <sup>Pr</sup>	215.1 <sup>b</sup>	187.6	237.8
S <sup>Pr</sup>	215.5	198.5	221.1
Se <sup>Pr</sup>	216.5	199.4	219.1
Te <sup>Pr</sup>	217.8	200.8	201.4

<sup>a</sup>Measured in CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>One of the two rotamers observed in solution.

Variable temperature NMR studies of the isomeric mixture of [W( $\eta^2$ -*i*PrSeC≡CPh)(CO)Cl(Tp\*)] failed to demonstrate signal coalescence up to 378 K, suggesting that the barrier to alkyne rotation is high as expected for complexes of this type and discussed in detail by Templeton. In contrast to the cationic '(Tp\*)W(CO)<sub>2</sub><sup>+</sup>' fragment with identical adjacent CO co-ligands, the neutral '(Tp\*)W(CO)Cl' fragment is more  $\pi$ -basic and presents a pair of retrodonative orbitals that differ significantly in energy depending on their involvement with the  $\pi$ -acidic CO or alternatively  $\pi$ -basic Cl co-ligand. This is illustrated for the frontier orbitals for the '(Tp)W(CO)Cl' fragment (Figure 11) derived in the same way as for the '(Tp)W(CO)<sub>2</sub><sup>+</sup>' fragment. Thus coordination of the alkyne C–C vector parallel to the C–O vector maximizes both in plane  $\pi$ -retrodonation from the metal and orthogonal  $\pi$ -donation from the alkyne. The HOMO of the fragment lies in the W(CO)Cl plane, is preoccupied with CO binding and presents only  $\delta$ -symmetry along the metal-alkyne axis.



**Figure 11** Frontier orbitals of the hypothetical '(Tp)W(CO)Cl' fragment relevant to alkyne binding. Note different orientation *cf.* Figure 4.

**Electronic Spectra.** UV/Vis spectra provide the simplest experimental indication of the separation of the frontier orbitals of the free alkynes. The free alkynylchalcogenols all absorb strongly in the UV region (Table 5) and exhibit closely similar absorption maxima with weakly-structured bands. The spectra are characterized by intense, Laporte-allowed  $\pi-\pi^*$  transitions near 250 nm, with shoulders near 260 nm, and tails extending to 400 nm. As the  $\pi$ -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 the telluroether.

**Table 5. UV/Vis Data<sup>a</sup> for Free Alkynes RC≡CPh.**

R =	$\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )
O <sup>i</sup> Pr	249 (11,930)
S <sup>i</sup> Pr	242 (13,140), 264 (10,280)
Se <sup>i</sup> Pr	250 (10,850), 263 (8,820)
Te <sup>i</sup> Pr	255 (12,570), 269 (10,760), 291 (8,855), 350 (1,093)

<sup>a</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub>, *ca* 4 × 10<sup>-3</sup> M.

The energy level gradations shown in Figure 10 for MeC≡CMe suggest that the incorporation of increasingly heavier chalcogen atoms into the alkyne framework leads to contraction of the HOMO-LUMO energy gap and the experimental results agree well with this prediction. The introduction of increasingly  $\pi$ -basic 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 auxochromic 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 [1]BF<sub>4</sub> – [4]BF<sub>4</sub> are vividly colored, as is typical of [W( $\eta^2$ -RC≡CR)(L)(CO)(Tp\*)] compounds. The oxygen-, sulfur-, and selenium-containing salts are the characteristic bright green color but a dramatic color change to orange occurs upon coordination of the alkynyltelluroether. The absorption maxima that produce the brilliant visible green colors range from 14900 to 15500 cm<sup>-1</sup> ( $\lambda_{\max \text{ av}}$  657 nm) with  $\epsilon$  between 135 and 185 M<sup>-1</sup> cm<sup>-1</sup> (Table 6, Figure 12a) (NB: the color of the tellurium analogue is dictated by the strong absorption near 480 nm with  $\epsilon$  8200 M<sup>-1</sup> cm<sup>-1</sup>, as discussed below). A similar absorption near 700 nm is observed for a variety of [W( $\eta^2$ -RC≡CR)(L)(CO)(Tp\*)] compounds.<sup>13</sup> 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→LUMO transition localised in the d $\pi$  manifold of the d<sup>4</sup> tungsten centre, i.e., a symmetry-forbidden d→d transition between orbitals not intimately involved in metal–alkyne bonding.

