Hydrogenating an Organometallic Carbon Chain: Buten-yn-diyl (CH=CHC≡C) as a Missing Link

Michael J. Bartlett,^a Benjamin J. Frogley,^a Anthony F. Hill,^{a,*} Manab Sharma,^a Matthew K. Smith^a and Jas S. Ward^a

The sequential reaction of $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ with $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$, and *N*-chlorosuccinimide affords the binuclear tetracarbido complex $[\text{Ru}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$. This may be compared with the first example of a butenyndiyl bridged bimetallic complex $[\text{Ru}_2(\mu\text{-CH=CHC}\equiv\text{C})\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$ which is obtained from the reaction of $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ with $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ followed by carbonylation. Characterisation data are discussed with reference to constituent model complexes $[\text{Ru}(\text{C}\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{CH=CH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ in addition to DFT analysis of the bonding in the complexes $[\text{Ru}_2(\mu\text{-L})\text{Cl}_2(\text{CO})_4(\text{PMe}_3)_4]$ ($\text{L} = \text{C}\equiv\text{C-C}\equiv\text{C}$, $\text{CH=CHC}\equiv\text{C}$, CH=CH-CH=CH). A range of other tetracarbido complexes which may be prepared from $[\text{RuCl}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ is also described and includes $[\text{RuAu}(\mu\text{-C}_4)\text{Cl}(\text{CO})_3(\text{PPh}_3)_3]$, $[\text{RuIr}(\mu\text{-C}_4)\text{Cl}(\text{CO})_3(\text{PPh}_3)_4]$, $[\text{RuIr}(\mu\text{-C}_4)\text{H}(\text{NCMe})(\text{CO})_3(\text{PPh}_3)_4]\text{BF}_4$, $[\text{RuIr}(\mu\text{-C}_4)\text{Cl}(\eta^2\text{-O}_2)(\text{CO})_3(\text{PPh}_3)_4]$, $[\text{Ru}_2\text{Hg}(\mu\text{-C}_4)_2\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$, $[\text{Ru}_2\text{Pt}(\mu\text{-C}_4)_2\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_6]$ and $[\text{Ru}_2(\mu\text{-C}_4)\text{HCl}(\text{CO})_4(\text{PPh}_3)_4]$.

Introduction

While bimetallic complexes spanned by the butadiyn-diyl linkage $\text{L}_n\text{MC}\equiv\text{CC}\equiv\text{CML}_n$ are numerous,¹ a survey of the literature² would appear to suggest that those spanned by derivatives of the butenyndiyl connectivity $\text{L}_n\text{MCR}=\text{CRC}\equiv\text{CML}_n$ (Chart 1) are limited to one cyclometallated example described by Bruce.³ This is perhaps surprising, given the importance and ready availability of enynes in natural product chemistry⁴ and the growing interest in molecular wires in which two metals are spanned by an electronically conducting polycarbonyl chain.^{1,5}

Chart 1. Plausible diyl bridging modes for the C_4H_2 ligand.

Roper's complex $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**)⁶ reacts readily with internal alkynes and diynes to afford simple π -adducts,⁷ though

under more forcing conditions, more complex structures may arise including ruthenacyclopentadienes, and cyclopentadienones *via* alkyne coupling.⁸ Propargylic rearrangement of propargylphosphonium salts induced by **1** affords π -allene complexes⁹ and **1** has been shown to oxidatively add the internal C—C bond of dimetalla-octatetraynes to afford bis(tricarbido) complexes in a rare example of the cleavage of $\text{C}(\text{sp})\text{—C}(\text{sp})$ single bonds.¹⁰ In contrast, terminal alkynes undergo simple, albeit reversible, oxidative addition to afford hydrido-alkynyl complexes *via* facile C—H activation.^{6c,11} We have previously described the first example of a bimetallic construct in which the two metals are spanned by a C_4H bridge¹² that arises from such a reaction of **1** with butadiyne to afford $[\text{RuH}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) followed by reaction with *N*-chlorosuccinimide or chloroform to generate $[\text{RuCl}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ (**3**). This in turn reacts with $[\text{Ru}(\text{THF})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ to afford the mixed alkynyl-vinylidene complex $[\text{Ru}_2(\mu\text{-C}_4\text{H})(\text{CO})_2(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ (Scheme 1). We have therefore now considered whether the intermediate butadiynyl complexes **2** or **3** might also afford access to unprecedented $\text{MCH=CHC}\equiv\text{CM}$ linkages.

Results and discussion

As indicated in Scheme 1,¹² the reaction of **1** with butadiyne results in oxidative addition of the terminal C—H bond to afford **2**. This reaction is reversible, as indicated by the subsequent reaction of **2** with dioxygen (air) to afford $[\text{Ru}(\eta^2\text{-O}_2)(\text{CO})_2(\text{PPh}_3)_2]$, implicating the intermediacy of 'Ru(CO)₂(PPh₃)₂'. Notably, when **1** is treated with only one half an equivalent of butadiyne, or when isolated **2** is treated with a second equivalent of **1**, no further reaction of the remaining terminal C—H bond is apparent, suggesting that if the complex $[\text{Ru}_2\text{H}_2(\mu\text{-C}_4)(\text{CO})_4(\text{PPh}_3)_4]$ (**4**) forms, it does so reversibly and does not accumulate in spectroscopically observable amounts

^a Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.

* Corresponding author. E-mail: a.hill@anu.edu.au

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(IR, $^{31}\text{P}\{^1\text{H}\}$ NMR). Reasoning that the reversibility of C–H activation was responsible for the failure to observe **4**, we con-

Scheme 1. Synthesis of a C_4H -bridged bimetallic ($\text{L} = \text{PPh}_3$). (i) $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**1**); (ii) CHCl_3 or N -chlorosuccinimide; (iii) $[\text{Ru}(\text{THF})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$; (iv) DBU; (v) HPF_6 .

verted **2** to the corresponding chloro derivative **3** which is stable with respect to haloalkyne reductive elimination.¹² In a similar manner, **2** may be converted to the phenylselenolato complex $[\text{Ru}(\text{C}\equiv\text{C}\equiv\text{CH})(\text{SePh})(\text{CO})_2(\text{PPh}_3)_2]$ (**5**) *via* reaction with diphenyldiselenide and again this complex was not found to be prone to alkynylselenoether reductive elimination.

Heterobi- and trimetallic complexes spanned by butadiyn-diyl ($\mu\text{-C}\equiv\text{C}\equiv\text{C}$) ligands.

Further to the previously reported bimetallic complex $[\text{Ru}_2(\mu\text{-C}_4)\text{Cl}(\text{CO})_2(\text{PPh}_3)_4(\eta\text{-C}_5\text{H}_5)]$,¹² the heterobimetallic tetracarbido-bridged complex $[\text{RuAu}(\mu\text{-C}_4)\text{Cl}(\text{CO})_3(\text{PPh}_3)_3]$ (**6**) was obtained *via* the reaction of **3** with $[\text{AuCl}(\text{PPh}_3)]$ in the presence of diethylamine and cuprous iodide (Scheme 2). Gold-terminated polycarbonyl complexes have been shown by Bruce and Zaitseva to serve as remarkably effective transfer agents for the modular elaboration of highly extended carbon-wired bi- and polymetallics.¹³ The most striking feature of the IR spectrum of **6** is the diminished intensity of the $\text{C}\equiv\text{C}$ stretching band, a result arising from the decrease in polarity of the diynyl linkage, which is now capped at either end by a heavy metal. The frequency of this vibration is also lower, a phenomenon typical of substituted acetylides. The shift in the positions of the carbonyl absorptions is marginal (DCM: 2056, 1997 cm^{-1}) suggesting that replacement of the acetylenic proton by a distal 'AuPPh₃' fragment does not significantly influence the net acceptor properties of the butadiynyl ligand. The substitution is further confirmed by the absence of the terminal proton resonance in the ^1H NMR spectrum and the presence of a somewhat broad resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 42.3$, integrating for one phosphorus against the two residing on the ruthenium. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** shows the expected resonances for the carbonyl and triphenylphosphine ligands. The phenyl resonances for the phosphines bound to ruthenium appear as conventional virtual triplets, confirming the *trans*- $\text{Ru}(\text{PPh}_3)_2$ geometry, while the corresponding

resonances for the gold-bound phosphine appear as doublets. The metal-bound carbons of the carbon chain show two bond couplings to the respective phosphine ligand ^{31}P nuclei on the ruthenium ($t, {}^2J_{\text{CP}} = 20.5$ Hz) and gold centres ($d, {}^2J_{\text{CP}} = 26.2$ Hz). Resonances

Scheme 2. Synthesis of bi- and polymetallic tetracarbido bridged complexes ($\text{L} = \text{PPh}_3$). (i) ClAuL , Et_3N ; (ii) $\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2$; (iii) cat. $\text{RhCl}(\text{CO})\text{L}_2$; (iv) $[\text{Ir}(\text{NCMe})(\text{CO})\text{L}_2]\text{BF}_4$; (v) DBU; (vi) $[\text{IrCl}(\text{CO})\text{L}_2]$, HNMe_2 , CuI ; (vii) O_2 (air); (viii) $[\text{Co}_2(\text{CO})_8]$; (ix) *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$, HNMe_2 , CuI .

for the two internal carbons appearing at $\delta_{\text{C}} = 102.2$ and 119.5 could be assigned on the basis of chemical shifts typical for the carbon β to the ruthenium and do not show any resolvable ${}^3J_{\text{PC}}$ or ${}^4J_{\text{PC}}$ couplings.

The neutral mixed ruthenium-iridium tetracarbido complex $[\text{RuIr}(\mu\text{-C}_4)\text{Cl}(\text{CO})_3(\text{PPh}_3)_4]$ (**7**) was obtained *via* two routes, either the reaction of **3** with Vaska's complex in the presence of Et_2NH and CuI , or alternatively *via* a two-step sequence involving the oxidative addition of **3** to $[\text{Ir}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ to afford $[\text{RuIr}(\mu\text{-C}_4)\text{H}(\text{NCMe})(\text{CO})_3(\text{PPh}_3)_4]\text{BF}_4$ [**8**] BF_4 which could be deprotonated (DBU) to afford **7**. By analogy with the simple alkynyl complex $[\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2]$,^{14,15} the complex **7** is air sensitive and readily forms the dioxygen adduct $[\text{RuIr}(\mu\text{-C}_4)\text{Cl}(\eta^2\text{-O}_2)(\text{CO})_3(\text{PPh}_3)_4]$ (**9**), the infrared spectrum of which contains a weak band at 837 cm^{-1} in a region characteristic of iridium dioxygen complexes (835 cm^{-1} for $[\text{Ir}(\text{C}\equiv\text{CPh})(\text{CO})(\text{O}_2)(\text{PPh}_3)_2]$).^{14a} Oxidation is reflected by the movement of the iridium ν_{CO} absorption to a higher frequency,

such that it becomes obscured by that of the antisymmetric ruthenium ν_{CO} mode, an upfield shift of the iridium PPh_3 $^{31}\text{P}\{^1\text{H}\}$ NMR signal to $\delta_{\text{P}} = 3.1$ and a colour change from orange to yellow.

The intermediate salt $[\mathbf{8}]\text{BF}_4$ gives rise to only two resolvable carbonyl bands in the IR spectrum (2053 , 1987 cm^{-1}). Presumably these are the two ruthenium carbonyl modes with the weaker iridium carbonyl absorption being hidden underneath the lower frequency peak at 1987 cm^{-1} . The presence of a hydride on iridium is confirmed by a triplet resonance at $\delta_{\text{H}} = -17.50$ ($^2J_{\text{PH}} = 11.0\text{ Hz}$) in the ^1H NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two resonances, integrating equally at $\delta_{\text{P}} = 21.9$ and -1.8 , however, the higher field iridium resonance appears as a doublet (unless the decoupler is offset from the usual decoupler range) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, providing further evidence for an iridium hydride.

The neutral ruthenium-iridium complex **7** was by necessity characterised under strictly air-free conditions. The IR spectrum showing a low energy carbonyl vibration (1953 cm^{-1}) typical of simpler alkynyl iridium analogues.¹⁴ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum measured at 25°C curiously shows only one peak. Variable temperature NMR spectroscopy was therefore carried out to ascertain if this was due to a fluxional process. Reducing the temperature to -25°C revealed a second peak in the spectrum, at $\delta_{\text{P}} = 21.2$ integrating 1:1 with the ruthenium peak at $\delta_{\text{P}} = 22.5$, confirming that the unexpectedly simple room temperature spectrum simply corresponds to circumstantial coincidence of the Ir–P and Ru–P resonances.

The reaction of $[\text{Co}_2(\text{CO})_8]$ with **3** in benzene under exclusion of light followed by chromatographic purification of the reaction mixture provided an almost quantitative yield of a single brown-black product $[\text{RuCo}_2(\mu\text{-C}_4\text{H})\text{Cl}(\text{CO})_8(\text{PPh}_3)_2]$ (**10**). The formation of **10** involves selective addition of a dicobalt unit to the terminal $\text{C}\equiv\text{C}$ triple bond, no doubt reflecting the steric encumbrance exerted by the phosphines surrounding the $\text{C}\equiv\text{C}$ bond directly attached to ruthenium. There is very little change in the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift from **3**, but a rather large change in the chemical shift for the terminal proton in the ^1H NMR spectrum (from $\delta_{\text{H}} = 1.43$ to 5.64), consistent with the addition having occurred at the $\text{C}\equiv\text{C}$ triple bond most remote from the ruthenium centre. The acquisition of $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound was somewhat compromised by low solubility, although some useful data were obtained. There are three carbonyl resonances; two triplets are observed for the chemically inequivalent ruthenium bound carbonyls, while the broad singlet at $\delta_{\text{C}} = 200.1$ arises from the six carbonyls residing on the dicobaltatetrahedrane. The broadening of this signal is characteristic of coordination to two quadrupolar ($I = 7/2$) ^{59}Co nuclei.

Trimetallic bis(tetracarbido) complexes were obtained *via* the cuprous iodide mediated reactions of **3** with metal dihalides under basic conditions. Thus the reaction of **3** with *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ in the presence of CuI and Et_2NH was complete in five minutes (monitored by solution IR spectroscopy), affording $[\text{Ru}_2\text{Pt}(\mu\text{-C}_4)_2\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_6]$ (**11**). The IR spectrum contains two new carbonyl bands and the $\nu_{\text{C}\equiv\text{C}}$ stretching mode could no longer be seen, presumably due to a gain in symmetry

consistent with a *trans*-phosphine geometry at platinum. The rearrangement from *cis*- $\text{Pt}(\text{PPh}_3)_2$ to the *trans* geometry adopted by **11** most likely reflects a response to the steric clutter about platinum. Examples of platinum complexes with two *trans*-disposed metallated butadiyn-diyl ligands remain rare, with the previous examples each containing group ten metal termini, $[\{\text{L}_n\text{M}\}\text{-C}\equiv\text{C}\text{-C}\equiv\text{C}\text{-Pt}(\text{P}^n\text{Bu}_3)_2\text{-C}\equiv\text{C}\text{-C}\equiv\text{C}\text{-}\{\text{ML}_n\}]$, ($\text{ML}_n = \text{PtCl}(\text{P}^n\text{Bu}_3)_2$ and $\text{PdCl}(\text{P}^n\text{Bu}_3)_2$).¹⁶ The *cis*-bis(tetracarbido)platinum unit has however proven useful for the construction of $\text{Pt}_4(\mu\text{-C}_4)_4$ molecular squares.¹⁷

In a similar manner, treating **3** with $[\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2]$ affords the mercurial derivative $[\text{Ru}_2\text{Hg}(\mu\text{-C}_4)_2\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$ (**12**). The mercury bis(tetracarbido) complexes $\text{Hg}(\text{C}_4\text{ML}_n)_2$ [$\text{ML}_n = \text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$,^{16a} $\text{Ru}(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{Ph}$, $\text{C}_6\text{H}_4\text{Me-4}$),¹⁸ $\text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$, $\text{Ru}(\text{dppe})(\eta\text{-C}_5\text{Me}_5)$ ¹⁹] have been described previously. The complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (**13**) is capable of catalysing the demercuration of bis(alkynyl)mercurials to afford 1,3-dienes,²⁰ and of bis(tricarbido)mercurials to afford dimetalladiyne and tetrayne connectivities.²¹ We find that a similar process occurs when **12** is treated with *ca* 5 mol% of **13** to afford the octacarbido complex $[\text{Ru}_2(\mu\text{-C}_8)\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$ (**14**) although as with **12**, the NMR characterisation is equivocal due to poor solubility and the apparent operation of a fluxional process involving the phosphine ligands. Thus while the formulations of **12** and **14** are plausible, and supported by ESI-MS data, the quality of other characterisation data is insufficient to unambiguously substantiate their identities. Nevertheless, dimetallated octacarbidos $\text{L}_n\text{M}(\text{C}\equiv\text{C})_4\text{-ML}_n$ are a well-established class of compound, extensively documented by Gladysz, Bruce and Low.^{1,22}

The preceding set of reactions (Scheme 2) are generally unremarkable and many are based on previous precedent from related systems developed by Bruce or Gladysz. Taken together, they do however serve to confirm that once the butadiynyl ligand is 'locked in' by conversion of **2** to **3** to obviate reductive elimination, subsequent transformations of the butadiynyl ligand proceed without issue and by analogy with growing precedent. Each however fails when the protocol is applied to **2**.

