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Some transition-metal complexes derived from silylated 1,3-diynes

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The complexes $[Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(CO)_4(cp)_2]$, $[Pt(\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(PPh_3)_2]$ and $Ru_3(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(\mu\text{-}CO)(CO)_9]$ have been prepared. Further reaction of the first with $[Co_2(CO)_8]$ gives $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2:\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$. Desilylation of $[Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(\mu\text{-}dppm)_n(CO)_{6-2n}]$ (n = 0 or 1, dppm = $Ph_2PCH_2PPh_2$) gave $[Co_2(\mu\text{-}\eta^2\text{-}RC_2C\equiv CH)(\mu\text{-}dppm)_n(CO)_{6-2n}]$ (n = 0, R = H; n = 1, R = $SiMe_3$ or H). The first dppm complex adds across the M–M bonds in $[Re_2(CO)_8(NCMe)_2]$ and $[Ru_3(CO)_{12}]$ to give $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_8]$ and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_9]$, respectively, while both dppm complexes react with $[WCl(CO)_3(cp)]$ to give $[Co_2\{\mu\text{-}\eta^2\text{-}RC_2C\equiv C[W(CO)_3(cp)]\}(\mu\text{-}dppm)(CO)_4]$ (R = H or $SiMe_3$). Auration of the $HC_2C_2SiMe_3$ complex with $[AuCl(PPh_3)]$–1,8-diazabicyclo[5.4.0]undec-7-ene gave $[Co_2\{\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv C[Au(PPh_3)]\}(\mu\text{-}dppm)(CO)_4]$. Addition of $HC\equiv CC\equiv CSiMe_3$ to $[Ru_3(\mu\text{-}dppm)_2(CO)_8]$ gave $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C\equiv CSiMe_3)(\mu\text{-}dppm)_2(CO)_5]$. The complex $[Os_3(CO_{10}(NCMe)_2]$ reacts with $HC\equiv CC\equiv CSiMe_3$ to give isomers of $[Os_3(\mu_3\text{-}\eta^2\text{-}HC_2C_2SiMe_3)(\mu\text{-}CO)(CO)_9]$; the mixture reacts with $[Co_2(CO)_8]$ to give one isomer of $[Os_3\{\mu_3\text{-}\eta^2;\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$ in which the Co_2 moiety bridges the $C\equiv CSiMe_3$ portion of the diyne. The crystal structures of five of the complexes have been determined.

The current interest in complexes of transition metals derived from di- and poly-ynes is partially due to the stabilising influence of the metal on reactive unsaturated carbon chains and polycarbon ligands.[1–5] In conjunction with our studies of the chemistry of complexes containing the C_4 ligand,[6,7] we have had occasion to prepare several complexes containing 1,3-diyne units, which are described in this paper. The structures of $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2:\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ (cp = $\eta\text{-}C_5H_5$), $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_8]$, $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-}dppm)(CO)_4]\}(CO)_9]$, $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C\equiv CSiMe_3)(\mu\text{-}dppm)_2(CO)_5]$ and $[Os_3\{\mu_3\text{-}\eta^2:\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$ are also reported.

Results and Discussion

Reactions of $Me_3SiC_2C_2SiMe_3$

Reactions of $Me_3SiC_2C_2SiMe_3$ with $[\{Mo(CO)_2(cp)\}_2]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ afforded the expected complexes $[Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(CO)_4(cp)_2]$ **1** and $[Pt(\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(PPh_3)_2]$ **3** respectively. The platinum complex forms a pale yellow powder (86% yield) and is analogous to the R_2C_4 complexes (R = Me or Ph) described by Heyns and Stone[8] some years ago.

The new complexes **1** and **3** were readily characterised by the usual methods, details of which are given in the Experimental section below. These complexes contain an uncomplexed $C\equiv C$ triple bond, which gives a ν(CC) absorption at 2125 (**1**) or 2132 and 2094 cm^{-1} (**3**). The electrospray (ES) mass spectrum of **3** contains an intense $[M + H]^+$ ion at m/z 914, which fragments by loss of $SiMe_3$, C_6H_6 and $C_4(SiMe_3)_2$ groups.

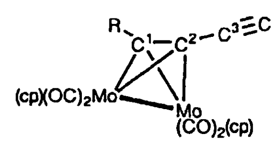
The simple alkyne cluster $[Ru_3(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(\mu\text{-}CO)(CO)_9]$ **5** was obtained from the reaction between $[Ru_3(CO)_{10}(NCMe)_2]$ and $Me_3SiC_2C_2SiMe_3$. The low yield of **5** (10%) and difficulties experienced in crystallising the product precluded full characterisation. However, the ν(CO) spectrum of this red complex is very similar to those of the related alkyne clusters $[Ru_3(\mu_3\text{-}\eta^2\text{-}RC_2R')(\mu\text{-}CO)(CO)_9]$ (*e.g.* R = R′ = Me, Ph; R = H, R′ = CO_2H),[9] with the absorption for the bridging CO ligand at 1883 cm^{-1}, while ν(CC) for the unco-ordinated $C\equiv C$ triple bond is at 2108 cm^{-1}. The ^1H NMR spectrum contained only one resonance at δ 0.21, suggesting either a rapid exchange of co-ordinated and free alkyne moieties or accidental equivalence of the two $SiMe_3$ resonances.

Further complexation of metal–ligand groups to the free $C\equiv C$ triple bond can be achieved readily. Reaction between $[Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(CO)_4(cp)_2]$ and $[Co_2(CO)_8]$ gave deep green crystals of the mixed Mo_2Co_2 complex **6**. Also isolated from the reaction mixture was $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2,\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ (6%).[10] The identity of **6** was deduced from analytical and spectroscopic data and confirmed by a single-crystal structure determination (see below). The ν(CO) spectrum contained ten absorptions; overall, the pattern approximates a superposition of the component ν(CO) spectra, *i.e.* there is little or no electronic interaction between the two metal carbonyl groups. No absorptions were found in the ν(CC) region. In the ^{13}C NMR spectrum the signals at δ 201 and 231.5 are assigned to the CO groups on Co and Mo respectively (*cf.* corresponding resonances at δ 227.68 and 230.0 for **1**). There are CO-exchange processes localised on each metal centre. The diyne C resonances were not observed, even with long pulse delays in the ^{13}C NMR experiment, suggesting a lack of efficient relaxation processes for these carbon nuclei.

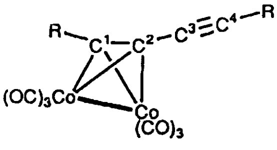
Under mild oxidative conditions, $[Co_2(\mu\text{-}\eta^2\text{-}RC_2R')(CO)_6]$ complexes often decompose to liberate the alkyne.[11] Prolonged exposure of **6** to atmospheric oxygen on silica was sufficient to remove the co-ordinated $Co_2(CO)_6$ group and regenerate **1**. This effect at least partially accounts for the moderate yield of **6** when isolated by preparative TLC (33%).

Desilylation reactions

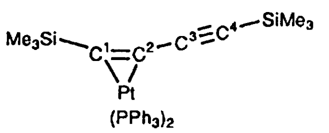
Desilylation of complex **1** with tetrabutylammonium fluoride proceeded readily. In moist tetrahydrofuran (thf) the complex $[Mo_2(\mu\text{-}\eta^2\text{-}HC_2C\equiv CH)(CO)_4(cp)_2]$ **7** was isolated in 22% yield. Desilylation of the analogous cobalt complex $[Co_2(\mu\text{-}\eta^2\text{-}$



1 R = SiMe$_3$
7 R = H



2 R = SiMe$_3$
8 R = H



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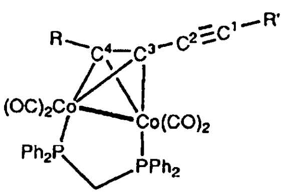
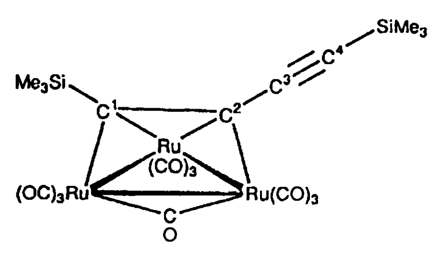
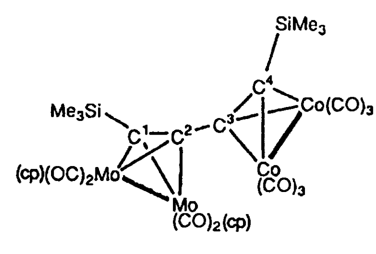


4 R = R' = SiMe$_3$
9 R = SiMe$_3$, R' = H
10 R = R' = H
13 R = SiMe$_3$, R' = W(CO)$_3$(cp)
14 R = H, R' = W(CO)$_3$(cp)
15 R = H, R' = Au(PPh$_3$)



5 R = SiMe$_3$



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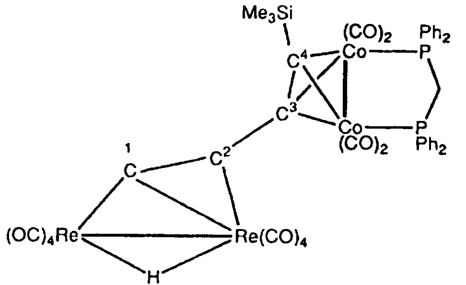
$Me_3SiC_2C{\equiv}CSiMe_3)(CO)_6]$ **2**[10] was performed with KF in methanol to give $[Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_6]$ **8**. These buta-1,3-diynyl complexes were readily characterised from their spectroscopic properties, which included resonances in the ^1H NMR spectra for the two types of HC≡ protons around δ 2.73 and 5.63 (**7**) or 3.73 and 6.20 (**8**), assigned to protons on the free and co-ordinated C≡C systems, respectively. These assignments were made by comparison with the chemical shifts of terminal acetylenes and $[Co_2(\mu\text{-}\eta^2\text{-}HC_2R)(CO)_6]$ complexes.[12] The FAB mass spectrum of **7** contained the expected molecular ions and fragment ions formed by loss of CO groups. Complex **8** is remarkably volatile, codistilling with MeOH at 1 mmHg (*ca.* 133 Pa); it decomposed rapidly at −20 °C under dry nitrogen and thus proved to be unsuitable as a reagent for further metallation reactions. A much more stable complex was obtained by replacing two CO ligands in **2** by bis(diphenylphosphino)methane (dppm) prior to desilylation as reported by Diederich and co-workers.[2] The product, $[Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_4]$, undergoes stepwise desilylation to give the stable crystalline derivatives $[Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4]$ **9** and $[Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4]$ **10**.[2]

Reactions of $[Co_2(\mu\text{-}\eta^2\text{-}RC_2C{\equiv}CH)(\mu\text{-dppm})(CO_4)]$

We were able to use the unco-ordinated –C≡CH-portion of complex **9** to form mixed Co_2Re_2 and Co_2Ru_3 complexes by oxidative addition of the C–H bond across the Re–Re bond in $[Re_2(CO)_8(NCMe)_2]$ or an Ru–Ru bond in $[Ru_3(CO)_{12}]$. Both complexes, namely $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1{:}\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_8]$ **11** and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1{:}\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9]$ **12** were fully characterised by single-crystal structures: other spectroscopic data were in accord with the solid-state structures.



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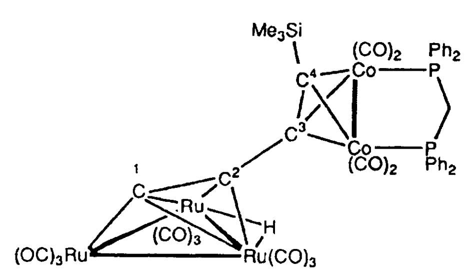

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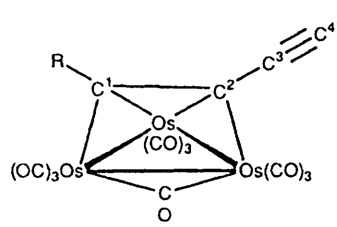
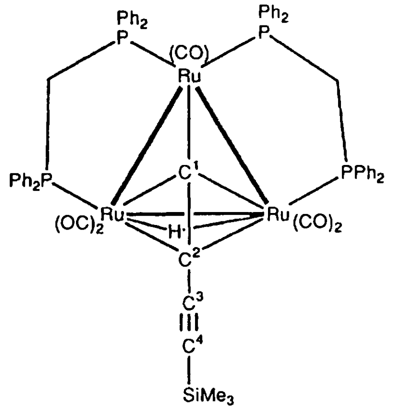


16a R = H, R' = SiMe$_3$
16b R = SiMe$_3$, R' = H



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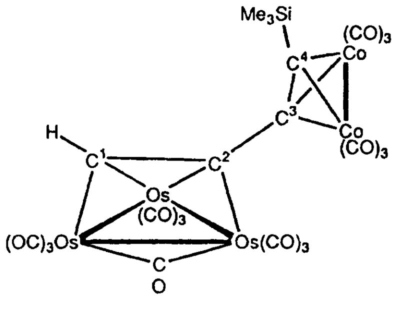

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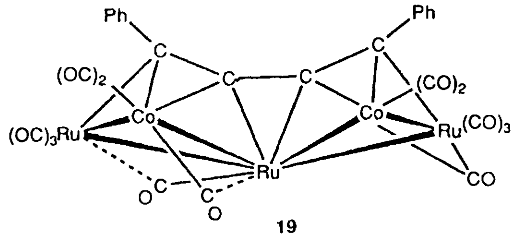

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The former product, obtained in 85% yield, contained a characteristic Re–H resonance at δ −12.88 in the ^{1}H NMR spectrum. The analogous octacarbonyl complex $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_2Ph)(CO)_8]$ has been prepared from either $[Re_2(CO)_{10}]$ or $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}\textit{trans}\text{-}CH{=}CHMe)(CO)_8]$ and phenylacetylene.[13] Similar reactions of $[Re_2(CO)_8(NCMe)_2]$ with phenylacetylene or α-ethynylestradiol [17α-ethynylestra-1,3,5(10)-triene-3,17β-diol] gave acetonitrile-substituted derivatives of general formula $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_2R)(CO)_7(NCMe)]$.[14] In these cases it was suggested that the incorporation of NCMe into these products was due to thermal substitution of one of the axial CO ligands of an undetected octacarbonyl intermediate by the MeCN liberated from the dirhenium precursor during the course of reaction. Curiously, however, **11** retains all eight carbonyl ligands on the dirhenium core.