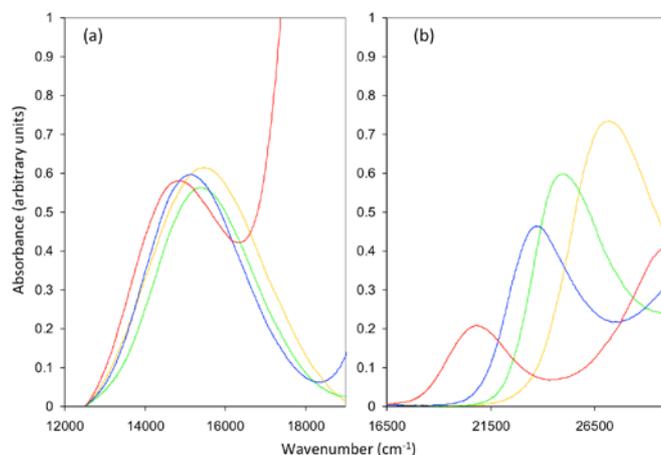
**Table 6. UV/Vis Data<sup>a</sup> for Alkyne Complexes [W( $\eta^2$ -RC≡CPh)(CO)<sub>2</sub>(Tp\*)]BF<sub>4</sub>.**

R =	$\lambda_1/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) <sup>b</sup>	$\lambda_2/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) <sup>c</sup>
O <sup>i</sup> Pr	646 (152)	368 (18,100)
S <sup>i</sup> Pr	650 (135)	401 (14,410)
Se <sup>i</sup> Pr	661 (138)	422 (11,960)
Te <sup>i</sup> Pr	674 (183)	481 (8,200)
(6)	694 (144)	345 (8,040)

<sup>a</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup>4 × 10<sup>-5</sup> M; <sup>c</sup>7.5 × 10<sup>-5</sup> M.

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 ( $\epsilon > 20\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) as well as a second, less intense absorption between 350 and 500 nm ( $\epsilon_{\text{av}}$  1400 M<sup>-1</sup> cm<sup>-1</sup>). The latter absorption shifts towards lower energy upon descending Group 16 as displayed in Figure 12b. The trend in this second  $\lambda_{\max}$  with alkyne substituents suggests that the electronic transition is highly responsive to substituent factors impinging on the alkyne  $\pi$ -donor orbital, favoring its assignment as Laporte-allowed ligand-to-metal-charge-transfer (LMCT) in origin, i.e., involving electron transfer from the filled  $\pi$ -donor orbital of the alkyne to the vacant metal d $\pi$  orbital. In the case of the Te<sup>i</sup>Pr auxochrome, extensive conjugation results in the LMCT absorption protruding strongly into the visible region of the spectrum ( $\lambda_{\max} = 481\text{ nm}$ ,  $\epsilon$  8200 M<sup>-1</sup> cm<sup>-1</sup>), which accounts for the observed orange coloration of [4][BF<sub>4</sub>].

Conversion of the *cis*-W(CO)<sub>2</sub> salt [3]BF<sub>4</sub> to the neutral complex [W( $\eta^2$ -iPrSeC≡CPh)(CO)Cl(Tp\*)] (6) is accompanied by a red-shift for the forbidden d→d transition from 661 nm ( $\epsilon$  138 M<sup>-1</sup> cm<sup>-1</sup>) to 695 nm ( $\epsilon$  135 M<sup>-1</sup> cm<sup>-1</sup>). The lowered energy of this transition can be attributed to the altered d $\pi$  splitting pattern. Both filled d $\pi$  levels are stabilized by  $\pi$ -acceptor carbonyl ligands in the cationic [3]<sup>+</sup>, but in neutral 6, 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 alkyne to metal  $\pi$ -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 cationic dicarbonyl precursor.



**Figure 12** UV-visible spectra of the salts [W( $\eta^2$ -PhCCE<sup>i</sup>Pr)(CO)<sub>2</sub>(Tp\*)]BF<sub>4</sub> (E = O — ; S — ; Se — ; Te —) recorded in CH<sub>2</sub>Cl<sub>2</sub>. (a) d→d transitions; (b) LMCT transitions

## Conclusions

Systematic variation of the  $\pi$ -system of the alkyne, by the inclusion of substituents of increasing  $\pi$ -donor strength that augment  $\pi$ -conjugation, contributes to an understanding of the influence upon  $\pi$ -bonding properties of *this class* of compounds. The geometric and spectroscopic data for the series of alkyne complexes **[1]<sup>+</sup>** - **[4]<sup>+</sup>**, differing only in the identity of the chalcogen atom, provide a basis for interpreting the  $\pi$ -donor contribution to bonding in these complexes.