Diruthenium complexes spanned by butadiyn-diyl ($\mu\text{-C}\equiv\text{CC}\equiv\text{C}$) ligands

As noted above, **2** does not react appreciably with a further equivalent of **1**. In contrast, the reaction of **3** with **1** results in the formation of the binuclear complex $[\text{Ru}_2(\mu\text{-C}_4)\text{HCl}(\text{CO})_4(\text{PPh}_3)_4]$ (**15**, Scheme 3). While this reaction is slowly reversible, treatment with *N*-chlorosuccinimide or chloroform affords the stable symmetrical bimetallic complex $[\text{Ru}_2(\mu\text{-C}_4)\text{Cl}_2(\text{CO})_4(\text{PPh}_3)_4]$ (**16**). The symmetrical nature of the complex is indicated by the appearance of a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and two resonances for the C_4 bridge in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum corresponding to the ruthenium-bound ($\delta_{\text{C}} = 89.9$, tt , $^2J_{\text{CP}} = 20.9$, $^5J_{\text{CP}} = 2.2$) and internal alkynyl carbon nuclei ($\delta_{\text{C}} = 104.6$, $^3J_{\text{CP}} \approx ^4J_{\text{CP}} \approx 3\text{ Hz}$). In addition to the two strong ν_{CO} infrared absorptions (CH_2Cl_2 : 2055 , 1995 cm^{-1}), a weak band was observed at 1952 cm^{-1} , which on the basis of the spectrum calculated for $[\text{Ru}_2(\mu\text{-C}_4)\text{Cl}_2(\text{CO})_4(\text{PMe}_3)_4]$ (*vide infra*)

Scheme 3. Synthesis of enyne-diyl and related complexes ($L = PPh_3$). (i) $\frac{1}{2} Ph_2Se_2$; (ii) $Ru(CO)_2L_3$; (iii) O_2 ; (iv) $CHCl_3$ or N -chlorosuccinimide; (v) $RuHCl(CO)L_3$; (vi) CO ; (vii) NaS_2CNMe_2 .

may be assigned to ν_{as} for the $RuC\equiv CC\equiv CRu$ spine. The formulation of **16** was confirmed by a crystallographic analysis, the results of which are summarised in Figure 1. A wealth of structural data have been provided for symmetrical diruthenium tetracarbido complexes, primarily by Bruce and Low (Table 1).²³ Those observed for **16** do not depart significantly from the emerging norms, other than to note that **16**, which has the longest $Ru-C$ bond length, is the only example involving coordination of a π -acid (CO) *trans* to the butadiynyl ligand, a situation that would be expected to reduce ruthenium-alkynyl retrodonation. With the exceptions of $[Ru_2(\mu-C_4)Cl(dppe)_3(\eta-C_5Me_5)]$,²²ⁱ $[Ru_2(\mu-C_4)Cl(CO)_2(PPh_3)_4(\eta-C_5H_5)]$ ¹² and $[Ru_2(\mu-C_4)(4-Phterpy)_2(PPh_3)_4][PF_6]_2$ ^{23d} all structurally characterised examples involve both termini being of the half-sandwich (3-legged piano-stool) $Ru(PR_3)_2(\eta-C_5R'_5)$ ($R' = H, Me$) type which allows the bulky phosphines on adjacent metals to avoid entanglement (approximate C_i symmetry). There is however indication that significant steric clash occurs between phosphine ligands on adjacent ruthenium centres in **16** such that the $Ru2-C4-P4-P3-C8$ and $Ru1-P2-C6-P1-C1$ coordination planes are canted by 44.5° (Figure 1b) so as to allow the interweaving of the 12 phenyl groups (Figure 1c). This steric clutter also most likely contributes to the bowing of the $RuC\equiv CC\equiv CRu$ spine ($Ru1-C1\cdots Ru2 = 166.7^\circ$; $Ru1\cdots C4-Ru2 = 164.5^\circ$). Notably, a similar twisting of coordination planes is

apparent in Gladysz's diplatinum complex $[Pt_2(\mu-C_4)(C_6F_5)_2\{P(C_6H_4Me-4)_3\}_4]$.²⁴ Thus while *trans*-disposed phosphines may be accommodated *cis* to the butadiynyl on either terminus, this clearly calls for some torsional twisting to avoid steric clash. The differential *trans* influence of chloride and $\mu-C_4$ ligands is manifest such that the $Ru-CO$ bonds *trans* to the alkynyl are marginally elongated relative to those *trans* to the chloride.

Figure 1. (a) Molecular structure of **16** in a crystal of **16**.(CH_2Cl_2)₂ (50% displacement ellipsoids, hydrogens omitted, phenyl groups simplified for clarity). Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $Ru1-C1$ 2.054(6), $Ru2-C4$ 2.051(7), $Ru1-C5$ 1.867(7), $Ru1-C6$ 1.935(7), $Ru2-C7$ 1.875(8), $Ru2-C8$ 1.948(7), $C1-C2$ 1.216(9), $C2-C3$ 1.392(10), $C3-C4$ 1.225(9), $Ru1-C1-C2$ 171.3(6), $C1-C2-C3$ 176.7(7), $C2-C3-C4$ 175.8(7), $Ru2-C4-C3$ 169.3(6). (b) Torsional twist of $Ru2-C4-P4-P3-C8$ and $Ru1-P2-C6-P1-C1$ coordination planes. (c) Space filling representations indicating interweaving of adjacent phosphine ligands.

The possibility that a bimetallic zerovalent diruthenium complex $[Ru_2(\mu-C_4)(CO)_4(PPh_3)_2]$ might be accessible was briefly explored, given that on electron-counting grounds, this would be expected to have a cumulenetic $Ru=C=C=C=Ru$ bond localisation so as to satisfy the 16-electron termini. Unfortunately, while **15** reacted with $AgPF_6$ in acetonitrile to provide $AgCl$ and presumably the rather labile bimetallic $[Ru_2(\mu-C_4)H(CO)_4(NCMe)(PPh_3)_2]PF_6$, subsequent treatment with base (DBU , Et_2NH) failed to result in reductive deprotonation of the metal centre. Similarly, attempts to reduce the dichloro complex **16** with either cobaltocene or amalgamated magnesium failed to result in any observable reduction. Thus although cumulenetic (dimetallahexapentatriene) $[Ru_2(\mu-C_4)(CO)_4(PPh_3)_2]$ remains a plausible complex, synthetic access routes have yet to be identified.

Table 1. Mean geometric parameters for symmetrical diruthenium butadiyndiyls [Ru₂L_{2n}(μ-C₄)]²³

RuL _n	Ru–Cα	Cα≡Cβ	Cβ–Cβ'
Ru(dppm)(C ₅ H ₅) ^{23a}	2.018	1.220	1.385
Ru(dppe)(C ₅ Me ₅) ^{23a,i}	2.002	1.221	1.382
Ru(PPh ₃) ₂ (C ₅ H ₅) ^{23b,d}	1.992	1.225	1.378
Ru(dppe)(C ₅ H ₅) ^{23b}	2.011	1.218	1.396
Ru(μ-dppp)(C ₅ H ₅) ^{23c,b}	2.010	1.218	1.384
Ru(PPh ₃) ₂ (4-Phterpy) ^{23d}	2.001	1.228	1.372
Ru(dppf)(C ₅ H ₅) ^{23j,c}	2.001	1.201	1.411
RuCl(CO) ₂ (PPh ₃) ₂ 16	2.053	1.221	1.392
RuCl(CO) ₂ (PMe ₃) ₂ ^d	2.095	1.208	1.393

^aFor structures with crystallographically distinct bond lengths, the mean value is given; ^bμ-dppp = μ-P,P'-Ph₂P(CH₂)₅PPh₂; ^cdppf = 1,1'-bis(diphenylphosphino)-ferrocene; ^dCalculated (*vide infra*).

Diruthenium complexes spanned by buten-yn-diyl (μ-C≡CCH=CH) ligands

The complex [RuHCl(CO)(PPh₃)₃]²⁵ readily and regioselectively hydroruthenates alkynes, diynes, phosphalkynes and dimetallaocstatetraynes.^{26–28} Amongst the diynes investigated was butadiyne itself, which was found to provide the bimetallic complex [Ru₂(μ-CHCHCHCH)Cl₂(CO)₂(PPh₃)₄].²⁸ A smooth reaction ensues between **3** and [RuHCl(CO)(PPh₃)₃] over 5 minutes at reflux in dichloromethane to afford the dark red bimetallic complex [Ru₂(μ-C₄H₂)Cl₂(CO)₃(PPh₃)₄] (**17**). This compound exhibits three carbonyl absorptions in the infrared spectrum with the carbonyl of the 16-electron fragment appearing at a typically low frequency of 1934 cm⁻¹ (CH₂Cl₂). The ¹H NMR spectrum of this compound contains a doublet resonance at δ_H = 5.23 for the Hβ proton, coupling to the Hα proton of the α carbon; the magnitude of this coupling (³J_{HH} = 15.6 Hz) is consistent with the *trans*-CHα=CHβ regiochemistry expected for concerted hydroruthenation. Satisfactory ¹³C{¹H} NMR data for this compound could not be obtained as decomposition occurred over the acquisition period (confirmed by subsequent ³¹P{¹H} NMR spectroscopy). For further studies, this compound was therefore generally prepared freshly and, where possible, used *in situ*. Thus the reaction of a red solution of **17** with carbon monoxide (1 atmosphere) resulted in an immediate colour change to yellow, indicating rapid reaction to afford [Ru₂(μ-C₄H₂)Cl₂(CO)₄(PPh₃)₄] (**18**) which was found to be much more stable than its precursor. Consistent with the formulation as a tetracarbonyl derivative, the infrared spectrum included four strong absorptions (CH₂Cl₂: 2052, 2035, 1987, 1975 cm⁻¹). Since alkenyl ligands are less effective *net* π-acids than alkynyls, the carbonyl ligands bound to the vinylic end of the molecule participate in retrodonation to a greater extent and hence show lower frequency absorptions. For comparative purposes, the complexes [RuCl(C≡CH)(CO)₂(PPh₃)₂] (2059, 1995 cm⁻¹, *vide infra*) and [RuCl(CH=CH₂)(CO)₂(PPh₃)₂] (2033, 1973 cm⁻¹) have very similar individual absorptions to those found for the 'composite' complex **18**, suggesting little if any mutual coupling between oscillators on the remote ruthenium centres.

The ¹H NMR spectrum of **18** shows the expected resonances for the vinylic protons, which appear as a doublet at δ_H = 5.35 for Hβ and a broadened doublet of triplets at δ_H = 8.07 for the Hα proton (³J_{HH} = 18.3). The ¹³C{¹H} NMR spectrum of **18** revealed a curious reversal in the typical δ_C trend for the alkynyl

carbons with the Ru-C≡C resonance appearing as a triplet at δ_C = 98.2, and the Ru-C≡C- resonance appearing as a singlet at δ_C = 121.4. The carbon nuclei of the vinylic component of the bridge were found as a singlet at δ_C = 124.5, and a triplet at δ_C = 163.4 (²J_{PC} = 14.2 Hz).

The complex **18** was characterised crystallographically (Figure 2) and while this study confirmed the gross formulation, it also revealed a recalcitrant crystallographic problem. The packing of the molecules and accordingly the resulting space group is determined primarily by the bulky 'RuCl(CO)₂(PPh₃)₂' units which effectively conceal the C₄H₂ unit's more subtle influence. The result is that while the local molecular geometry can have no symmetry element other than the identity and (ideally) a mirror plane orthogonal to the P–P vectors, the globular topology that dictates packing allows the molecule to crystallise in a centrosymmetric space group (C2/c) with the encapsulated C₄H₂ linkage being disordered about the crystallographic '2' axis. The molecular geometry is depicted in Figure 2, however this disorder and the requisite modelling constraints obviate a detailed discussion of the geometry of the RuC₄H₂Ru linkage, *i.e.*, the actual point of primary interest. This unanticipated problem is likely to compromise the crystallographic characterisation of any such complex with bulky and identical end groups. Attempts to circumvent this problem involved the synthesis of a less symmetrical compound of the same bridging connectivity. The reaction of Na[S₂CNMe₂] with **17** proceeded rather slowly due to the insolubility of the former in CH₂Cl₂, but was complete within five hours, as marked by the gradual colour change from red to yellow accompanying formation of [Ru₂(μ-C₄H₂)Cl(S₂CNMe₂)(CO)₃(PPh₃)₄] (**19**). The replacement of the chloride on the 18-electron alkynyl ruthenium terminus does not proceed under these conditions. The characterisation of **19** was not significantly different from that of **18**, the exception being that there is one less carbonyl absorption in the infrared spectrum. The ¹H NMR spectrum revealed the two inequivalent methyl resonances of the dithiocarbamate ligand at δ_H = 2.55 and 2.68 indicating restricted rotation about the C–N multiple bond. The vinylic protons of **19** show similar splitting (*trans*-³J_{HH} = 15.6 Hz) to that of the tetracarbonyl analogue **18**, however the resonances are further upfield, *viz.* δ_H = 4.86 for Hβ, Hα obscured by the phenyl resonances (revealed by COSY measurements). The ¹³C{¹H} NMR spectrum is very similar to that of the tetra-carbonyl derivative in regard to the bridging carbon resonances (δ_C = 93.2 (t), 119.8 (s), 121.1 (s) and 158.5 (s)), except that the carbon α to the ruthenium bearing the dithiocarbamate does not appear as a triplet but is slightly broadened, suggesting a small but unresolved triplet coupling to phosphorus.

Figure 2. (a) Molecular structure of **18** in a crystal (50% displacement ellipsoids, aryl hydrogen atoms omitted, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg.): Cl1–Ru1 2.469(1), P1–Ru1 2.392(1), P2–Ru1 2.3939(13), Ru1–C1 1.949(5), Ru1–C2 1.854(5), Ru1–C5 2.13(2), Ru1–C3 2.06(2), C5–C6 1.32(2), C4–C6 1.51(2), C4–C3 1.13(2), P2–Ru1–P1 174.41(4), Ru1–C5–C6 137(1), C6–C4–C3 160(2), Ru1–C3–C4 165(3). (b) Modeling of C≡C–H bridge disorder about the crystallographic 2 axis).

