Phosphorus–Carbon Bond Formation in Heterobimetallic Molybdenum–Tungsten Alkyne Complexes†

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The heterobimetallic complexes $[MoW(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = Ph **1a**, Me **1b** or H **1c**; $R^1 = R^2 = CO_2Me$ **1d** or Me **1e**) have been isolated from the reaction of a mixture of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with the corresponding alkyne $R^1C{\equiv}CR^2$ in diglyme (2,5,8-trioxanonane). Thermolysis of complexes **1a**–**1d** with PPh_2Cl proceeded *via* P–Cl bond cleavage and coupling of the diphenylphosphide unit with the alkyne in one of four different ways, depending on the nature of R^1 and R^2, to give the products $[MoW(\mu\text{-}Cl)(\mu\text{-}Ph_2PCR^1{=}CR^2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = Ph **2a**; $R^1 = R^2$ = H **2c** or CO_2Me **2d**), $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHR^2)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ (R^2 = Ph **3a**, Me **3b** or H **3c**), $[MoWCl_2(\mu\text{-}Ph_2PC{=}CHR^2)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ (R^2 = Ph **4a** or Me **4b**) and $[WMo(\mu\text{-}Cl)\{\mu\text{-}Ph_2PC(CO_2Me){=}CCO_2Me\}(CO)_2(\eta\text{-}C_5H_5)_2]$ **5d**. The formation of complexes **2** and **3** can be rationalised as resulting from initial substitution of a molybdenum carbonyl ligand by the halogenophosphine and that of **4** and **5** by initial substitution of a tungsten carbonyl. The significantly higher yield of the former two complexes suggests that initial substitution of a molybdenum carbonyl is the preferred pathway. Attempts at the preparation of an organophosphine-substituted derivative of **1a** *via* its reaction with PPh_3 gave $[WMo(O)(\mu\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ **6** as the only product. A single-crystal X-ray structure determination of complex **3a** shows a Mo–W distance compatible with a double bond. The phosphorus atom and the α carbon of the four-membered metallacycle are σ bonded to tungsten and the carbon–carbon double bond is π-co-ordinated to molybdenum.

Heterobimetallic complexes are of interest because they open up possibilities for the study of the relative reactivities of two different metal sites, and of the co-operative interaction between two metal centres. The reactions of organophosphines with heterodinuclear carbonyl complexes containing $\mu\text{-}R^1\text{-}C{\equiv}CR^2$ ligands generally give, in the first instance, substitution of a carbonyl ligand at one of the metal centres preferentially.[2]

In the reactions of chlorodiphenylphosphine with the homobimetallic complexes $[M_2(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Mo or W) no stable complexes involving simple substitution of a terminal carbonyl ligand were isolated; instead a variety of complexes were obtained involving P–Cl bond cleavage, the nature of which depended on both the identity of the metal centres and the R substituents of the alkyne group.[1,3] In this paper we report for comparative purposes the preparation and reactions of the heterodinuclear species $[MoW(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = Ph **1a**, Me **1b** or H **1c**; $R^1 = R^2 = CO_2Me$ **1d**) with chlorodiphenylphosphine.

Results and Discussion

(1) *Synthesis of* $[MoW(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = Ph **1a**, Me **1b** *or* H **1c**; $R^1 = R^2 = CO_2Me$ **1d** *or* Me **1e**).—These complexes were prepared by treating a freshly prepared mixture of the three triply bonded species[4] $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, $[MoW(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[W_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with an excess of alkyne, $R^1C{\equiv}CR^2$. Separation of the alkyne-bridged molybdenum–tungsten species from the ditungsten- and dimolybdenum-alkyne complexes was achieved by column and thin-layer chromatography.

The complexes $[MoW(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = Ph **1a**, Me **1b** or H **1c**; $R^1 = R^2 = CO_2Me$ **1d** or Me **1e**) were characterised by microanalysis, mass spectrometry, IR, ^1H and ^{13}C NMR spectroscopy (see Table 1 and Experimental section). Either three or four ν(CO) absorption bands are seen in the IR spectra of each of the complexes **1a**–**1e**, the overall pattern being similar to that of the analogous dimolybdenum and ditungsten complexes.[1,5,6] One of the absorptions in each case is in the range 1827–1845 cm^{-1} and may be assigned to a semi-bridging carbonyl group. There is an additional absorption at 1693 cm^{-1} in the IR spectrum of **1d** due to the C=O stretch of the CO_2Me groups.

The ^1H NMR spectra for **1a**–**1e** show two singlet resonances due to the inequivalent cyclopentadienyl ligands for each complex. The acetylenic proton signals in **1a**–**1c** are seen as a singlet at δ 5.13 (**1a**), a quartet at δ 5.21 [^4J(HMe) 0.7 Hz] (**1b**) and a singlet at δ 4.46 (**1c**).

In the $^{13}C\text{-}\{^1H\}$ NMR spectra of **1a**–**1e** at 293 K, resonances due to the four carbonyl ligands are present, with those due to the carbonyls on tungsten being further upfield than those due to the carbonyls attached to molybdenum. When the alkyne is symmetrical (**1c**–**1e**) only two peaks are observed at 293 K, but when the alkyne is unsymmetrical (**1a** and **1b**) then four individual peaks are resolved. The observation of separate signals for the tungsten- and molybdenum-bound carbonyl ligands is not unexpected, since carbonyl scrambling between metal atoms is a very high energy process in systems of this type and does not normally occur at room temperature.[6] The difference in the ^{13}C NMR spectra for the complexes containing the symmetrical and unsymmetrical alkynes can be accounted for as shown in Scheme 1 which shows a possible fluxional process that renders carbonyls a/b and c/d equivalent in the symmetrical transverse alkyne complexes (**1c**–**1e**) and involves partial rotation of cp^1 (cp = $\eta\text{-}C_5H_5$), CO^a and CO^b

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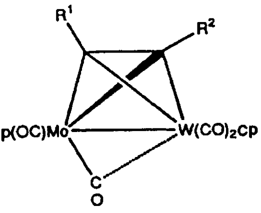
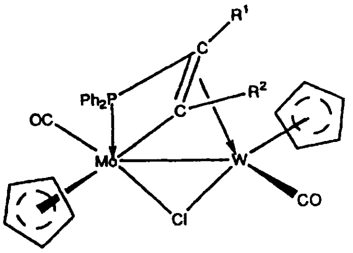
† Reactivity of Halogenophosphines towards Transition-metal Complexes. Part 2.[1]

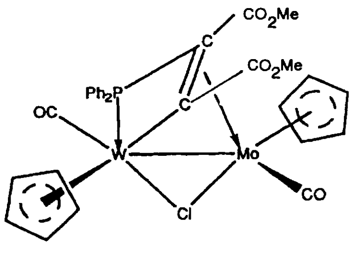
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



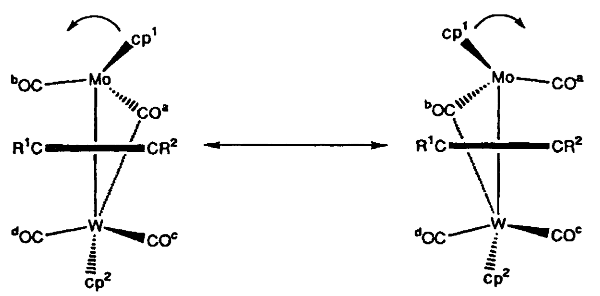
1a $R^1 = H, R^2 = Ph$
1b $R^1 = H, R^2 = Me$
1c $R^1 = R^2 = H$
1d $R^1 = R^2 = CO_2Me$
1e $R^1 = R^2 = Me$



2a $R^1 = H, R^2 = Ph$
2c $R^1 = R^2 = H$
2d $R^1 = R^2 = CO_2Me$



5d



Scheme 1 Proposed fluxional process for complex **1** that renders CO^a and CO^b equivalent in symmetrical alkyne complexes (**1c**–**1e**) but not in unsymmetrical alkyne complexes (**1a** and **1b**)

around the Mo–W bond. For unsymmetrical alkynes a similar process may also occur but the different nature of the two R groups means that equivalence of the carbonyls does not ensue.