The reaction involving unactivated $[Ru_3(CO)_{12}]$ is notable for the very high yield (96%) of complex **12**. This product is similar to those reported earlier from alk-1-ynes and $[Ru_3(CO)_{12}]$ or $[Ru_3(CO)_{10}(NCMe)_2]$,[15] and is characterised by an Ru–H resonance at δ −19.99.

Formation of a σ-bonded acetylide was found in the copper-catalysed reaction between complex **9** and $[WCl(CO)_3(cp)]$ run in $NHEt_2$. Deep red needles of $[Co_2\{\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C[W(CO)_3(cp)]\}(\mu\text{-dppm})(CO)_4]$ **13** were obtained in 70% yield. A similar reaction with **10** afforded brick-red $[Co_2\{\mu\text{-}\eta^2\text{-}HC_2C{\equiv}C[W(CO)_3(cp)]\}(\mu\text{-dppm})(CO)_4]$ **14** in 50% yield. In the ^{13}C NMR spectrum, broad Co–CO resonances were at δ 202.7 and 207.5 (**13**), 203.2 and 206.2 (**14**); sharp singlets at δ 210.9 and 230.2 (**13**) or 210.9 and 229.8 (**14**) were assigned to the W–CO groups. Similarly, in **13** the C_2 unit co-ordinated to Co (triplets at δ 84.4 and 86.8 by coupling to the dppm ^{31}P nuclei) could be distinguished from the singlets for the C_2 σ-bonded to W (δ 95.8 and 109.0). The acetylenic proton in **14** resonated at δ 6.04 in the ^{1}H NMR spectrum.

As expected, the reaction between complex **10** and $[AuCl(PPh_3)]$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) resulted in replacement of the acetylenic H atom by the isolobal $Au(PPh_3)$ group. The resulting complex, $[Co_2\{\mu\text{-}\eta^2\text{-}HC_2C{\equiv}C[Au(PPh_3)]\}(\mu\text{-dppm})(CO)_4]$ **15**, was obtained in 48% yield as deep red needles. The acetylenic proton resonance was found at δ 5.98 (^{1}H NMR spectrum); only the carbons attached to Co could be located in the ^{13}C NMR spectrum at δ 70.63 and 78.74.

Reactions of $HC_2C_2SiMe_3$

Reaction of $HC_2C_2SiMe_3$ with $[Os_3(CO)_{10}(NCMe)_2]$ afforded the alkyne complex $[Os_3(\mu_3\text{-}\eta^2\text{-}HC_2C_2SiMe_3)(\mu\text{-}CO)(CO)_9]$ **16**. This compound was obtained as a 2 : 1 mixture of the two possible isomers containing the Os_3 cluster co-ordinated to either of the C≡C triple bonds, as determined by ^{1}H NMR spectroscopy. The isomer with the Os_3 group co-ordinated to the C_2H part of the diyne (**16a**) was identified as the major component. We did not find any evidence for the formation of the hydridoalkynyl complex in this reaction. This contrasts

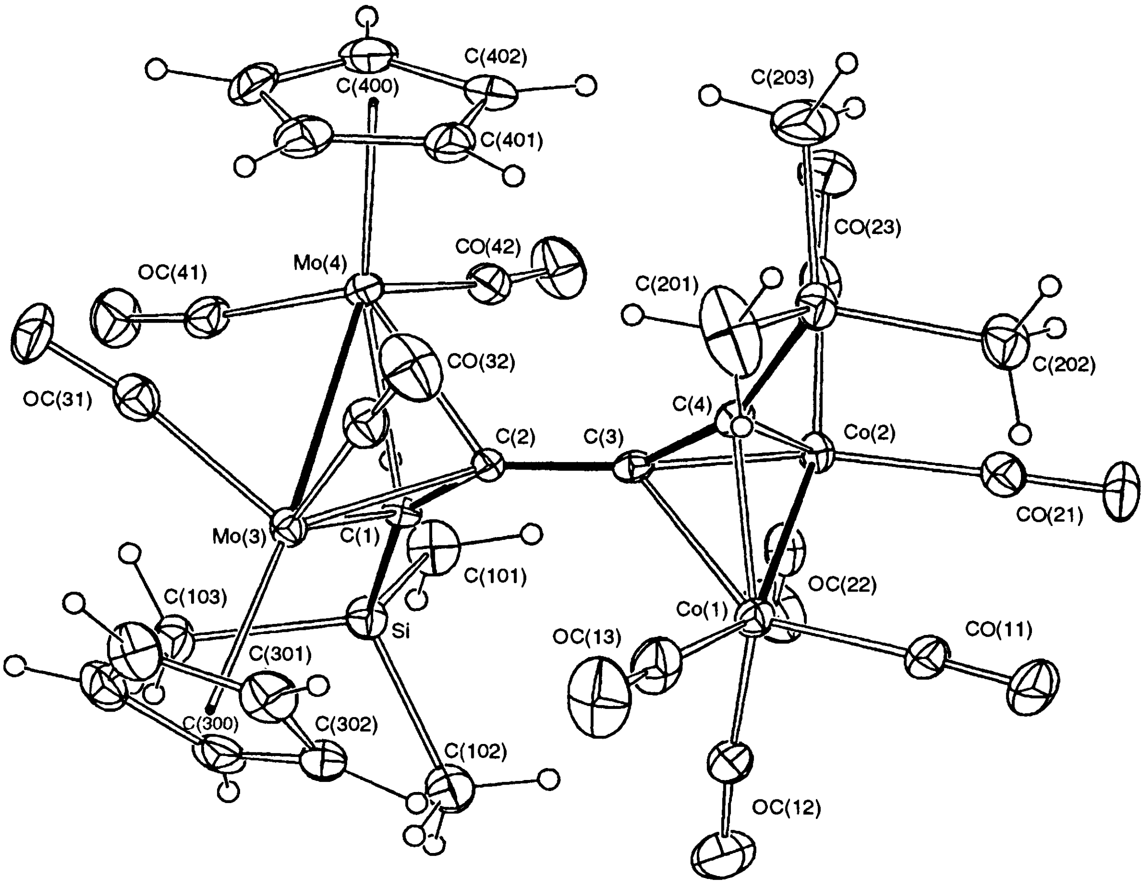

Fig. 1 Plot of a molecule of $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2:\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ **6**, showing the atom numbering scheme. In this and subsequent figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å

with the situation found with $[Ru_3(\mu\text{-dppm})_2(CO)_8]$ where formation of $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C{\equiv}CSiMe_3)(\mu\text{-dppm})_2(CO)_5]$ **17**, which was fully characterised by a single-crystal X-ray study (see below), was found. The ^1H NMR spectrum of **17** contained a high-field resonance at δ −19.40. The bis(dppm) complex does not display any evidence for isomerisation or fluxional behaviour. The solid-state structure indicates that the diyne ligand is constrained between the phenyl rings of the bulky dppm ligands (see Molecular structures section).

Cluster **16** reacts readily with $[Co_2(CO)_8]$ to give a dark green 1:1 adduct **18** identified by a single-crystal X-ray study as $[Os_3\{\mu_3\text{-}\eta^2:\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$, formed by addition of a $Co_2(CO)_6$ fragment to the uncoordinated C≡C triple bond of **16a**, *i.e.* the Co_2 moiety is attached to the C_2 unit adjacent to the $SiMe_3$ group. There was no evidence for the formation of the other isomer. It is interesting that addition to the C≡C triple bond has occurred in this reaction, since the analogous reaction with $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-}CO)(CO)_9]$ afforded the Co_2Ru_3 bow-tie cluster **19**, apparently by insertion of the cobalt reagent into an Ru–Ru bond,[16] and that with $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C{\equiv}CPh)(\mu\text{-dppm})(\mu\text{-}CO)(CO)_7]$ afforded a complex in which the diyne had been cleaved to form two C_2Ph units.[17]

Molecular structures

(*i*) $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2:\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ **6.** A picture of a molecule of complex **6** is given in Fig. 1 and some significant bond parameters are collected in Tables 1 and 2. It can be seen that each C≡C triple bond is co-ordinated to a dimetal system, C(1)–C(2) to Mo(3)–Mo(4) and C(3)–C(4) to Co(1)–Co(2). The metal–metal distances [Co(1)–Co(2) 2.470(1), Mo(3)–Mo(4) 2.958(1) Å] are similar to those found in $[Co_2(\mu\text{-}\eta^2\text{-}C_2R_2)(CO)_6]$ [2.460(1) (R = Bu^t); 2.476(1) Å (R = Ph)][18] and $[Mo_2\{\mu\text{-}\eta^2\text{-}C_2(SiMe_3)_2\}(CO)_4(cp)_2]$ [2.952(1) Å].[19] The metal–carbon distances [Mo(3,4)–C(1) 2.185(6), 2.244(6); Mo(3,4)–C(2) 2.208(6), 2.220(6); Co(1,2)–C(3) 2.029(6), 2.009(6); Co(1,2)–C(4) 1.979(6), 2.008(6) Å] are within the ranges found for the similar Mo_2– or Co_2–η^2-alkyne complexes mentioned above. The C(1)–C(2) and C(3)–C(4) distances [1.358(8), 1.345(8) Å] show the expected lengthening on co-ordination and the angles Si(1)–C(1)–C(2), C(1)–C(2)–C(3), C(2)–C(3)–C(4) and C(3)–C(4)–Si(2) are 151.6(5), 140.5(5), 147.3(5) and 157.5(5)°, respectively. The total deviation from linearity as defined by summation of the angles along the Si–C_4–Si chain is 123.1°. The co-ordination about the respective metal centres also shows no significant differences from the parameters found in related Mo_2 and Co_2 complexes.[18,19]

Table 1 Selected bond parameters (lengths in Å, angles in °) for $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2:\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ **6**

Co(1)–Co(2)	2.470(1)	Mo(4)–C(1)	2.244(6)
Mo(3)–Mo(4)	2.958(1)	Mo(4)–C(2)	2.220(6)
Co(1)–C(3)	2.029(6)	Si(1)–C(1)	1.872(6)
Co(1)–C(4)	1.979(6)	C(1)–C(2)	1.358(8)
Co(2)–C(3)	2.009(6)	C(2)–C(3)	1.444(8)
Co(2)–C(4)	2.008(6)	C(3)–C(4)	1.345(8)
Mo(3)–C(1)	2.185(6)	C(4)–Si(2)	1.869(6)
Mo(3)–C(2)	2.208(6)		
Si(1)–C(1)–C(2)	151.6(5)	C(2)–C(3)–C(4)	147.3(6)
C(1)–C(2)–C(3)	140.5(5)		

Dihedral Mo(3)–Mo(4)/Co(1)–Co(2): 12.1°.

(*ii*) $[Re_2(\mu\text{-H})\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_8]$ **11.** Fig. 2 shows a plot of a molecule of complex

Table 2 Geometries (bond lengths in Å, angles in °) of $Co_2(CO)_4(L–L)$ [L–L = $(CO)_2$ or μ-dppm] complexes

	6	**18***	**11**	**12***
R =	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$
R′ =	$C_2SiMe_3\{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2\}$	$C_2H\{Os_3(CO)_{10}\}$	$C_2\{Re_2(\mu\text{-}H)(CO)_8\}$	$C_2\{Ru_3(\mu\text{-}H)(CO)_9\}$
L–L =	$(CO)_2$	$(CO)_2$	μ-dppm	μ-dppm
Co(1)–Co(2)	2.470(1)	2.465(5)	2.472(3)	2.478(5), 2.497(5)
Co(1)–C(3)	2.029(6)	1.98(1)	1.98(1)	1.97(2), 1.98(2)
Co(1)–C(4)	1.979(6)	1.98(1)	1.99(1)	1.94(2), 1.95(2)
Co(2)–C(3)	2.009(6)	1.99(2)	1.96(1)	1.98(2), 1.98(2)
Co(2)–C(4)	2.008(6)	2.04(2)	2.00(1)	1.94(2), 1.93(2)
Co(1)–P(1)	—	—	2.219(4)	2.225(9), 2.214(8)
Co(2)–P(2)	—	—	2.221(4)	2.256(8), 2.243(8)
C(3)–C(4)	1.345(8)	1.32(2)	1.36(2)	1.32(3), 1.35(3)
R–C(4)–C(3)	157.5(5)	159(1)	155(1)	151(2), 149(2)
R′–C(3)–C(4)	147.3(6)	151(1)	144(1)	147(2), 143(2)

* For Co(1,2), read Co(4,5).

