

Cationic linear triphos, L [PhP(CH₂CH₂PPh₂)₂], alkyne complexes of molybdenum(II) and tungsten(II); crystal structures of [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)]₂[W₆O₁₉], [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)][BPh₄] and [MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-*P,P',O*}]

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Equimolar quantities of [MoX(Y)(CO)(NCMe)(η²-RC₂R)₂] and L [= PhP(CH₂CH₂PPh₂)₂] reacted in CH₂Cl₂ at room temperature to give the cationic tridentate linear triphos complexes [MoX(CO)(L-*P,P',P''*)(η²-RC₂R)]Y **1–5** (X = Y = Br, R = Me or Ph; X = Cl, Y = I, R = Me or Ph; X = Br, Y = I, R = Me) in high yield. Refluxing the tungsten complexes [WX₂(CO)(L-*P,P',P''*)(η²-RC₂R')] in dry acetonitrile afforded the cationic complexes, [WX(CO)(L-*P,P',P''*)(η²-RC₂R')]X **6–8** (X = Br or I, R = R' = Me; X = I, R = Me, R' = Ph), whereas refluxing [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)] in slightly wet acetonitrile yielded the unusual crystallographically characterised complex [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)]₂[W₆O₁₉] **9**. Silver tetrafluoroborate reacted with an equimolar amount of [M(CO)(L-*P,P',P''*)(η²-RC₂R')] in acetonitrile to give the cationic complexes [M(CO)(L-*P,P',P''*)(η²-RC₂R')] [BF₄] **10–13** (M = Mo, R = R' = Me or Ph; M = W, R = R' = Me, R = Me, R' = Ph). The tetraphenylborate complexes [W(CO)(L-*P,P',P''*)(η²-RC₂R')] [BPh₄] (R = R' = Me **14**, R = Me, R' = Ph **15**) were prepared by an iodide exchange reaction of [W(CO)(L-*P,P',P''*)(η²-RC₂R')]I with Na[BPh₄] in acetonitrile. The crystal structure for **14** has been determined. The dicationic complexes [W(CO)(NCMe)(L-*P,P',P''*)(η²-RC₂R')] [BF₄]₂ **16–18** (R = R' = Me or Ph; R = Me, R' = Ph) were prepared by treating [W(CO)(L-*P,P',P''*)(η²-RC₂R')] with 2 equivalents of Ag[BF₄] in acetonitrile. The cationic bromomolybdenum complexes [MoBr(CO)(L-*P,P',P''*)(η²-RC₂R)]Br (R = Me or Ph) rearrange in refluxing CHCl₃ in air to give the unusual molybdenum(IV) product [MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-*P,P',O*}] **19**, which has been crystallographically characterised.

Alkynes have been shown to be able to donate two or four electrons to a transition-metal centre.^{1–6} In molybdenum(II) and tungsten(II) complexes the co-ordinated alkyne generally donates four electrons to the metal.⁷ In 1977, Bottrill and Green⁸ described the synthesis and characterisation of a series of cationic cyclopentadienyl and indenyl molybdenum(II) complexes of the type [Mo(CO)(η²-RC₂R')₂(η⁵-C₅H₅ or C₉H₇)] [BF₄] (R = R' = Me or Ph; R = H, R' = Me; R = H, R' = Bu^t), and investigated their reactions.^{9,10} Since these early reports a wide range of cationic alkyne complexes of molybdenum(II) and tungsten(II) have been described.^{11–18}

Since our initial report on the synthesis and crystallographic characterisation of the bis(alkyne) tungsten complexes [W(CO)(NCMe)(η²-RC₂R)₂] (R = Me or Ph) in 1988¹⁹ the chemistry of these and related complexes has been extensively investigated,^{20,21} including the formation of a number of cationic alkyne derivatives.^{22–24} In 1996²⁵ we described the reactions of [W(CO)(NCMe)(η²-RC₂R')₂] (R = R' = Me or Ph; R = Me, R' = Ph) with equimolar amounts of L {PhP(CH₂CH₂PPh₂)₂} in CH₂Cl₂ at room temperature which gave the bidentate linear triphos complexes, [W(CO)(L-*P,P',P''*)(η²-RC₂R')] (R = R' = Me or Ph), crystallographically characterised for R = R' = Me and R = Me, R' = Ph. Linear triphos, Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂, means the three phosphorus atoms are in a linear mode, with two CH₂ groups separating each phosphorus atom. In this paper we describe the conversion of these [W(CO)(L-*P,P',P''*)(η²-RC₂R')] and related complexes to the cationic tridentate linear triphos complexes of the type [MX(CO)(L-*P,P',P''*)(η²-RC₂R')]Y (M = Mo or W; X = Cl, Br or I; R = R' = Me or Ph; R = Me, R' = Ph; Y = Br, I, $\frac{1}{2}$ W₆O₁₉, BF₄ or BPh₄) and