In the one known crystal structure of a molybdenum–tungsten alkyne-bridged complex $[\mathrm{MoW}\{\mu\text{-}\mathrm{C_2(C_7H_7)_2}\}(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})\{\eta\text{-}\mathrm{C_7H_6(COMe)}\}]$ a semi-bridging carbonyl group, as with the homometallic analogues, is revealed and furthermore it is the molybdenum carbonyl that is seen to be semi-bridging.[7] The IR spectra of complexes **1a**–**1e** in dichloromethane solution confirm that for these complexes in this solvent a semi-bridging carbonyl is also present.

(2) *Reactions of* $[\mathrm{MoW}(\mu\text{-}\mathrm{R^1CCR^2})(\mathrm{CO})_4(\eta\text{-}\mathrm{C_5H_5})_2]$ (R^1 = H, R^2 = Ph **1a**, Me **1b** *or* H **1c**; $R^1 = R^2 = CO_2Me$ **1d**) *with* PPh_2Cl.—The complexes **1a**–**1d** were refluxed in toluene for 18 h, with an excess of PPh_2Cl, to give a range of products **2**–**5**, the particular combination of products obtained in any given reaction depending on the R groups. The products were characterised, in general, by microanalysis, mass spectrometry, IR, ^{1}H, ^{31}P and ^{13}C NMR spectroscopy (see Table 1 and Experimental section). Complex **3a** has also been the subject of a crystal structure determination.

The ordering of Mo and W in the chemical formulae for complexes **2**–**5** indicates the orientation of the organic or organophosphorus bridging ligand. All such ligands in these products can be regarded as variations on simple vinyl ligands. The vinyl ligand is σ-bonded to either molybdenum or tungsten, and whichever metal atom participates in this σ bond is placed first in the molecular formula.

(*a*) *Characterisation of* $[\mathrm{MoW}(\mu\text{-}\mathrm{Cl})(\mu\text{-}\mathrm{Ph_2PCR^1{=}CR^2})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})_2]$ (R^1 = H, R^2 = Ph **2a**; $R^1 = R^2$ = H **2c** *or* CO_2Me **2d**) *and* $[\mathrm{WMo}(\mu\text{-}\mathrm{Cl})\{\mu\text{-}\mathrm{Ph_2PC(CO_2Me){=}CCO_2Me}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})_2]$ **5d**. Complexes **2a** and **2c** were obtained as minor products from the reactions of PPh_2Cl with **1a** and **1c** respectively. In contrast, **2d** is the major product of the reaction of **1d** with PPh_2Cl. Complex **5d** is a minor product of the same reaction.

The electron-impact (EI) mass spectra of complexes **2a**, **2c**, **2d** and **5d** each show peaks at *m*/*z* values corresponding to their respective molecular ions and to fragment ions obtained by loss of one and two carbonyl ligands from the molecular ions. The IR spectrum of each complex has one band in the terminal carbonyl region. In addition, the spectra of **2d** and **5d** each show an absorption due to the C=O stretch of the CO_2Me substituents (1669 and 1680 cm^{-1}). These spectra are similar to the IR spectra of the dimolybdenum and ditungsten analogues.[1,3]

The ^{1}H NMR spectra of **2a** and **2c** each show two cyclopentadienyl resonances. In both cases the more downfield of the two cyclopentadienyl signals is a doublet coupled to phosphorus [^3J(HP) 1.9 Hz]. This signal is attributed to the protons on the cyclopentadienyl ring attached to molybdenum because, from ^{31}P NMR data (see later), it has been established that the phosphorus is also directly bonded to molybdenum. The more upfield cyclopentadienyl signal is a singlet and is assigned to the cyclopentadienyl ligand on tungsten. A signal due to the proton on the β-carbon of the vinyl ligand ($\mathrm{Ph_2PC_\beta H{=}C_\alpha R}$) (R = Ph **2a** or H **2c**) is seen in each of the two spectra at δ 4.73 (**2a**) [doublet ^2J(HP) 7.7 Hz] and δ 4.40 (**2c**) [doublet of doublets ^2J(HP) 8.6, ^3J(HH) 4.9 Hz]. In the spectrum of **2c** an additional doublet of doublets at δ 6.16 is due to the proton on the α carbon coupled to phosphorus [^3J(HP) 12.7 Hz] and to the β proton. The ^{1}H NMR spectra of **2d** and **5d** each show two cyclopentadienyl signals and two methyl signals. In the case of **2d** the upfield cyclopentadienyl resonance is a doublet coupled to phosphorus [^3J(HP) 1.9 Hz] and is attributed to the protons on the cyclopentadienyl ligand bonded to molybdenum. No splitting could be resolved for either of the cyclopentadienyl resonances in the spectrum of **5d**.

The ^{31}P-{^{1}H} NMR spectrum of **2d** shows a single peak at δ −115.4 [relative to $P(OMe)_3$ δ 0.0] while that of **5d** has a peak at δ −150.2 with clearly resolved ^{183}W satellites [^1J(PW) 232 Hz]. The presence of ^{183}W satellites in the spectrum of **5d**, but not in that of **2d**, implies that in **2d** the phosphorus is directly bonded to molybdenum, whereas in **5d** it is bonded to tungsten. The chemical shift values in each case are indicative of the phosphorus atom being part of a four-membered metallacycle, $\overline{\mathrm{M{-}C{=}C{-}P}}$.[1,3,8]

From the above data it can be deduced that **2a**, **2c**, **2d** and **5d** have the structures indicated above, which are analogous to those of the related dimolybdenum[3] and ditungsten[1] complexes; the structure of the ditungsten analogue of **5d** has