Table 3 Selected bond parameters (lengths in Å, angles in °) for $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_8]$ **11**

Co(1)–Co(2)	2.472(3)	C(1)–C(2)	1.24(2)
Re(3)–Re(4)	3.0651(9)	C(2)–C(3)	1.43(2)
Re(3)–C(1)	2.35(1)	C(3)–C(4)	1.36(2)
Re(3)–C(2)	2.50(1)	C(4)–Si	1.85(1)
Re(4)–C(1)	2.11(1)		
Re(4)–C(1)–C(2)	168(1)	C(2)–C(3)–C(4)	144(1)
C(1)–C(2)–C(3)	161(1)		

Table 4 Selected bond parameters (lengths in Å, angles in °) for $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C_2SiMe_3)(\mu\text{-dppm})_2(CO)_5]$ **17** and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9]$ **12**

	17	**12** (two molecules)
Ru(1)–Ru(2)	2.756(2)	2.790(4), 2.805(4)
Ru(1)–Ru(3)	2.821(2)	2.800(4), 2.790(4)
Ru(2)–Ru(3)	2.850(3)	2.775(4), 2.785(4)
Ru(1)–P(11)	2.343(4)	
Ru(1)–P(22)	2.304(4)	
Ru(2)–P(12)	2.338(4)	
Ru(3)–P(21)	2.302(4)	
Ru(1)–C(1)	2.11(1)	2.17(2), 2.19(2)
Ru(1)–C(2)	2.24(1)	2.31(2), 2.33(2)
Ru(2)–C(1)	2.19(1)	2.15(3), 2.21(3)
Ru(2)–C(2)	2.24(1)	2.28(3), 2.30(2)
Ru(3)–C(1)	1.93(1)	1.97(3), 1.98(2)
Si–C(4)	1.83(1)	1.90(2), 1.93(3)
C(1)–C(2)	1.33(2)	1.26(4), 1.29(3)
C(2)–C(3)	1.41(2)	1.45(3), 1.40(3)
C(3)–C(4)	1.20(2)	1.32(3), 1.35(3)
Ru(3)–C(1)–C(2)	159(1)	159(2), 157(2)
C(1)–C(2)–C(3)	138(1)	148(2), 147(2)
C(2)–C(3)–C(4)	176(1)	147(2), 143(2)
C(3)–C(4)–Si	174(1)	151(2), 149(2)

Dihedral angles for **12**: Co(4)–Co(5)/Ru(1)–Ru(2) 1.7,3.2, Co(4)–Co(5)/Ru(1,2,3) plane 88.36(8), 87.13(7).

11 and selected bond parameters are given in Tables 2 and 3. The molecule consists of an $Re_2(CO)_8$ fragment [Re(3)–Re(4) 3.0651(9) Å] which is bridged by a hydrogen (not detected in the X-ray study) and C(1)–C(2) of the $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2)(\mu\text{-dppm})(CO)_4$ fragment in the $\eta^1:\eta^2$ mode [Re(3)–C(1,2) 2.35(1), 2.50(1); Re(4)–C(1) 2.11(1); C(1)–C(2) 1.24(2) Å]. These parameters are similar to those found in $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^2\text{-}C_2Ph)(CO)_7(NCMe)]$ for example, which has Re–Re 3.0788(4), Re–C(σ) 2.059(7), Re–C(π) 2.307(6), 2.446(7) and C–C 1.216(9) Å.[14] The geometry of the $Co_2(\mu\text{-dppm})(CO)_4$ unit is also normal (Table 7).[2,5] Not surprisingly, the latter part of the molecule is placed so that there is minimum steric interference between the two parts of the molecule. The torsion angles C(1)–C(2)/C(3)–C(4) and Co(1)–Co(2)/Re(3)–Re(4) are 153(4) and 66.1°, respectively.

(*iii*) **$[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;$ $\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9]$ 12.** The molecular structure of complex **12** is depicted in Fig. 3 and some structural parameters are collected in Tables 2 and 4. The triangular Ru_3 cluster is capped by the $C_2C_2SiMe_3\{Co(\mu\text{-dppm})(CO)_4\}$ moiety in the usual $\eta^1:\eta^2$ mode [values for molecules 1, 2: Ru(1)–C(1,2) 2.17(2), 2.19(2); 2.31(2), 2.33(2); Ru(2)–C(1,2) 2.15(3), 2.21(2); 2.28(3), 2.30(2); Ru(3)–C(1) 1.97(3), 1.98(2); C(1)–C(2) 1.26(4), 1.29(3) Å] with the putative μ-H atom bridging Ru(1)–Ru(2). Again we find that the geometry of the two parts of the molecule is in accord with previously reported examples,[2,5,20] with the $Co_2(\mu\text{-dppm})(CO)_4$ fragment disposed as far away from the Ru_3 cluster as possible. The torsion angles C(1)–C(2)/C(3)–C(4) and Co(4)–Co(5)/Ru(1)–Ru(2) are −179(4), 176(4) and 1.7, 3.2°, respectively, *i.e.* the two metal–metal bonds are essentially parallel. In this complex the total deviation of the C_4 chain from linearity is 94°.

(*iv*) **$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C{\equiv}CSiMe_3)(\mu\text{-dppm})_2(CO)_5]$ 17.** A molecule of this complex is illustrated in Fig. 4 and some bond lengths and angles are given in Tables 2 and 4. There are no surprises in the structure, the two dppm ligands bridging two of the three Ru–Ru bonds [Ru(1)–Ru(2,3) 2.756(2), 2.821(2) Å]; the hydride ligand (located in the structural determination) and the alkynyl group bridge Ru(1)–Ru(2) [Ru(1)–C(1,2) 2.11(1), 2.24(1); Ru(2)–C(1,2) 2.19(1), 2.24(1) Å], C(1) also being σ-bonded to Ru(3) [Ru(3)–C(1) 1.93(1) Å]. Comparisons with $[Ru_3(\mu\text{-dppm})_2(CO)_8]$[21] show that there has been a shortening of the average Ru–Ru separation from 2.839 Å in the parent carbonyl to 2.778 Å in **17**. In the parent complex the four Ru–P bonds are not coplanar with the Ru_3 triangle; in **17**, P(11), P(12), P(21), P(22) lie 0.011(5), −0.164(2), 0.672(5), 1.078(4) Å out of the Ru_3 plane respectively, torsions in the adjacent P–C bonds in the metallacycle being 41.2(9), −46.1(9), −25.1(10), 34.7(10)°. The C_2SiMe_3 group is bent up away from the cluster [angle C(1)–C(2)–C(3) 138(1)°] while the C(2)–C(3)–C(4)–$SiMe_3$ group is nearly linear [C(2)–C(3)–C(4) 176(1); C(3)–C(4)–Si 174(1)°]; the total deviation from linearity of the C_4 chain is 52°.

Overall the alkynyl group interacts closely with the dppm ligands and there is no evidence for any fluxional processes; it would be difficult for the alkynyl group to move around the cluster as it is essentially trapped between the phenyl groups of the dppm ligands.

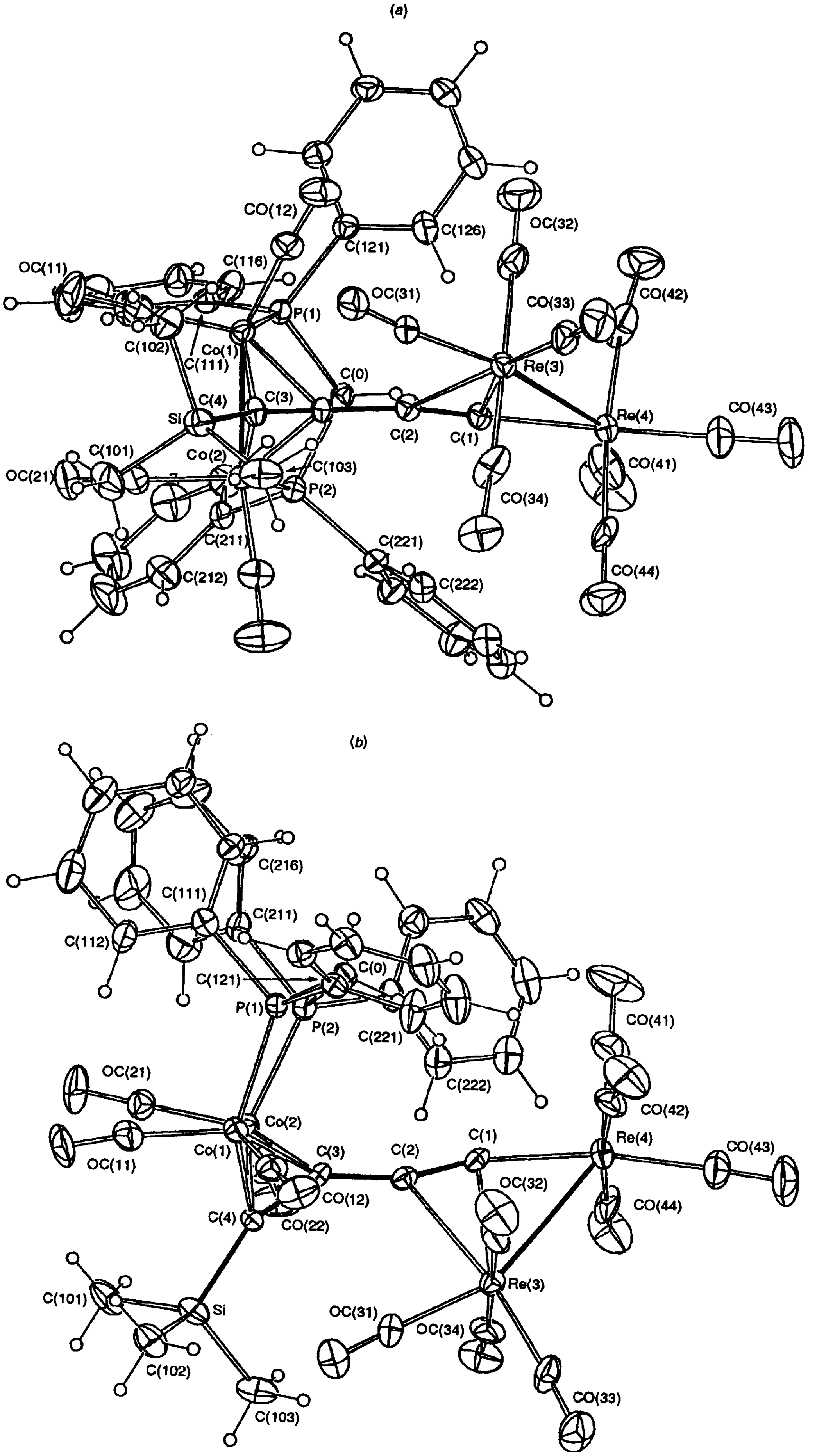

Fig. 2 Plots of a molecule of $[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-}dppm)(CO)_4)]\}(CO)_8]$ **11**, (*a*) perpendicular to and (*b*) looking down the Co–Co bond, showing the atom numbering scheme

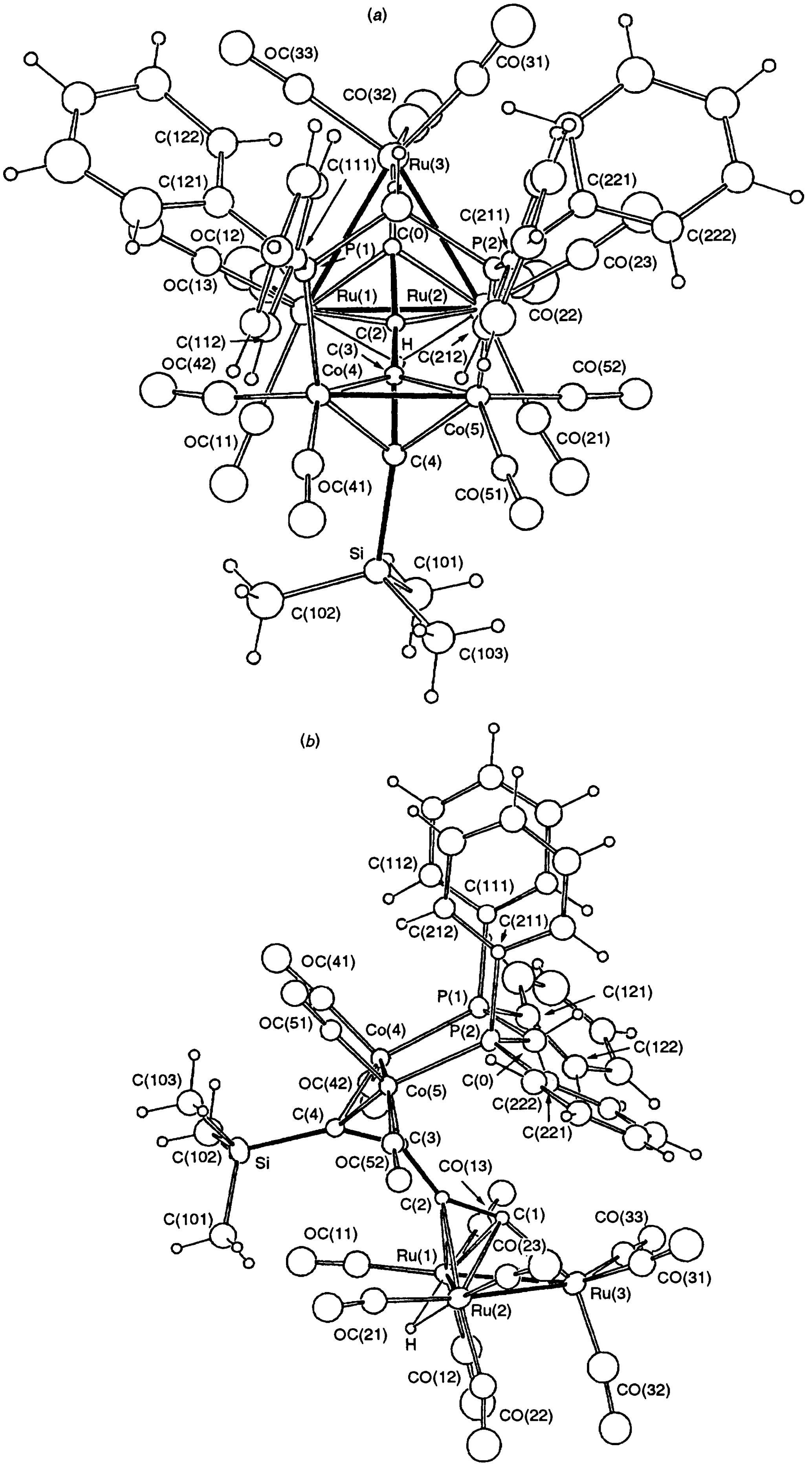

Fig. 3 Plots of one of the two independendent molecules of $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9]$ **12**, (*a*) perpendicular to and (*b*) oblique to the Ru_3 triangle, showing the atom numbering scheme