Calculations for free alkynyl chalcogenides MeC≡CEMe (E = O, S, Se, Te) suggest that whilst the  $\pi$ -basicity of the alkyne increases upon successive incorporation of heavier chalcogens, the  $\pi$ -acid capacity of the alkyne ligand is also increased. Nevertheless, the opposing interactions do not entirely cancel one another. The cationic nature of the 'W(CO)<sub>2</sub>(Tp\*)<sup>+</sup>' fragment would be expected to enhance the former leading to a systematic increase in the net basicity of the alkyne ligands (increasing in the order E = O < S < Se < Te) as evident in the lowering in energy of the  $\nu_{CO}$  absorptions across the series **[1]<sup>+</sup>** - **[4]<sup>+</sup>**.

UV-visible analyses show that the LMCT transition is highly responsive to substituent factors decreasing in energy as the  $\pi$ -basicity of the alkyne increases with heavier chalcogens. In contrast, the key d→d transition is barely effected consistent with it involving essentially metal-based orbitals. Despite modest trends being apparent from spectroscopic data, these do not translate to significant geometric responses, with the inter- and intra-molecular stacking of aromatic moieties dictating many of the geometric properties.

## Experimental

**General Considerations.** All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line and inert atmosphere (argon) dry-box techniques with dried and degassed solvents. NMR spectra were recorded at 25 °C on a Varian Mercury 300 (<sup>1</sup>H at 300.1 MHz, <sup>31</sup>P at 121.5 MHz), Varian Inova 300 (<sup>1</sup>H at 299.9 MHz, <sup>13</sup>C at 75.47 MHz, <sup>31</sup>P at 121.5 MHz), Varian Mercury 400 (<sup>1</sup>H at 399.9 MHz, <sup>13</sup>C at 100.5 MHz, <sup>31</sup>P at 161.9 MHz, 11B at 128.4 MHz) or Bruker Avance 600 (<sup>1</sup>H at 600.0 MHz, <sup>13</sup>C at 150.9 MHz) spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm and referenced to the solvent peak (<sup>1</sup>H, <sup>13</sup>C) or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) with coupling constants given in Hz. Infrared spectra were obtained from solution and in the solid state (KBr pellets) using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalytical data were obtained from the ANU Research School of Chemistry microanalytical service. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. Data for X-ray crystallography were collected with a Nonius Kappa (Mo) CCD diffractometer (CCDC 1502220-1502226).

**Synthesis of [W( $\eta^2$ -*i*-PrSeC≡CPh)(CO)<sub>2</sub>(Tp\*)][BF<sub>4</sub>]**[3]BF<sub>4</sub>**. In a representative synthesis, a dark brown dichloromethane solution (10 mL) containing [W(CO)<sub>3</sub>(Tp\*)] (**5**: 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<sub>4</sub> (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 equipped with a**

diatomaceous earth 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 **[1]BF<sub>4</sub>**. Yield 0.560 g (65%). IR (Nujol): 2562 w ( $\nu_{BH}$ ), 2043 s, 1958 s ( $\nu_{CO}$ ), 1715 w ( $\nu_{C=C}$ ), 1543 ( $\nu_{C=N}$ ) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2047, 1974 ( $\nu_{CO}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz):  $\delta$  8.24, 7.83 (m × 2, 5 H, C<sub>6</sub>H<sub>5</sub>), 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<sub>3</sub>), 2.65 (septet, 1 H, <sup>i</sup>PrCH), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 7.2, 6 H, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz):  $\delta$  219.1 (PhC≡CSe), 216.5 (WCO), 199.4 (PhC≡CSe), 155.7, 152.5, 150.5, 147.9 (1:2:1:2, Tp\*CCH<sub>3</sub>), 134.7, 134.3, 133.4, 130.7 (C<sub>6</sub>H<sub>5</sub>), 110.1, 108.7 (1:2, Tp\*CH), 42.8 (<sup>i</sup>PrCH), 24.5 (<sup>i</sup>PrCH<sub>3</sub>), 16.8, 15.3, 13.4, 12.6 (1:2:1:2, Tp\*CCH<sub>3</sub>). MS (ESI): *m/z* (%) 761.2 (100) [M]<sup>+</sup>, 733.2 (49) [M - CO]<sup>+</sup>, 705.2 (18) [M - 2CO]<sup>+</sup>. Anal. Found: C, 39.23; H, 4.15; N, 10.22%. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>SeW: C, 39.70; H, 4.05; N, 9.92%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  422 nm ( $\epsilon$  = 11 960 M<sup>-1</sup> cm<sup>-1</sup>), 661 nm ( $\epsilon$  = 138 M<sup>-1</sup> cm<sup>-1</sup>). *Crystal data for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>SeW*, *M<sub>r</sub>* = 847.04, monoclinic, C2/c, *a* = 30.2338(5), *b* = 14.2584(2), *c* = 16.1047(2) Å,  $\beta$  = 109.2096(7)°, *V* = 6556.0(2) Å<sup>3</sup>, *Z* = 8,  $\rho_{calcd}$  = 1.716 Mg m<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 4.693 mm<sup>-1</sup>, *T* = 200(2) K, green plate, 7533 independent measured reflections ( $2\theta \leq 54^\circ$ ), *R*<sub>1</sub> = 0.0231, *wR* = 0.0257 for 5121 independent observed absorption-corrected reflections (*I* > 3 $\sigma$ (*I*)), 437 parameters, CCDC 1502224. 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.