Model ruthenium ethynyl complexes

To assess the nature of the enyn-diyl bridge, model complexes comprising the constituent links were sought. The reaction of **1** with ethynyltrimethylsilane affords the hydrido-alkynyl complex $[\text{RuH}(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (**20**) in 97% yield, as reported by Lavigne previously (Scheme 4).^{6c} As with complex **2**, solutions of **20** exposed to air deteriorate rapidly with formation of the dioxygen adduct $[\text{Ru}(\eta^2\text{-O}_2)(\text{CO})_2(\text{PPh}_3)_2]$, however **20** may be converted to the air-stable derivative $[\text{Ru}(\text{C}\equiv\text{CSiMe}_3)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (**21**, Scheme 4) upon treatment with chloroform. The conversion of **20** to **21** was accompanied by an increase in the energy of the carbonyl stretching frequencies, the disappearance of the metal hydride ^1H NMR resonance, and an upfield shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance. The complex **21** was crystallographically characterised, confirming its geometry (Figure 3). Analysis of the molecular structure reveals the alkynyl Ru–C(3) length is 2.080(2) Å (*i.e.*, longer than in **16**), C(3)–C(4) is 1.173(4) Å and the C(4)–Si length is 1.824(3) Å. Comparison to the previously published complex of similar connectivity, $[\text{trans-Ru}(\text{C}\equiv\text{CSiMe}_3)_2(\text{CO})_2(\text{PEt}_3)_2]$,²⁹ shows only subtle, barely significant, deviation from these bond lengths, Ru–C(1) 2.062(2) Å, C(1)–C(2) 1.221(2) Å and C(2)–Si 1.812(2) Å. The slightly shorter C≡C bond length of **21** possibly reflects the *trans*-coordination of the strong π -acid ligand (CO) to the acetylide compromising retrodonation to the C≡C π^* orbitals.

Scheme 4. Synthesis of ethynyl and related complexes (L = PPh₃). (i) HC≡CSiMe₃; (ii) CHCl₃; (iii) HC≡CH; (iv) *N*-chlorosuccinimide; (v) *N*-bromosuccinimide; (vi) $\frac{1}{2}$ (SC₆H₄Me-4)₂; (vii) HCl; (viii) $\frac{1}{3}$ Ph₂Se₂; (ix) CO.

Figure 3. Molecular structure of **21** (50% displacement ellipsoids, aryl hydrogen atoms omitted, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg.): Cl1–Ru1 2.4452(9), P1–Ru1 2.4092(8), P2–Ru1 2.4002(8), Ru1–C3 2.080(3), Si1–C4 1.825(3), C3–C4 1.172(4), Ru1–C3–C4 177.0(2), Si1–C4–C3 175.5(3).

It was presumed that the parent ruthenium alkynyl could be synthesised from **20** *via* a fluoride assisted proto-desilylation reaction, typically carried out using moist $[\text{nBu}_4\text{N}]\text{F}$ (TBAF) as the

fluoride source. Attempts at desilylation were, however, unsuccessful resulting in partial decomposition to the dioxygen adduct $[\text{Ru}(\text{O}_2)(\text{CO})_2(\text{PPh}_3)_2]$, although most of the material reacted to form an unidentified brown solid. Literature accounts of the attempted proto-desilylation of similar acetylides also report variable success.¹⁹ The presence of the dioxygen adduct suggests that the desired reaction may actually occur, however it was thought that the terminal acetylide was reductively eliminating ethyne, allowing the dioxygen adduct to form. Since decomposition products compromised this synthetic approach, alternative routes to the terminal acetylide were sought. Ethyne itself was found to oxidatively add to the $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2]$ fragment formed in solution from **1** to give $[\text{RuH}(\text{C}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ (**22**) quantitatively. Isolation of the white solid revealed it to be air-stable in the solid state, only undergoing reductive elimination of ethyne in solution. The properties of this compound are similar to those of the silylated analogue, the infrared spectra revealing two carbonyl stretching frequencies (CH_2Cl_2 : 1988, 1959 cm^{-1}), confirming the *cis*-arrangement of carbonyl ligands. The $\nu_{\text{C}\equiv\text{C}}$ stretching frequency is significantly lower than that of **20**, appearing at 2038 cm^{-1} (CH_2Cl_2). That substituted acetylides, in general, display higher $\nu_{\text{C}\equiv\text{C}}$ stretching frequencies than their terminal partners is well established.³⁰ Both of the non-aryl proton resonances in the molecule show coupling to the *trans*-phosphine ^{31}P nuclei, the hydride showing a stronger two bond coupling, $^2J_{\text{HP}} = 20.1$ Hz. Presumably the weaker four bond coupling ($^4J_{\text{HP}} = 2.7$ Hz) of the acetylenic proton is only observable due to enhanced communication through the *sp*-hybridised $\text{C}\equiv\text{C}$ moiety. A solution of **22** in deuterated benzene is completely converted to $[\text{Ru}(\text{O}_2)(\text{CO})_2(\text{PPh}_3)_3]$ during three hours of exposure to air, while a mixture of **22** and diphenyl acetylene in deuterated benzene was found to completely convert to $[\text{Ru}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]$ within five hours under anaerobic conditions.

Several attempts to synthesise $[\text{Ru}(\text{C}\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (**23**) *via* reaction with chloroform were unsuccessful. Initially the conversion proceeded to yield two products, as evident by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. It was suspected that the presence of residual acid (HCl in commercial CHCl_3) was diverting the reaction to partially provide the corresponding metal alkenyl complex (see Scheme 4). This reaction must have been disfavoured in the case of the silylated alkynyl **20**, where a clean reaction was observed. Independent synthesis of the suspected alkenyl side-product $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (**24**) was carried out by low pressure carbonylation of $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (**25**).³¹ Furthermore, careful addition of one equivalent of HCl to **22** cleanly afforded **25**, presumably *via* the vinylidene salt $[\text{RuH}(\text{C}=\text{CH}_2)(\text{CO})_2(\text{PPh}_3)_2]\text{Cl}$ resulting from protonation at the carbon β to ruthenium followed by hydride migratory insertion. The reaction of **22** with *N*-chlorosuccinimide in THF was however found to rapidly effect the desired substitution to form $[\text{Ru}(\text{C}\equiv\text{CH})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (**23**) in high yield and purity. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **23**, the two chemically inequivalent carbonyl carbon nuclei appear as triplets at $\delta_{\text{C}} \sim 190$ showing coupling, to the two chemically equivalent triphenylphosphine ^{31}P nuclei ($^2J_{\text{CP}} \sim 18$ Hz). The

carbon nuclei of the ethynyl ligand were identified at $\delta_{\text{C}} = 101.4$ (t, $^2J_{\text{CP}} = 19.2$, C_α) and 102.3 (s, C_β).

Replacement of the labile hydride ligand of **22** by more strongly coordinating bromo, selenolato or thiolato ligands could be achieved by the reaction of **22** with *N*-bromosuccinimide, diphenyldiselenide or di-4-tolyldisulfide to afford the complexes $[\text{Ru}(\text{C}\equiv\text{CH})\text{X}(\text{CO})_2(\text{PPh}_3)_2]$ (X = Br **26**, SePh **27**, $\text{SC}_6\text{H}_4\text{Me-4}$ **28**), none of which were prone to reductive elimination. The reactions of ruthenium hydrido complexes with disulphides have been described previously by James.³² All four compounds **23**, **26–28** showed very little deviation in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, however the variation between the halo and chalcogenolato complexes in the infrared spectra reflects their relative π -donative capacities. The data in Table 2 suggest, as expected, that the chalcogenolato ligands are stronger π -donors relative to the halides, enhancing retrodonation to the $\pi^*\text{CO}$ orbitals, manifested in lower ν_{CO} infrared frequencies.

Table 2. Selected spectroscopic data for *cis,cis,trans*- $[\text{Ru}(\text{C}\equiv\text{CH})\text{X}(\text{CO})_2(\text{PPh}_3)_2]$

X =	$^{31}\text{P}\{^1\text{H}\}^a$ δ_{P}	ν_{CO} (cm^{-1}) (CH_2Cl_2)	k_{CK}^b (Ncm^{-1})
H (22)	45.1	1988, 1959	15.71
SeC ₆ H ₅ (27)	21.6	2047, 1984	16.38
SC ₆ H ₄ Me-4 (28)	22.1	2048, 1985	16.40
Cl (23)	22.8	2059, 1995	16.57
Br (26)	21.1	2059, 1995	16.57

^a Measured in CD_2Cl_2 (**1**) or CDCl_3 (**2–8**) (ppm). ^b Cotton-Kraihanzel force constant

Although similar arguments might apply to the alkynyl $\nu_{\text{C}\equiv\text{C}}$ frequencies, in practice this reporter appears far less sensitive to such changes in metal π basicity. The complex **23** was structurally characterised, however positional disorder between the ethynyl, carbonyl and chloro ligands rendered the structural model of little interpretive use beyond confirming the identity. The complex **28** was however structurally characterised with more success as a dichloromethane solvate (Figure 4). Structural data associated with the Ru–S–C linkage of non-chelated octahedral ruthenium thiolato complexes cover the comparatively wide ranges 2.396 – 2.528 Å (Ru–S) and 106 – 123° (Ru–S–C)³³ such that those for **28** (2.468 Å, 110.3°) are unremarkable.

Attempted synthesis of 1,3-dimetallated $\mu\text{-C}_4\text{H}_2$ complexes

The methodology employed to prepare **18** was specifically chosen to provide the 1,4-dimetallated geometry (*E*-1,4 Chart 1). We did however briefly consider alternative 1,3-dimetallation but were unable to obtain the necessary building blocks. As noted above, $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (**16**) has been shown to hydroruthenate diphenylbuta-1,3-diyne to provide the coordinatively unsaturated enynyl complex $[\text{Ru}\{\text{C}(\text{C}\equiv\text{Ph})=\text{CHPh}\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$,^{26f} and this was subsequently extended by others to afford the complexes $[\text{Ru}\{\text{C}(\text{C}\equiv\text{CR})=\text{CHR}\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, (R = SiMe₃ (**29**),²⁸ ^{*t*}Bu,³⁴ ^{*n*}Bu³⁵). The crystal structures of both ^{*n*}Bu and ^{*t*}Bu derivatives have been described and provide a point of contrast in that the ^{*t*}Bu derivative clearly involves 5-coordinate ruthenium while the ^{*n*}Bu example displays an interaction between the α -alkynyl group and the ruthenium centre (Table 3).

Figure 4. Molecular structure of **28** in a crystal of **28**.CH₂Cl₂ (50% displacement ellipsoids, phenyl hydrogen atoms omitted, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg.): Ru1–C2 1.887(3), Ru1–C1 1.919(3), Ru1–C3 2.099(3), Ru1–P1 2.413(1), Ru1–P2 2.416(1), Ru1–S1 2.468(1), C3–C4 1.150(4), P1–Ru1–P2 176.41(3), C11–S1–Ru1 110.3(1), C4–C3–Ru1 177.6(3).

Table 3. Selected geometric data for [Ru{C(C≡CR)=CHR}Cl(CO)(PPh₃)₂] and **31**.

R=	α (°)	β (°)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
^t Bu ³⁵	97.8	187.0	2.029	2.631	3.444
ⁿ Bu ³⁶	79.8	211.0	2.081	2.300	2.558
SiMe ₃ (29A) ^d	89.3	195.5	2.058	2.489	3.106
SiMe ₃ (29B) ^d	86.6	204.7	2.066	2.438	2.877
31	112.7	182.7	2.109	2.968	3.928

^dOne of two crystallographically independent molecules.

The molecular structure of **29** has not been described and the initial report noted uncertainty as to the coordination mode.²⁸ Accordingly, the crystal structure of **29** was determined (Figure 5) and found to also involve weak coordination of the α -alkynyl group. Consideration of the structural data for **29** with those for the previously reported butyl derivatives (Table 3) and the more general class of enynyl ligands bound to otherwise 4-coordinate ruthenium,³⁶ [Ru{C(C≡CR)=CHR}L₄]^{0/+} reveals a considerable variation in the degree of coordination of the α -alkynyl substituent, even for very similar ligand sets, *e.g.*, the thiocarbonyl complex [Ru{C(C≡CPh)=CHPh}Cl(CS)(PPh₃)₂]³⁶ⁱ has a near linear (170.1°) C α -C≡C linkage with the alkynyl group too remote to infer any significant interaction with the nevertheless coordinatively unsaturated ruthenium centre. In contrast, the cationic complex [Ru{C(C≡CPh)=CHPh}(CO)₂(PPh₃)₂]⁺ has the most pronounced deformation of the alkynyl group (C α -C≡C = 147.0 Å) arising from significant interaction with the ruthenium

centre (Ru–C = 2.169, 2.231, 2.322 Å), even though this association has been shown to be hemilabile.^{7c} We therefore suggest that little energetic expenditure is associated with the variable nature of this interaction, which most likely responds in part to crystal packing forces, as seen for **29** in which two crystallographically distinct molecules (**29A**, **29B**, Table 3) coexist in the unit cell.

Figure 5. (a) Molecular structure of **29** in a crystal (50% displacement ellipsoids, phenyl groups simplified for clarity). Selected bond lengths (Å) and angles (deg.) for **29B**: Cl1–Ru1 2.495(1), P1–Ru1 2.372(1), P2–Ru1 2.386(1), Ru1–C1 1.808(5), Ru1–C15 2.066(4), Ru1–C16 2.438(4), Ru1–C15–C14 143.9(4), Ru1–C15–C16 86.6(3), C14–C15–C16 129.3(4), C15–C16–C17 155.3(5), Ru1–C16–C17 97.7(3), Cl1–Ru1–C1 106.8(1). (b) Superposition of the equatorial coordination planes of the two independent molecules of **29** (**29A**, **29B**).

Carbonylation of **29** under mild conditions afforded the *cis*-dicarbonyl complex [Ru{C(C≡SiMe₃)=CHSiMe₃}Cl(CO)₂(PPh₃)₂] (**30**). Several attempts at fluoride-assisted (moist TBAF), protodesilylation of **30** also failed to provide the desired parent compound, as did treatment with methanolic KOH, which resulted in the decomposition of the starting material. As also observed by Jia,²⁸ we have been unsuccessful in identifying conditions appropriate for the desilylation of **29** to provide the hypothetical parent complex [Ru{C(C≡CH)=CH₂}Cl(CO)(PPh₃)₂]. The parent enynyl ligand has only very rarely been observed. Thus Werner has shown that carbonylation of [Rh(C≡CH)=(C=CH₂)(PⁱPr₃)₂] results initially in the complex [Rh{C(C≡CH)=CH₂}{CO}(PⁱPr₃)₂] which however rearranges thermally to the butatrienyl isomer [Rh(CH=C=C=CH₂)(CO)(PⁱPr₃)₂] or photochemically to the alkynyl [Rh(C≡CCH=CH₂)(CO)(PⁱPr₃)₂].³⁷ Stang has suggested that the cobalt complex [Co{C(C≡CH)=CH₂}{dmgH}₂(py)] (dmgH =

dimethylglyoximate) may be obtained *via* nucleophilic attack by the $[\text{Co}(\text{dmgH})_2(\text{py})]^-$ anion on alkynylvinyl triflates.³⁸

The reaction of **29** with $\text{Na}[\text{S}_2\text{CNMe}_2]$ afforded the dithiocarbamate complex $[\text{Ru}\{\text{C}(\text{C}\equiv\text{CSiMe}_3)=\text{CHSiMe}_3\}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ (**31**) which was crystallographically characterised. The spectroscopic data for **31** are generally unremarkable other than to note that the $\nu_{\text{C}\equiv\text{C}}$ absorption in the infrared spectra is some 18 cm^{-1} higher than in the precursor, consistent with the $\text{C}\equiv\text{C}$ bond no longer interacting with the now coordinatively saturated metal centre. The dimethyldithiocarbamate ligand was chosen due to its tendency to form robust and inert chelates, which it was hoped would preserve the complex under more aggressive desilylation conditions. However, neither TBAF nor methanolic KOH effected desilylation. For the present, routes to the alternative $\text{M}-\text{C}\equiv\text{C}-\text{C}(\text{M})=\text{CH}_2$ isomeric connectivity remain to be established.