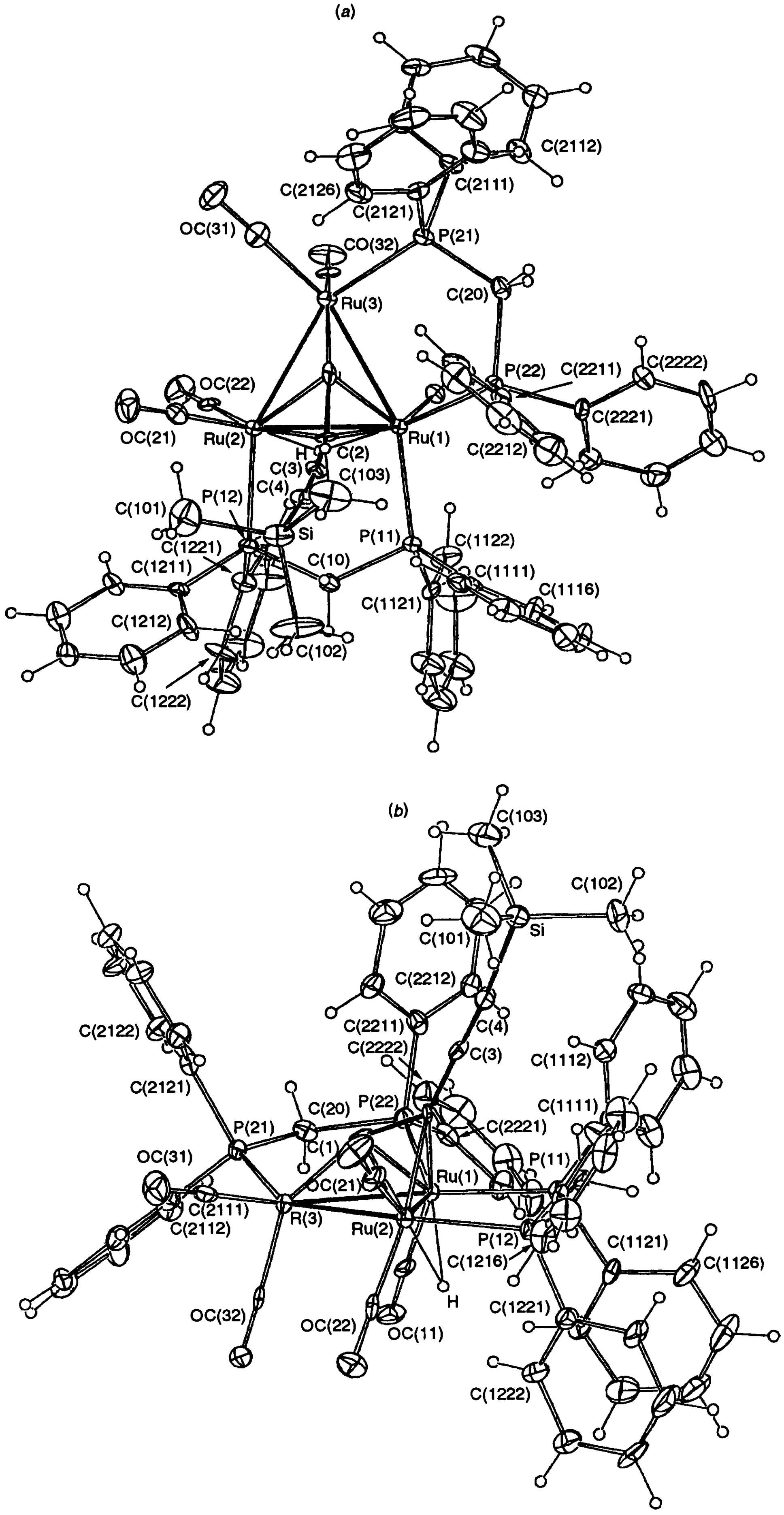

Fig. 4 Plots of a molecule of [$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2\text{-}C_2C{\equiv}CSiMe_3)(\mu\text{-dppm})_2(CO)_5$] **17**, (*a*) perpendicular to and (*b*) oblique to the Ru_3 triangle, showing the atom numbering scheme

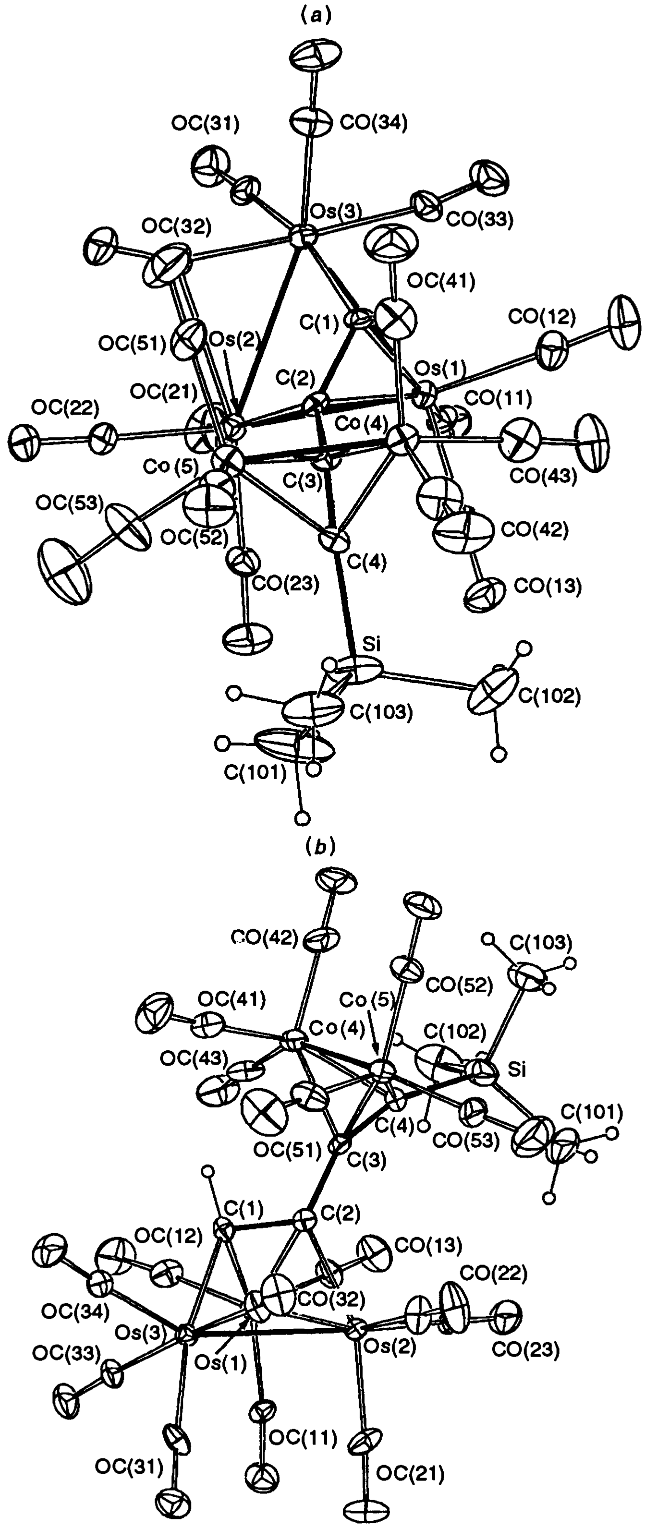

Fig. 5 Plots of a molecule of $[Os_3\{\mu_3\text{-}\eta^2:\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$ **18**, (*a*) perpendicular to and (*b*) oblique to the Os_3 triangle, showing the atom numbering scheme

Table 5 Selected structural parameters (lengths in Å, angles in °) for $[Os_3\{\mu_3\text{-}\eta^2:\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$ **18**

Os(1)–Os(2)	2.720(1)	C(1)–C(2)	1.37(2)
Os(1)–Os(3)	2.817(1)	C(2)–C(3)	1.45(2)
Os(2)–Os(3)	2.885(2)	C(3)–C(4)	1.32(2)
Os(1)–C(1)	2.13(2)	C(4)–Si	1.87(1)
Os(1)–C(2)	2.32(2)	Os(3)–C(32)	1.96(3)
Os(2)–C(2)	2.12(1)	Os(2)–C(32)	2.60(2)
Os(3)–C(1)	2.13(2)		
C(1)–C(2)–C(3)	121(1)	Os(2)–C(32)–O(32)	123(1)
C(2)–C(3)–C(4)	151(1)	Os(3)–C(32)–O(32)	159(1)
C(3)–C(4)–Si	159(1)		

Dihedral angles: Os(1)–Os(2)/Co(4)–Co(5) 5.26, Os(2)–Os(3)/C(1)–C(2) 9.34, Os(2)–Os(3)/Co(4)–Co(5) 63.10, Os(1,2,3) plane/Co(4)–Co(5) 85.51(3).

(*v*) $[Os_3\{\mu_3\text{-}\eta^2:\mu\text{-}\eta^2\text{-}HC_2C_2SiMe_3[Co_2(CO)_6]\}(\mu\text{-}CO)(CO)_9]$ **18.** A plot of a molecule of complex **18** is shown in Fig. 5 and relevant structural data are collected in Tables 2 and 5. The Os_3 cluster is capped by an $HC_2C_2SiMe_3$ ligand in the expected μ_3-η^2-(||) mode, with the C(1)–C(2) vector being approximately parallel to the Os(1)–Os(2) edge. The bridging CO(32) leans towards Os(2) so that it assumes a semibridging mode: the Os(2)–C(32) separation [2.60(2) Å] and slight bending of the Os(3)–C(32)–O(32) vector at the carbon atom [159(1)°] [also found with Os(3)–C(33)–O(3) 170(2)°] suggest some incipient bridging of the CO groups.

The geometry of the Os_3C_2 unit in complexes $[Os_3(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}CO)(CO)_9]$ has been found to vary from nearly symmetrical [with respect to the relative orientations of the Os(2)–Os(3) and C(1)–C(2) bonds], as with R = Et,[22a] to skewed, for R = Ph.[22b] The CO group bridging Os(2)–Os(3) adopts a symmetrical mode in the former case, but tends to become semibridging along with CO(12), with these changes occurring in concert in the latter case.[23] In the case of **18**, Os(1)–C(1) [2.13(2) Å] is considerably shorter than Os(1)–C(2) [2.32(2) Å], with CO(32) and CO(13) taking up semibridging positions. While the immediate cause of the asymmetry is probably steric interaction between the CO groups on the $Co_2(CO)_6$ fragment with those on Os(1), it is clear that the resulting electronic imbalance is compensated by the usual mechanism associated with semibridging CO groups.

The second C≡C triple bond of the $HC_2C_2SiMe_3$ ligand bridges the Co–Co bond [Co(4)–C(3,4) 1.98(1), 1.98(1); Co(5)–C(3,4) 1.99(2), 2.04(2) Å] in the usual manner. Angles at the carbon atoms of the two C≡C triple bonds [C(1)–C(2)–C(3) 121(1), C(2)–C(3)–C(4) 151(1), C(3)–C(4)–Si 159(1)°] indicate the expected bending occurring on co-ordination, but that at C(4) is rather greater than usually observed: the total deviation from linearity is 113°. There is no obvious explanation for this structural feature, but one possibility is the pronounced steric hindrance between the Os-bound CO groups and the $SiMe_3$ group of the ligand.

Conclusion

The complexes described herein represent further examples of η^2-alkyne complexes of Mo, Co or Pt; several reactions of either the unco-ordinated C≡C triple bond, of the acetylenic proton, or of both, have generated novel mixed-metal complexes. The further elaboration of these and related derivatives into complexes containing unsubstituted C_4 ligands will be reported elsewhere.

Experimental

General reaction conditions

All reactions were carried out under dry, high-purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed before use. Light petroleum refers to a fraction of b.p. 60–80 °C. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumental conditions

Infrared: Perkin-Elmer 1700X FT-IR. NMR: Bruker ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.98 MHz, ^{13}C at 50.29 MHz). FAB mass spectra: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV). ES mass spectra: samples dissolved in acetonitrile–water (1 : 1) and injected into a 10 µl injection loop attached to a VG Platform II mass spectrometer. Nitrogen was used as the drying and nebulising gas. Samples were examined over a range of cone voltages (20–90 V) to find the best conditions.