Table 1 Infrared, ^{1}H and ^{31}P NMR data for the complexes

Compound	ν(CO)[a]/cm^{-1}	^{1}H NMR (δ)[b]	^{31}P-{^{1}H} NMR (δ)[c]
1a	1989s, 1922vs, 1830s	7.3–7.0 (m, 5 H, Ph), 5.38 (s, 5 H, cp), 5.27 (s, 5 H, cp), 5.13 [s, ^2J(HW) 3.2, 1 H, CH]	
1b	1991s, 1925vs, 1915vs, 1841s[d]	5.34 (s, 5 H, cp), 5.27 (s, 5 H, cp), 5.21 [q, ^4J(HMe) 0.7, 1 H, CH], 2.56 (d, 3 H, Me)	
1c	1989s, 1919vs, 1827s	5.38 [s, ^2J(HW) 1.1, 5 H, W-cp], 5.33 (s, 5 H, Mo-cp), 4.46 [s, ^2J(HW) 3.5, 2 H, CH]	
1d	2021s, 1958vs, 1845s, 1693m	5.39 [s, ^2J(HW) 1.2, 5 H, W-cp], 5.32 (s, 5 H, Mo-cp), 3.73 (s, 6 H, Me)	
1e	1984s, 1913vs, 1840s[d]	5.29 (s, 5 H, cp), 5.21 (s, 5 H, cp), 2.57 (s, 6 H, Me)	
2a	1866s	7.9–7.0 (m, 15 H, Ph), 4.89 [d, ^3J(HP) 1.9, 5 H, Mo-cp], 4.85 (s, 5 H, W-cp), 4.73 [d, ^2J(HP) 7.7, 1 H, Ph$_2$PC*H*]	
2c	1863s	7.5–7.2 (m, 10 H, Ph), 6.16 [dd, ^3J(HP) 12.7, ^2J(HH) 4.9, 1 H, Ph$_2$PCH=C*H*], 4.94 [d, ^3J(HP) 1.9, 5 H, Mo-cp], 4.88 (s, 5 H, W-cp), 4.40 [dd, ^2J(HP) 8.6, 1 H, Ph$_2$PC*H*]	
2d	1926s, 1890s, 1669m	8.1–7.2 (m, 10 H, Ph), 4.94 (s, 5 H, W-cp), 4.90 [d, ^3J(HP) 1.9, 5 H, Mo-cp], 3.79 (s, 3 H, Me), 3.64 (s, 3 H, Me)	−115.4 [s, μ-Ph$_2$*P*C(CO$_2$Me)=CCO$_2$Me]
3a	*e*	8.4–7.2 (m, 25 H, Ph), 4.39 [t, ^3J(HP) 0.8, 5 H, W-cp], 3.93 [dd, ^3J(HP) 1.6, ^4J(HP) 0.3, 5 H, Mo-cp], 3.34 [dd, ^3J(HP) 12.2, ^3J(HP) 1.5, 1 H, C*H*Ph]	11.6 [d, ^2J(PP) 62, ^1J(PW) 300, μ-PPh$_2$], −241.1 [d, ^1J(PW) 115, μ-PPh$_2$C=CHPh]
3b	*e*	8.2–7.2 (m, 20 H, Ph), 4.39 (s, 5 H, cp), 4.12 (s, 5 H, cp), 2.83 [q, ^3J(HMe) 5.2, C*H*Me], 2.63 (d, 3 H, Me)	17.2 [d, ^2J(PP) 65, ^1J(PW) 314, μ-PPh$_2$], −256.0 [d, ^1J(PW) 97, μ-Ph$_2$PC=CHMe]
3c	*e*		11.4 [d, ^2J(PP) 64, μ-PPh$_2$], −261.0 [d, μ-Ph$_2$PC=CH$_2$][f]
4a	*e*	8.5–6.9 (m, 25 H, Ph), 4.27 [t, ^3J(HP) 0.8, 5 H, Mo-cp], 3.97 [dd, ^3J(HP) 1.6, ^4J(HP) 0.3, 5 H, W-cp], 2.65 [dd, ^3J(HP) 6.4, ^3J(HP) 1.1, 1 H, C*H*Ph]	−7.6 [d, ^2J(PP) 53, ^1J(PW) 314, μ-PPh$_2$], −233.4 [d, μ-Ph$_2$PC=CHPh]
4b	*e*	8.3–7.1 (m, 20 H, Ph), 4.25 (s, 5 H, cp), 4.16 (s, 5 H, cp), 2.99 [d, ^3J(MeH) 5.5, 3 H, Me], 2.28 [q, ^3J(HMe) 5.5, 1 H, C*H*Me]	12.2 [d, ^2J(PP) 52, μ-PPh$_2$],[f] −236.3 [d, μ-Ph$_2$PC=CHMe]
5d	1929s, 1897s, 1680m	8.1–7.0 (m, 10 H, Ph), 5.51 (s, 5 H, cp), 5.24 (s, 5 H, cp), 3.95 (s, 3 H, Me), 3.66 (s, 3 H, Me)	−150.2 [s, ^1J(PW) 232, μ- Ph$_2$PC(CO$_2$Me)=CCO$_2$Me]
6[g]	1843s	9.03 [dd, ^3J(HH) 10.7, ^3J(HP) 1.3, ^2J(HW) 7.2, 1 H, C*H*=CHPh], 8.2–7.1 (m, 15 H, Ph), 5.29 [d, ^3J(HP) 0.6, 5 H, cp], 4.41 [d, ^3J(HP) 1.6, 5 H, cp], 3.95 [d, *J*(HW) 1.8, 1 H, CH=C*H*Ph]	24.2 [s, ^1J(PW) 367, μ-PPh$_2$]

[a] Recorded in CH$_2$Cl$_2$ solution unless stated otherwise. [b] Proton chemical shifts (δ) relative to SiMe$_4$ (δ = 0), coupling constants in Hz in CDCl$_3$ at 293 K. [c] Phosphorus-31 chemical shifts (δ) relative to external P(OMe)$_3$ (δ = 0.0) (upfield shifts negative), {^{1}H}-gated decoupled, measured in CDCl$_3$ at 293 K. [d] Recorded in *n*-hexane solution. [e] No peaks in carbonyl region. [f] ^{183}W satellites not resolved. [g] ν(W=O) 826 cm^{-1} recorded using a KBr disc.

been previously determined by X-ray crystallography.[1] The molybdenum–tungsten complexes are presumed, therefore, to have a Mo–W single bond, two terminal carbonyls, two cyclopentadienyl ligands, a bridging chloride and a bridging vinyl group. In addition the diphenylphosphine substituent on the β carbon of the vinyl group is bonded to the same metal atom to which the α carbon is σ bonded.

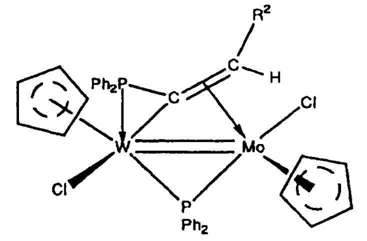
For complex **2a** the formation of the μ-Ph$_2$PCH=CPh bridging ligand is regiospecific, with the bulky phenyl group positioned only on the carbon atom (C$_\alpha$) remote from the phosphine group. Such regiospecificity has been noted previously in related complexes.[9]

(*b*) *Characterisation of* [WMoCl$_2$(μ-Ph$_2$PC=CHR^2)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] (R^2 = Ph **3a**, Me **3b** *or* H **3c**) *and* [MoWCl$_2$(μ-Ph$_2$PC=CHR^2)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] (R^2 = Ph **4a** *or* Me **4b**). Compounds **3a** and **3b** are the major products of the reactions of [MoW(μ-HCCR^2)(CO)$_4$(η-C$_5$H$_5$)$_2$] (R^2 = Ph **1a** or Me **1b**) with PPh$_2$Cl while **4a** and **4b** are the minor products of these reactions. Complex **3c** is isolated in only very low yield from the reaction of [MoW(μ-HCCH)(CO)$_4$(η-C$_5$H$_5$)$_2$] **1c** with PPh$_2$Cl.

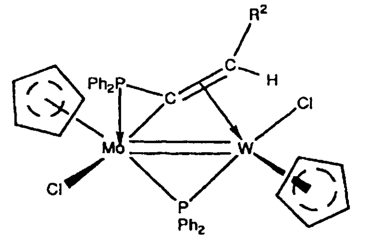
The EI mass spectra of **3a**, **3b**, **4a** and **4b** show peaks due to their parent molecular ions. Complex **3c** has no molecular ion peak in the EI spectrum, but in the fast atom bombardment (FAB) mass spectrum the molecular ion is seen together with a fragment ion resulting from the loss of two Cl atoms.

None of the complexes **3a**–**3c**, **4a** and **4b** shows any absorption in the carbonyl region of their IR spectra. The ^{1}H NMR spectra of **3a** and **3b** both show multiplets in the phenyl region and signals of appropriate relative intensity due to the cyclopentadienyl rings. In addition, the spectrum of **3a** shows a doublet of doublets [^3J(HP) 12.2, ^3J(HP) 1.5 Hz] centred at δ 3.34 due to the proton on the β carbon of the vinyl ligand. In the spectrum of **3b** a quartet is seen at δ 2.83 and is attributed to the β proton coupling to the methyl group [^3J(HMe) 5.2 Hz]. Coupling to phosphorus is not resolved in this spectrum. A ^{1}H NMR spectrum could not be obtained for **3c**. The compound was extremely unstable in solution and is formulated as [WMoCl$_2$(μ-Ph$_2$PC=CH$_2$)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] on the basis of mass spectrometry, the absence of carbonyl absorptions in the IR spectrum, ^{31}P NMR spectroscopy and by comparison with complexes **3a** and **3b**.