**Synthesis of [W( $\eta^2$ -*i*-PrSC≡CPh)(CO)<sub>2</sub>(Tp\*)][BF<sub>4</sub>]**[2]BF<sub>4</sub>**. Compound **[2]BF<sub>4</sub>** was prepared as a bright green powder following the procedure described for **[3]BF<sub>4</sub>** from isopropyl(2-phenylethynyl)sulfane (0.061 g, 0.35 mmol), [W(CO)<sub>3</sub>(Tp\*)] (**5**: 0.200 g, 0.29 mmol), and AgBF<sub>4</sub> (0.056 g, 0.29 mmol). Yield 0.091 g (40%). IR (Nujol): 2575 w ( $\nu_{BH}$ ), 2052 s, 1969 vs ( $\nu_{CO}$ ), 1718 w ( $\nu_{C=C}$ ), 1544 ( $\nu_{C=N}$ ) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2049, 1975 ( $\nu_{CO}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz):  $\delta$  8.25, 7.81 (m × 2, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.15, 6.07 (s × 2, 1:2 H, Tp\*H), 2.82, 2.59, 2.45, 1.68 (s × 4, 3:6:3:6 H, Tp\*CH<sub>3</sub>), 2.50 (septet, 1 H, <sup>i</sup>PrCH), 0.97 (d(br), <sup>3</sup>J<sub>HH</sub> = 6.0, 6 H, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz):  $\delta$  221.1 (PhC≡CS), 215.5 (WCO), 198.5 (PhC≡CS), 155.7, 152.5, 150.5, 147.9 (1:2:1:2, Tp\*CCH<sub>3</sub>), 134.7, 134.2, 133.1, 130.7 (C<sub>6</sub>H<sub>5</sub>), 110.1, 108.7 (1:2, Tp\*CH), 45.6 (*i*-PrCH), 23.4 (*i*-PrCH<sub>3</sub>), 16.8, 15.2, 13.4, 12.7 (1:2:1:2, Tp\*CCH<sub>3</sub>). MS (ESI): *m/z* (%) 713.2 (100) [M]<sup>+</sup>, 685.2 (78) [M - CO]<sup>+</sup>, 657.2 (29) [M - 2CO]<sup>+</sup>. Anal. Found: C, 41.95; H, 4.25; N, 10.43; S, 4.07%. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>SW: C, 42.03; H, 4.28; N, 10.50; S, 4.01%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  401 nm ( $\epsilon$  = 14 410 M<sup>-1</sup> cm<sup>-1</sup>), 650 nm ( $\epsilon$  = 135 M<sup>-1</sup> cm<sup>-1</sup>). *Crystal data for C<sub>28</sub>H<sub>34</sub>BN<sub>6</sub>O<sub>2</sub>SW·BF<sub>4</sub>*, *M<sub>r</sub>* = 800.15, monoclinic, P2<sub>1</sub>/n, *a* = 10.1686(1), *b* = 24.4955(2), *c* = 13.1753(1) Å,  $\beta$  = 103.1297(5)°, *V* = 3195.98(5) Å<sup>3</sup>, *Z* = 4,  $\rho_{calcd}$  = 1.663 Mg m<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 3.739 mm<sup>-1</sup>, *T* = 200(2) K, green plate, 7324 independent measured reflections ( $2\theta \leq 54^\circ$ ), *R*<sub>1</sub> = 0.0190, *wR* = 0.0218 for 5356 independent observed absorption-corrected reflections (*I* > 3 $\sigma$ (*I*)), 397 parameters, CCDC 1502225.**