Reagents

The compounds $[\{Mo(CO)_2(cp)\}_2]$,[24] $Me_3SiC_2C_2SiMe_3$,[25] $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$,[26] $[Ru_3(CO)_{12}]$,[27] $[Re_2(CO)_8(NCMe)_2]$,[28] $[Ru_3(CO)_{10}(NCMe)_2]$,[29] $[Os_3(CO)_{10}(NCMe)_2]$,[29] $[Ru_3(\mu\text{-dppm})_2(CO)_8]$,[30] $[WCl(CO)_3(cp)]$[31] and $[AuCl(PPh_3)]$[32] were prepared by literature methods. Tetrabutylammonium fluoride (1 mol dm^{-3} solution in thf) (Aldrich), dbu (Aldrich) and $[Co_2(CO)_8]$ (Strem) were used as received.

Minor modifications of published methods were used for the syntheses of $HC_2C_2SiMe_3$[33] and the complexes $[Co_2(\mu\text{-dppm})_n(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_{6-2n}]$ [n = 0 **2**[10] or 1 **4**[2]], $[Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4]$ **9**[2] and $[Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4]$ **10**,[2] as detailed below.

$HC_2C_2SiMe_3$. The compound $Me_3SiC_2C_2SiMe_3$ (1.0 g, 5.15 mmol) in Et_2O (50 cm^3) was treated with LiMe•LiBr (7.8 cm^3 of 1.5 mol dm^{-3} solution in Et_2O, 5.15 mmol). After 3 h at room temperature MeOH (0.21 cm^3) was added and the solution was washed successively with saturated aqueous NH_4Cl and NaCl solutions. Distillation of a dried ($MgSO_4$) pentane extract gave $HC_2C_2SiMe_3$ (406 mg, 65%) (b.p. 35–37 °C, 27 mmHg).

Complex 2. The complex $[Co_2(CO)_8]$ (1.75 g, 5.12 mmol) and $Me_3SiC_2C_2SiMe_3$ (1 g, 5.12 mmol) were stirred in light petroleum (100 cm^3) for 1 h. The solvent was removed *in vacuo* and the red-brown residue purified by column chromatography on Al_2O_3. Light petroleum eluted a red-brown band, which yielded **2** (1.86 g, 75%) as a red oil.

Complex 4. Complex **2** (1 g, 2 mmol) and dppm (800 mg, 2 mmol) were dissolved in benzene (50 cm^3) and heated to reflux for 12 h. Evaporation and recrystallisation (CH_2Cl_2–MeOH) gave deep red crystals of **3** (1.54 g, 91%).

Complex 9. Complex **4** (1.3 g, 1.77 mmol) was dissolved in thf (100 cm^3 containing 2% MeOH) and 20 µl of a 1 mol dm^{-3} thf solution of NBu_4F was added. The reaction solution was allowed to stir until TLC analysis indicated complete conversion (1–2 h). The solvent was removed and the red residue obtained was dissolved in MeOH (15 cm^3). Upon standing crystallisation began giving deep red crystals of **9** (0.95 g, 80%).

Complex 10. This complex was prepared and isolated in the same manner as for **9** except that the reaction solvent contained 10% MeOH. If the reaction failed to go to completion a further 20 µl of the NBu_4F solution was added. Yield 75%.

Reactions of $Me_3SiC_2C_2SiMe_3$

$[Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4(cp)_2]$ 1. The complex $[\{Mo(CO)_2(cp)\}_2]$ (520 mg, 1.2 mmol) and $Me_3SiC_2C_2SiMe_3$ (233 mg, 1.2 mmol) were heated in refluxing toluene (50 cm^3). After 2.5 h the solvent was removed to give a deep red residue. This was extracted with pentane, filtered, and concentrated to give **1** as a deep red microcrystalline solid (620 mg, 82%) (Found: C, 45.7; H, 4.45. Calc. for $C_{24}H_{28}Mo_2O_4Si_2$: C, 45.85; H, 4.45%). IR (cyclohexane): ν(C≡C) 2125w; ν(CO) 2001s, 1949s, 1934s and 1851s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.17 (9 H, s, $SiMe_3$), 0.23 (9 H, s, $SiMe_3$) and 5.32 (5 H, s, cp), ^{13}C, δ −0.53 (s, $SiMe_3$), −0.15 (s, $SiMe_3$) 85.93 [s, C(4)], 87.93 [s, C(3)], 92.22 (s, cp), 97.59 [s, C(1)], 108.93 [s, C(2)], 227.68 (s, CO) and 230.00 (s, CO). FAB mass spectrum: m/z 628, M^+ and 571–515, $[M - n\text{CO}]^+$ (n = 1–3).

$[Pt(\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(PPh_3)_2]$ 3. The compound $Me_3SiC_2C_2SiMe_3$ (100 mg, 0.52 mmol) was added to a suspension of $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (385 mg, 0.52 mmol) in light petroleum (40 cm^3) and stirred at room temperature (r.t.) for 18 h. The suspension was filtered to remove the unreacted $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (90 mg, 23%), and the filtrate evaporated to dryness. The sticky residue obtained was triturated with MeOH (3 × 5 cm^3) to give complex **3** as a pale yellow powder (305 mg, 86% based on Pt consumed) (Found: C, 60.90; H, 6.30. Calc. for $C_{46}H_{48}P_2PtSi_2$: C, 60.45; H, 5.25%). IR (Nujol): ν(C≡C) 2132m, 2094s, ν(C=C) 1663s cm^{-1}. NMR ($CDCl_3$): ^1H, δ −0.16 (9 H, s, $SiMe_3$), 0.09 (9 H, s, $SiMe_3$) and 7.11–7.38 (30 H, m, Ph); ^{13}C, δ −0.26 (s, $SiMe_3$), 0.12 (s, $SiMe_3$), 86.19, 88.26 [2 s, C≡C (unco-ordinated)], and 127.68–137.68 (m, Ph). ES mass spectrum: m/z 914, $[M + H]^+$; 840, $[M - SiMe_3]^+$; 761, $[M - SiMe_3 - C_6H_6]^+$ and 720, $[Pt(PPh_3)_2 + H]^+$.

$[Ru_3(\mu_3\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(\mu\text{-CO})(CO)_9]$ 5. A freshly made solution of $[Ru_3(CO)_{10}(NCMe)_2]$ in CH_2Cl_2–MeCN {from $[Ru_3(CO)_{12}]$ (100 mg, 0.16 mmol)} was filtered through degassed silica gel (2 cm) and kept at −10 °C. The yellow solution was treated with $Me_3SiC_2C_2SiMe_3$ (32 mg, 0.16 mmol) and allowed to warm to room temperature. It turned orange after 45 min. After removal of solvent, the dark red residue was dissolved in CH_2Cl_2 and purified by preparative thin-layer chromatography (TLC) (light petroleum–acetone, 10 : 3). Band 1 (R_f 0.85) contained complex **5** (12 mg, 10%). IR (cyclohexane): ν(CC) 2108m; ν(CO) 2095w, 2069vs, 2021m, 1996m, 1974w (sh), 1962w (sh), 1910w (br) and 1883w (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.21 (s, $SiMe_3$). A second band (R_f 0.75) contained recovered $[Ru_3(CO)_{12}]$.

Preparation of $[\{Mo_2(CO)_4(cp)_2\}\{Co_2(CO)_6\}(\mu\text{-}\eta^2 : \mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ 6

The complex $[Co_2(CO)_8]$ (103 mg, 0.30 mmol) was added in portions to a solution of $[Mo_2(\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4(cp)_2]$ **1** (100 mg, 0.24 mmol) in light petroleum (15 cm^3) and allowed to stir. The reaction was stopped when all the starting material had been consumed (IR spectroscopy). After removal of solvent, recrystallisation of the residue (CH_2Cl_2–MeOH) gave deep green crystals of complex **6** (110 mg, 50%). Alternatively, attempted purification of the reaction mixture by preparative TLC (light petroleum–acetone, 9 : 1) gave three bands after repeated development. The first band was identified as $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2 : \mu\text{-}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)]$ (5 mg, 6%) by comparison with an authentic sample. The second band contained **1** (20 mg, 20%). The third broad, deep green band contained **6** (55 mg, 33%) (Found: C, 39.15; H, 3.10. Calc. for $C_{30}H_{28}Co_2Mo_2O_{10}Si_2$: C, 39.40; H, 3.05%). IR (cyclohexane): ν(CO) 2076vs, 2040vs, 2015vs, 2009vs, 1998m, 1989s, 1959m, 1930s, 1925m and 1847s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.49 (9 H, br, $SiMe_3$) and 5.36 (5 H, s, cp); ^{13}C, δ 3.32 (s, $SiMe_3$), 5.63 (s, $SiMe_3$), 92.48 (s, cp), 200.99 (s, CO), and 231.45 (s, CO). FAB mass spectrum: m/z 830–634, $[M - n\text{CO}]^+$ (n = 3–10). Prolonged exposure of the reaction mixture on the TLC plates to air before or after development resulted in the conversion of deep green **6** back into red **1**.

Desilylation of $Me_3SiC_2C_2SiMe_3$ complexes

$[Mo_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_4(cp)_2]$ 7. To a solution of complex **1** (150 mg, 0.24 mmol) in thf (10 cm^3) was added methanol (1 cm^3) and NBu_4F (0.24 mmol as 1 mol dm^{-3} thf

Table 6 Crystal data and refinement details for complexes **6**, **11**, **12**, **17** and **18**

Complex	**6**	**11**	**12**	**17**	**17a**	**18**
Formula	$C_{30}H_{28}Co_2Mo_2O_{10}Si_2$	$C_{44}H_{32}Co_2O_{12}P_2Re_2Si$	$C_{45}H_{32}Co_2O_{13}P_2Ru_3Si$	$C_{62}H_{54}O_5P_4Ru_3Si{\cdot}2CH_2Cl_2$	$C_{62}H_{54}O_5P_4Ru_3Si$	$C_{23}H_{10}Co_2O_{16}Os_3Si$
M	914.5	1333.0	1291.9	1504.2	1334.3	1258.9
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	*Pccn* (no. 56)	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	*Pc* (no. 7)
a/Å	18.940(3)	43.683(10)	13.914(7)	12.232(4)	20.74(3)	9.036(3)
b/Å	10.057(6)	17.804(3)	18.620(9)	15.163(10)	13.37(3)	18.596(9)
c/Å	17.971(7)	12.185(4)	38.348(14)	17.721(10)	11.95(2)	12.656(4)
α/°					111.0(1)	
β/°	92.83(2)		96.14(3)	99.85(4)	92.1(1)	131.49(3)
γ/°					103.6(1)	
U/Å^3	3419	9477	9878	3238	2980	1593
Z	4	8	8	2	2	2
D_c/g cm^{-3}	1.78	1.87	1.74	1.54	1.49	2.62
F(000)	1816	5120	5088	1512	1344	1144
Crystal size/mm	0.11 × 0.19 × 0.18	0.13 × 0.50 × 0.53	0.18 × 0.13 × 0.07	0.12 × 0.45 × 0.37	0.14 × 0.10 × 0.15	0.21 × 0.11 × 0.24
$A^*_{\mathrm{min,max}}$	1.21,1.35	2.36, 8.0	1.08, 1.24	1.09, 1.39	1.09, 1.14	3.6, 11.8
μ/cm^{-1}	17.9	59.3	17.0	10.2	9.3	130
$2\theta_{\mathrm{max}}$/°	50	50	50	50	45	55
N	6009	8327	17 349	5919	7774	3783
N_o	3900	5095	4784	4441	3176	3405
R	0.039	0.054	0.078	0.050	0.11	0.032
R'	0.039	0.057	0.076	0.049	0.11	0.033

Table 7 Non-hydrogen positional parameters for complex **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.892 23(5)	0.528 39(9)	0.348 08(5)	O(42)	0.644 4(3)	0.782 7(6)	0.198 7(3)
Co(2)	0.846 36(5)	0.684 82(9)	0.251 42(5)	Si(1)	0.631 1(1)	0.412 7(2)	0.275 8(1)
Mo(3)	0.684 50(3)	0.507 64(6)	0.463 60(3)	C(101)	0.604 0(4)	0.481 7(8)	0.182 6(4)
Mo(4)	0.638 73(3)	0.738 33(6)	0.371 24(3)	C(102)	0.691 2(4)	0.271 5(7)	0.256 5(4)
C(11)	0.986 9(4)	0.534 7(7)	0.333 8(4)	C(103)	0.548 1(4)	0.347 2(7)	0.313 9(4)
O(11)	1.045 5(3)	0.532 8(6)	0.325 6(3)	C(1)	0.675 1(3)	0.533 0(6)	0.342 8(3)
C(12)	0.870 0(4)	0.378 4(8)	0.298 4(5)	C(2)	0.732 0(3)	0.605 1(6)	0.368 0(3)
O(12)	0.859 8(3)	0.283 8(6)	0.265 0(4)	C(3)	0.802 6(3)	0.638 8(6)	0.347 7(3)
C(13)	0.899 6(4)	0.472 3(9)	0.442 5(5)	C(4)	0.860 5(3)	0.713 9(6)	0.361 7(3)
O(13)	0.907 0(3)	0.437 1(8)	0.502 1(3)	Si(2)	0.916 2(1)	0.848 4(2)	0.406 0(1)
C(21)	0.931 1(4)	0.707 4(7)	0.210 8(4)	C(201)	0.930 9(5)	0.818(1)	0.506 3(4)
O(21)	0.983 2(3)	0.718 1(6)	0.182 6(3)	C(202)	1.003 7(4)	0.858 7(8)	0.364 9(4)
C(22)	0.802 9(4)	0.573 9(8)	0.184 0(4)	C(203)	0.875 2(5)	1.014 9(8)	0.391 8(7)
O(22)	0.779 3(3)	0.506 2(6)	0.139 1(3)	C(301)	0.743 8(5)	0.355 3(8)	0.541 8(4)
C(23)	0.808 6(4)	0.842 4(8)	0.224 7(4)	C(302)	0.741 6(4)	0.298 5(7)	0.470 4(5)
O(23)	0.787 1(3)	0.943 1(6)	0.208 2(3)	C(303)	0.670 1(5)	0.273 9(7)	0.449 7(4)
C(31)	0.601 5(4)	0.596 0(7)	0.500 1(4)	C(304)	0.628 9(4)	0.316 1(8)	0.507 1(5)
O(31)	0.552 4(3)	0.634 0(6)	0.530 4(3)	C(305)	0.674 6(5)	0.366 0(9)	0.563 7(4)
C(32)	0.744 1(4)	0.635 6(8)	0.516 3(4)	C(401)	0.703 7(4)	0.908 5(7)	0.435 1(5)
O(32)	0.781 7(3)	0.706 1(6)	0.551 1(3)	C(402)	0.678 9(4)	0.955 1(7)	0.365 7(5)
C(41)	0.542 3(4)	0.666 8(7)	0.350 7(4)	C(403)	0.603 1(5)	0.956 5(7)	0.363 0(5)
O(41)	0.484 0(3)	0.639 5(6)	0.339 1(3)	C(404)	0.583 3(4)	0.910 1(8)	0.432 8(5)
C(42)	0.643 2(3)	0.759 2(7)	0.260 8(4)	C(405)	0.645 1(5)	0.881 1(8)	0.477 3(5)