Complexes **4a** and **4b** have similar ^{1}H NMR spectra to **3a** and **3b**. In the spectrum of **4a** a doublet of doublets at δ 2.65 [^3J(HP)



3a $R^2 = Ph$
3b $R^2 = Me$
3c $R^2 = H$



4a $R^2 = Ph$
4b $R^2 = Me$

6.4, ^3J(HP) 1.1 Hz] arises from the β proton coupling to the two phosphorus atoms. In that of **4b** a quartet at δ 2.28 [^3J(HMe) 5.5 Hz] is due to the β proton coupling to the methyl group; as with the corresponding proton in **3b** no coupling to phosphorus could be resolved.

The $^{31}P-\{^1H\}$ NMR spectra for complexes **3a**–**3c**, **4a** and **4b** are extremely informative. Each of the spectra of the five complexes shows two doublets at very different chemical-shift values with coupling constants in the range ^2J(PP) 52–65 Hz. The downfield doublet in each case appears at a chemical shift around δ 10 and is assigned to the bridging phosphido moiety. This signal, in the cases of **3a**, **3b**, **4a** and **4b**, displays ^{183}W satellites [av. ^1J(PW) 300 Hz]. The upfield doublets appear in the region δ −220 to −260 and are indicative of a phosphorus atom in a strained three-membered metallacycle, similar chemical-shift values having been previously observed in related dimolybdenum,[3] ditungsten[1] and diiron systems.[10] These doublets show tungsten satellites for **3a** and **3b** [^1J(PW) 115 **3a**, 97 Hz **3b**] but not for **4a** and **4b**. This suggests that the phosphorus atom of the μ-$Ph_2PC{=}CR^1R^2$ ligand is bonded to tungsten for complexes **3a**–**3c** and to molybdenum for **4a** and **4b**.

In view of the above spectroscopic data it is proposed that complexes **3a**–**3c**, **4a** and **4b** adopt the structures shown. For **3a** this assignment has been confirmed by X-ray crystallography.

Suitable crystals of **3a** were grown from a dichloromethane solution by slow diffusion of hexane at 273 K. The structure of **3a** is depicted in Fig. 1 while Table 2 lists selected bond lengths and bond angles.

The two metal centres, molybdenum and tungsten, in complex **3a** are bridged by a diphenylphosphide group and an α-phosphine-substituted μ-vinyl ligand. The 18-electron rule suggests that a molybdenum–tungsten double bond should exist between the two metal centres. The bond distance [2.772(3) Å] is, however, considerably longer than previously reported Mo=W double bonds [2.702(1)–2.718(2) Å],[11] although shorter than the reported Mo–W single bonds [3.3102(4)–2.938(1) Å][12] and considerably longer than the reported Mo≡W triple bonds [2.275(1)–2.207(1) Å].[13] It is also slightly longer than the Mo=Mo distance [av. 2.714(1) Å] in $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$[3] and the W=W distance [av. 2.657(1) Å] in $[W_2Cl(\mu\text{-}PhC_2Ph)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$.[1]

The cyclopentadienyl and chloride ligands adopt a *trans* configuration. The Mo–Cl [2.456(8) Å] and W–Cl bond length [2.450(7) Å] are equivalent within error limits as are the average Mo–C(cp) [2.381(35) Å] and average W–C(cp) bond lengths [2.372(50) Å].

Table 2 Selected bond lengths (Å) and angles (°) for $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **3a** with estimated standard deviations given in parentheses

Mo(1)–W(1)	2.772(3)	Mo(1)–Cl(1)	2.456(8)
Mo(1)–P(2)	2.420(8)	Mo(1)–C(20)	2.065(25)
Mo(1)–C(21)	2.292(34)	W(1)–Cl(2)	2.450(7)
W(1)–P(1)	2.424(8)	W(1)–P(2)	2.410(8)
W(1)–C(20)	2.105(25)	C(20)–C(21)	1.514(43)
Mo(1)–C(cp)	2.336(32)–2.447(36)		
W(1)–C(cp)	2.308(26)–2.462(52)		
W(1)–Mo(1)–Cl(1)	107.6(2)	W(1)–Mo(1)–P(2)	54.8(2)
Cl(1)–Mo(1)–P(2)	93.9(3)	W(1)–Mo(1)–C(20)	49.0(7)
Cl(1)–Mo(1)–C(20)	113.2(7)	P(2)–Mo(1)–C(20)	103.4(7)
W(1)–Mo(1)–C(21)	79.7(9)	Cl(1)–Mo(1)–C(21)	80.4(9)
P(2)–Mo(1)–C(21)	130.2(9)	C(20)–Mo(1)–C(21)	40.3(11)
Mo(1)–W(1)–Cl(2)	122.9(2)	Mo(1)–W(1)–P(1)	81.9(2)
Cl(1)–W(1)–P(1)	89.6(3)	Mo(1)–W(1)–P(2)	55.1(2)
Cl(2)–W(1)–P(2)	87.3(3)	P(1)–W(1)–P(2)	124.6(3)
Mo(1)–W(1)–C(20)	47.7(7)	Cl(2)–W(1)–C(20)	127.6(7)
P(1)–W(1)–C(20)	42.7(7)	P(2)–W(1)–C(20)	102.5(7)
W(1)–P(1)–C(20)	58.4(9)	Mo(1)–P(2)–W(1)	70.0(2)
Mo(1)–C(20)–W(1)	83.9(9)	Mo(1)–C(20)–P(1)	131.7(15)
W(1)–C(20)–P(1)	78.9(10)	Mo(1)–C(20)–C(21)	78.0(17)
W(1)–C(20)–C(21)	128.3(20)	P(1)–C(20)–C(21)	145.5(21)
Mo(1)–C(21)–C(20)	61.8(15)		

The bridging phosphide ligand is symmetrically placed [Mo–P(2) 2.420(8), W–P(2) 2.410(8) Å] which is slightly surprising in view of the fact that this is a heterobimetallic complex and that the other bridging ligand is unsymmetrical. In the analogous homobimetallic complex $[Mo_2Cl_2(\mu\text{-}Ph_2PC{=}CHMe)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ there is a significant difference in the two Mo–P(μ-phosphide) bond lengths (*ca.* 0.04 Å).[3]

The μ-vinyl ligand carries a phosphine substituent on the α carbon atom. This phosphine substituent, like the α carbon itself, bonds to the tungsten atom. The β carbon of the vinyl ligand carries a phenyl group *cis* to the phosphine group and a hydrogen *trans* to it. The three-membered metallacycle created by the phosphine substituent bonding to tungsten is extremely strained, the angles being C(20)–W(1)–P(1) 42.7(7), W(1)–P(1)–C(20) 58.4(9) and P(1)–C(20)–W(1) 78.9(10)°. The C(20)–C(21) bond length [1.514(43) Å] in complex **3a** is considerably longer than the equivalent C_α–C_β bond length of 1.409(18) Å in $[Mo_2Cl_2(\mu\text{-}Ph_2PC{=}CHMe)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$.[3]

(3) *Reaction Pathways for the Formation of Complexes* **2**–**5**.—Reaction pathways have been previously postulated which show how the products obtained in the reactions of both the molybdenum and tungsten homobimetallic analogues of complex **1** with PPh_2Cl may be formed and some intermediates were isolated.[1,3] Scheme 2, which is modelled on the schemes previously proposed for the homobimetallic complexes, is capable of accounting for the fact that complexes **2** and **3** are obtained in far greater yield than complexes **4** and **5**.