Figure 6. Molecular structure of **31** in a crystal (50% displacement ellipsoids, aryl hydrogen atoms omitted, phenyl groups simplified for clarity, rotational disorder of SiMe_3 about $\text{C17}-\text{Si2}$). Selected bond lengths (Å) and angles (deg.): $\text{P1}-\text{Ru1}$ 2.372(1), $\text{P2}-\text{Ru1}$ 2.373(1), $\text{Ru1}-\text{S1}$ 2.504(1), $\text{Ru1}-\text{S2}$ 2.476(1), $\text{Ru1}-\text{C4}$ 1.829(4), $\text{Ru1}-\text{C15}$ 2.104(4), $\text{C14}-\text{C15}$ 1.350(6), $\text{C15}-\text{C16}$ 1.430(6), $\text{C16}-\text{C17}$ 1.207(7), $\text{P2}-\text{Ru1}-\text{P1}$ 177.90(3), $\text{S1}-\text{Ru1}-\text{S2}$ 70.12(4), $\text{Ru1}-\text{C15}-\text{C14}$ 130.2(3), $\text{Ru1}-\text{C15}-\text{C16}$ 113.0(3), $\text{C14}-\text{C15}-\text{C16}$ 116.8(4), $\text{C15}-\text{C16}-\text{C17}$ 176.4(5). Inset: View along $\text{P1}-\text{P2}$ vector.

Computational analysis.

Given the crystallographic caveats associated with the characterisation of **18**, specifically the acquisition of robust geometrical data for the disordered C_4H_2 bridge, we have turned to computational methods to interrogate the bonding of this linkage relative to $\text{M}-\text{C}_4-\text{M}$ and $\text{M}-(\text{CH})_4-\text{M}$ bridges. Copious data are already available for dimetallated butadiynediyl complexes^{1,12,23,39} and while many of these relate to diruthenium systems, ‘ $\text{RuCl}(\text{CO})_2(\text{PR}_3)_2$ ’ termini have not yet been considered. Complexes based on the $\text{L}_n\text{MCH}=\text{CH}=\text{CH}=\text{CHML}_n$ connectivity are scarce⁴⁰ and have only been computationally studied in two cases ($\text{L}_n\text{M} = \text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$,^{40d} $\text{RuCl}(\text{CO})(\text{PMe}_3)_3$ ^{40g}). No computational investigations of the $\text{L}_n\text{MC}\equiv\text{CCH}=\text{CHML}_n$ connectivity have appeared

previously. From the outset it should be noted that what sets the ‘ $\text{RuCl}(\text{CO})_2(\text{PR}_3)_2$ ’ termini apart from other studies is the presence of a strongly π -acidic CO ligand *trans* to the bridging organyl of interest that would be expected to compromise any π -component to the $\text{Ru}-\text{C}$ bonding.

For computational simplicity and economy, we have therefore considered the bimetallic complexes $[\text{Ru}_2(\mu\text{-L})\text{Cl}_2(\text{CO})_4(\text{PMe}_3)_4]$ ($\text{L} = -\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ **A**, $-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-$ **AH₂**, $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ **AH₄**). The frontier orbitals of interest for **A**, **AH₂** and **AH₄** are presented in Figures 7, 8 and 9, respectively. For **A**, the essentially degenerate HOMO pair correspond, as might be expected, to the π -system of the butadiynediyl unit with $\text{Ru}-\text{C}$ π -antibonding character. Given that protonation of $[\text{Ru}_2(\mu\text{-C}_4)\text{Cl}(\text{CO})_2(\text{PPh}_3)_4(\eta\text{-C}_5\text{H}_5)]$ occurs at a β -alkynyl carbon,¹² and that protonation at the β -carbon of **22** is implicit in the formation of **24**, this is not surprising. The HOMO-7 and HOMO-8 pair which are again near degenerate, comprise considerable $p\pi-p\pi$ bonding character between the two internal carbons, consistent with conjugation along the entire spine and the rather short C-C ‘single’ bond (1.393 Å for **A**, 1.393 Å for **16**). The LUMO is primarily $\text{Ru}-\text{Cl}$ σ -antibonding in nature, despite the failure discussed above, to reduce **16** to $[\text{Ru}_2(\mu\text{-C}_4)(\text{CO})_4(\text{PPh}_3)_2]$. The topology and energy of this primarily metal-based LUMO are essentially invariant across the series **A**, **AH₂** and **AH₄**. Notably, the optimised geometry for **A** has the P–P vectors on adjacent ruthenium centres close to orthogonal, in contrast to that adopted by **16** in the solid state in which these vectors are nearer to parallel (Figure 1). Thus with essentially free rotation about the $\text{RuC}\equiv\text{CC}\equiv\text{CRu}$ spine (and the near degeneracy of HOMO and HOMO-1), the geometry reflects the minimisation of intramolecular (bulkier phosphines for **16**) and intermolecular non-bonding interactions rather than any more subtle electronic factors.

For **AH₂**, the HOMO is again associated with the Ru_2Ru π -system, having conjugated $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ π -bonding character and $\text{Ru}-\text{C}$ $d\pi-p\pi$ antibonding character. In contrast to **A**, however, the orthogonal π -orbitals are no longer degenerate, being substantially lower in energy and primarily localised in the $\text{C}\equiv\text{C}$ bond. Finally, for **AH₄** the HOMO is unique in character and separated by a large energy gap from a manifold of 6 orbitals (-9.12 to -9.76 eV), the lowest of which corresponds to the fully $\text{C}-\text{C}$ π -bonding butadiene system with $\text{Ru}-\text{C}$ $d\pi-p\pi$ antibonding character. Similar topologies were described by Winter for the complexes $[\text{Ru}_2(\mu\text{-C}_4\text{H}_4)\text{Cl}_2(\text{CO})_2(\text{PR}_3)_4]^{n+}$ ($\text{R} = \text{H}, \text{Me}$; $n = 0, 1, 2$; B3LYP/BP).^{40g} These orbitals are what would be expected qualitatively, however taken together it is possible to quantitatively compare the effect of sequential hydrogenation of the C_4 bridge upon the metal centre. The HOMO-LUMO gap increases significantly on going from **A** (2.57 eV) to **AH₂** (5.56 eV) but slightly less so for **AH₄** (5.26 eV).

Figure 7. Frontier orbitals of interest for the complex $[\text{Ru}]_2(\mu\text{-C}\equiv\text{C-C}\equiv\text{C})$ (**A**). $[\text{Ru}] = \text{RuCl}(\text{CO})_2(\text{PMe}_3)_2$.

Figure 8. Frontier orbitals of interest for the complex $[\text{Ru}]_2(\mu\text{-C}\equiv\text{C-CH=CH})$ (**AH₂**). $[\text{Ru}] = \text{RuCl}(\text{CO})_2(\text{PMe}_3)_2$.

Table 4 collates the various charges that follow from the calculations, which show remarkably little variation in the electron density at ruthenium on traversing the series, despite the significant differences in π -basicity implicit in the infrared data for complexes **16** and **18** (Table 5). Infrared data for **18** correlate remarkably well with those for the complexes **21** and **24** that serve as models for the constituent components of the butenyndiyl bridge. Although calculated frequencies significantly overestimate observed fundamentals, those derived for **A**, **AH₂** and **AH₄** reproduce the trends, if not the absolute values. They also confirm remarkably little coupling between the ν_{CO} and ν_{CC} oscillators.

Table 4. Calculated atomic charges for the complexes **A**, **AH₂** and **AH₄**.

Complex	Atom	Mulliken	NBO	Hirshfeld
A	Ru	-0.97	-1.47	-0.46
	$\equiv\text{C1/4}$	-0.46	-0.04	-0.11
	$\equiv\text{C2/3}$	+0.39	-0.17	-0.09
AH₂	Ru1	-0.99	-1.47	-0.41
	$\equiv\text{C1}$	+0.01	-0.08	-0.13
	$\equiv\text{C2}$	+0.03	-0.13	-0.19
	$\equiv\text{C3}$	-0.27	-0.34	-0.03
	$=\text{C4}$	-0.15	-0.28	-0.05
AH₄	Ru4	-0.97	-1.46	-0.42
	$=\text{C1/4}$	-0.18	-0.31	-0.07
	$=\text{C2/3}$	-0.14	-0.30	-0.05

Figure 9. Frontier orbitals of interest for the complex $[\text{Ru}]_2(\mu\text{-CH=CH-CH=CH})$ (**AH₄**). $[\text{Ru}] = \text{RuCl}(\text{CO})_2(\text{PMe}_3)_2$.

Natural bond order analysis of the ruthenium alkenyl and alkynyl connections indicates that in all cases the σ -component comprises approximately 69–67% Ru d^2sp^3 and 31–33% C sp or sp^2 character, respectively. The π -component to the Ru–C bonding is however of interest in the context of inter-metallic communication. The NBO second order analysis suggests that for **A**, the rather modest π -component contributes only *ca* 12 kJmol⁻¹ to the Ru–C bond enthalpy. For both **AH₂** and **AH₄** the Ru–C=C π -component is also found to be rather modest, contributing in the order of 18 kJmol⁻¹.

These effects taken together account for the comparatively invariant charges on ruthenium in the series **A**, **AH₂** and **AH₄**. It should be re-stated that the ‘ $\text{RuCl}(\text{CO})_2(\text{PR}_3)_2$ ’ ($\text{R} = \text{Me}, \text{Ph}$) fragments are somewhat distinct from the vast majority of ruthenium carbon-chain termini for which computational results are available. These typically relate to half-sandwich ‘ $\text{Ru}(\text{PR}_3)_2(\eta^5\text{-C}_5\text{R}'_5)$ ’ moieties such that the alkynyl is effectively the only substantial π -acid present. Winter has computationally interrogated the complex $[\text{Ru}_2(\mu\text{-C}_4\text{H}_4)\text{Cl}_2(\text{CO})_2(\text{PMe}_3)_6]$, which however places strong σ -donor PMe_3 ligands *trans* to the

polycarbonyl chain.^{40g} The 'RuCl(CO)₂(PR₃)₂' terminus places a π -acidic CO ligand *trans* to the carbon chain ligand of interest, which will therefore competitively compromise π -retrodonation from ruthenium.

Finally, it should be noted that although concerted alkyne hydorruthenation places the newly formed C–Ru and C–H bonds in a *cis*-relationship, hence the regioisomer structure considered for **AH₄** (now designated *EE*-**AH₄**) we have also considered alternative regioisomers (Figure 10). Interestingly, *EE*-**AH₄** is *not* the thermodynamically ($\Delta G_{298.2K}$ or $\Delta H_{298.2K}$) preferred isomer, but rather lies some 60 kJmol⁻¹ above *EZ*-**AH₄** and 90 kJmol⁻¹ above *ZZ*-**AH₄** though these results in part reflect the choice of a smaller phosphine (PMe₃) in the model compounds. Steric factors will contribute more significantly to the real system in terms of inter-ligand repulsion.

Table 5. Selected infrared data for complexes *cis*, *cis*, *trans*-[RuCl(CO)₂(PPh₃)₂]

R =	ν_{CO} (cm ⁻¹)	k_{CK}^a (Ncm ⁻¹)
C≡CH (23)	2058, 1991	16.56
C≡CSiMe ₃ (21)	2038, 1994	16.41
C≡CC≡CH (3)	2057, 1997	16.60
C≡CC≡CRu... (16)	2051, 1989	16.48
C≡CCH=CHRu... (18)	2052, 1987	16.47
	2035, 1975	16.24
CH=CH ₂ (24)	2036, 1974	16.24
H ⁴²	2040, 1965	16.20
C ₆ H ₄ Me ⁴³	2055, 1952	16.22
Cl ⁴⁴	2050, 1990	16.48
A ^b	2013, 1964	15.97
AH₂ ^b	2009, 1961	15.91
	1999, 1946	15.71
AH₄ ^b	1997, 1947	15.72

^aCotton-Kraihanzel force constant for *cis*-Ru(CO)₂. ^bCalculated at the BP86-6-31G(d) level of theory.

Figure 10. Relative energies for **AH₄** regioisomers ($\Delta G_{298.2K}$, gas phase, MO6/BS2//BP86/BS1)).

Although the synthetic strategy that afforded **18** was chosen for its regioselectivity, for completeness we have also considered the butatriendiyl RuCH=C=C=CHRu connectivity although this has yet to be experimentally observed for any transition metal. This complex lies only 3 kJmol⁻¹ above **AH₂** and is therefore certainly viable. The failure to observe this in the presence of **AH₂** thus most likely indicates the absence of any kinetically accessible prototropic interconversion route.

In the characterization of polyynediyl (and alkynyl) complexes, MC α ≡C β ..., ligated by phosphines, the assignment of ¹³C NMR chemical shifts to C α and C β respectively is usually

performed with recourse to the magnitude of ^{2,3}J_{PC} on the reasonable assumption that this will be greater for C α than C β . This is required given that the chemical shifts range considerably for the two carbon nuclei and these ranges overlap. Thus whilst, *e.g.*, the butadiynyl complexes [Re(C₄R)(NO)(PPh₃)(η -C₅Me₅)] (R = H, SiMe₃) have C α to higher field (R = H 103.0, SiMe₃ 107.0 ppm) of C β (R = H 111.4, SiMe₃ 112.8 ppm), this is reversed for the bimetallic butadiynediyl complex [Re₂(μ -C₄)(NO)₂(PPh₃)₂(η -C₅Me₅)₂] (C α 96.6, 95.7; C β 118.0 ppm).⁴⁴ Similarly, the complex [Ru₂(μ -C₄)(dppm)₂(η -C₅Me₅)₂] has C α (93.3 ppm) to marginally higher field of C β (100.4 ppm). We therefore calculated the chemical shifts for the polycarbonyl linkers in **16** and **18** by taking two different approaches. Data for the actual complexes were obtained beginning with the crystallographically derived atomic coordinates for **16** and **18**, with the GIAO method implemented within Gaussian09[®] using BS1 (see Experimental section). Alternatively, the optimized geometries for **A**, **AH₂** and **AH₄** were used, bearing in mind the more electron donating nature of PMe₃ relative to PPh₃. Table 6 collates these data and reveals a peculiar observation, *i.e.*, that it would appear that the resonances to lower field for both **16** and **A** correspond to C α whilst those to higher field derive from C β . For the C₄H₂ complex **AH₂**, the resonances follow the expected trend including those observed for **18**. We might therefore surmise that caution should be exercised when applying the accepted assumptions about δ_C and ¹J_{PC} when assigning resonances in polycarbonyl chains.

Table 6. Observed and calculated NMR data for complexes [Ru₂(μ -L)Cl₂(CO)₄(PR₃)₄] and [RuCl(C≡CC≡CH)(CO)₂(PPh₃)₂] (**3**)

L	R	δ_C [ppm]			
3	Ph	104.0	97.3	71.9	58.3
C≡C–C≡C					
16	Ph	89.9	104.6	104.6	89.9
16	Ph	96.2	90.5	91.1	97.3 ^a
A	Me	97.0	85.1	85.1	97.0
CH=CH–C≡C					
18	Ph	163.4	124.5	98.2	121.4
AH₂	Me	171.7	112.2	102.7	110.3
CH=CH–CH=CH					
AH₄	Me	157.7	134.2	134.2	157.7

^aNon-optimised structure taken from crystallographic coordinates.