Table 8 Non-hydrogen positional parameters for complex **11**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.401 83(4)	0.591 1(1)	0.734 5(1)	C(114)	0.452 8(5)	0.474(1)	1.165(2)
Co(2)	0.419 53(4)	0.478 9(1)	0.633 3(2)	C(115)	0.422 0(4)	0.454 3(9)	1.172(1)
Re(3)	0.310 23(1)	0.584 98(3)	0.487 19(5)	C(116)	0.403 2(4)	0.472 2(8)	1.086(1)
Re(4)	0.282 17(1)	0.437 44(3)	0.569 01(5)	C(121)	0.353 4(3)	0.563 5(7)	0.952(1)
C(11)	0.437 1(4)	0.639 0(9)	0.765(1)	C(122)	0.355 7(4)	0.607 1(8)	1.044(1)
O(11)	0.458 6(3)	0.673 6(7)	0.778(1)	C(123)	0.329 7(4)	0.637 7(9)	1.094(1)
C(12)	0.375 2(4)	0.665 8(9)	0.746(1)	C(124)	0.301 8(4)	0.626(1)	1.051(2)
O(12)	0.356 8(3)	0.711 1(6)	0.751(1)	C(125)	0.299 9(4)	0.586(1)	0.959(2)
C(21)	0.458 4(4)	0.493 1(9)	0.677(1)	C(126)	0.324 5(4)	0.556(1)	0.908(1)
O(21)	0.482 6(3)	0.501 7(8)	0.706(1)	C(0)	0.374 8(3)	0.431 0(7)	0.843(1)
C(22)	0.425 3(4)	0.427 8(8)	0.511(1)	P(2)	0.403 30(9)	0.390 4(2)	0.747 8(3)
O(22)	0.429 9(4)	0.396 4(7)	0.432(1)	C(211)	0.432 8(3)	0.344 5(8)	0.833(1)
C(31)	0.340 3(4)	0.664 3(9)	0.477(1)	C(212)	0.460 6(4)	0.327(1)	0.783(2)
O(31)	0.356 5(3)	0.713 5(6)	0.476(1)	C(213)	0.483 6(5)	0.294(1)	0.841(2)
C(32)	0.294 8(4)	0.634(1)	0.614(1)	C(214)	0.478 9(6)	0.279(1)	0.952(2)
O(32)	0.284 8(4)	0.669 0(7)	0.688(1)	C(215)	0.451 2(5)	0.294(1)	1.000(2)
C(33)	0.283 9(4)	0.641 1(9)	0.394(2)	C(216)	0.428 2(4)	0.327 4(8)	0.942(1)
O(33)	0.269 5(3)	0.677 6(7)	0.336(1)	C(221)	0.382 2(3)	0.308 7(8)	0.694(1)
C(34)	0.325 9(5)	0.538(1)	0.361(1)	C(222)	0.367 8(4)	0.313 4(8)	0.593(1)
O(34)	0.337 7(4)	0.504 8(6)	0.287(1)	C(223)	0.350 6(4)	0.254(1)	0.551(2)
C(41)	0.287 7(5)	0.349(1)	0.661(2)	C(224)	0.348 9(4)	0.191(1)	0.614(2)
O(41)	0.290 0(4)	0.299 3(9)	0.719(2)	C(225)	0.362 7(5)	0.185 3(9)	0.711(2)
C(42)	0.265 0(5)	0.483(1)	0.699(1)	C(226)	0.380 0(4)	0.242 6(9)	0.753(1)
O(42)	0.250 4(4)	0.510 7(7)	0.768(1)	C(1)	0.326 1(3)	0.482 8(7)	0.595(1)
C(43)	0.241 9(4)	0.410(1)	0.523(2)	C(2)	0.350 6(3)	0.518 1(7)	0.595(1)
O(43)	0.217 2(3)	0.395(1)	0.494(1)	C(3)	0.381 9(3)	0.537 1(7)	0.612(1)
C(44)	0.294 9(4)	0.387(1)	0.436(1)	C(4)	0.405 8(3)	0.577 9(7)	0.573(1)
O(44)	0.302 9(4)	0.353 2(8)	0.360(1)	Si	0.426 2(1)	0.636 7(2)	0.471 5(4)
P(1)	0.387 06(8)	0.527 5(2)	0.881 9(3)	C(101)	0.466 7(4)	0.608(1)	0.462(2)
C(111)	0.413 0(3)	0.508 9(7)	0.996(1)	C(102)	0.426 2(4)	0.737 3(8)	0.517(1)
C(112)	0.442 8(4)	0.532(1)	0.991(1)	C(103)	0.409 3(5)	0.625 2(9)	0.335(1)
C(113)	0.463 2(5)	0.516(1)	1.078(2)				

solution). After 4 h the solvent was removed and the residue purified by TLC (light petroleum–acetone, 8 : 2). The major red band yielded complex **7** (25 mg, 22%) after crystallization (toluene–pentane) (Found: C, 44.95; H, 2.55. Calc. $C_{18}H_{12}Mo_2O_4$: C, 44.65; H, 2.50%). IR (cyclohexane): ν(C≡C) 2078w; ν(CO) 2002vs, 1948vs, 1941 (sh) and 1853vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 2.73 (1 H, s, C≡CH), 5.39 (5 H, s, cp), and 5.63 [1 H, s, $HC_2(Mo_2)$]; ^{13}C, δ 74.89 [s, ≡C(1)H], 79.41 [s, C(2)], 88.45 [s, C(4)], 90.77 [s, C(3)], 92.30 (s, cp), 226.66, 230.28 (2 s, CO). FAB mass spectrum: *m*/*z* 485, M^+ and 428–378, $[M - nCO]^+$ (*n* = 2–4).

[$Co_2(\mu$-η^2-$HC_2C{\equiv}CH)(CO)_6$] 8. Complex **2** (250 mg, 0.52 mmol) and KF (60 mg, 1.04 mmol) were dissolved in methanol (15 cm^3) and the solution warmed to 35–40 °C. After 30 min the solvent was removed at room temperature on a rotary evaporator and the resulting dark oil purified by flash chromatography on alumina (light petroleum eluent) to give complex **8** as a bright red oil (70–80%) which decomposed over several hours at -20 °C under nitrogen to a brown intractable polymer. IR (thf): ν(C≡C) 2113w; ν(CO) 2024s, 2000vs and 1973vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.73 (1 H, s, C≡CH) and 6.20 [1 H, s, $HC_2(Co_2)$].

Table 9 Non-hydrogen positional parameters for complex **12**

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.354 2(2)	1.029 4(2)	0.776 82(7)	0.580 1(2)	0.840 5(1)	0.538 62(6)
Ru(2)	0.352 9(2)	0.987 1(1)	0.706 98(6)	0.596 5(2)	0.701 4(1)	0.566 74(7)
Ru(3)	0.292 7(2)	0.891 5(1)	0.755 71(7)	0.531 9(2)	0.813 7(1)	0.606 18(6)
Co(4)	0.077 0(3)	1.167 5(2)	0.741 2(1)	0.305 2(3)	0.758 5(2)	0.466 93(9)
Co(5)	0.080 9(3)	1.129 1(2)	0.679 48(9)	0.329 6(3)	0.635 1(2)	0.491 81(9)
C(11)	0.398(3)	1.124(2)	0.785(1)	0.609(2)	0.846(2)	0.491 6(8)
O(11)	0.422(2)	1.184(2)	0.784 8(7)	0.631(1)	0.848(1)	0.464 0(5)
C(12)	0.458(2)	0.983(2)	0.803 1(8)	0.679(2)	0.893(2)	0.558 6(9)
O(12)	0.523(2)	0.952(1)	0.816 9(6)	0.750(2)	0.927(1)	0.571 8(6)
C(13)	0.288(3)	1.035(2)	0.818(1)	0.503(2)	0.923(2)	0.534 0(7)
O(13)	0.254(2)	1.032(1)	0.842 4(6)	0.453(1)	0.974(1)	0.531 4(5)
C(21)	0.396(2)	1.060(2)	0.677 7(8)	0.634(2)	0.630(2)	0.533 9(7)
O(21)	0.432(2)	1.103(1)	0.660 9(6)	0.661(1)	0.585(1)	0.518 3(5)
C(22)	0.462(2)	0.924(2)	0.704 9(8)	0.706(2)	0.699(2)	0.598 1(8)
O(22)	0.527(1)	0.890(1)	0.703 8(5)	0.787(2)	0.696(1)	0.612 0(6)
C(23)	0.280(2)	0.940(2)	0.668 9(7)	0.539(2)	0.632(2)	0.594 0(7)
O(23)	0.245(1)	0.906(1)	0.646 5(5)	0.504(2)	0.595(1)	0.614 0(6)
C(31)	0.234(2)	0.828(2)	0.727 1(8)	0.470(2)	0.768(2)	0.639 9(8)
O(31)	0.198(2)	0.780(1)	0.707 8(6)	0.422(2)	0.745(1)	0.660 3(6)
C(32)	0.403(3)	0.834(2)	0.768(1)	0.636(2)	0.828(2)	0.636 6(9)
O(32)	0.471(2)	0.798(2)	0.767 8(7)	0.714(2)	0.834(1)	0.655 3(6)
C(33)	0.238(2)	0.861(2)	0.795 8(8)	0.476(2)	0.903(2)	0.612 5(7)
O(33)	0.208(2)	0.843(1)	0.820 9(6)	0.447(1)	0.961(1)	0.616 3(5)
C(41)	0.009(2)	1.249(1)	0.739 9(6)	0.249(2)	0.734(2)	0.428 1(7)
O(41)	−0.023(1)	1.304(1)	0.737 6(5)	0.213(1)	0.710(1)	0.400 3(5)
C(42)	0.139(2)	1.180(2)	0.781 9(8)	0.351(2)	0.842(2)	0.458 4(8)
O(42)	0.184(2)	1.188(1)	0.809 1(6)	0.382(1)	0.899(1)	0.457 5(5)
C(51)	0.005(2)	1.199(2)	0.661 1(7)	0.276(2)	0.581(1)	0.458 0(6)
O(51)	−0.043(1)	1.246(1)	0.650 9(5)	0.239(1)	0.543(1)	0.437 0(5)
C(52)	0.148(2)	1.110(1)	0.644 5(6)	0.401(2)	0.571(1)	0.514 9(7)
O(52)	0.195(1)	1.097(1)	0.622 5(5)	0.446(1)	0.530(1)	0.531 0(5)
P(1)	−0.025 2(5)	1.082 1(4)	0.754 2(2)	0.193 3(5)	0.794 1(4)	0.500 1(2)
C(111)	−0.153(2)	1.102(1)	0.749 7(7)	0.062(2)	0.786(1)	0.484 3(6)
C(112)	−0.190(2)	1.151(2)	0.725 7(7)	0.034(2)	0.782(1)	0.448 6(7)
C(113)	−0.294(2)	1.166(2)	0.718 0(8)	−0.058(2)	0.778(1)	0.435 6(7)
C(114)	−0.353(3)	1.121(2)	0.736 8(9)	−0.127(2)	0.774(2)	0.457 7(7)
C(115)	−0.319(3)	1.073(2)	0.759 1(9)	−0.103(2)	0.780(2)	0.493 1(8)
C(116)	−0.218(2)	1.059(2)	0.765 8(8)	−0.007(2)	0.785(1)	0.506 6(7)
C(121)	−0.007(2)	1.049(1)	0.799 1(7)	0.191(2)	0.885(2)	0.514 8(7)
C(122)	0.024(2)	0.980(2)	0.808 0(8)	0.240(2)	0.910(2)	0.546 1(7)
C(123)	0.039(2)	0.954(2)	0.843 1(8)	0.232(2)	0.983(2)	0.559 3(8)
C(124)	0.023(2)	1.006(2)	0.867 7(7)	0.187(2)	1.029(2)	0.537 0(7)
C(125)	−0.002(3)	1.072(2)	0.860 4(9)	0.151(3)	1.011(2)	0.505(1)
C(126)	−0.021(2)	1.097(2)	0.825 5(9)	0.146(3)	0.938(2)	0.495 5(9)
C(0)	−0.015(2)	1.002(1)	0.726 3(5)	0.209(2)	0.745(2)	0.540 3(7)
P(2)	−0.016 1(5)	1.032 3(4)	0.680 9(2)	0.220 7(5)	0.648 0(4)	0.530 4(2)
C(211)	−0.144(2)	1.041(1)	0.664 5(7)	0.096(2)	0.619(1)	0.518 3(5)
C(212)	−0.168(2)	1.089(2)	0.638 2(8)	0.059(2)	0.611(1)	0.483 2(7)
C(213)	−0.260(3)	1.103(2)	0.621 6(9)	−0.036(2)	0.590(2)	0.474 6(8)
C(214)	−0.332(2)	1.057(2)	0.635 5(7)	−0.095(2)	0.582(2)	0.500 7(8)
C(215)	−0.315(2)	1.012(2)	0.661 7(7)	−0.061(2)	0.593(2)	0.534 6(8)
C(216)	−0.217(2)	1.002(2)	0.676 2(7)	0.032(2)	0.612(2)	0.545 0(7)
C(221)	0.007(2)	0.950(1)	0.657 7(7)	0.249(2)	0.605(1)	0.572 9(7)
C(222)	0.015(2)	0.955(2)	0.621 4(7)	0.249(2)	0.531(2)	0.575 2(7)
C(223)	0.019(2)	0.894(2)	0.598 9(8)	0.269(2)	0.495(2)	0.607 9(7)
C(224)	0.018(2)	0.829(2)	0.616 4(8)	0.279(2)	0.533(2)	0.636 9(8)
C(225)	0.013(3)	0.820(2)	0.649 6(9)	0.274(2)	0.611(2)	0.635 7(8)
C(226)	0.009(2)	0.879(2)	0.671 0(8)	0.260(2)	0.643(1)	0.603 9(7)
C(1)	0.238(2)	0.985(1)	0.740 5(7)	0.472(2)	0.775(1)	0.561 0(6)
C(2)	0.236(2)	1.050(1)	0.731 0(6)	0.469(2)	0.747(1)	0.530 3(6)
C(3)	0.178(2)	1.113(1)	0.720 4(6)	0.411(2)	0.721(1)	0.500 5(6)
C(4)	0.177(2)	1.181(1)	0.710 2(6)	0.416(2)	0.694(1)	0.468 1(6)
Si	0.243 1(6)	1.267 6(5)	0.701 7(3)	0.490 0(6)	0.679 7(5)	0.428 9(2)
C(101)	0.342(3)	1.254(2)	0.675(1)	0.616(2)	0.661(2)	0.442 8(7)
C(102)	0.276(3)	1.316(2)	0.742 4(9)	0.485(2)	0.758(2)	0.400 5(8)
C(103)	0.157(3)	1.331(2)	0.674(1)	0.441(2)	0.602(2)	0.403 3(7)