Thus if it is assumed that the bond between the metal and the phosphorus atom of the PPh_2Cl ligand, once this bond is formed, is difficult to break then this can account for the preferential formation of **2** over **5**. Thus carbonyl groups bonded to molybdenum are more labile than those attached to tungsten[1,3,14] and the molybdenum atom will therefore be the preferred initial site of substitution. This substitution of PPh_2Cl at molybdenum will lead to the major product **2** as shown in Scheme 2. Complexes **3** and **4** are postulated to arise from intermediate **III**. In these complexes the α-phosphine substituent on the μ-vinyl ligand must be derived from attack of a further

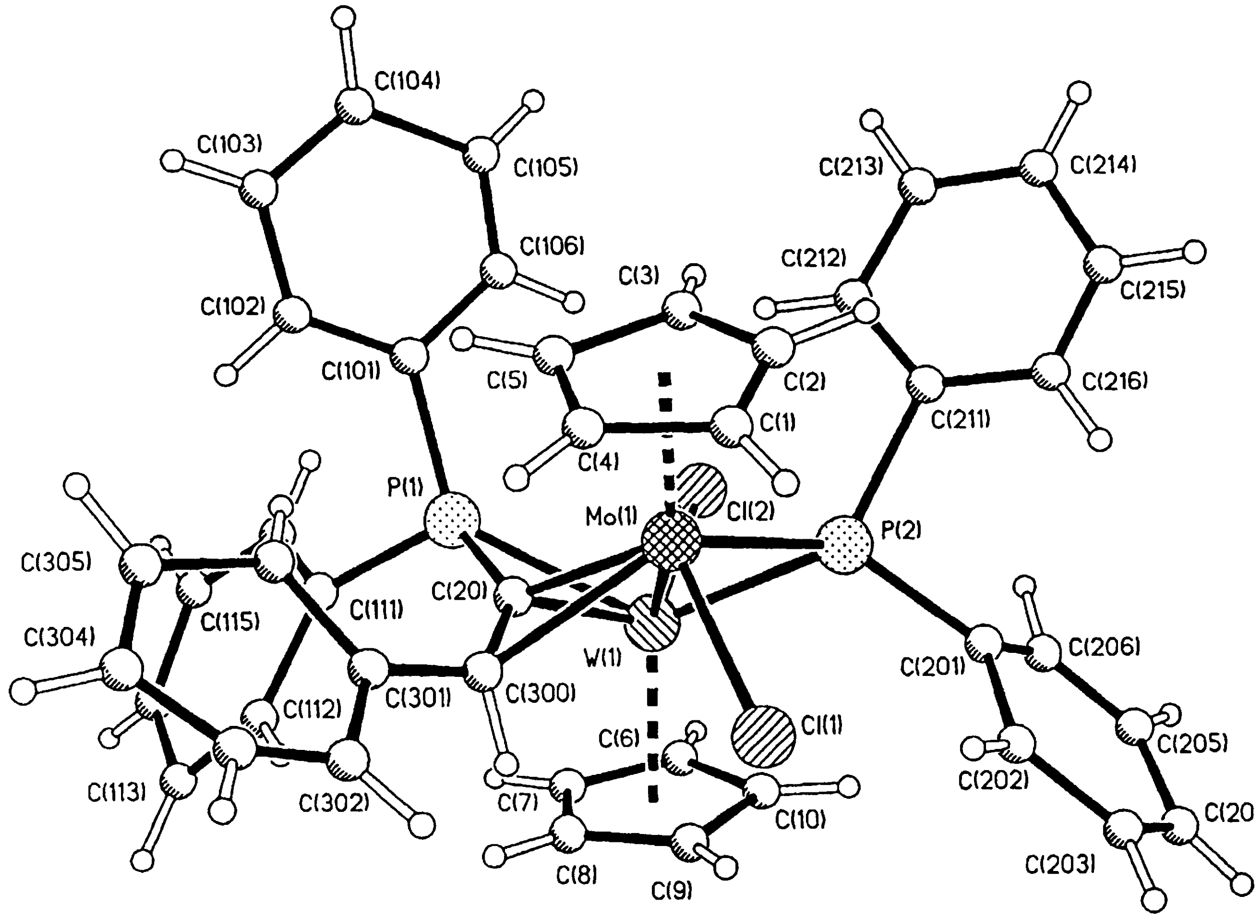


Fig. 1 Molecular structure of [WMoCl$_2$(μ-Ph$_2$PC=CHPh)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] **3a** including the atom numbering scheme

molecule of PPh$_2$Cl. This can only take place in intermediate **III** at the metal atom which retains a carbonyl group and was more difficult to substitute initially. Hence the preferential formation of **3** over **4**.

Attempts in this work to isolate a stable analogue of intermediate **I** in Scheme 2 proved unsuccessful. Thus, the photolytic reaction of **1a** with PPh$_3$ gave only [WMo(O)(μ-CH=CHPh)(μ-PPh$_2$)(CO)(η-C$_5$H$_5$)$_2$] **6** rather than a simple phosphine-substituted derivative (Scheme 3). Knox and co-workers[15] have, however, reported the substitution of a triphenylphosphine molecule for a carbonyl group in the homobimetallic complex [Mo$_2$(μ-RCCH)(CO)$_4$(η-C$_5$H$_5$)$_2$] under similar photolytic conditions.

In principle, complexes **4** could be obtained directly from **3** or *vice versa via* an isomerisation involving a vinyl-flipping type mechanism.[16] However, separate refluxing of complexes **3a** and **4a** in toluene in the presence of PPh$_2$Cl, which replicates the conditions of the reaction in which these complexes were originally obtained as a mixture, did not lead to interconversion.