**Preparation of [W( $\eta^2$ -*i*-PrTeC $\equiv$ CPh)(CO)<sub>2</sub>(Tp\*)][BF<sub>4</sub>] (**[4]BF<sub>4</sub>**).** Compound **[4]BF<sub>4</sub>** was prepared as a brick-red powder following the procedure described for **[3]BF<sub>4</sub>** from isopropyl(2-phenylethynyl)tellane (0.094 g, 0.35 mmol), [WI(CO)<sub>3</sub>Tp\*] (**5**): 0.200 g, 0.29 mmol), and AgBF<sub>4</sub> (0.056 g, 0.29 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 ( $\nu_{\text{C=N}}$ ) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2043, 1970 s ( $\nu_{\text{CO}}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz):  $\delta$  8.19, 7.83 (m  $\times$  2, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.15, 6.07 (s  $\times$  2, 1:2 H, Tp\*H), 2.78, 2.61, 2.45, 1.65 (s  $\times$  4, 3:6:3:6 H, Tp\*CH<sub>3</sub>), 2.65 (septet, 1 H, *i*-PrCH), 1.31 (d, <sup>3</sup>J<sub>HH</sub> = 6.9, 6 H, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz):  $\delta$  217.8 (WCO), 201.4 (PhC $\equiv$ CTe), 200.8 (PhC $\equiv$ CTe), 155.9, 152.3, 150.6, 147.7 (1:2:1:2, Tp\*CCH<sub>3</sub>), 134.9, 134.6, 133.6, 130.7 (C<sub>6</sub>H<sub>5</sub>), 110.1, 108.9 (1:2, Tp\*CH), 27.5 (*i*-PrCH), 26.8 (*i*-PrCH<sub>3</sub>), 16.8, 15.6, 13.4, 12.6 (1:2:1:2, Tp\*CCH<sub>3</sub>). MS (ESI):  $m/z$  (%) 809.1 (100) [M]<sup>+</sup>, 781.1 (50) [M - CO]<sup>+</sup>, 753.1 (10) [M - 2CO]<sup>+</sup>. Anal. Found: C, 37.73; H, 4.01; N, 9.06%. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>TeW: C, 37.55; H, 3.83; N, 9.38%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  481 nm ( $\epsilon$  = 8200 M<sup>-1</sup> cm<sup>-1</sup>), 674 nm ( $\epsilon$  = 183 M<sup>-1</sup> cm<sup>-1</sup>). *Crystal data for* C<sub>28</sub>H<sub>34</sub>BN<sub>6</sub>O<sub>2</sub>TeW•BF<sub>4</sub>,  $M_r$  = 896.68, monoclinic, *C*2/*c*,  $a$  = 30.5636(5),  $b$  = 14.4234(2),  $c$  = 15.9962(2) Å,  $\beta$  = 109.5840(7)°,  $V$  = 6643.7(2) Å<sup>3</sup>,  $Z$  = 8,  $\rho_{\text{calcd}}$  = 1.791 Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 4.396 mm<sup>-1</sup>,  $T$  = 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, CCDC 1502226. 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 $\equiv$ CPh)(CO)<sub>2</sub>(Tp\*)][BF<sub>4</sub>] *syn/anti-1*BF<sub>4</sub>.