dicationic tungsten complexes [W(CO)(NCMe)(L-*P,P',P''*)(η²-RC₂R')] [BF₄]₂ (R = R' = Me or Ph; R = Me, R' = Ph). The oxidative rearrangement of the cationic molybdenum bromo complexes [MoBr(CO)(L-*P,P',P''*)(η²-RC₂R)]Br (R = Me or Ph) to give the novel crystallographically characterised molybdenum(IV) complex, [MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-*P,P',O*}] is also described. The crystal structures of the complexes [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)]₂[W₆O₁₉] and [W(CO)(L-*P,P',P''*)(η²-MeC₂Me)] [BPh₄] are also discussed.

Results and discussion

Reaction of equimolar quantities of [MoX(Y)(CO)(NCMe)(η²-RC₂R)]^{19,26} and L {PhP(CH₂CH₂PPh₂)₂} in CH₂Cl₂ at room temperature for 24 h gives the tridentate linear triphos complexes [MoX(CO)(L-*P,P',P''*)(η²-RC₂R)]Y **1–5** (X = Y = Br, R = Me or Ph; X = Cl, Y = I, R = Me or Ph; X = Br, Y = I, R = Me) in excellent yield. Complexes **1–5** have been characterised by elemental analysis (C, H and N) and IR (Table 1) and ¹H and ³¹P NMR spectroscopy (Table 2). The complex [MoCl(CO)(L-*P,P',P''*)(η²-MeC₂Me)]·CH₂Cl₂ **3** was confirmed as a CH₂Cl₂ solvate by repeated elemental analyses and ¹H NMR spectroscopy. They are all soluble in chlorinated solvents such as CH₂Cl₂ and CHCl₃, but as expected totally insoluble in hydrocarbon solvents and diethyl ether. They are air-sensitive in solution, but are stable for long periods when stored in the solid state under dinitrogen. For the mixed halide complexes **3–5** we have previously shown²⁷ that reaction of the mixed halide tungsten complex [WCl(I)(CO)(NCMe)(η²-MeC₂Me)]₂ with an equimolar amount of 2,2'-bipy afforded

Table 1 Physical, analytical^a and IR^b data for the cationic and dicationic linear triphos alkyne complexes