Conclusion

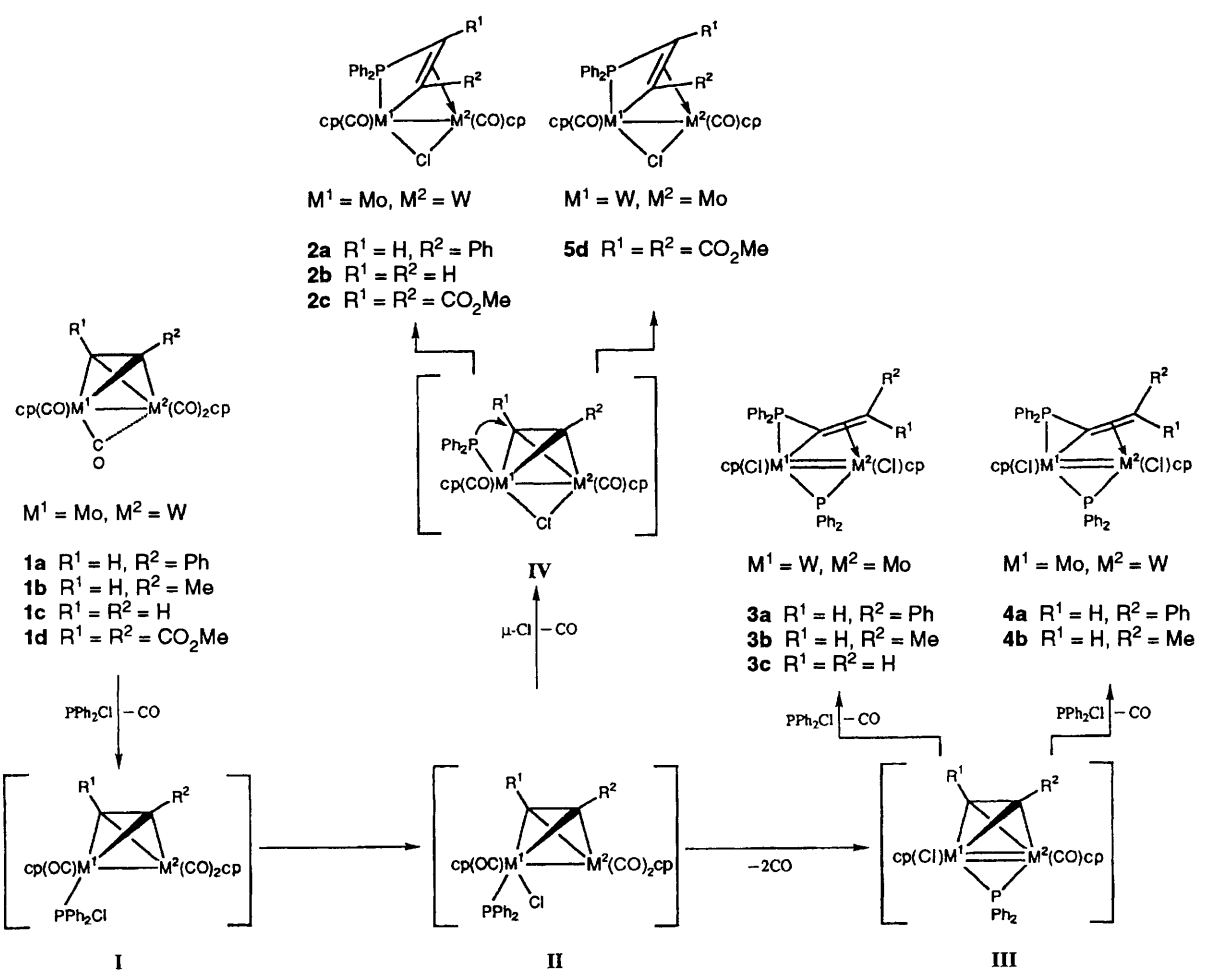
The reactions of [MoW(μ-R^{1}CCR^2)(CO)$_4$(η-C$_5$H$_5$)$_2$] (R^1 = H, R^2 = Ph **1a**, Me **1b** or H **1c**; R^1 = R^2 = CO$_2$Me **1d**) with PPh$_2$Cl in refluxing toluene show a closer similarity in outcome to those of the dimolybdenum[3] rather than to those of the ditungsten system.[1] The fact that simple *mono*-substituted PPh$_2$Cl complexes could not be obtained may indicate that initial substitution of a carbonyl group has the highest activation energy and hence is the rate-determining step. Substitution of a molybdenum-carbonyl group can be inferred as the preferred initial step in the reaction sequence.

Experimental

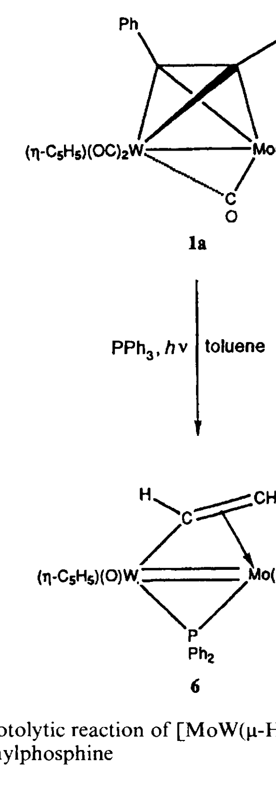
All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain the spectroscopic data has been described previously.[17] All reagents were obtained from commercial suppliers and used without further purification.

(*i*) *Preparation of* [MoW(μ-R^{1}CCR^2)(CO)$_4$(η-C$_5$H$_5$)$_2$] (R^1 = H, R^2 = Ph **1a**, Me **1b** *or* H **1c**; R^1 = R^2 = CO$_2$Me **1d** *or* Me **1e**).—(*a*) R^1 = H, R^2 = Ph **1a**. Complexes [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (1.00 g, 2.04 mmol) and [W$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (1.35 g, 2.03 mmol) were dissolved in diglyme (2,5,8-trioxanonane) (150 cm^3) and refluxed for 3 h, while a stream of N$_2$ was bubbled through.[4] The solution was then cooled to room temperature and an excess of phenylacetylene was added. Further stirring of the solution for 3 h was followed by removal of solvent at reduced pressure to give a dark red residue. The residue was then dissolved in the minimum quantity of CH$_2$Cl$_2$ and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–CH$_2$Cl$_2$ (19:1) gave three intense red bands which were identified as [Mo$_2$(μ-HCCPh)(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.22 g, 20%), [MoW(μ-HCCPh)(CO)$_4$(η-C$_5$H$_5$)$_2$] **1a** (0.41 g, 32%) and [W$_2$(μ-HCCPh)(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.07 g, 5%). Complex **1a** (Found: C, 42.25; H, 2.70. C$_{22}$H$_{16}$MoO$_4$W requires C, 42.35;



Scheme 2 Possible reaction pathways for the formation of complexes **2**–**5** from complex **1**



Scheme 3 Photolytic reaction of [MoW(μ-HCCPh)(CO)$_4$(η-C$_5$H$_5$)$_2$] **1a** with triphenylphosphine

H, 2.60%): EI mass spectrum, *m/z* 624 (M^+) and $M^+ - n$CO (n = 2–4); ^{13}C NMR (CDCl$_3$, 293 K, ^{1}H composite pulse decoupled), δ 230.6 (s, Mo–CO), 229.6 (s, Mo–CO), 217.3 (s, W–CO), 217.0 (s, W–CO), 146.1–125.4 (m, Ph), 91.7 (s, cp), 89.7 (s, cp) and 63.6 (s, CH).

(*b*) R^1 = H, R^2 = Me **1b**. In an analogous procedure to (*a*), [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (2.30 g, 4.69 mmol) and [W$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (3.10 g, 4.69 mmol) were dissolved in diglyme (150 cm^3) and refluxed for 3 h, while a stream of N$_2$ was bubbled through. When the solution had cooled to room temperature methylacetylene was bubbled through the solution for 20 min and then the reaction mixture stirred for a further 2.5 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH$_2$Cl$_2$ and applied to the base of the TLC plates. Elution with hexane–CH$_2$Cl$_2$ (7:3) gave red crystalline [Mo$_2$(μ-HCCMe)(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.56 g, 25%), [MoW(μ-HCCMe)(CO)$_4$(η-C$_5$H$_5$)$_2$] **1b** (0.95 g, 36%) and [W$_2$(μ-HCCMe)(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.12 g, 4%). Complex **1b** (Found: C, 36.15; H, 2.40. C$_{17}$H$_{14}$MoO$_4$W requires C, 36.30; H, 2.50%): EI mass spectrum, *m/z* 562 (M^+) and $M^+ - n$CO (n = 1–4); ^{13}C NMR (CDCl$_3$, 293 K, ^{1}H composite pulse decoupled), δ 230.9 (s, Mo–CO), 229.4 (s, Mo–CO), 218.3 (s, W–CO), 216.9 (s, W–CO), 91.1 (s, cp), 89.3 (s, cp), 69.4 (s, CH), 53.1 (s, *C*Me) and 22.5 (s, Me).

(*c*) R^1 = R^2 = H **1c**. In an analogous procedure to (*a*), [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (1.50 g, 3.06 mmol) and [W$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (2.03 g, 3.06 mmol) were refluxed and then acetylene bubbled through the cooled solution for 3 h. TLC separation with hexane–CH$_2$Cl$_2$ (78:22) as eluent gave red crystalline

$[Mo_2(\mu\text{-}HCCH)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.14 g, 10%), $[MoW(\mu\text{-}HCCH)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1c** (0.30 g, 18%) and $[W_2(\mu\text{-}HCCH)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.04 g, 2%). Complex **1c** (Found: C, 35.00; H, 2.25. $C_{16}H_{12}MoO_4W$ requires C, 35.05; H, 2.20%): EI mass spectrum, *m/z* 548 (M^+) and $M^+ - n$CO (n = 0, 2–4); ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 230.1 (s, Mo–CO), 216.7 (s, W–CO), 90.7 (s, cp), 88.9 (s, cp) and 61.6 (s, CH).