** NB: The isopropyl(2-phenylethynyl)ether obtained according to the published procedure contained an inseparable iodobenzene contaminant and was used in excess in subsequent reactions without further purification. The preparation of the salt **[1]BF<sub>4</sub>** as a bright green powder followed a procedure similar to those used for **[3]BF<sub>4</sub>** from isopropoxy(2-phenylethynyl)ether (0.261 g, 1.63 mmol), [WI(CO)<sub>3</sub>(Tp\*)] (**5**): 0.805 g, 1.16 mmol), and AgBF<sub>4</sub> (0.227 g, 1.16 mmol). Due to low alkyne purity it was necessary to subject the crude residue to chromatographic purification (silica gel, 3:1 dichloromethane-acetonitrile, -33 °C), collecting only the major green band. Solvent removal and recrystallisation from dichloromethane-diethyl ether provided pure **[1]BF<sub>4</sub>** as a mixture of the *syn*-**[1]BF<sub>4</sub>** and *anti*-**[1]BF<sub>4</sub>** isomers and data provided relate to the mixture. Yield 0.282 g (31%). IR (Nujol): 2564 w ( $\nu_{\text{BH}}$ ), 2056 s, 1979 s ( $\nu_{\text{CO}}$ ), 1681 w(br) ( $\nu_{\text{C=C}}$ ), 1541 ( $\nu_{\text{C=N}}$ ) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2054, 1978 ( $\nu_{\text{CO}}$ ) cm<sup>-1</sup>. *Anti*-**[1]**<sup>+</sup>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz):  $\delta$  8.23, 7.77 (m  $\times$  2, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.13, 6.10, (s  $\times$  2, 1:2 H, Tp\*H), 3.96 (septet, <sup>3</sup>J<sub>HH</sub> = 6.2, 1 H, *i*-PrCH), 2.82, 2.59, 2.43, 1.78 (s  $\times$  4, 3:6:3:6 H, Tp\*CH<sub>3</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.3, 6 H, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz):  $\delta$  237.8 (PhC $\equiv$ CO), 215.1 (WCO), 187.6 (PhC $\equiv$ CO), 155.6, 152.2, 150.2, 148.2 (1:2:1:2, Tp\*CCH<sub>3</sub>), 133.1 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 134.7, 132.0, 130.5 (C<sub>6</sub>H<sub>5</sub>), 109.9, 108.7 (1:2, Tp\*CH), 87.9 (*i*-PrCH), 22.9 (*i*-PrCH<sub>3</sub>), 16.7, 16.0, 13.3, 12.8 (1:2:1:2, Tp\*CCH<sub>3</sub>). *Syn*-**[1]**<sup>+</sup>: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz):  $\delta$  7.56, 7.33, 6.90 (m  $\times$  3, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.10, 5.95 (s  $\times$  2, 1:2 H, Tp\*H), 5.53 (septet, <sup>3</sup>J<sub>HH</sub> = 6.14, 1 H, *i*-PrCH), 2.63, 2.62, 2.45, 1.48 (s  $\times$  4, 3:6:3:6 H, Tp\*CH<sub>3</sub>), 1.69 (d, <sup>3</sup>J<sub>HH</sub> = 6.3, 6 H, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR

(CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz):  $\delta$  216.1 (WCO), 213.2 (PhC $\equiv$ CO), 211.0 (PhC $\equiv$ CO), 155.4, 152.0, 150.2, 147.6 (1:2:1:2, Tp\*CCH<sub>3</sub>), 135.1 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 133.9, 131.6, 130.0 (C<sub>6</sub>H<sub>5</sub>), 109.7, 108.8 (1:2, Tp\*CH), 88.9 (*i*-PrCH), 23.0 (*i*-PrCH<sub>3</sub>), 16.4, 15.7, 13.3, 12.8 (1:2:1:2, Tp\*CCH<sub>3</sub>). MS (ESI):  $m/z$  (%) 697.1 (47) [M]<sup>+</sup>, 626.1 (100) [M - CO - *i*-Pr]<sup>+</sup>, 598.1 (43) [M - 2CO - *i*-Pr]<sup>+</sup>. Anal. Found: C, 42.24; H, 4.45; N, 10.63%. Calcd. for C<sub>28</sub>H<sub>34</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>3</sub>W•H<sub>2</sub>O: C, 41.93; H, 4.52; N, 10.48%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  368 nm ( $\epsilon$  = 18 100 M<sup>-1</sup> cm<sup>-1</sup>), 646 nm ( $\epsilon$  = 152 M<sup>-1</sup> cm<sup>-1</sup>). *Crystal data for* C<sub>28</sub>H<sub>34</sub>BN<sub>6</sub>O<sub>3</sub>W•BF<sub>4</sub> [**1**]BF<sub>4</sub>,  $M_r$  = 784.0, triclinic,  $P\bar{1}$ ,  $a$  = 10.3774(3),  $b$  = 12.1348(2),  $c$  = 12.8498(3) Å,  $\alpha$  = 77.136(1),  $\beta$  = 88.384(1),  $\gamma$  = 82.709(1)°,  $V$  = 1564.77(6) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{\text{calcd}}$  = 1.664 Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 3.755 mm<sup>-1</sup>,  $T$  = 200(2) K, green plate, 7188 independent measured reflections ( $2\theta \leq 54^\circ$ ),  $R_1$  = 0.0232,  $wR$  = 0.0274 for 5958 independent observed absorption-corrected reflections ( $I > 3\sigma(I)$ ), 437 parameters, CCDC 1502223. 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 [WI(CO)<sub>3</sub>(Tp\*)] (**5**).** Anhydrous K[HB(pzMe<sub>2</sub>)<sub>3</sub>] (10.0 g, 0.0297 mol) and [W(CO)<sub>6</sub>] (9.418 g, 0.0268 mol) were combined in a Schlenk flask containing a magnetic stirring bar. The flask was evacuated and filled with nitrogen gas three times. The nitrogen gas continued flow through the side-arm of the flask as propionitrile (50 mL) was added. The mixture was then deoxygenated by bubbling nitrogen through it via a syringe for 10 minutes. A condenser, which had been separately evacuated and charged with nitrogen, was quickly fitted to the flask under a counter-flow of nitrogen. The flask was placed in an oil bath and heated for 18 hours under reflux and then allowed to cool to room temperature followed by cooling in an ice bath. Iodine (6.80 g, 26.8 mmol) was added portionwise to the yellow-brown solution over 5 minutes and the mixture then allowed to stir for 1 h, after which time methanol (20 mL) was added and the mixture stored in a freezer overnight. The resulting black-brown crystals were isolated by filtration (porosity #3 frit) and washed with cold methanol (2  $\times$  15 mL), dried in vacuo and then stored under nitrogen. Yield 15.11 g (81.6%). A further crop (3-4%) or crystals could be obtained by extended storing of the filtrate at -18 °C. *Crystal data for* C<sub>57</sub>H<sub>71</sub>B<sub>3</sub>I<sub>3</sub>N<sub>19</sub>O<sub>9</sub>W<sub>3</sub> (**5**•3NCEt),  $M_r$  = 2131.01, monoclinic, *C*2/*c*,  $a$  = 49.9924(2),  $b$  = 11.0135(1),  $c$  = 28.9124(2) Å,  $\beta$  = 114.9920(2)°,  $V$  = 14428.38(18) Å<sup>3</sup>,  $Z$  = 8,  $\rho_{\text{calcd}}$  = 1.962 Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha)$  = 6.120 mm<sup>-1</sup>,  $T$  = 200(2) K, brown plate, 16,529 independent measured reflections ( $2\theta \leq 55^\circ$ ),  $R_1$  = 0.0224,  $wR$  = 0.0261 for 10,714 independent observed absorption-corrected reflections ( $I > 3\sigma(I)$ ), 847 parameters, CCDC 1502221.