Concluding Remarks

There now exist a multitude of bimetallic complexes spanned by a tetracarbydo (butadiynediyl) C₄ bridge, for which the motivation has included their fundamental intrigue as models for molecular wires in which a degree of inter-metallic communication might be manifest. In contrast, a very small number of bimetallic complexes spanned by the butadiendiyl C₄H₄ linkage have been isolated, to which has recently been added the complex [Fe₂{ μ -C₄H₂(OMe)₂}(CO)₂(PMe₃)₂(η -C₅Me₅)₂]⁴⁵ which features the inclusion of positively mesomeric substituents (**M**⁺ OMe) as a means of further moderating the electronic nature of the hydrocarbon bridge. We have now shown that the missing link, a butenyndiyl C₄H₂ linkage, is viable

and on the basis of computational interrogation have been shown to retain frontier orbitals of suitable energy and delocalisation to also allow intimate communication between the metal termini. Unfortunately, the ease of direct synthesis of butadiynyl complexes does not extend to the installation of C₄H₂ linkages for call for more circuitous synthetic routes. Nevertheless, one such route has been demonstrated here, the individual steps of which in principle offer some generality.

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 obtained at 25°C on Bruker AVANCE 400 (¹H at 399.9 MHz, ³¹P at 162.0 MHz) or Varian Gemini 300BB (¹H at 300.8 MHz, ¹³C at 75.4 MHz, ¹³P at 121.4 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peak (¹H, ¹³C) or external reference (³¹P: H₃PO₄) with coupling constants given in Hz. *t*_v refers to characteristic virtual triple resonances for the *trans*-M(PPh₃)₂ unit with apparent coupling constants given. Infrared spectra were obtained from solution and in the solid state (Nujol or KBr) using a Perkin-Elmer Spectrum One FT-IR spectrometer. Electrospray ionisation mass spectrometry (ESI-MS, +ve ion, MeCN matrix) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. Elemental microanalytical data were provided by the ANU Microanalytical Service. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer. Reaction progress was typically monitored by *in situ* solution IR spectroscopy and thin layer chromatography (silica gel). The complexes [Ru(CO)₂(PPh₃)₃] (**1**),^{6b} [RuHCl(CO)(PPh₃)₃] (**17**),²⁵ [IrCl(CO)(PPh₃)₂],⁴⁶ [RuH(κ²-S₂CNMe₂)(CO)(PPh₃)₂],⁴⁷ [AuCl(PPh₃)],⁴⁸ [Hg{N(SiMe₃)₂}₂]⁴⁹ and *cis*-[PtCl₂(PPh₃)₂]⁵⁰ are available *via* published procedures. All other reagents were used as received from commercial sources.

Computational details. All computational works were performed using the *Gaussian 09*TM suite of programs.⁵¹ All complexes were geometrically optimised using a combined basis set (BS1) which comprised a 28-core-electron relativistic effective core potential (SDD) for Ru and 6-31G(d) basis sets for all other atoms. Frequency calculations were performed to confirm that the optimized structures were minima using the BP86 level of theory.⁵²⁻⁵⁴ Single-point energy calculations for all the optimized structures were carried out with a larger combination basis set (BS2) comprising the quadruple-ζ valence Def2-QZVPD basis set for Ru along with the 28-core-electron corresponding effective core potential and the 6-311+G(2d,p) basis set for all other atoms. NBO calculations were performed using the NBO5 implementation within *Gaussian 09*TM.⁵¹ Chemical shifts were calculated relative to SiMe₄ using the GIAO method implemented within Gaussian09 using BS1.

Preparation of [RuH(C≡CC≡CH)(CO)₂(PPh₃)₂] (2**).** [Ru(CO)₂(PPh₃)₃] (**1**: 6.00 g, 6.35 mmol) was suspended in THF (100 mL). In a separate flask 1,4-bis(trimethylsilyl)-1,3-butadiyne (2.47 g, 12.7 mmol) was suspended in ethanol (20

mL) and with stirring, commercial [ⁿBu₄N]F (50.4 mL, 50.4 mmol, 1.0 mol L⁻¹ in THF, 3-5% H₂O) was added and the resulting solution was stirred for 15 minutes. This solution was then added dropwise *via* cannula to the flask containing **1** with stirring. After 10 minutes the reaction was complete, a clear solution having resulted and after stirring for 5 minutes further, white crystals of the product began to form. The solvent volume was reduced to *ca* 20 mL under reduced pressure and the white solid was isolated by filtration and recrystallised from CH₂Cl₂/ethanol to yield light brown crystals. Yield: 3.96 g (85%). IR CH₂Cl₂: 2143 ν_{C≡C}, 2040 ν_{CO}, 1999 ν_{RuH}, 1987 ν_{CO} cm⁻¹. Nujol: 2141 ν_{C≡C}, 2040, 1989 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = -5.30 (t, 1 H, RuH, ²J_{HP} = 20.0), 1.21 (t, 1 H, C≡CH, ⁶J_{HP} = 1.20 Hz), 6.97, 7.92 (m × 2, 30 H, C₆H₅). ³¹P{¹H}: δ 44.1. Satisfactory ¹³C NMR data were not acquired due to complications arising from the elimination of butadiyne over prolonged periods in solution. ESI-MS: *m/z* 772.8 [M + H + NCMe]⁺. Anal. Found: C, 68.87; H, 4.79; N, 0.00%. Calcd. for C₄₂H₃₂O₂P₂Ru: C, 68.84; H, 4.40; N, 0.00%.

Preparation of [RuCl(C≡CC≡CH)(CO)₂(PPh₃)₂] (3**).** [RuH(C≡CC≡CH)(CO)₂(PPh₃)₂] (**2**: 0.18 g, 0.25 mmol) and *N*-chlorosuccinimide (0.04 g, 0.30 mmol) were dissolved in THF (30 mL) and stirred for 5 minutes. During this time two new carbonyl stretching frequencies (2058, 1999 cm⁻¹) developed in the infrared solution spectrum. Ethanol was added and the solvent volume reduced until a pale yellow solid formed. This was isolated by filtration and recrystallised from CH₂Cl₂/ethanol to provide straw coloured crystals. Yield: 0.16 g (85%). IR CH₂Cl₂: 2150 ν_{C≡C}, 2058, 1999 ν_{CO} cm⁻¹. Nujol: 2147 ν_{C≡C}, 2057, 1997 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = 1.43 (t, 1 H, C≡CH, ⁶J_{HP} = 1.20 Hz), 6.97, 8.19 (m × 2, 30 H, C₆H₅). ¹³C{¹H}: δ = 58.3 (C≡CC≡CH), 71.9 (C≡CC≡CH), 97.3 (RuC≡C), 104.0 (t, ²J_{CP} = 19.7, RuC≡C), 128.5 [*t*_v, *J*_{CP} = 5.0, C^{3,5}(C₆H₅)], 130.7 [C⁴(C₆H₅)], 132.9 [*t*_v, *J*_{CP} = 24.2, C¹(C₆H₅)], 134.4 [*t*_v, *J*_{CP} = 5.3, C^{2,6}(C₆H₅)], 191.7 (t, ²J_{CP} = 9.0, RuCO), 193.8 (t, ²J_{CP} = 10.6 Hz, RuCO). ³¹P{¹H}: δ 22.1. ESI-MS: *m/z* 806.8 [M + H + NCMe]⁺. Anal. Found: C, 62.65; H, 4.04; N, 0.00%. Calcd. for C₄₂H₃₁ClO₂P₂Ru.0.66CH₂Cl₂: C, 62.32; H, 3.97; N, 0.00%.

Preparation of [Ru(C≡CC≡CH)(SePh)(CO)₂(PPh₃)₂] (5**).** [RuH(C≡CC≡CH)(CO)₂(PPh₃)₂] (**2**: 0.30 g, 0.41 mmol) and diphenyldiselenide (0.064 g, 0.21 mmol) were dissolved in THF (35 mL). The resulting solution was then stirred for 4 hours, by which time the solution had turned from yellow to orange. Hexane was added and the solvent volume reduced under vacuum to precipitate the crude orange product. The orange solid was recrystallised from CH₂Cl₂/hexane as a dichloromethane monosolvate. Yield: 0.08 g (22%). IR CH₂Cl₂: 2146, 2091 ν_{C≡C}, 2043, 1984 ν_{CO} cm⁻¹. Nujol: 2036, 1976 ν_{CO} cm⁻¹. NMR (CDCl₃, 25°C) ¹H: δ = 1.86 (t, 1 H, C≡CH, ⁶J_{HP} = 2.53 Hz), 6.65 (m, 5 H, SeC₆H₅), 7.05, 8.21 (m × 2, 30 H, C₆H₅). ¹³C{¹H}: δ = 68.2 (RuC≡CC≡CH), 115.5 (RuC≡CC≡CH), 116.5 (RuC≡C), 118.4 (t, RuC≡C, ²J_{HP} = 2.5), The quaternary carbon of the SeC₆H₅ group could not be unambiguously identified, 128.3 [*t*_v, *J*_{CP} = 4.8, C^{3,5}(PC₆H₅)], 130.2 [C⁴(PC₆H₅)], 132.5 [C^{2,6}Se(C₆H₅)], the C¹(C₆H₅) resonance is obscured by the C^{2,6}(C₆H₅) resonance, 134.4 [*t*_v, *J*_{CP} = 5.2, C^{2,6}(PC₆H₅)], 137.3 [C^{3,5}Se(C₆H₅)], 193.5 (t, ²J_{CP} = 10.7, RuCO), 194.2 (t, ²J_{CP} = 7.7 Hz, RuCO). ³¹P{¹H}: δ 20.9. ESI-MS: *m/z*

887.9 [M + H]⁺. Anal. Found: C, 60.68; H, 4.31; N, 0.00%; Calcd. for C₄₈H₃₆O₂P₂RuSe.CH₂Cl₂: C, 60.49; H, 3.94; N, 0.00%

Preparation of [(PPh₃)₂(CO)₂ClRuC≡C–C–Au(PPh₃)] (6). [Ru(C≡C=CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.20 g, 0.26 mmol) and [AuCl(PPh₃)] (0.13 g, 0.26 mol) were dissolved in THF (35 mL) and stirred while CuI (*ca* 2 mg, cat.) and Et₂NH (1 mL) were added. The solution was stirred for 10 min, the solvents were removed *in vacuo* and the crude product extracted into CH₂Cl₂. Ethanol was added to the filtered extracts and on reduction of the solvent volume, a cream solid precipitated which was isolated by filtration, washed with ethanol and dried *in vacuo*. Yield: 0.20 g (63%). IR CH₂Cl₂: 2141 $\nu_{C\equiv C}$, 2056, 1997 ν_{CO} cm⁻¹. Nujol: 2140 $\nu_{C\equiv C}$, 2047, 1985 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = 6.97, 7.20, 8.33 (m $\times$ 3, 45 H, C₆H₅). ¹³C{¹H}: δ = 91.3 (d, C≡CAu, ²J_{CP} = 26.2), 93.2 (t, RuC≡C, ²J_{CP} = 20.5), 102.2 (RuC≡CCAu), 119.5 (RuC≡CCAu), the RuPPh₃ C^{3,5} resonance could not be unambiguously identified, 129.0 [d, ³J_{CP} = 11.2, C^{3,5}(AuPC₆H₅)], 130.1 [C⁴(RuPC₆H₅)], 131.1 [C⁴(AuPC₆H₅)], 134.0 [t^v, J_{CP} = 23.9, C¹(RuPC₆H₅)], the AuPPh₃ C¹ resonance could not be unambiguously identified, 134.3 [d, ²J_{CP} = 13.8, C^{2,6}(AuPC₆H₅)], 134.7 [t^v, J_{CP} = 5.3, C^{2,6}(RuPC₆H₅)], 192.1 (t, ²J_{CP} = 8.9, RuCO), 194.7 (t, ²J_{CP} = 10.9 Hz, RuCO). ³¹P{¹H}: δ 42.3, 21.6. ESI-MS: *m/z* 1224.6 [M+H]⁺ Anal. Found: C, 58.67; H, 3.84; N, 0.00%. Calcd. for C₆₀H₄₅AuClO₂P₃Ru: C, 58.81; H, 3.70; N, 0.00%.

Preparation of [RuIr(μ-C₄)Cl(CO)₃(PPh₃)₄] (7) (a) [RuIr(μ-C₄)HCl(CO)₃(NCMe)(PPh₃)₄]BF₄ (**8**: 0.20 g, 0.12 mmol) was dissolved in THF (15 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.5 mL) was added. The solution turned from light orange to dark orange instantly. Air free hexane was added and the solvents reduced to precipitate an orange solid. Yield: 0.15 g (81%). IR CH₂Cl₂: 2054, 1994 ν_{RuCO} , 1956 ν_{IrCO} cm⁻¹. Nujol: 2048, 1986 ν_{RuCO} , 1953 ν_{IrCO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: 6.94, 7.92, 8.11, 8.22 (m $\times$ 4, 60 H, C₆H₅). ³¹P{¹H} (CH₂Cl₂, -25°C): δ 21.2, 22.5. ESI-MS: *m/z* 1510.3 [M + H]⁺. Suitable microanalytical data could not be collected due to air-sensitivity resulting in formation of the dioxygen adduct **9**, which however provided satisfactory data (*vide infra*). (b) A mixture of [Ru(C≡C=CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.10 g, 0.13 mmol) and [IrCl(CO)(PPh₃)₂] (0.10 g, 0.13 mmol) was stirred in THF (30 mL). Diethylamine (1 mL) was then added and the solution was stirred for 10 minutes, during which time no reaction was evident by *in situ* IR spectroscopy. Cuprous iodide (*ca* 1 mg, 4 mol%) was added to the solution, which was accompanied by an instant colour change from yellow to orange. Air free hexane was then added and the solvents reduced *in vacuo* to form an orange precipitate with spectroscopic data identical to those obtained in (a) above. Yield: 0.18 g (92%). IR CH₂Cl₂: 2054, 1994, 1956 ν_{CO} cm⁻¹. Nujol: 2048, 1986, 1953 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 6.94, 7.92, 8.11, 8.22 (m $\times$ 4, 60 H, C₆H₅). ³¹P{¹H}(CH₂Cl₂, -25°C): δ = 21.2, 22.5.

Preparation of [RuIr(μ-C₄)HCl(CO)₃(NCMe)(PPh₃)₄]BF₄ (8**).** [Ru(C≡C=CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.25 g, 0.33 mmol) and [Ir(CO)(NCMe)(PPh₃)₂]BF₄ (0.28 g, 0.33 mmol) were dissolved in THF (20 mL) and stirred for 10 minutes, during which time the solution became orange in colour. The solvents were then removed and the residue extracted with CH₂Cl₂. The filtered extracts were concentrated and then diluted with ethanol to provide a beige microcrystalline solid. Yield: 0.45 g (84%). IR

CH₂Cl₂: 2060, 1996 ν_{CO} cm⁻¹. Nujol: 2053, 1987 [ν (CO)] cm⁻¹. The salt [IrH(C≡CPh)(NCMe)(CO)(PPh₃)₂]ClO₄⁵⁶ has ν_{CO} = 2060 cm⁻¹ and so we presume that this band overlaps with the symmetric stretch for the Ru(CO)₂ unit. NMR (C₆D₆, 25°C) ¹H: δ = -17.5 (t, 1 H, IrH, ²J_{HP} = 11.0 Hz), 1.74 (s, 3 H, NCCH₃), 6.93, 7.05, 7.82, 8.11 [m $\times$ 4, 60 H, C₆H₅]. ¹³C{¹H} data collected indicated decomposition of the product in solution during acquisition, confirmed by subsequently re-measuring the ¹H NMR spectrum. ³¹P{¹H}: δ = -1.8 (d, IrP, ²J_{HP} = 9.71 Hz, incomplete {¹H} decoupling), 21.9. ESI-MS: *m/z* 1511.6 [M – BF₄ – NCMe]⁺ Anal. Found: C, 57.78; H, 4.14; N, 0.74%. Calcd. for C₈₁H₆₄BClF₄IrNO₃P₄Ru.0.75CH₂Cl₂: C, 57.63; H, 3.88; N, 0.82%.