(d) $R^1 = R^2 = CO_2Me$ **1d**. In an analogous procedure to *(a)*, $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (1.50 g, 3.06 mmol) and $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2.03 g, 3.06 mmol) were refluxed and an excess of dimethyl acetylenedicarboxylate added to the cooled solution which was refluxed for a further 3 h. TLC separation with ethyl acetate–light petroleum b.p. (60–80 °C) (2:3) as eluent gave red crystalline $[Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.41 g, 23%), $[MoW\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **1d** (0.59 g, 29%) and $[W_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.16 g, 7%). Complex **1d** (Found: C, 35.80; H, 2.35. $C_{20}H_{16}MoO_8W$ requires C, 36.15; H, 2.40%): EI mass spectrum, *m/z* 664 (M^+) and $M^+ - n$CO (n = 0, 2–4); ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 225.7 (s, Mo–CO), 212.4 (s, W–CO), 175.6 (s, *C*O$_2$Me), 91.7 (s, cp), 89.7 (s, cp) and 52.3 (s, Me).

(e) $R^1 = R^2 = Me$ **1e**. In an analogous procedure to *(a)*, $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2.30 g, 4.69 mmol) and $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (3.10 g, 4.69 mmol) were refluxed and an excess of dimethylacetylene added to the cooled solution which was stirred for a further 3 h. TLC separation with hexane–CH_2Cl_2 (1:4) as eluent gave red crystalline $[Mo_2(\mu\text{-}MeCCMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.21 g, 9%), $[MoW(\mu\text{-}MeCCMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1e** (0.41 g, 15%) and $[W_2(\mu\text{-}MeCCMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.06 g, 2%). Complex **1e** (Found: C, 37.60; H, 2.80. $C_{18}H_{16}MoO_4W$ requires C, 37.50; H, 2.80%): EI mass spectrum, *m/z* 576 (M^+) and $M^+ - n$CO (n = 2–4); ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 230.5 (s, Mo–CO), 216.2 (s, W–CO), 91.4 (s, cp), 89.5 (s, cp), 72.8 (s, *C*Me) and 21.9 (s, Me).

(ii) Reaction of $[MoW(\mu\text{-}R^1CCR^2)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1a**–**1d** *with* PPh_2Cl.—*(a)* $R^1 = H$, $R^2 = Ph$ **1a**. Complex $[MoW(\mu\text{-}HCCPh)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1a** (0.230 g, 0.37 mmol) and PPh_2Cl (0.20 cm^3, 1.11 mmol) were dissolved in toluene (100 cm^3) and the solution was refluxed for 18 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum quantity of CH_2Cl_2. TLC separation with hexane–CH_2Cl_2 (1:3) as eluent gave orange crystalline $[MoW(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH{=}CPh)(CO)_2(\eta\text{-}C_5H_5)_2]$ **2a** (0.002 g, 1%), red crystalline $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **3a** (0.044 g, 13%) and red crystalline $[MoWCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **4a** (0.013 g, 4%). Complex **2a** (Found: C, 48.70; H, 3.30; P, 3.65. $C_{32}H_{26}ClMoO_2PW$ requires C, 48.70; H, 3.30; P, 3.95%): EI mass spectrum, *m/z* 788 (M^+) and $M^+ - n$CO (n = 1 or 2). Complex **3a** (Found: C, 52.80; H, 3.95; P, 6.40. $C_{42}H_{36}Cl_2MoP_2W$ requires C, 52.90; H, 3.80; P, 6.50%): EI mass spectrum, *m/z* 952 (M^+), $M^+ - PPh_2$ and $M^+ - PPh_2 - Cl$; ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 148.6–124.2 (m, Ph), 97.5 (s, cp), 95.5 (s, cp) and 76.4 (s, *C*HPh). Complex **4a** (Found: C, 52.80; H, 3.75; P, 6.25. $C_{42}H_{36}Cl_2MoP_2W$ requires C, 52.90; H, 3.80; P, 6.50%): EI mass spectrum, *m/z* 952 (M^+), $M^+ - PPh_2$ and $M^+ - PPh_2 - Cl$.

(b) $R^1 = H$, $R^2 = Me$ **1b**. Complex $[MoW(\mu\text{-}HCCMe)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1b** (0.200 g, 0.36 mmol) and PPh_2Cl (0.20 cm^3, 1.11 mmol) were used in an analogous procedure to *(a)* above to give red crystalline $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHMe)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **3b** (0.064 g, 20%) and red crystalline $[MoWCl_2(\mu\text{-}Ph_2PC{=}CHMe)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **4b** (0.007 g, 2%). Complex **3b** (Found: C, 49.75; H, 3.80; P, 6.85. $C_{37}H_{34}Cl_2MoP_2W$ requires C, 49.85; H, 3.85; P, 6.95%): EI mass spectrum, *m/z* 890 (M^+) and $M^+ - Cl$; ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 146.9–126.7 (m, Ph), 97.5 (s, cp), 93.6 (s, cp), 70.4 [d, ^2J(CP) 12, *C*HMe] and 29.7 (s, Me). Complex **4b** (Found: C, 49.70; H, 3.80; P, 6.80. $C_{37}H_{34}Cl_2MoP_2W$ requires C, 49.85; H, 3.85; P, 6.95%): EI mass spectrum, *m/z* 890 (M^+) and $M^+ - Cl$.

(c) $R^1 = R^2 = H$ **1c**. Complex $[MoW(\mu\text{-}HCCH)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1c** (0.400 g, 0.73 mmol) and PPh_2Cl (0.40 cm^3, 2.22 mmol) were used in an analogous procedure to *(a)* above to give yellow $[MoW(\mu\text{-}Cl)(\mu\text{-}Ph_2PCH{=}CH)(CO)_2(\eta\text{-}C_5H_5)_2]$ **2c** (0.005 g, 1%) and red $[WMoCl_2(\mu\text{-}Ph_2PC{=}CH_2)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **3c** (0.013 g, 2%). Complex **2c**: EI mass spectrum, *m/z* 712 (M^+) and $M^+ - n$CO (n = 1 or 2). Complex **3c**: EI mass spectrum, *m/z* 876 (M^+) and $M^+ - 2Cl$.

(d) $R^1 = R^2 = CO_2Me$ **1d**. Complex $[MoW\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ **1d** (0.140 g, 0.21 mmol) and PPh_2Cl (0.15 cm^3, 0.83 mmol) were used in an analogous procedure to *(a)* above to give red crystalline $[MoW(\mu\text{-}Cl)\{\mu\text{-}Ph_2PC(CO_2Me){=}CCO_2Me\}(CO)_2(\mu\text{-}C_5H_5)_2]$ **2d** (0.070 g, 40%) and red crystalline $[WMo(\mu\text{-}Cl)\{\mu\text{-}Ph_2PC(CO_2Me){=}CCO_2Me\}(CO)_2(\eta\text{-}C_5H_5)_2]$ **5d** (0.011 g, 6%). Complex **2d** (Found: C, 43.20; H, 3.15; P, 3.60. $C_{30}H_{26}ClMoO_6PW$ requires C, 43.45; H, 3.15; P, 3.75%): EI mass spectrum, *m/z* 828 (M^+) and $M^+ - n$CO (n = 1 or 2); ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled), δ 251.2 [d, ^2J(CP) 11.9, Mo–CO], 223.1 (s, W–CO), 180.9 [d, ^2J(CP) 3.9, *C*O$_2$Me], 174.0 [d, ^3J(CP) 4.6, *C*O$_2$Me], 140.9–128.1 (m, Ph), 108.7 [d, ^2J(CP) 7.8, $Ph_2PC(CO_2Me){=}$*C*CO_2Me], 93.3 (s, cp), 92.2 (s, cp), 51.1 (s, Me), 50.8 (s, Me) and 30.4 [d, ^1J(CP) 41.5, Ph_2P*C*CO_2Me]. Complex **5d** (Found: C, 43.25; H, 3.20; P, 3.55. $C_{30}H_{26}ClMoO_6PW$ requires C, 43.45; H, 3.15; P, 3.75%): EI mass spectrum, *m/z* 828 (M^+) and $M^+ - n$CO (n = 1 or 2).