Complex	Colour	Yield (%)	Analysis (%)			$\tilde{\nu}(\text{C}=\text{O})/\text{cm}^{-1}$	$\tilde{\nu}(\text{C}\equiv\text{C})/\text{cm}^{-1}$
			C	H	N		
1 [MoBr(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)]Br	Brown	90	53.8 (53.7)	4.3 (4.5)	—	1960s	1601w
2 [MoBr(CO)(L- <i>P,P',P''</i>)(η^2 -PhC ₂ Ph)]Br	Orange-brown	83	59.6 (59.0)	4.1 (4.3)	—	1966s	1590w
3 [MoCl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)]I·CH ₂ Cl ₂	Brown	82	49.7 (49.4)	4.0 (4.0)	—	1974s	1666w
4 [MoCl(CO)(L- <i>P,P',P''</i>)(η^2 -PhC ₂ Ph)]I	Brown	85	59.0 (58.8)	4.2 (4.3)	—	1979s	1671w
5 [MoBr(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)]I	Red-brown	87	51.2 (50.9)	4.6 (4.3)	—	1976s	1665w
6 [WBr(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)]Br	Purple	61	48.2 (48.9)	4.4 (4.1)	—	1967s	1601w
7 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)]I	Brown	66	44.8 (44.4)	3.8 (3.0)	—	1961s	1585w
8 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Ph)]I	Brown	87	47.7 (47.7)	4.3 (3.7)	—	1969s	1587w
9 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)] ₂ [W ₆ O ₁₉]	Brown	18	29.5 (28.7)	2.1 (2.4)	—	1969s	1522w
10 [MoI(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)][BF ₄]	Brown	53	50.2 (50.3)	4.1 (4.2)	—	1963s	1600w
11 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)][BF ₄]	Purple	66	45.1 (45.6)	4.1 (4.1)	—	1967s	1601w
12 [MoI(CO)(L- <i>P,P',P''</i>)(η^2 -PhC ₂ Ph)][BF ₄]	Brown	62	55.4 (55.9)	3.6 (4.1)	—	1965s	1590w
13 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Ph)][BF ₄]	Purple	45	48.6 (49.0)	4.7 (4.8)	—	1968s	1570w
14 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)][BPh ₄]+0.5CH ₂ Cl ₂	Red-purple	67	59.6 (59.1)	4.7 (4.7)	—	1970s	1579w
15 [Wl(CO)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Ph)][BPh ₄]	Red-purple	73	61.8 (62.3)	5.3 (4.8)	—	1971s	1579w
16 [W(CO)(NCMe)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Me)][BF ₄] ₂	Red	36	48.3 (48.5)	4.2 (4.2)	1.3 (1.4)	1959s	1600w
17 [W(CO)(NCMe)(L- <i>P,P',P''</i>)(η^2 -MeC ₂ Ph)][BF ₄] ₂	Red	39	51.0 (51.2)	4.1 (4.2)	1.6 (1.3)	1966s	1629w
18 [W(CO)(NCMe)(L- <i>P,P',P''</i>)(η^2 -PhC ₂ Ph)][BF ₄] ₂	Red-brown	34	53.0 (53.7)	3.8 (4.1)	1.2 (1.3)	1973s	1601w
19 [MoBr ₂ (O){Ph ₂ P(CH ₂) ₂ PPh(CH ₂) ₂ POPPh ₂ - <i>P,P',O</i> }]	Green	62	49.6 (49.6)	4.4 (4.1)	—	—	—

^a Calculated values in parentheses. ^b Spectra recorded as thin films in CHCl₃ between NaCl plates; s = strong, w = weak.

Table 2 Proton^a and ³¹P^b NMR data for the cationic and dicationic linear triphos alkyne complexes of molybdenum(II) and tungsten(II) 1–18