Reactions of $[Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CH)(\mu\text{-dppm})(CO)_4]$ 9

$[Re_2(\mu\text{-}H)\{\mu\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_8]$ 11. The complexes $[Re_2(CO)_8(NCMe)_2]$ (100 mg, 0.15 mmol) and **9** (108 mg, 0.15 mmol) were heated in refluxing light petroleum (15 cm^3). After 3 h all the $[Re_2(CO)_8(NCMe)_2]$ had been consumed although a significant amount of the cobalt diyne was still present (TLC). Another equivalent of $[Re_2(CO)_8(NCMe)_2]$ was added and reflux continued. The remaining diyne was rapidly consumed. The

Table 10 Non-hydrogen positional parameters for complex **17**·$2CH_2Cl_2$

Atom	*x*	*y*	*z*
Ru(1)	0.721 69(9)	0.5*	0.240 22(6)
Ru(2)	0.528 21(9)	0.456 00(9)	0.291 29(6)
Ru(3)	0.551 2(1)	0.627 1(1)	0.229 23(6)
C(11)	0.702(1)	0.514 5(9)	0.136 2(8)
O(11)	0.697 6(9)	0.523 3(7)	0.069 4(5)
C(21)	0.448(1)	0.473(1)	0.367(1)
O(21)	0.398(1)	0.482 8(8)	0.418 0(7)
C(22)	0.404(1)	0.436 7(9)	0.219 3(9)
O(22)	0.325(1)	0.422 1(8)	0.173 1(7)
C(31)	0.433(1)	0.690(1)	0.256 3(8)
O(31)	0.360(1)	0.727 7(9)	0.273 1(8)
C(32)	0.480(1)	0.617 5(9)	0.127 1(9)
O(32)	0.432(1)	0.613 0(7)	0.063 7(6)
P(11)	0.809 8(3)	0.364 2(3)	0.270 3(2)
C(1111)	0.952(1)	0.361 1(9)	0.320 8(8)
C(1112)	0.978(1)	0.389(1)	0.397(1)
C(1113)	1.085(2)	0.391(1)	0.437(1)
C(1114)	1.170(2)	0.367(1)	0.400(1)
C(1115)	1.150(1)	0.342(1)	0.327(1)
C(1116)	1.038(1)	0.339(1)	0.286(1)
C(1121)	0.813(1)	0.279 5(9)	0.194 7(9)
C(1122)	0.777(2)	0.298(1)	0.120 3(9)
C(1123)	0.775(2)	0.229(2)	0.065(1)
C(1124)	0.815(2)	0.149(1)	0.088(1)
C(1125)	0.847(2)	0.131(1)	0.161(1)
C(1126)	0.850(2)	0.194(1)	0.217(1)
C(10)	0.736(1)	0.305 7(9)	0.337 2(8)
P(12)	0.585 7(3)	0.310 8(2)	0.318 8(2)
C(1211)	0.544(1)	0.258 1(9)	0.401 9(9)
C(1212)	0.615(1)	0.243(1)	0.469 3(9)
C(1213)	0.577(2)	0.202(1)	0.529(1)
C(1214)	0.470(2)	0.177(1)	0.523(1)
C(1215)	0.399(2)	0.193(1)	0.455(1)
C(1216)	0.435(2)	0.233(1)	0.396(1)
C(1221)	0.547(1)	0.229(1)	0.243 4(8)
C(1222)	0.522(2)	0.251(1)	0.168 2(9)
C(1223)	0.499(2)	0.188(1)	0.111(1)
C(1224)	0.503(2)	0.101(1)	0.130(1)
C(1225)	0.528(2)	0.075(1)	0.204(1)
C(1226)	0.551(2)	0.136(1)	0.261 3(9)
P(21)	0.666 6(3)	0.742 9(2)	0.212 7(2)
C(2111)	0.628(1)	0.810 3(9)	0.126 2(8)
C(2112)	0.702(1)	0.838(1)	0.080(1)
C(2113)	0.665(2)	0.887(1)	0.015(1)
C(2114)	0.554(2)	0.907(1)	−0.006 5(9)
C(2115)	0.480(1)	0.881(1)	0.039(1)
C(2116)	0.517(1)	0.831(1)	0.104 5(9)
C(2121)	0.685(1)	0.830(1)	0.287 2(8)
C(2122)	0.756(2)	0.903(1)	0.280(1)
C(2123)	0.765(2)	0.969(1)	0.336(1)
C(2124)	0.709(2)	0.966(1)	0.394(1)
C(2125)	0.640(2)	0.893(1)	0.401(1)
C(2126)	0.629(1)	0.827(1)	0.347(1)
C(20)	0.806(1)	0.709(1)	0.205 7(8)
P(22)	0.862 8(3)	0.602 3(2)	0.250 1(2)
C(2211)	0.937(1)	0.629(1)	0.345 3(8)
C(2212)	1.041(2)	0.603(1)	0.370(1)
C(2213)	1.096(2)	0.622(2)	0.443(1)
C(2214)	1.039(2)	0.665(1)	0.491(1)
C(2215)	0.934(2)	0.687(1)	0.470(1)
C(2216)	0.881(1)	0.673(1)	0.395(1)
C(2221)	0.976(1)	0.585(1)	0.195 1(8)
C(2222)	1.056(1)	0.651(1)	0.191(1)
C(2223)	1.138(2)	0.637(2)	0.148(1)
C(2224)	1.143(2)	0.563(2)	0.109(1)
C(2225)	1.068(2)	0.496(1)	0.113(1)
C(2226)	0.984(1)	0.507(1)	0.155 7(9)
C(1)	0.639(1)	0.570 1(9)	0.316 5(7)
C(2)	0.687(1)	0.505 3(9)	0.360 2(7)
C(3)	0.732(1)	0.491 5(9)	0.438 2(7)
C(4)	0.765(1)	0.476 3(9)	0.504 7(8)
Si	0.804 3(4)	0.461 4(4)	0.608 2(2)
C(101)	0.677(2)	0.461(2)	0.649(1)
C(102)	0.883(2)	0.357(1)	0.627(1)
C(103)	0.893(2)	0.553(1)	0.648(1)
Cl(11)	0.802(1)	0.672 0(9)	−0.171 9(7)
Cl(12)	0.895(1)	0.693(1)	−0.019 3(7)
C(01)	0.806(4)	0.705(4)	−0.087(2)
Cl(21)	0.781(1)	0.400(1)	−0.125 7(9)
Cl(22)	1.002(1)	0.414 3(8)	−0.118 7(9)
C(02)	0.894(3)	0.426(3)	−0.069(2)

* Defines origin.

solution was cooled, filtered and purified by preparative TLC (light petroleum–acetone, 8 : 2). Two major bands were isolated. The top brown band (R_f 0.8) gave deep red complex **11** (60 mg, 30%) after recrystallisation (CH_2Cl_2–MeOH) (Found: C, 39.6; H, 2.45. Calc. for $C_{44}H_{32}Co_2O_{12}P_2Re_2Si$: C, 39.50; H, 2.70%). IR (cyclohexane): ν(CO) 2115m, 2089m, 2026vs, 2022vs, 2006s, 2001s, 1995s, 1982m, 1972vs, 1959m and 1937w cm^{-1}. NMR ($CDCl_3$): ^1H, δ −12.88 (1 H, s, μ-H), 0.54 (9 H, s, $SiMe_3$), 3.63 (1 H, m, CH_2P_2), 4.09 (1 H, m, CH_2P_2), and 7.02–7.50 (20 H, m, Ph); ^{13}C, δ 2.09 (s, $SiMe_3$), 31.81 (t, CH_2P_2, J_{CP} = 19.62 Hz), 80.01 [br, C(4)], 86.77 [br, C(3)], 94.37 [s, C(2)], 96.86 [s, C(1)], 127.9–137.2 (m, Ph), 181.33, 182.06, 184.78 [s, Re(CO)], 202.35, 206.59 [s, Co(CO)]. FAB mass spectrum: *m*/*z* 1248–1080, $[M - nCO]^+$ (*n* = 3–9). The purple band (R_f 0.5) gave an unidentified compound [IR (cyclohexane): ν(CO) 2096m, 2036s, 2020s, 2001vs, 1994vs, 1982m, 1970s, 1968s, 1962s, 1954m, 1945m, 1939m, 1933m and 1930m cm^{-1}] which isomerised to **11** (110 mg, 55%) during crystallisation (CH_2Cl_2–Bu^iOH). Total yield of **11**: 170 mg, 85%.

$[Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1:\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9]$ 12. A mixture of complexes **9** (50 mg, 0.068 mmol) and $[Ru_3(CO)_{12}]$ (40 mg, 0.06 mmol) was heated in refluxing thf (10 cm^3). The reaction was followed by the disappearance of the bond of 2061 cm^{-1} in the IR spectrum and TLC. After 2 h the solvent was removed and the residue taken up in CH_2Cl_2 (10 cm^3). Methanol (5 cm^3) was added and the solution concentrated to give complex **12** as flaky, red-brown crystals. The mother-liquor was evaporated and the residue purified by TLC (light petroleum–acetone, 8 : 2) to give 27 mg more of the product. Total yield 70 mg, 96%. Crystals suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2–MeOH solution (Found: C, 41.40; H, 2.60%. Calc. for $C_{45}H_{32}Co_2O_{13}P_2Ru_3Si$: C, 41.75; H, 2.50%). IR (cyclohexane): ν(CO) 2095m, 2073vs, 2061m, 2048vs, 2024vs, 2016m, 2010 (sh), 1998s, 1986w, 1974s and 1958w cm^{-1}. NMR ($CDCl_3$): ^1H, δ −19.99 (1 H, s, μ-H), 0.48 (9 H, s, $SiMe_3$), 3.64 (1 H, m, CH_2P_2), 4.48 (1 H, m, CH_2P_2) and 6.84–7.58 (20 H, m, Ph); ^{13}C, δ 2.94 (s, $SiMe_3$), 30.70 (t, CH_2P_2, J_{CP} = 20.49 Hz), 92.78 [s, C(1)], 127.75–138.09 (m, Ph), 165.10 [s, C(2)], 186.16, 188.95 [s, Co(CO)], 202.92, 206.74 [s, Ru(CO)]. FAB mass spectrum: *m*/*z* 1178, $[M - 4CO]^+$; 1122–926, $[M - nCO]^+$ (*n* = 6–13).