Preparation of [RuIr(μ-C₄)(η²-O₂)Cl(CO)₃(PPh₃)₄] (9). Solid [RuIr(μ-C₄)Cl(CO)₃(PPh₃)₄] (**7**) was exposed to air for 20 minutes in which time the solid had turned from orange to yellow. The material was recrystallized from a mixture of CH₂Cl₂ and hexane under aerobic conditions. Yield quantitative. IR CH₂Cl₂: 2054, 1994 ν_{CO} cm⁻¹. Nujol: 2048, 1986 ν_{CO} , 837 ν_{O_2} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = 6.90, 6.96, 7.92, 8.22 (m $\times$ 4, 60 H, C₆H₅). ¹³C{¹H}: δ 50.3 (br.s, RuC≡CClIr), 90.4 (t, RuC≡CClIr, ²J_{CP} = 24.5), 98.5 (RuC≡CClIr), 104.8 (RuC≡CClIr), Both C^{3,5}(C₆H₅) resonances are obscured by the solvent peak, 129.3 [t^v, J_{CP} = 29.0, C¹(IrPC₆H₅)], 130.1 [C⁴(IrPC₆H₅)], 130.7 [C⁴(RuPC₆H₅)], 134.1 [t^v, J_{CP} = 23.6, C¹(RuPC₆H₅)], 134.7 [t^v, J_{CP} = 5.4, C^{2,6}(RuPC₆H₅)], 135.2 [t^v, J_{CP} = 5.4 Hz, C^{2,6}(IrPC₆H₅)], 168.5 (IrCO), 191.4 (RuCO), 195.3 (RuCO). ³¹P{¹H}: δ 3.1 (IrP), 22.1 (RuP). ESI-MS: *m/z* 1542.6 [M + H]⁺ Anal. Found: C, 61.55; H, 4.23; N, 0.00%. Calcd. for C₇₉H₆₀ClIrO₅P₄Ru: C, 61.47; H, 3.92; N, 0.00%.

Preparation of [RuCo₂(μ-C₄)Cl(CO)₈(PPh₃)₂] (10). [Ru(C≡C=CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.20 g, 0.26 mmol) and [Co₂(CO)₈] (0.090 g, 0.26 mmol) were dissolved in benzene (40 mL), in the absence of light. The resulting solution was stirred for 30 minutes, ethanol was added and the solvents reduced *in vacuo*. The residue was extracted into dichloromethane and purified by column chromatography (silica gel, CH₂Cl₂/hexane 1:1). The product eluted as a thin, dark brown band, which upon the addition of hexane yielded a crystalline brown solid. Yield: 0.25 g (91%). IR (C₆H₆): 2089w, 2070w, 2050vs, 2022m, 1999w, *ca* 1960 w.sh. ν_{CO} cm⁻¹. IR (CH₂Cl₂): 2090w, 2051vs, 2022m, *ca* 1990 w.sh. ν_{CO} cm⁻¹. Nujol: 2088m, 2047sh, 2044s, 2003vs, 1995s, *ca* 1960vw, 1950vw ν_{CO} cm⁻¹. NMR (CHCl₃, 25°C) ¹H: δ 5.64 (s, 1 H, CH), 7.39, 7.92 (m $\times$ 2, 30 H, C₆H₅). ¹³C{¹H} (C₆D₆, 25 °C): δ 73.12 (Co₂CH), 76.39 (Co₂CC=C), 109.8 (t, RuC≡C, ³J_{CP} = 2.4), 128.4 [t^v, J_{CP} = 4.60, C^{3,5}(C₆H₅)], 129.2 (t, RuC≡C, ²J_{CP} = 20.4), 130.4 [C⁴(C₆H₅)], 133.5 [t^v, J_{CP} = 29.5, C¹(C₆H₅)], 134.5 [t^v, J_{CP} = 5.3, C^{2,6}(C₆H₅)], 192.8 (t, ²J_{PC} = 8.9, RuCO), 194.5 (t, ²J_{PC} = 10.4 Hz, RuCO), 200.1 (br. CoCO). ³¹P{¹H}: δ 22.8. ESI-MS: *m/z* 1062.9 [M – Cl]⁺ Anal. Found: C, 54.27; H, 2.97; N, 0.00%.⁵⁷ Calcd. for C₄₈H₃₁ClCo₂O₈P₂Ru: C, 54.80; H, 2.97; N, 0.00%.

Preparation of [Ru₂Pt(μ-C₄)₂Cl₂(CO)₄(PPh₃)₆] (11). [Ru(C≡C=CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.20 g, 0.26 mmol) and *cis*-[PtCl₂(PPh₃)₂] (0.10 g, 0.13 mmol) were suspended in THF (15 mL). Diethylamine (1 mL) and CuI (1 mg, 4 mole%) were then added and the mixture was stirred for 1 hour during which time the platinum complex dissolved to provide a pale green solution and, as indicated by the solution IR spectroscopy, the reaction had proceeded to completion. Ethanol was then added and solvent volume was reduced *in vacuo*. The resulting yellow solid

was isolated by filtration and recrystallised from CH₂Cl₂/ethanol. Yield: 0.24 g (84%). IR CH₂Cl₂: 2054, 1993 ν_{CO} cm⁻¹. Nujol: 2047, 1985 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = 6.97, 7.93, 8.12 ($m \times 3$, 90 H, C₆H₅). Poor solubility precluded acquisition of useful ¹³C{¹H} NMR data. ³¹P{¹H}: δ 21.73 (RuP), 17.29 (PtP: ¹J_{PTP} = 2600 Hz). ESI-MS: m/z 2256.1 [M – Cl + NCMe]⁺ and 2215.0 [M – Cl]⁺. Anal. Found: C, 58.96; H, 4.13; N, 0.00%. Calcd. for C₁₂₀H₉₀Cl₂O₄P₆PtRu₂·3CH₂Cl₂: C, 58.98; H, 3.86; N, 0.00%.

Preparation of [Ru₂Hg(μ-C₄)Cl₂(CO)₄(PPh₃)₄] (12). [Ru(C≡C–C≡CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.20 g, 0.26 mmol) was dissolved in THF (30 mL) and the solution was stirred while [Hg{N(SiMe₃)₂}₂] (0.50 mL, 0.15 mmol, 0.3 M in toluene) was added *via* syringe. The solution turned light brown instantly and was filtered through diatomaceous earth. Hexane was added and the solvent volume reduced to precipitate a beige solid, which was recrystallized from CH₂Cl₂/hexane. Yield 0.13 g (58%). IR CH₂Cl₂: 2147 $\nu_{\text{C}\equiv\text{C}}$, 2048, 1991 [$\nu(\text{CO})$] cm⁻¹. IR THF: 2148 $\nu_{\text{C}\equiv\text{C}}$, 2051, 1994 1963sh ν_{CO} cm⁻¹. Nujol: 2146w $\nu_{\text{C}\equiv\text{C}}$, 2044, 1986 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 6.98, 8.20 ($m \times 2$, 60 H, C₆H₅). ³¹P{¹H}: An unresolvable (–50 to +50 °C) fluxional process involving two (non-coupled) phosphorus environments at δ = 26 and 22 ppm remains to be explained but most likely rotation of the Ru(PPh₃)₂ groups about the Ru₄HgC₄Ru spine. The complex however slowly degrades during extended data acquisition. ESI-MS: m/z 1744.1 [M – 2Cl + 2NCMe]. Anal. Found: C, 59.69; H, 3.88; N, 0.00%. Calcd. for C₈₄H₆₀Cl₂HgO₄P₄Ru₂·C₆H₁₄: C, 59.40; H, 4.10; N, 0.00%.

Preparation of [Ru₂(μ-C₈)Cl₂(CO)₄(PPh₃)₆] (14). [Ru₂Hg(μ-C₄)₂Cl₂(CO)₄(PPh₃)₄] (**12**: 0.05 g, 0.03 mmol) and [RhCl(CO)(PPh₃)₂] (**13**: *ca* 1 mg, *ca* 5 mol%) were dissolved in THF (15 mL) and stirred for 20 min when, although no shift in the IR spectrum was observed, elemental mercury was deposited on the bottom of the flask. The solution was filtered through diatomaceous earth to remove mercury, diluted with ethanol and the solvents reduced to provide a brown precipitate. Yield: 0.03 g (68%). IR CH₂Cl₂: 2146, 2127 $\nu_{\text{C}\equiv\text{C}}$, 2051, 1992 ν_{CO} cm⁻¹. IR THF: 2147 $\nu_{\text{C}\equiv\text{C}}$, 2046, 1990 ν_{CO} cm⁻¹. Nujol: 2146 $\nu_{\text{C}\equiv\text{C}}$, 2044, 1986 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = 6.96, 8.25 ($m \times 2$, 60 H, C₆H₅). ³¹P{¹H}: A fluxional process similar to that described above for **12** (δ = 25.3, 21.8) hindered meaningful peak assignment. ESI-MS: 1459.4 [M – 2Cl]⁺, 1500.8 [M – 2Cl + MeCN]⁺. Anal. Found: C, 63.46; H, 4.29; N, 0.00%. Calcd. for C₈₄H₆₀Cl₂O₄P₄Ru₂·CH₂Cl₂: C, 63.20; H, 3.87; N, 0.00%.

Preparation of [Ru₂(μ-C₄)HCl(CO)₄(PPh₃)₄] (15). [Ru(C≡C–C≡CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.05 g, 0.07 mmol) and [Ru(CO)₂(PPh₃)₃] (**1**: 0.06 g, 0.07 mmol) were dissolved in THF (30 mL) and stirred for 4 hours. Ethanol was then added and the solvents were reduced to precipitate a pale yellow powder. The solid was recrystallized from CH₂Cl₂/ethanol providing light yellow crystals. Yield: 0.08 g (85%) IR CH₂Cl₂: 2052, 2034, 1984 br. ν_{CO} cm⁻¹. Nujol: 2049, 2032, 1981 br. ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ = –5.25 (t, 1 H, RuH, ²J_{HP} = 20.4 Hz), 6.94, 7.45, 8.05, 8.19 ($m \times 4$, 60 H, C₆H₅). ¹³C{¹H} data collected indicated decomposition of the product in solution during acquisition. ³¹P{¹H}: δ 22.5, 42.1. ESI-MS: m/z 1453.8 [M – Cl + NCMe]⁺, 1412.7 [M – Cl]⁺. Anal. Found: C, 65.64; H, 4.44; N, 0.00%. Calcd.

for C₈₀H₆₁ClO₄P₄Ru₂: C, 66.37; H, 4.22; N, 0.00%. Calcd. for C₈₀H₆₁ClO₄P₄Ru₂(CH₂Cl₂)_{0.25}: C, 65.55; H, 4.25; N, 0.00%.

Preparation of [Ru₂(μ-C₄)Cl₂(CO)₄(PPh₃)₄] (16). [Ru₂(μ-C₄)HCl(CO)₄(PPh₃)₄] (**15**: 0.13 g, 0.09 mmol) and *N*-chlorosuccinimide (0.02 g, 0.15 mmol) were dissolved in THF (35 mL) and the solution was stirred for 5 minutes. Ethanol was then added and the solvents reduced *in vacuo* until a brown precipitate formed which was isolated by filtration and recrystallised from CH₂Cl₂/ethanol to yield a yellow solid. Yield: 0.12 g (95%). IR CH₂Cl₂: 2055, 1995 ν_{CO} cm⁻¹. Nujol: 2051, 1989 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 6.92, 8.23 ($m \times 2$, 60 H, C₆H₅). (CDCl₃, 25°C) ¹³C{¹H}: δ = 89.9 (tt, RuC≡C, ²J_{CP} = 20.9, ⁵J_{CP} = 2.2), 104.6 (t, RuC≡C, ³J_{CP} = 2.8), 128.1 [t^v, J_{CP} = 4.9, C^{3,5}(C₆H₅)], 130.2 [C⁴(C₆H₅)], 133.5 [t^v, J_{CP} = 24.0, C¹(C₆H₅)], 134.6 [t^v, J_{CP} = 5.3, C^{2,6}(C₆H₅)], 191.3 (t, ²J_{CP} = 8.6, CO), 194.3 (t, ²J_{CP} = 11.0 Hz, CO). ³¹P{¹H}: δ = 22.4. ESI-MS: m/z 1488.9 [M – Cl + NCMe]⁺. Anal. Found: C, 63.92; H, 4.27; N, 0.00%. Grinding and storage under high vacuum failed to completely remove the CH₂Cl₂ solvate apparent from the crystal structure. Calcd. for C₈₀H₆₀Cl₂O₄P₄Ru₂(CH₂Cl₂)_{0.25}: C, 64.11; H, 4.06; N, 0.00%. Calcd. for C₈₀H₆₀Cl₂O₄P₄Ru₂: C, 64.82; H, 4.08; N, 0.00%. **Crystal data** for C₈₂H₆₄Cl₆O₄P₄Ru₂: M_r = 1652.16, monoclinic, $P2_1/c$, a = 27.361(5), b = 10.355(5), c = 29.764(5) Å, β = 112.705(5)°, V = 7779(4) Å³, Z = 4, ρ_{calcd} = 1.411 Mg m⁻³, T = 173(2) K, light yellow block, 0.101 x 0.140 x 0.160 mm, $\mu(\text{Mo-K}\alpha)$ = 0.725 mm, F^2 refinement, R_1 = 0.077, wR_2 = 0.193, for 9079 independent observed absorption corrected reflections ($I > 2\sigma(I)$), $2\theta_{\text{max}}$ = 48.20°, 883 parameters, 24 restraints.

Preparation of [Ru₂(μ-C₄H₂)Cl₂(CO)₃(PPh₃)₄] (17). [Ru(C≡C≡CH)Cl(CO)₂(PPh₃)₂] (**3**: 0.05 g, 0.07 mmol) and [RuHCl(CO)(PPh₃)₃] (**17**: 0.06 g, 0.07 mmol) were dissolved in THF (30 mL) and the solution was heated gently to dissolve the solids, during which time the solution had turned deep red in colour. Ethanol was added and the solvents were reduced, to precipitate a red solid which was recrystallised from CH₂Cl₂/ethanol to yield a deep red solid. Yield: 0.07 g (74%). IR CH₂Cl₂: 2050, 1988, 1934 ν_{CO} cm⁻¹. Nujol: 2045, 1983, 1925 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 5.23 [d, 1 H, RuCH=CH, ³J_{HH} = 15.6 Hz], 6.99, 7.82, 8.29, 8.19 ($m \times 4$, 61 H, C₆H₅ and RuCH=CH). ¹³C{¹H} NMR data collected indicated decomposition of the product during data acquisition. ³¹P{¹H}: δ 22.6, 32.1. ESI-MS: m/z 1456.5 [M + H]⁺. HR ESI-MS: Found: 1462.1726. Calcd for C₈₁H₆₅³⁵ClNO₃P₄¹⁰²Ru₂ [M – Cl + CH₃CN]: 1462.1716. Anal. Found: C, 63.97; H, 4.40; N, 0.00%. Calcd. for C₇₉H₆₂Cl₂O₃P₄Ru₂(CH₂Cl₂)_{0.5}: C, 63.68; H, 4.24; N, 0.00%.