Complex	¹ H (δ)	³¹ P (δ , J/Hz)
1	7.8–7.5 (m, 25 H, Ph), 3.0 (s, 6 H, C ₂ Me), 2.4–2.2 (m, 8 H, CH ₂)	97.5 (s, 1P), 42.0 (s, 2P)
2	7.8–7.5 (m, 35 H, Ph), 3.4–3.2 (m, 8 H, CH ₂)	98.9 (s, 1P), 44.7 (s, 2P)
3	7.8–7.1 (m, 35 H, Ph), 5.3 (s, 2 H, CH ₂ Cl ₂), 3.0–2.8 (m, 8 H, CH ₂)	97.7 (s, 1P), 47.1 (s, 2P)
4	7.8–7.1 (m, 35 H, Ph), 2.8–2.4 (m, 8 H, CH ₂)	97.6 (s, 1P), 46.9 (s, 2P)
5	7.8–7.4 (m, 25 H, Ph), 3.0 (s, 6 H, C ₂ Me), 2.8–2.4 (m, 8 H, CH ₂)	97.0 (s, 1P), 47.1 (s, 2P)
6	7.7–7.5 (m, 25 H, Ph), 3.1, 3.0, 2.95, 2.9 (4s, 6 H, C ₂ Me), 2.8–2.6 (m, 8 H, CH ₂)	70.3 (s, 1P, <i>J</i> _{WP} = N.O.), 39.9 (s, 2P, <i>J</i> _{WP} = N.O.)
7	7.7–7.4 (m, 25 H, Ph), 3.1 (s, 6 H, C ₂ Me), 2.8–2.6 (m, 8 H, CH ₂)	67.7 (s, 1P, <i>J</i> _{WP} = N.O.), 33.2 (s, 2P, <i>J</i> _{WP} = 261.9)
8	7.8–7.4 (m, 35 H, Ph), 3.1 (s, 3 H, C ₂ Me), 2.6–2.4 (m, 8 H, CH ₂)	67.7 (s, 1P, <i>J</i> _{WP} = N.O.), 33.2 (s, 2P, <i>J</i> _{WP} = N.O.)
9	7.8–7.4 (m, 25 H, Ph), 3.1 (s, 6 H, C ₂ Me), 2.6–2.4 (m, 8 H, CH ₂)	68.0 (s, 1P, <i>J</i> _{WP} = 262.1), 33.3 (s, 2P, <i>J</i> _{WP} = N.O.)
10	7.9–7.6 (m, 25 H, Ph), 3.1 (s, 6 H, C ₂ Me), 2.8–2.7 (m, 8 H, CH ₂)	59.6 (s, 1P), 42.9 (s, 2P)
11	7.8–7.4 (m, 25 H, Ph), 3.1 (s, 6 H, C ₂ Me), 2.6–2.4 (m, 8 H, CH ₂)	—
12	7.7–7.6 (m, 35 H, Ph), 2.8–2.6 (m, 8 H, CH ₂)	58.4 (s, 1P), 42.0 (s, 2P)
13	7.7–6.9 (m, 30 H, Ph), 3.0 (s, 3 H, CH ₂), 2.95–2.6 (m, 8 H, CH ₂)	59.5 (s, 1P, <i>J</i> _{WP} = 228.5), 42.8 (s, 2P, <i>J</i> _{WP} = 266.6)
14	7.6–7.1 (m, 45 H, Ph), 5.3 (s, H, CH ₂ Cl ₂), 3.1 (s, 6 H, C ₂ Me), 2.8–2.7 (m, 8 H, CH ₂)	66.8 (s, 1P, <i>J</i> _{WP} = 263.1), 32.5 (s, 2P, <i>J</i> _{WP} = 276.8)
15	7.6–7.9 (m, 50 H, Ph), 3.1 (s, 3 H, C ₂ Me), 2.9–2.7 (m, 8 H, CH ₂)	66.8 (s, 1P, <i>J</i> _{WP} = N.O.), 32.3 (s, 2P, <i>J</i> _{WP} = 254.6)
16	7.8–7.3 (m, 25 H, Ph), 3.1 (s, 6 H, C ₂ Me), 2.9–2.7 (m, 8 H, CH ₂), 2.1 (s, 3 H, NCMe)	58.5 (s, 1P, <i>J</i> _{WP} = N.O.), 42.0 (s, 2P, <i>J</i> _{WP} = 260.3)
17	7.6–7.2 (m, 30 H, Ph), 3.0 (s, 3 H, C ₂ Me), 2.8–2.6 (m, 8 H, CH ₂), 2.1 (s, 3 H, NCMe)	59.8 (s, 1P, <i>J</i> _{WP} = N.O.), 42.9 (s, 2P, <i>J</i> _{WP} = 260.3)
18	7.6–7.1 (m, 35 H, Ph), 2.6–2.4 (m, 8 H, CH ₂), 2.2 (s, 3 H, NCMe)	61.3 (s, 1P, <i>J</i> _{WP} = N.O.), 42.9 (s, 2P, <i>J</i> _{WP} = 234.2)

^a Spectra recorded in CDCl₃ (+25 °C) and referenced to SiMe₄; m = multiplet, s = singlet. ^b Spectra recorded in CDCl₃ and referenced to 85% H₃PO₄; N.O. = not observed.

the crystallographically characterised chloro-co-ordinated cation [WCl(CO)(2,2'-bipy)(η^2 -MeC₂Me)]I, thus iodide as expected is displaced in preference to chloride in these complexes, in accord with the formulation of 3–5 as iodide salts. The IR spectra of 1–5 all have a single carbonyl band at, for example, 1960 cm⁻¹ for complex 1, which is in the expected

range for this type of complex. Complexes 1–5 also have alkyne stretching bands at considerably lower wavenumber compared to those of the “free” alkyne. The most likely structure of 1–5 is similar to that of the crystallographically characterised tungsten complexes [Wl(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)]₂[W₆O₁₉] 9 and [Wl(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)][BPh₄] 14 (see Figs. 1

and 3), which are discussed later. The ^{31}P - $\{^1\text{H}\}$ NMR spectra (CDCl_3 , $+25^\circ\text{C}$) of complexes **1–5** (see Table 2) also show two resonances with an intensity ratio of 1:2. For example, $[\text{MoBr}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]\text{Br}$ **1** shows resonances at δ 97.5 (central phosphorus atom) and 42.0 (terminal phosphorus atoms), in accord with the crystallographically determined structures for the closely related tungsten complexes **9** and **14**.