$[Co_2\{\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C[W(CO)_3(cp)]\}(\mu\text{-dppm})(CO)_4]$ 13. The complexes $[WCl(CO)_3(cp)]$ (50 mg, 0.136 mmol) and **9** (100 mg, 0.136 mmol) were stirred in dry, degassed $NHEt_2$ (15 cm^3) with a catalytic amount of CuI (5 mg). After 18 h the solvent was removed and the residue purified by preparative TLC (light petroleum–acetone, 8 : 2). The only significant bands were a brown baseline and a deep red band (R_f 0.3). Crystallisation of the red band gave complex **13** as deep red needles (101 mg, 70%) (Found: C, 48.55; H, 3.30. Calc. for $C_{44}H_{36}Co_2O_7P_2SiW$: C, 49.55; H, 3.40%). IR (cyclohexane): ν(CO) 2038m, 2021s, 1998s (br), 1971s, 1958 and 1943s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.41 (s, 9 H, $SiMe_3$), 3.40 (1 H, m, CH_2P_2), 4.04 (1 H, m,

Table 11 Non-hydrogen positional parameters for complex **18**

Atom	*x*	*y*	*z*
Os(1)	0.376 2(1)	0.153 17(3)	0.117 46(8)
Os(2)	0.321 3(1)	0.121 63(3)	0.299 28(8)
Os(3)	0.0*	0.103 10(3)	0.0*
Co(4)	0.249 2(3)	0.389 7(1)	0.159 0(2)
Co(5)	0.191 6(3)	0.349 9(1)	0.315 0(3)
C(11)	0.514(2)	0.067 2(8)	0.150(2)
O(11)	0.579(2)	0.011 3(7)	0.158(1)
C(12)	0.352(3)	0.190(1)	−0.036(2)
O(12)	0.334(3)	0.208 1(9)	−0.126(2)
C(13)	0.625(2)	0.200 1(9)	0.251(2)
O(13)	0.770(2)	0.226 6(8)	0.330(2)
C(21)	0.396(3)	0.022(1)	0.329(2)
O(21)	0.440(2)	−0.038 3(7)	0.341(2)
C(22)	0.240(2)	0.124(1)	0.405(2)
O(22)	0.188(2)	0.124(1)	0.466(2)
C(23)	0.586(2)	0.143 4(9)	0.466(2)
O(23)	0.738(2)	0.154 8(8)	0.563(2)
C(31)	−0.053(2)	0.002(1)	−0.006(2)
O(31)	−0.078(2)	−0.058 2(8)	−0.004(2)
C(32)	−0.062(3)	0.119(1)	0.120(2)
O(32)	−0.153(2)	0.121 7(9)	0.153(2)
C(33)	0.057(2)	0.077(1)	−0.123(2)
O(33)	0.068(2)	0.055 0(8)	−0.199(1)
C(34)	−0.255(3)	0.137(1)	−0.159(2)
O(34)	−0.407(2)	0.159 3(8)	−0.253(1)
C(1)	0.123(2)	0.208 5(8)	0.055(1)
C(2)	0.252(2)	0.221 8(7)	0.196(1)
C(3)	0.309(2)	0.294 8(8)	0.251(1)
C(4)	0.442(2)	0.342 3(8)	0.345(1)
Si	0.690 5(7)	0.381 0(3)	0.495 4(7)
C(101)	0.848(4)	0.320(2)	0.645(3)
C(102)	0.819(4)	0.403(1)	0.423(3)
C(103)	0.664(3)	0.465(1)	0.564(3)
C(41)	−0.006(4)	0.390(1)	0.003(3)
O(41)	−0.165(2)	0.393(1)	−0.094(2)
C(42)	0.316(3)	0.487(1)	0.197(3)
O(42)	0.355(3)	0.543 6(8)	0.217(2)
C(43)	0.355(3)	0.373(1)	0.080(2)
O(43)	0.424(3)	0.362 0(9)	0.035(2)
C(51)	−0.056(3)	0.312(1)	0.188(2)
O(51)	−0.206(2)	0.289(1)	0.108(2)
C(52)	0.162(3)	0.441(1)	0.347(2)
O(52)	0.143(2)	0.497 1(8)	0.367(2)
C(53)	0.282(4)	0.312(1)	0.479(2)
O(53)	0.343(4)	0.290(1)	0.584(2)

* Defines origin.

CH$_2$P$_2$), 5.55 (5 H, s, cp) and 7.05–7.54 (20 H, m, Ph). ^{13}C, δ 0.48 (s, SiMe$_3$), 35.58 (t, J_{CP} = 20.95, CH$_2$P$_2$), 84.43 [t, J_{CP} = 7.62, C(4)], 86.80 [t, J_{CP} = 10.45 Hz, C(3)], 91.76 (s, cp), 95.77 [s, C(2)], 108.97 [s, C(1)], 127.8–139.4 (m, Ph), 202.70 [br, Co(CO)], 207.53 [br, Co(CO)], 210.86 [s, W(CO)] and 230.21 [s, W(CO)]. FAB mass spectrum: *m*/*z* 1068, M^+ and 1040–872, $[M - n\mathrm{CO}]^+$ (n = 1–7).

Reactions of [Co$_2$(μ-η^2-HC$_2$C≡CH)(μ-dppm)(CO)$_4$] 10

[Co$_2${μ-η^2-HC$_2$C≡C[W(CO)$_3$(cp)]}(μ-dppm)(CO)$_4$] 14. The complexes [WCl(CO)$_3$(cp)] (55 mg, 0.15 mmol) and **10** (100 mg, 0.15 mmol) were stirred in degassed NHEt$_2$ (15 cm^3) with CuI (5 mg, catalyst) for 10 h. Preparative TLC gave one major deep red band (R_f 0.4). Trituration of the residue gave complex **14** as a brick red powder (70 mg, 50%) which was recrystallised (CH$_2$Cl$_2$–hexane) (Found: C, 49.20; H, 2.85. Calc. for C$_{41}$H$_{28}$Co$_2$O$_7$P$_2$W: C, 49.40; H, 2.80%). IR (cyclohexane): ν(CO) 2038s, 2025vs, 2002vs, 1975vs, 1958br and 1943vs cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 3.40 (1 H, m, CH$_2$P$_2$), 3.79 (1 H, m, CH$_2$P$_2$), 5.59 (5 H, s, cp), 6.04 (1 H, s, HC$_2$Co$_2$) and 7.06–7.56 (20 H, m, Ph); ^{13}C, δ 35.35 (t, J_{CP} = 21.09 Hz, CH$_2$P$_2$), 127.9–138.7 (m, Ph), 203.15, 206.24 [br, Co(CO)], 210.92 and 229.84 [s, W(CO)]. FAB mass spectrum: *m*/*z* 912–798, $[M - n\mathrm{CO}]^+$ (n = 3–7).

[Co$_2${μ-η^2-HC$_2$C≡C[Au(PPh$_3$)]}(μ-dppm)(CO)$_4$] 15. The complexes [AuCl(PPh$_3$)] (100 mg, 0.20 mmol) and **10** (135 mg, 0.20 mmol) were dissolved in thf (10 cm^3) with an excess of dbu (two drops). The red solution was allowed to stir at room temperature overnight. The solvent was then removed and the red residue obtained purified by preparative TLC (light petroleum–acetone, 7:3). The major band (R_f 0.5) was collected and recrystallised (CH$_2$Cl$_2$–hexane) to give complex **15** as deep red needles (107 mg, 48%) (Found: C, 54.75; H, 3.85. Calc. for C$_{51}$H$_{38}$AuCo$_2$O$_4$P$_3$: C, 54.55; H, 3.40%). IR (thf): ν(CO) 2021s, 1997s (br), 1967s (br) and 1948 (sh) cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 3.39 (1 H, m, CH$_2$P$_2$), 3.82 (1 H, m, CH$_2$P$_2$), 5.98 [1 H, s, Co$_2$(μ-C$_2$H)] and 7.12–7.61 (35 H, m, Ph); ^{13}C, δ 36.77 (t, J_{CP} = 18.87 Hz, CH$_2$P$_2$), 70.63 [br, C(4)], 78.74 [br, C(3)], 127.62–134.16 (m, Ph), 203.43 [br, Co(CO)] and 204.87 [br, Co(CO)]. FAB mass spectrum: *m*/*z* 1581, $[M + \mathrm{Au(PPh_3)}]^+$ and 1066–1010, $[M - n\mathrm{CO}]^+$ (n = 2–4).

Reactions of HC$_2$C$_2$SiMe$_3$

[Os$_3$(μ$_3$-η^2-HC$_2$C$_2$SiMe$_3$)(μ-CO)(CO)$_9$] 16. The complex [Os$_3$(CO)$_{10}$(NCMe)$_2$] (100 mg, 0.18 mmol) in thf (30 cm^3) was treated with HC$_2$C$_2$SiMe$_3$ (50 mg, 0.4 mmol) at r.t. The solution immediately darkened and was stirred overnight at r.t. to complete the reaction. After removal of solvent, the residue was dissolved in CH$_2$Cl$_2$ and purified by TLC (light petroleum). The main orange-yellow band (R_f 0.375) contained complex **16** (41.9 mg, 24%). IR (cyclohexane): ν(CC) 2140w; ν(CO) 2102m, 2066vs, 2060vs, 2028s, 2010m, 2003 (sh), 1986 (sh) and 1852m (br) cm^{-1}. ^{1}H NMR (CDCl$_3$): isomer **16a**, [Os$_3$(μ$_3$-η^2-HC$_2$C≡CSiMe$_3$)(μ-CO)(CO)$_9$], δ 0.15 (18 H, s, SiMe$_3$) and 9.41 (2 H, s, C$_2$H); isomer **16b**, [Os$_3$(μ$_3$-η^2-Me$_3$SiC$_2$C≡CH)(μ-CO)(CO)$_9$], δ 0.86 (9 H, s, SiMe$_3$) and 3.98 (1 H, s, C$_2$H). FAB mass spectrum: *m*/*z* 972, M^+ and 944–692, $[M - n\mathrm{CO}]^+$ (n = 1–10).

[Ru$_3$(μ-H)(μ$_3$-η^1:η^2-C$_2$C≡CSiMe$_3$)(μ-dppm)$_2$(CO)$_5$] 17. The complex [Ru$_3$(CO)$_8$(μ-dppm)$_2$] (95 mg, 0.08 mmol) in thf (30 cm^3) was treated with HC$_2$C$_2$SiMe$_3$ (12.2 mg, 0.1 mmol). The mixture was refluxed for 36 h. After removal of solvent the residue was dissolved in CH$_2$Cl$_2$ and purified by TLC (light petroleum–acetone, 10:3). An orange fraction (R_f 0.45) contained complex **17** (34 mg, 32%). IR (cyclohexane): ν(CC) 2119w (br); ν(CO) 2016vs, 1983s, 1956s, 1940m and 1906w (br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −19.40 (1 H, m, μ-H), 0.09 (9 H, s, SiMe$_3$), 3.05 (1 H, dt, CH$_2$P$_2$), 3.64 (2 H, m, CH$_2$P$_2$), 4.17 (1 H, dt, CH$_2$P$_2$) and 6.85–7.45 (m, Ph). FAB mass spectrum: *m*/*z* 1333, M^+.

Preparation of [Os$_3${μ$_3$-η^2:μ-η^2-HC$_2$C$_2$SiMe$_3$[Co$_2$(CO)$_6$]}(μ-CO)(CO)$_9$] 18

Complex **16** (56 mg, 0.06 mmol) in light petroleum (20 cm^3) was treated with [Co$_2$(CO)$_8$] (20 mg, 0.06 mmol) at r.t. The solution immediately turned dark green; after 3 h all starting material was consumed. The solution was reduced to dryness and the residue recrystallised from hexane containing a few drops of benzene to give black crystals of complex **18**. IR (cyclohexane): ν(CO) 2104m, 2086 (sh), 2080s, 2067vs, 2058vs, 2045 (sh), 2029s, 2022vs, 2009s, 2003s and 1854w (br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.37 (9 H, s, SiMe$_3$) and 9.30 (1 H, s, C$_2$H).

FAB mass spectrum: m/z 1174, M^+; 1101, $[M - \text{SiMe}_3]^+$; 1073–737 and $[1101 - n\text{CO}]^+$ (n = 1–13).

Crystallography

Structure determinations. Unique room-temperature diffractometer data sets (monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å; 2θ–θ scan mode; T ca. 295 K) were measured within the specified $2\theta_{\text{max}}$ limit, yielding N independent reflections, N_o of these with $I > 3\sigma(I)$ being considered 'observed' and used in the large block/full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{\text{iso}})_{\text{H}}$ being included at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being employed. Computation used the XTAL 3.2 program system[34] implemented by S. R. Hall. Details of the crystal data and refinement are given in Table 6.*

Abnormal features/variations in procedure. *Complex* **11**. The putative Re$_2$(μ-H) atom was not evident as any significant residue in any reasonable location in difference maps and was ignored in the processing. An analytical absorption correction was applied.

Complex **12**. Major residues in the final difference maps coincided with plausible cluster-bound Ru$_3$(μ-H) locations and were included constrained as such in the final refinement; the limited data, however, consequent on use of a small inferior specimen, would only support anisotropic thermal parameter refinement for Ru, Co, P and Si. For both complexes **11** and **12**, in consequence of the long axial lengths, data sets were measured by the ω-scan technique in an attempt to diminish any effects arising from possible reflection overlap.

Complex **17**. As also with complex **18**, space-group chirality was assigned for the preferred hand in the refinement. The cluster-bound hydrogen expected from the chemistry was included in the refinement at a plausible location. Solvent site occupancies were set at unity after trial refinement. An initial determination on inferior unsolvated material is recorded as **17a**, all data other than those in Table 6 being deposited (anisotropic thermal parameter refinement for Ru, Si and P only).

Complex **18**. Atom H(1) was evident in difference maps and included constrained.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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* The structure of complex **6** was reported after submission of this paper. Precursor **1** was formed by heating [Mo(C≡CSiMe$_3$)(CO)$_3$(cp)] in toluene and the W$_2$ analogue was also described.[35]