(iii) Photolytic Reaction of $[MoW(\mu\text{-}HCCPh)(CO)_4(\eta\text{-}C_5H_5)_2]$ **1a** *with* PPh_3.—Complex **1a** (0.210 g, 0.34 mmol) and triphenylphosphine (0.097 g, 0.37 mmol) were dissolved in toluene (120 cm^3) and irradiated for 18 h. The solvent was then removed under reduced pressure and the residue dissolved in the minimum quantity of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–CH_2Cl_2 (2:3) gave unreacted starting material and orange $[WMo(O)(\mu\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ **6** (0.005 g, 1%) as the only product. Complex **6**: EI mass spectrum, *m/z* 742 (M^+) and M^+ −CO.

(iv) Thermolysis of $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **3a** *and* $[MoWCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]$ **4a**.—*(a)* In an attempt to convert **3a** into **4b**, complex **3a** (0.045 g, 0.05 mmol) and PPh_2Cl (0.03 cm^3, 0.15 mmol) were dissolved in toluene (50 cm^3) and refluxed for 20 h. Spot TLC showed only complex **3a** and decomposition products.

(b) Complex **4a** (0.030 g, 0.03 mmol) and PPh_2Cl (0.02 cm^3, 0.10 mmol) were treated as in *(a)* above. Spot TLC showed only complex **4a** and decomposition products.

(v) Crystal Structure Determination of Complex **3a**.—Suitable single crystals of $[WMoCl_2(\mu\text{-}Ph_2PC{=}CHPh)(\mu\text{-}PPh_2)(\eta\text{-}C_5H_5)_2]\cdot C_5H_{12}$ **3a** were grown from a dichloromethane solution by slow diffusion of hexane at 273 K. A single crystal was mounted on a goniometer head using epoxy resin and transferred to a Stoe four-circle diffractometer.

Crystal data. $C_{42}H_{36}Cl_2MoP_2W$, M = 954.0, monoclinic, space group $P2_1/c$, a = 12.924(8), b = 18.137(13), c = 17.741(13) Å, β = 90.14(5)°, U = 4158(1) Å^3, Z = 4, D_c = 1.524 g cm^{-3}, $F(000)$ = 2040, μ(Mo-Kα) = 33.04 cm^{-1}.

Data collection and refinement. A red block-shaped crystal with approximate dimensions 0.24 × 0.48 × 0.49 mm was used. Accurate cell dimensions were obtained from 25 reflections in the range $20 \leqslant 2\theta \leqslant 25°$. Intensity data were recorded using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), and an ω–2θ scan mode to a maximum 2θ value of 45°. Three standard reflections were monitored every 60 min throughout the data collection and showed no significant variation in intensity.

A total of 5659 intensities were measured within the range $-13 \leqslant h \leqslant 13$, $-19 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 18$ and averaged to

Table 3 Atomic coordinates (× 10^4) for complex **3a**

Atom	*x*	*y*	*z*
W(1)	9 614(1)	4 331(1)	1 705(1)
Mo(1)	9 788(1)	3 588(1)	3 067(1)
Cl(1)	9 024(4)	4 374(3)	4 054(3)
Cl(2)	9 193(5)	3 705(3)	513(3)
C(1)	9 655(17)	2 768(14)	4 067(14)
C(2)	9 372(24)	2 362(17)	3 656(18)
C(3)	9 963(20)	2 329(15)	2 767(16)
C(4)	10 716(14)	2 913(11)	3 911(11)
C(5)	10 950(21)	2 629(15)	3 275(15)
C(6)	9 040(23)	5 318(17)	899(19)
C(7)	10 027(13)	5 509(9)	1 260(10)
C(8)	10 098(27)	5 539(17)	2 250(19)
C(9)	9 139(26)	5 417(19)	2 526(22)
C(10)	8 432(14)	5 283(10)	1 616(10)
P(1)	11 399(4)	3 928(3)	1 583(4)
C(101)	11 953(15)	2 993(11)	1 477(12)
C(102)	12 953(21)	2 831(16)	1 600(16)
C(103)	13 367(21)	2 124(16)	1 634(15)
C(104)	12 693(32)	1 570(24)	1 412(24)
C(105)	11 594(20)	1 772(15)	1 017(16)
C(106)	11 312(18)	2 433(12)	1 150(13)
C(111)	12 376(14)	4 538(11)	1 228(11)
C(112)	12 724(17)	5 251(13)	1 658(14)
C(113)	13 317(22)	5 803(18)	1 277(17)
C(114)	13 651(17)	5 536(12)	477(13)
C(115)	13 453(16)	4 858(12)	170(12)
C(116)	12 797(14)	4 377(11)	483(12)
C(301)	11 984(14)	4 412(10)	3 614(11)
C(302)	12 069(16)	4 723(12)	4 401(12)
C(303)	12 881(19)	4 678(14)	4 652(15)
C(304)	13 763(20)	4 405(14)	4 435(15)
C(305)	13 755(15)	3 979(11)	3 887(12)
C(306)	12 803(16)	3 993(12)	3 227(13)
C(20)	10 875(13)	4 156(10)	2 408(10)
C(300)	11 101(14)	4 432(11)	3 209(11)
P(2)	8 271(4)	3 604(3)	2 305(4)
C(201)	6 985(17)	4 054(13)	2 298(13)
C(202)	6 823(19)	4 438(14)	3 082(15)
C(203)	5 834(19)	4 853(14)	3 062(15)
C(204)	5 172(19)	4 929(14)	2 492(14)
C(205)	5 476(17)	4 503(13)	1 898(14)
C(206)	6 367(18)	4 128(13)	1 925(14)
C(211)	7 745(17)	2 650(12)	1 929(13)
C(212)	8 391(15)	2 232(11)	1 597(12)
C(213)	7 969(18)	1 532(13)	1 399(14)
C(214)	7 057(18)	1 301(14)	1 630(13)
C(215)	6 523(17)	1 767(12)	2 077(13)
C(216)	6 822(17)	2 433(12)	2 197(13)
C(01)	6 166(24)	6 857(18)	1 104(20)
C(02)	5 709(59)	7 151(44)	477(43)
C(03)	4 783(24)	7 316(18)	809(18)
C(04)	4 199(24)	7 620(18)	179(18)
C(05)	3 083(28)	7 725(21)	409(21)

give 5387 unique reflections ($R_{\text{int}} = 0.0485$) of which 3885 were judged as significant using the criterion $F_o > 4\sigma(F_o)$. Corrections for Lorentz and polarisation effects were applied. A numerical absorption correction was applied; minimum and maximum transmission factors 0.2198 and 0.3200. The structure was solved by a combination of direct methods (W and Mo atoms) and Fourier-difference techniques. The structure was refined by full-matrix least squares with all non-hydrogen atoms assigned anisotropic displacement parameters.[18] Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom with C–H 0.96 Å; hydrogen-atom displacement parameters were set at 0.08 Å^2. In the final cycles of refinement a weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.010F^2$ which gave satisfactory agreement analysis was introduced. The refinement converged to $R = 0.088$ and $R' = 0.101$,[17] goodness-of-fit = 1.32. Final non-hydrogen atomic coordinates are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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