The previously described tungsten complexes, $[\text{W}_2(\text{CO})(\text{L-}P,P')(\eta^2\text{-RC}_2\text{R}')] (\text{R} = \text{R}' = \text{Me}, \text{R} = \text{Me}, \text{R}' = \text{Ph})$ ²⁵ do not rearrange at room temperature in CH_2Cl_2 for 48 h to give the cationic complexes $[\text{WX}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-RC}_2\text{R}')]\text{X}$, only the neutral bidentate linear triphos starting materials are isolated. However, refluxing the complexes $[\text{WX}_2(\text{CO})(\text{L-}P,P')(\eta^2\text{-RC}_2\text{R}')]$ in dry acetonitrile for 24 h gives the cationic complexes $[\text{WX}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-RC}_2\text{R}')]\text{X}$ **6–8** ($\text{X} = \text{Br}, \text{R} = \text{R}' = \text{Me}; \text{X} = \text{I}, \text{R} = \text{R}' = \text{Me}, \text{R} = \text{Me}, \text{R}' = \text{Ph}$) in good yield. The much greater lability of molybdenum complexes compared to their tungsten analogues is very well known. Complexes **6–8** have been characterised in the normal manner (see Tables 1 and 2), and are slightly more stable than their molybdenum analogues, and of similar solubility. It is interesting that refluxing the but-2-yne complex $[\text{W}_2(\text{CO})(\text{L-}P,P')(\eta^2\text{-MeC}_2\text{Me})]$ in slightly wet acetonitrile gives the unusual $[\text{W}_6\text{O}_{19}]^{2-}$ dianion complex $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]_2[\text{W}_6\text{O}_{19}]$ **9** which has been crystallographically characterised. Complex **9** has been fully characterised (see Tables 1 and 2). The $[\text{W}_6\text{O}_{19}]^{2-}$ dianion is apparently very stable and has been crystallographically characterised in association with a variety of different cations.^{28–33} The rearrangement/oxidation of $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]^+$ to its $[\text{W}_6\text{O}_{19}]^{2-}$ salt is strange, and very difficult to explain, except that the dianion $[\text{W}_6\text{O}_{19}]^{2-}$ is in a potential well and occurs in many structures.^{28–33} In 1993, McCann and co-workers³⁴ also found that addition of $[\text{NBu}_4][\text{ClO}_4]$ to the filtrate which remains after the synthesis of $[\text{Mo}_2(\mu\text{-O}_2\text{-CMe}_2)_4]$ {from $[\text{Mo}(\text{CO})_6]$, MeCO_2H and $(\text{MeCO})_2\text{O}$ } followed by exposure to air affords $[\text{NBu}_4]_2[\text{W}_6\text{O}_{19}]$.

Suitable single crystals of complex **9** were grown by cooling a concentrated solution of it in CH_2Cl_2 to -17°C for 24 h. Single crystals of the identical cation $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ **14**, which has a tetraphenylborate counter anion, have been grown from a CDCl_3 solution at room temperature for 24 h. The structures of the cations in **9** and **14** are shown in Figs. 1 and 3 together with the common atomic numbering scheme. As is apparent from the figures and the dimensions in Table 3, the structures of the cations are equivalent. The metal co-ordination can best be considered as octahedral with the but-2-yne occupying one site *trans* to the iodide ligand. The tridentate phosphorus ligand occupies the *mer* arrangement with P(1) *trans* to P(7), while the central phosphorus P(4) is *trans* to the carbonyl group. The distortion from octahedral is considerable, mainly because of the constraints of the triphos ligand. Thus the P(1)–W(1)–P(7) angle is $152.7(3)^\circ$ and $152.6(1)^\circ$ in the two structures. There are no systematic variations in the W–P bond lengths and indeed all dimensions are as expected. The structure of the dianion in **9** is shown in Fig. 2. This $[\text{W}_6\text{O}_{19}]^{2-}$ dianion contains a crystallographic centre of symmetry. The structure of the dianion has been determined previously^{28–33} and the dimensions reported here are consistent with those in previous structures.