**Preparation of [W( $\eta^2$ -*i*-PrSeC $\equiv$ CPh)Cl(CO)(Tp\*)] (**6**).** Method 1. A green dichloromethane solution (10 mL) containing [W( $\eta^2$ -*i*-PrSeC $\equiv$ CPh)(CO)<sub>2</sub>(Tp\*)][BF<sub>4</sub>] (**[3]BF<sub>4</sub>**: 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 *syn/anti* isomers. Yield 0.092 g (99%). IR (Nujol): 1902s (vco), 1715w (v<sub>C=C</sub>) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1907s (vco) cm<sup>-1</sup>. Low temperature recrystallisation from dichloromethane–pentane yielded isomer *syn-6*; room temperature dichloromethane–pentane or diethyl ether–pentane recrystallisation yielded the *anti-6* isomer. The *syn* and *anti* isomers were distinguished on the basis of arguments provided by Templeton and Pregosin.<sup>14</sup> *Anti-6*: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz): δ 7.95, 7.61, 7.49 (m × 3, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.01, 5.89, 5.83 (s × 3, 3 H, Tp\*H), 3.16 (septet, <sup>3</sup>J<sub>HH</sub> = 6.8, 1 H, *i*-PrCH), 2.86, 2.53, 2.49, 2.36, 2.29, 1.58 (s × 6, 18 H, Tp\*CH<sub>3</sub>), 1.24, 0.72 (d × 2, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 75.421 MHz): δ 241.3 (WCO), 199.7 (PhC≡CSe), 193.2 (PhC≡CSe), 154.7, 154.6, 150.4, 146.4, 145.4, 144.7 (Tp\*CCH<sub>3</sub>), 139.1 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 130.8, 130.1, 129.0 (C<sub>6</sub>H<sub>5</sub>), 108.1, 108.0, 107.7 (Tp\*CH), 35.5 (*i*-PrCH), 25.2, 23.3 (*i*-PrCH<sub>3</sub>), 16.3, 16.2, 16.0, 12.9, 12.7, 12.6 (Tp\*CCH<sub>3</sub>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> 345 nm (ε = 8040 M<sup>-1</sup> cm<sup>-1</sup>), 694 nm (ε = 144 M<sup>-1</sup> cm<sup>-1</sup>). *Crystal data for C<sub>27</sub>H<sub>34</sub>BClN<sub>6</sub>OSeW*, *M<sub>r</sub>* = 767.68, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 10.8646(1), *b* = 19.5161(2), *c* = 14.7036(2) Å, β = 101.7898(7)°, *V* = 3051.90(6) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.671 Mg m<sup>-3</sup>, μ(Mo Kα) = 5.095 mm<sup>-1</sup>, *T* = 200(2) K, green plate, 6973 independent measured reflections (2θ ≤ 54°), *R*<sub>1</sub> = 0.0179, *wR* = 0.0180 for 5340 independent observed absorption-corrected reflections (*I* > 3σ(*I*)), 343 parameters, CCDC 1502220. *Syn-6*: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 300.075 MHz): δ 7.16, 6.57 (m × 2, 5 H, C<sub>6</sub>H<sub>5</sub>), 5.88, 5.76, 5.72 (s × 3, 3 H, Tp\*H), 4.52 (septet, <sup>3</sup>J<sub>HH</sub> = 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<sub>3</sub>), 1.61, 1.48 (d × 2, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.9, *i*-PrCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 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\*CCH<sub>3</sub>), 137.9 [C<sup>1</sup>(C<sub>6</sub>H<sub>5</sub>)], 128.9, 128.7, 128.2 (C<sub>6</sub>H<sub>5</sub>), 108.3, 108.0, 107.5 (Tp\*CH), 35.9 (*i*-PrCH), 26.7, 23.0 (*i*-PrCH<sub>3</sub>), 16.8, 16.1, 15.0, 12.9, 12.8, 12.7 (Tp\*CCH<sub>3</sub>). (ESI): *m/z* (%) 791.2 (83) [M + Na]<sup>+</sup>, 769.3 (48) [M]<sup>+</sup>, 740.3 (63) [M – CO]<sup>+</sup>, 733.3 (100) [M – Cl]<sup>+</sup>, 705.3 (47) [M – Cl – CO]<sup>+</sup>. Anal. Found: C, 42.39; H, 4.55; N, 10.71%. Calcd. for C<sub>27</sub>H<sub>34</sub>BClN<sub>6</sub>OSeW: C, 42.24; H, 4.46; N, 10.95%. *Crystal data for C<sub>27</sub>H<sub>34</sub>BClN<sub>6</sub>OSeW*, *M<sub>r</sub>* = 767.68, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 10.1041(1), *b* = 18.3646(3), *c* = 16.4175(2) Å, β = 95.6786(8)°, *V* = 3031.44(7) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.682 Mg m<sup>-3</sup>, μ(Mo Kα) = 5.130 mm<sup>-1</sup>, *T* = 200(2) K, green block, 6949 independent measured reflections (2θ ≤ 54°), *R*<sub>1</sub> = 0.0186, *wR* = 0.0190 for 5105 independent observed absorption-corrected reflections (*I* > 3σ(*I*)), 343 parameters, CCDC 1502222.

Method 2. Compound **6** could also be prepared in an analogous manner from excess [Bu<sub>4</sub>N]I (0.26 g, 0.70 mmol) and [W(η<sup>2</sup>-*i*-PrSeC≡CPh)(CO)<sub>2</sub>Tp\*][BF<sub>4</sub>] (0.107 g, 0.126 mmol) in dichloromethane (20 mL) over a period of 6 days.

**Kinetic Study of the formation of *syn-6* and *anti-6*** - [W(η<sup>2</sup>-*i*-PrSeC≡CPh)(CO)<sub>2</sub>Tp\*][BF<sub>4</sub>] (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-*d*<sub>2</sub> in a sealed NMR tube under argon at 25 °C. A <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 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 *K*<sub>eq</sub> = [*anti-6*]/[*syn-6*] = 1.08 (*t*<sub>1/2</sub> ≈ 2 h).

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## Notes and references

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