Preparation of [Ru₂(μ-C₄H₂)Cl₂(CO)₄(PPh₃)₄] (18). [Ru₂(μ-C₄H₂)Cl₂(CO)₃(PPh₃)₄] (**17**: 0.31 g, 0.21 mmol) was dissolved in THF (40 mL) and with stirring, CO gas was passed through the solution. The reaction was deemed complete on the colour change from red to yellow which occurred over 2 minutes and was confirmed by solution IR spectroscopy, including the appearance of a fourth carbonyl absorption. Ethanol was added to the solution and the solvents were reduced *in vacuo* to precipitate the product as a yellow powder. The solid was recrystallised from CH₂Cl₂/ethanol to yield a pale yellow solid. Yield: 0.30 g (96%). IR CH₂Cl₂: 2052, 2035, 1987, 1975 ν_{CO} cm⁻¹. Nujol: 2047, 2040, 1980, 1971 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 5.35 (d, 1 H, RuCH=CH, ³J_{HH} = 18.3), 8.07 (d, 1 H, RuCH, ³J_{HH} =

18.3 Hz, $^3J_{\text{PH}}$ not resolved) 6.91, 7.93, 8.33 ($m \times 3$, 60 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$: δ 98.2 (t, $^2J_{\text{CP}} = 19.83$, $\text{RuC}\equiv\text{C}$), 121.4 ($\text{RuC}\equiv\text{C}$), 124.5 ($\text{RuCH}=\text{CH}$), 128.1 [t^v , $J_{\text{CP}} = \text{obscured by solvent peak}$, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 130.2 [$\text{C}^4(\text{C}_6\text{H}_5)$], 133.2 [t^v , $J_{\text{CP}} = 22.2$, $\text{C}^1(\text{C}_6\text{H}_5)$], 134.4 [t^v , $J_{\text{CP}} = 22.2$, $\text{C}^1(\text{C}_6\text{H}_5)$], 134.8, 134.7 [$t^v \times 2$, $J_{\text{CP}} = 5.4$, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 163.4 (t, $^2J_{\text{CP}} = 14.2$, RuCH), 191.6 (t, $^2J_{\text{CP}} = 7.5$, CO), 194.5 (t, $^2J_{\text{CP}} = 9.4$, CO), 196.0 (t, $^2J_{\text{CP}} = 10.6$, RuCO), 199.0 (t, $^2J_{\text{CP}} = 10.2$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$: δ 22.5, 25.2. ESI-MS: m/z 1448.9 [$\text{M} - \text{Cl}$] $^+$. HR ESI-MS: Found: 1490.1680. Calcd for $\text{C}_{82}\text{H}_{65}^{35}\text{ClNO}_4\text{P}_4^{102}\text{Ru}_2$ [$\text{M} - \text{Cl} + \text{CH}_3\text{CN}$]: 1490.1656. Anal. Found: C, 64.94; H, 4.43; N, 0.00%. Calcd. For $\text{C}_{80}\text{H}_{62}\text{Cl}_2\text{O}_4\text{P}_4\text{Ru}_2$: C, 64.67; H, 4.21; N, 0.00%. *Crystal Data for* $\text{C}_{43}\text{H}_{30}\text{ClO}_2\text{P}_2\text{Ru}$, $M_r = 777.13$, monoclinic, $C2/c$, $a = 23.900(5)$ Å, $b = 10.450(2)$ Å, $c = 29.670(6)$ Å, $\beta = 101.90(3)^\circ$, $V = 7251(3)$ Å 3 , $Z = 8$, $\rho_{\text{calcd}} = 1.424$ Mg m $^{-3}$, $T = 200(2)$ K, yellow prisms, $R_1 = 0.055$, $wR_2 = 0.165$, for 6467 independent observed absorption corrected reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 50.2^\circ$), 421 parameters.

Preparation of $[\text{Ru}_2(\mu\text{-C}_4\text{H}_2)\text{Cl}(\text{S}_2\text{CNMe}_2)(\text{CO})_3(\text{PPh}_3)_4]$ (19). $[\text{Ru}_2(\mu\text{-C}_4\text{H}_2)\text{Cl}_2(\text{CO})_3(\text{PPh}_3)_4]$ (17: 0.10 g, 0.07 mmol) was dissolved in CH_2Cl_2 (25 mL) and $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ (0.01 g, 0.07 mmol) was added as a suspension. The mixture was stirred for five hours, during which time it turned from a red suspension to a yellow solution. The solution was then filtered through diatomaceous earth to remove NaCl, the solvent volume was reduced and ethanol was added resulting in the formation of a light yellow precipitate which was collected by vacuum filtration. Yield: 0.09 g (88%). IR CH_2Cl_2 : 2050, 1989, 1915 ν_{CO} cm $^{-1}$. Nujol: 2043, 1981, 1917 ν_{CO} cm $^{-1}$. NMR (CDCl_3 , 25°C) ^1H : δ = 2.55 (s, 3 H, NCH_3), 2.68 (s, 3 H, NCH_3), 4.86 (d, 1 H, $\text{RuCH}=\text{CH}$, $^3J_{\text{HH}} = 15.60$ Hz), 7.29, 7.57, 8.07 [$m \times 3$, 61 H, C_6H_5 , $\text{Ru}-\text{CH}=\text{CH}$]. $^{13}\text{C}\{^1\text{H}\}$: δ 38.5 [NCH_3], 38.9 [NCH_3], 93.2 [t, $^2J_{\text{CP}} = 18.25$, $-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-$], 119.8 [$-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-$], 121.1 [$-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-$], 127.3 [vt, $J_{\text{CP}} = 4.41$, $\text{Ru}(\text{S})\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 128.1 [vt, $J_{\text{CP}} = 4.37$, $\text{Ru}(\text{CO})\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 129.1 [$\text{Ru}(\text{S})\text{C}^4(\text{C}_6\text{H}_5)$], 130.1 [$\text{Ru}(\text{CO})\text{C}^4(\text{C}_6\text{H}_5)$], Both [$\text{C}^1(\text{C}_6\text{H}_5)$] resonances are obscured by other phenyl resonances. 134.7 [vt, $J_{\text{CP}} = 5.13$, $\text{Ru}(\text{CO})\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 134.9 [vt, $J_{\text{CP}} = 5.13$ Hz, $\text{Ru}(\text{S})-\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 158.8 ($\text{CH}=\text{CHRu}$), 191.8 (CO), 195.4 (CO), 205.4 (CO), 207.8 (S_2C). $^{31}\text{P}\{^1\text{H}\}$: δ 22.2, 37.6. ESI-MS: m/z 1540.7 [$\text{M}+\text{H}$] $^+$, 1505.8 [$\text{M} - \text{Cl}$] $^+$. Anal. Found: C, 62.95; H, 4.65; N, 0.94%. Calcd. For $\text{C}_{82}\text{H}_{68}\text{ClNO}_3\text{P}_4\text{Ru}_2\text{S}_2 \cdot (\text{CH}_2\text{Cl}_2)_{0.25}$: C 63.18; H, 4.41; N, 0.90%.

Preparation of $[\text{RuH}(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (20).^{6c} $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (1: 0.50 g, 0.53 mmol) was suspended in THF (25 mL) and ethynyltrimethylsilane (0.18 mL, 1.3 mmol) was added with stirring. The yellow suspension decolorized within 2 minutes. The solvent was then reduced and upon the addition of ethanol a snow-white precipitate formed which was isolated by filtration, washed with ether and dried *in vacuo*. Yield: 0.40 g (97%). IR CH_2Cl_2 : 2050 $\nu_{\text{C}\equiv\text{C}}$, 2022, 1983 ν_{CO} cm $^{-1}$. Nujol: 2052 $\nu_{\text{C}\equiv\text{C}}$, 2024 ν_{RuH} , 2015, 1977 ν_{CO} cm $^{-1}$. NMR (C_6D_6 , 25°C) ^1H : δ = 5.33 [t, 1 H, $\text{Ru}-\text{H}$, $^2J_{\text{HP}} = 20.7$ Hz], -0.06 [s, 9 H, $-\text{SiCH}_3$], 7.15, 7.99 [$m \times 2$, 30 H, C_6H_5]. $^{13}\text{C}\{^1\text{H}\}$ data collected indicated decomposition, confirmed by $^{31}\text{P}\{^1\text{H}\}$ measurements after data acquisition. $^{31}\text{P}\{^1\text{H}\}$: δ 45.4. ESI-MS: m/z 780.8 [$\text{M}+\text{H}$] $^+$. Anal. Found: C, 65.76; H, 5.28; N, 0.00%. Calcd. For $\text{C}_{43}\text{H}_{40}\text{O}_2\text{P}_2\text{RuSi}$: C, 66.14; H, 5.17; N, 0.00%.

Preparation of $[\text{RuCl}(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (21). $[\text{RuH}(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (20: 0.13 g, 0.17 mmol) was

dissolved in dry chloroform (25 mL) and stirred for 20 minutes. The progress of the reaction was monitored by *in situ* IR spectroscopy with two new $\nu(\text{CO})$ bands (2038, 1994 cm $^{-1}$) replacing those of the starting material (2022, 1983 cm $^{-1}$). The solvent was then removed and the residue extracted into DCM. The addition of ethanol yielded a pale cream solid, which was collected by filtration and dried *in vacuo*. Yield: 0.13 g (96%). IR CH_2Cl_2 : 2066 $\nu_{\text{C}\equiv\text{C}}$, 2038, 1994 ν_{CO} cm $^{-1}$. Nujol: 2063 $\nu_{\text{C}\equiv\text{C}}$, 2036, 1987 ν_{CO} cm $^{-1}$. NMR (C_6D_6 , 25°C) ^1H : δ 0.21 [s, 9 H, SiCH_3], 6.96, 7.08, 8.24 [$m \times 3$, 30 H, C_6H_5]. $^{31}\text{P}\{^1\text{H}\}$: δ 23.1. ESI-MS: m/z 758.8 [$\text{M} - \text{C}_2\text{SiMe}_3 + \text{NCMe}$] $^+$. Anal. Found: C, 62.50; H, 4.97; N, 0.00%. Calcd. For $\text{C}_{43}\text{H}_{39}\text{ClO}_2\text{P}_2\text{RuSi} \cdot (\text{CH}_2\text{Cl}_2)_{0.25}$: C, 62.15; H, 4.77; N, 0.00%. *Crystal Data for* $\text{C}_{43}\text{H}_{39}\text{ClO}_2\text{P}_2\text{RuSi}$, $M_r = 814.29$, monoclinic, $P2_1/n$, $a = 9.970(2)$ Å, $b = 19.640(4)$ Å, $c = 19.770(4)$ Å, $\beta = 94.55(3)^\circ$, $V = 3859.0(13)$ Å 3 , $Z = 4$, $\rho_{\text{calcd}} = 1.402$ Mg m $^{-3}$, $T = 200(2)$ K, colorless prisms, F^2 refinement, $R_1 = 0.035$, $wR_2 = 0.098$ for 8828 independent absorption corrected reflections ($I > 2\sigma(I)$, $2\theta_{\text{max}} = 55.0^\circ$), 454 parameters.

Preparation of $[\text{RuH}(\text{C}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ (22). $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (1: 0.25 g, 0.26 mmol) was suspended in THF (30 mL). Ethyne gas was then bubbled through this solution until it had turned from yellow to colourless. The solvent was then removed and the crude product was recrystallised from DCM/hexane to yield colourless microcrystals. Yield: 0.15 g (80%). IR CH_2Cl_2 : 2038 $\nu_{\text{C}\equiv\text{C}}$, 1988, 1959 ν_{CO} cm $^{-1}$. Nujol: 2030 $\nu_{\text{C}\equiv\text{C}}$, 1998, 1965 ν_{CO} cm $^{-1}$. NMR (C_6D_6 , 25°C) ^1H : δ = 5.22 [t, 1 H, $\text{Ru}-\text{H}$, $^2J_{\text{HP}} = 20.1$], 1.94 [t, 1 H, $\text{C}\equiv\text{C}-\text{H}$, $^4J_{\text{HP}} = 2.7$ Hz], 7.10, 7.79, 8.04 [$m \times 3$, 30 H, C_6H_5]. No useful $^{13}\text{C}\{^1\text{H}\}$ NMR data could be collected due to the facility of ethyne reductive elimination during data acquisition. Decomposition accompanied attempts to obtain crystallographic grade crystals. $^{31}\text{P}\{^1\text{H}\}$: δ 45.1. ESI-MS: m/z 682.3 [$\text{M} - \text{HCCH}$] $^+$. Anal. Found: C, 65.62; H, 3.99; N, 0.00%. Calcd. For $\text{C}_{40}\text{H}_{32}\text{O}_2\text{P}_2\text{Ru} \cdot (\text{CH}_2\text{Cl}_2)_{0.33}$: C, 65.77; H 4.47; N, 0.00%.

Reaction of $[\text{RuH}(\text{C}\equiv\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ with CHCl_3 . $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (1: 0.25 g, 0.26 mmol) was dissolved in THF (30 mL). Ethyne gas was then bubbled through this solution until it had turned from yellow to colourless. The solvent was then removed and the crude solid was dissolved in chloroform and stirred for 1 hour. The solvent was then removed and the yellow solid was recrystallized from CH_2Cl_2 /hexane to afford a straw coloured powder which was determined to be impure by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Yield: 0.20 g. $^{31}\text{P}\{^1\text{H}\}$: 22.8, 23.2, 60:40 relative intensity. The former resonance corresponds to the ethenyl complex $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})_2(\text{PPh}_3)_2]$ (24, *via* infrared spectroscopy CH_2Cl_2 : $\nu_{\text{CO}} = 2036$, 1974 cm $^{-1}$) the formation of which is presumably due to residual HCl in commercial chloroform.

Preparation of $[\text{Ru}(\text{CH}=\text{CH}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (25).^{32b} $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (1.00 g, 1.05 mmol) was suspended in dichloromethane (100 mL) and ethyne gas was bubbled through the solution until the yellow suspension had turned to a brown solution. Ethanol was added and the solvents were reduced, resulting in brown crystals of the product that were isolated by filtration, washed with hexane and dried *in vacuo*. Yield: 0.51 g (68%). IR CH_2Cl_2 : 1933 ν_{CO} cm $^{-1}$. Nujol: 1929 ν_{CO} cm $^{-1}$. NMR (C_6D_6 , 25°C) ^1H : δ 4.95 [d, 1 H, $\text{CH}=\text{CH}_2$, $\text{trans-}^3J_{\text{HH}} = 14.10$], 5.41 [d, 1 H, $\text{CH}=\text{CH}_2$, $^3J_{\text{HH}} = 3.3$], 7.85 [m, 30 H, C_6H_5], 8.34 [dt, 1 H, $\text{CH}=\text{CH}_2$, $^3J_{\text{HP}} = 7.80$, $^3J_{\text{HH}} = 14.01$ Hz]. $^{31}\text{P}\{^1\text{H}\}$: δ 32.1. ESI-MS: m/z

680.8 [M – Cl]⁺. Anal. Found: C, 64.84; H, 4.76; N, 0.00%. Calcd. For C₃₉H₃₃ClO₂P₂Ru.EtOH: C, 64.56; H, 5.16; N, 0.00%.

Preparation of [Ru(CH=CH₂)Cl(CO)₂(PPh₃)₂] (24). [Ru(CH=CH₂)Cl(CO)(PPh₃)₂] (**23**: 0.35 g, 0.49 mmol) was dissolved in dichloromethane (30 mL) and carbon monoxide was bubbled through the solution until the reaction was complete as indicated by *in situ* IR spectroscopy (2 minutes) and decolourisation to pale yellow. Ethanol was added and upon reduction of the solvent volume under reduced pressure, white crystals of the product formed. Yield: 0.25 g (69%). IR CH₂Cl₂: 2036, 1974 ν_{CO} cm⁻¹. Nujol: 2033, 1973 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 5.30 [d, 1 H, CH=CH₂, ³J_{HH} = 18.3], 6.12 [d, 1 H, CH=CH₂, ³J_{HH} = 10.8 Hz], 7.00, 8.08 [m × 2, 31 H, C₆H₅, CH=CH₂]. ³¹P{¹H}: δ 23.2. ESI-MS: *m/z* 708.8 [M – Cl]⁺. Anal. Found: C, 61.62; H, 4.40; N, 0.00%. Calcd. For C₄₀H₃₃ClO₂P₂Ru.0.5CH₂Cl₂: C, 61.83; H, 4.36; N, 0.00%.