The IR and NMR data conform with the structure of the cations shown in Figs. 1 and 3. The free phosphorus atoms of the two diastereoisomers of the crystallographically characterised neutral complex $[\text{W}_2(\text{CO})(\text{L-}P,P')(\eta^2\text{-MeC}_2\text{Me})]$ displace the iodide *trans* to the carbonyl to give the stereochemistry of the cation, $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]^+$, shown in Fig. 1. For example, the ^{31}P - $\{^1\text{H}\}$ NMR (CDCl_3 , $+25^\circ\text{C}$) of $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]_2[\text{W}_6\text{O}_{19}]$ **9** has two resonances at δ 68.0 (central phosphorus) and 33.3 (terminal phosphorus atoms) in a 1:2 ratio, which conforms with the structure

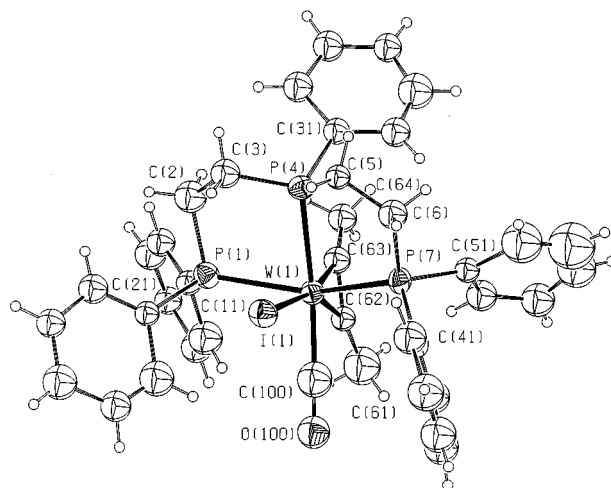


Fig. 1 Cation in complex **9** together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

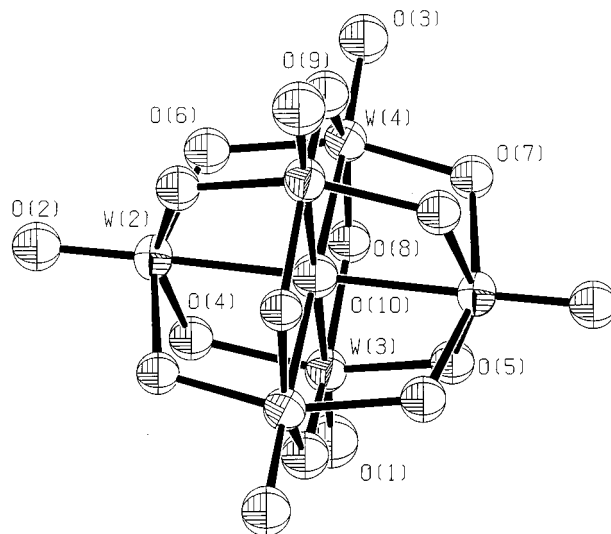


Fig. 2 Structure of the $[\text{W}_6\text{O}_{19}]^{2-}$ dianion in complex **9**. Ellipsoids shown at 30% probability.

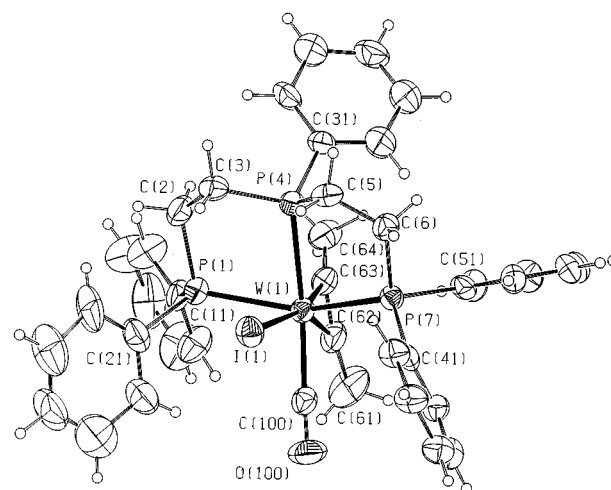


Fig. 3 Crystal structure of the $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]^+$ in complex **14**, together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