Preparation of [Ru(C≡CH)Cl(CO)₂(PPh₃)₂] (23). To a stirred solution of [RuH(C≡CH)(CO)₂(PPh₃)₂] (**22**: 0.05 g, 0.07 mmol) in THF (20 mL), was added *N*-chlorosuccinimide (0.01 g, 0.07 mmol). The solution turned from colourless to light brown and the reaction was monitored by IR spectroscopy (10 min). Once the reaction was complete, ethanol was added and the solvents reduced until a white precipitate formed. The white microcrystals were isolated by filtration and washed with ethanol and hexane. Yield: 0.04 g (76%). IR CH₂Cl₂: 2059, 1995 ν_{CO} cm⁻¹. Nujol: 2058, 1991 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 2.45 [t, 1 H, C≡CH ⁴J_{HP} = 2.01 Hz], 6.95, 8.26 [m × 2, 30 H, C₆H₅]. (CDCl₃, 25°C) ¹³C{¹H}: δ 101.4 [t, ²J_{CP} = 19.2, C≡CH], 102.3 [C≡CH], 128.1 [t^v, J_{CP} = 4.87, C^{3,5}(C₆H₅)], 130.4 [C⁴(C₆H₅)], 133.2 [t^v, J_{CP} = 23.8, C¹(C₆H₅)], 134.5 [t^v, J_{CP} = 5.4, C^{2,6}(C₆H₅)], 191.8 [t, ²J_{CP} = 17.7, CO], 194.8 [t, ²J_{CP} = 19.5 Hz, CO]. ³¹P{¹H}: δ 22.8. ESI-MS: *m/z* 758.7 [M – C₂H + NCMe]⁺. Anal. Found: C, 63.40; H, 4.58; N, 0.00%. Calcd. For C₄₀H₃₁ClO₂P₂Ru.(CH₂Cl₂)_{0.25}: C, 63.30; H 4.16; N 0.00%.

Preparation of [RuBr(C≡CH)(CO)₂(PPh₃)₂] (26). To a stirred solution of [RuH(C≡CH)(CO)₂(PPh₃)₂] (**22**: 0.05 g, 0.07 mmol) in THF (20 mL), *N*-bromosuccinimide (0.01 g, 0.07 mmol) was added. The solution turned from colourless to light brown and the reaction was monitored by IR spectroscopy. Once the reaction was complete, the solvents were removed and the residue was extracted into CH₂Cl₂. Addition of ethanol and the reduction of the solvent resulted in the precipitation of a white crystalline solid. The white micro-crystals were isolated by filtration and washed with ethanol and hexane. Yield: 0.05 g (90%). IR CH₂Cl₂: 2059, 1995 ν_{CO} cm⁻¹. Nujol: 2056, 1989 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 2.53 [t, 1 H, C≡CH, ⁴J_{HP} = 2.4 Hz], 6.96, 8.27 [m × 2, 30 H, C₆H₅]. ³¹P{¹H}: δ 21.1. ESI-MS: *m/z* 680.8 [M – Br – CO]⁺. Anal. Found: C, 59.48; H, 4.16; N, 0.00%. Calcd. For C₄₀H₃₁BrO₂P₂Ru.(CH₂Cl₂)_{0.33}: C, 59.48; H, 3.92; N, 0.00%.

Preparation of [Ru(C≡CH)(SePh)(CO)₂(PPh₃)₂] (27). [RuH(C≡CH)(CO)₂(PPh₃)₂] (**22**: 0.10 g, 0.14 mmol) and diphenyldiselenide (0.022 g, 0.07 mmol) were dissolved in THF (30 mL). The resulting solution was then stirred for four hours, by which time the solution had turned from yellow to orange. Hexane was added and the solution reduced under vacuum to precipitate the crude orange product. Thin layer chromatography revealed the product to be slightly impure. The residue was purified by column chromatography (silica gel,

CH₂Cl₂). The orange product was eluted and precipitated from CH₂Cl₂ by dilution with hexane. Yield: 0.09 g (74%). IR CH₂Cl₂: 2047, 1984 ν_{CO} cm⁻¹. Nujol: 2035, 1979 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 2.75 [t, 1 H, C≡CH, ⁴J_{HP} = 2.4 Hz], 6.74 [m, 5 H, SeC₆H₅], 7.05, 8.21 [m × 2, 30 H, PC₆H₅]. ¹³C{¹H} data collected indicated decomposition, confirmed by ³¹P{¹H} measurements after data acquisition. ³¹P{¹H}: δ 21.6. Anal. Found: C, 62.27; H, 4.41; N, 0.00%. Calcd. For C₄₆H₃₆O₂P₂RuSe.(CH₂Cl₂)_{0.33}: C, 62.34; H, 4.14; N, 0.00%.

Preparation of [Ru(C≡CH)(SC₆H₄CH₃-4)(CO)₂(PPh₃)₂] (28). [RuH(C≡CH)(CO)₂(PPh₃)₂] (**22**: 0.10 g, 0.14 mmol) and di(*p*-tolyl)disulfide (0.017 g, 0.07 mmol) were dissolved in THF (30 mL). The resulting solution was then stirred overnight. Hexane was added and the solution concentrated under vacuum to precipitate a crude bright yellow product. Thin layer chromatography revealed the product to be pure. The crude product was recrystallised from dichloromethane/ethanol to afford fine yellow crystals of the desired product. Yield: 0.08 g (66%). IR CH₂Cl₂: 2048, 1985 ν_{CO} cm⁻¹. Nujol: 2042, 1977 ν_{CO} cm⁻¹. NMR (C₆D₆, 25°C) ¹H: δ 2.00 [s, 3 H, CH₃], 2.65 [t, 1 H, C≡CH, ⁴J_{HP} = 2.4], 6.51, 6.55 [AA'BB' pattern, 4 H, SC₆H₄CH₃, ³J_{AB} = 8.1 Hz], 7.04, 8.17 [m × 2, 30 H, C₆H₅]. (CDCl₃, 25°C) ¹³C{¹H}: δ 25.9 [s, CH₃], 101.6 [t, Ru-C≡CH, ²J_{CP} = 19.8], 104.3 [RuC≡CH], the two quaternary carbons of the *p*-tolyl group could not be unambiguously assigned, 128.1 [vt, J_{CP} = 4.60, C^{3,5}(C₆H₅)], 130.2 [C⁴(C₆H₅)], 134.1 [vt, J_{CP} = 24.44, C¹(C₆H₅)], 134.6 [vt, J_{CP} = 4.53, C^{2,6}(C₆H₅)], 135.1 [C^{2,6}(S-C₆H₄)], 141.5 [C^{3,5}(S-C₆H₄)], 194.3 [t, ²J_{CP} = 7.62, -CO], 194.5 [t, ²J_{CP} = 10.7 Hz, -CO]. ³¹P{¹H}: δ 22.1. ESI-MS: *m/z* 803.0 [M – CO]⁺. Anal. Found: C, 68.12; H, 4.72; N, 0.00%. Calcd. For C₄₇H₃₉O₂P₂RuS: C, 67.86; H, 4.73; N, 0.00%. *Crystal Data for* C₄₈H₄₀Cl₂O₂P₂RuS, *M_r* = 914.77, triclinic, *P*-1 (No. 2), *a* = 9.997(5) Å, *b* = 13.079(5), *c* = 16.586 Å, α = 100.126(5), β = 91.282(5), γ = 93.454(5)°, *V* = 2130(1). Å³, *Z* = 2, ρ_{calcd} = 1.426 Mg m⁻³, *T* = 200(2) K, orange rod, 0.46 × 0.18 × 0.05 mm, μ(Mo-Kα) = 0.656 mm, *F*² refinement, *R*₁ = 0.044, *wR*₂ = 0.096, for 7234 independent observed absorption corrected reflections (*I* > 2σ(*I*), 2θ_{max} = 55.0°), 504 parameters.

Preparation of [Ru{C(=CHSiMe₃)C≡CSiMe₃}Cl(CO)(PPh₃)₂] (29)²⁹ [RuHCl(CO)(PPh₃)₃] (2.90 g, 3.05 mmol) was suspended in toluene (60 mL). A suspension of bis(trimethylsilyl)butadiyne) (0.60 g, 3.1 mmol) in toluene (20 mL) was then added and the mixture was heated until all the solid had dissolved, by which time the solution had turned bright orange. The mixture was heated at reflux for a further 5 minutes, by which time the solution had turned dark orange/red. The solvent was then removed to yield an oily residue. Diethyl ether was then added and the flask was placed in an ultrasonic bath for 20 minutes. The resulting solid was isolated by filtration and recrystallised from CH₂Cl₂/ethanol to yield orange crystals. Yield: 1.20 g (44%). IR CH₂Cl₂: 1921 ν_{CO}, 1270, 1259 ν_{CSi} cm⁻¹. Nujol: 2082 ν_{C≡C}, 1919 ν_{CO}, 1242 ν_{CSi} cm⁻¹. NMR (CDCl₃, 25°C) ¹H: δ -0.29 (s, 9 H, SiCH₃), 0.07 [s, 9 H, -SiCH₃], 6.24 [s, C=CH], 7.37, 7.66 [m × 2, 30 H, C₆H₅]. ³¹P{¹H}: δ 34.6. *Crystal Data for* C₉₄H₉₈Cl₂O₂P₂Ru₂Si₄, *M_r* = 1769.00, monoclinic, *P*2₁/c, *a* = 12.300(3) Å, *b* = 35.950(7) Å, *c* = 20.730(4) Å, β = 102.68(3)°, *V* = 8943(3) Å³, *Z* = 4, ρ_{calcd} = 1.314 g cm⁻³, *T* = 200(2) K, orange prisms, *F*² refinement, *R*₁ = 0.048, *wR*₂ = 0.148, for 15649 independent observed absorption corrected reflections (*I* > 2σ(*I*), 2θ_{max} = 50.2°), 986 parameters.

Preparation of [Ru{C(=CHSiMe₃)C≡CSiMe₃}Cl(CO)₂(PPh₃)₂] (30). [Ru{C(=CHSiMe₃)C≡CSiMe₃}Cl(CO)-(PPh₃)₂] (**29**: 0.50 g, 0.57 mmol) was dissolved in dichloromethane (20 mL) and carbon monoxide gas was then bubbled slowly through the solution. The solution immediately turned from deep orange to yellow. The solvent was then removed, leaving a yellow powder, which was recrystallized from CH₂Cl₂ and ethanol. Yield: 0.46 g (89%). IR CH₂Cl₂: 2105 $\nu_{C\equiv C}$, 1940, 1974 ν_{CO} , 1260 ν_{CSi} cm⁻¹. Nujol: 2104 $\nu_{C\equiv C}$, 2039, 1985, 1968 (solid state splitting) ν_{CO} , 1248 ν_{CSi} cm⁻¹. NMR (CDCl₃, 25°C) ¹H: δ - 0.24 [s, 9 H, -SiCH₃], 0.15 [s, 9 H, -SiCH₃], 7.40, 7.72 [m x 2, 30 H, C₆H₅]. ¹³C{¹H}: δ - 0.6 [SiCH₃], 0.5 [SiCH₃], 100.5 [C≡C-SiMe₃], 121.6 [C≡C-SiMe₃], 128.0 [t^v, J_{CP} = 4.6, C^{3,5}(C₆H₅)], 130.3 [C⁴(C₆H₅)], 132.5 [t^v, J_{CP} = 22.97, C¹(C₆H₅)], 134.9 [t^v, J_{CP} = 4.98, C^{2,6}(C₆H₅)], 137.7 [C=CHSiMe₃] 156.3 [Ru-C=C], 194.3 [t, $^2J_{CP}$ = 8.49, CO], 197.5 [t, $^2J_{CP}$ = 12.0 Hz, CO]. ³¹P{¹H}: δ 24.7. ESI-MS: m/z 876.9 [M - Cl]⁺. Anal. Found: C, 63.08; H, 5.72; N, 0.00%; Calcd. For C₄₈H₄₉ClO₂P₂RuSi₂: C, 63.18; H, 5.41; N 0.00%.

Preparation of [Ru{C(=CHSiMe₃)C≡CSiMe₃}S₂CNMe₂](CO)(PPh₃)₂] (31). [Ru{C(=CHSiMe₃)C≡CSiMe₃}Cl(CO)(PPh₃)₂] (**29**: 1.10 g, 1.24 mmol) was dissolved in dichloromethane (20 mL) and to this was added a solution of Na[S₂CNMe₂] (0.23 g, 1.3 mmol) in THF (20 mL). The solution turned immediately from deep orange to yellow. The NaCl formed as a by-product of the reaction was removed by filtration through diatomaceous earth. The solvent was then removed, leaving a yellow powder, which was shown to be impure by ³¹P{¹H} NMR spectroscopy. Recrystallization of the crude product was performed from CH₂Cl₂ with ethanol. Yield: 0.71 g (59%). IR CH₂Cl₂: 2101 $\nu_{C\equiv C}$, 1922 ν_{CO} , 1270, 1260 ν_{CSi} cm⁻¹. Nujol: 2100 $\nu_{C\equiv C}$, 1915 ν_{CO} , 1248 ν_{CSi} cm⁻¹. NMR (CDCl₃, 25°C) ¹H: δ 0.12 [s, 9 H, SiCH₃], 0.22 [s, 9 H, SiCH₃], 2.41 2.42 [s x 2, 3 H x 2, NCH₃], 7.26, 7.59 [m x 2, 30 H, C₆H₅]. ¹³C{¹H}: δ - 0.5 [SiCH₃], 1.1 [SiCH₃], 94.7 [C≡CSiMe₃], 116.2 [C≡C-SiMe₃], 126.6 [t^v, J_{CP} = 4.6, C^{3,5}(C₆H₅)], 128.8 [C⁴(C₆H₅)], 132.5 [t^v, J_{CP} = 11.7, C¹(C₆H₅)], 135.0 [t^v, J_{CP} = 5.0, C^{2,6}(C₆H₅)], the C=CHSiMe₃ resonance was obscured by the phenyl resonances, 144.0 [t, $^2J_{CP}$ = 10.8, Ru-C=C], 205.7 [t, $^2J_{CP}$ = 14.6 Hz, -CO], 206.5 [S₂CN]. ³¹P{¹H}: δ 38.6. ESI-MS: m/z 1007.3 [M + H]⁺. Anal. Found: C, 59.72; H, 5.44; N, 1.48%; Calcd. For C₅₀H₅₅NOP₂RuS₂Si₂.CH₂Cl₂: C, 60.11; H, 5.64; N 1.37%. *Crystal Data for* C₅₄H₆₃NO₂P₂RuS₂Si₂, M_r = 1041.36, triclinic, *P*-1 (No. 2), a = 12.434(5) Å, b = 13.181(5) Å, c = 17.570(5) Å, α = 80.940(5)°, β = 71.440(5)°, γ = 83.977(5)°, V = 2691.1(17) Å³, Z = 2, ρ_{calcd} = 1.285 Mg m⁻³, T = 200(2) K, yellow prisms, F^2 refinement, R_1 = 0.052, wR_2 = 0.146, for 12221 independent observed absorption corrected reflections ($I > 2\sigma(I)$), $2\theta_{max}$ = 49.13°, 627 parameters.

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Conflicts of Interest

The authors declare no conflicts of interest.

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