of the but-2-yne cation $[\text{W}(\text{CO})(\text{L-}P,P',P'')(\eta^2\text{-MeC}_2\text{Me})]^+$, whereby the two terminal phosphorus atoms are equivalent. It is interesting that refluxing the diphenylacetylene complexes $[\text{WX}_2(\text{CO})(\text{L-}P,P')(\eta^2\text{-PhC}_2\text{Ph})]$ ($\text{X} = \text{Br}$ or I) in acetonitrile

for 4 d, did not give the cation, only the starting complexes were isolated. It is likely the steric bulk of the diphenylacetylene group hinders the free phosphorus atom displacing the halide group.

Equimolar quantities of $[\text{M}_2(\text{CO})(\text{L}-P,P')(\eta^2\text{-RC}_2\text{R}')]]$ and $\text{Ag}[\text{BF}_4]$ react in acetonitrile at room temperature to afford the cationic tridentate triphos complexes $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R}')] [\text{BF}_4]_2$ **10–13** ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{R}' = \text{Me}$; $\text{M} = \text{Mo}$, $\text{R} = \text{R}' = \text{Ph}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) in good yield. Complexes **10–13** have been fully characterised (see Tables 1 and 2). Treatment of $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R}')]]$ with 1 equivalent of $\text{Na}[\text{BPh}_4]$ in acetonitrile gives the iodide exchanged products $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R}')] [\text{BPh}_4]$ ($\text{R} = \text{R}' = \text{Me}$ **14**; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ **15**) in good yield. The complex $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-MeC}_2\text{Me})] [\text{BPh}_4] \cdot 0.5\text{CH}_2\text{Cl}_2$ **14** was confirmed as a $0.5\text{CH}_2\text{Cl}_2$ solvate by repeated elemental analyses and ^1H NMR spectroscopy. The IR spectra of complexes **10–13** all show $\nu(\text{BF})(\text{CHCl}_3)$ broad bands at $\approx 1060\text{ cm}^{-1}$. The $^{11}\text{B}\{-\text{F}\}$ NMR (CDCl_3 , $+25^\circ\text{C}$) of **11** has a resonance at $\delta -1.2$. The ^{11}B NMR spectrum (CDCl_3 , $+25^\circ\text{C}$) for **14** has a single resonance at $\delta -6.9$. By this approach we have been able to prepare the only monocationic diphenylacetylene complex $[\text{Mo}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-PhC}_2\text{Ph})] [\text{BF}_4]$ **12**. However, treatment of the tungsten diphenylacetylene complex $[\text{W}_2(\text{CO})(\text{L}-P,P')(\eta^2\text{-PhC}_2\text{Ph})]$ with either an equimolar amount of $\text{Ag}[\text{BF}_4]$ or $\text{Na}[\text{BPh}_4]$ in acetonitrile did not give the expected cationic complex, and only the starting materials were isolated.

Suitable single crystals of the tetraphenylborate complex $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-MeC}_2\text{Me})] [\text{BPh}_4]$ **14** were grown from a CDCl_3 solution at room temperature for 24 h. The structure of the cation of **14** is shown in Fig. 3. The dimensions of the $[\text{BPh}_4]^-$ anion are as expected. The ^1H and ^{31}P NMR data conform with the structure of **14**. There are two resonances in the ^{31}P NMR spectrum, at δ 66.8 (1P) and 32.5 (2P) in a 1:2 intensity ratio. The second resonance is due to the equivalent terminal phosphorus atoms of the triphos ligand. It is important to note that, as expected, the ^{31}P NMR spectra of the three complexes $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-MeC}_2\text{Me})] \text{X}$ ($\text{X} = \text{I}$ **7**, $\frac{1}{2}\text{W}_6\text{O}_{19}$ **9** or BPh_4 **14**) have two resonances in very similar positions. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum (25°C , CD_2Cl_2) of **14** (see Experimental section) shows a resonance at δ 216.9 due to the alkyne ($\text{C}\equiv\text{C}$) atoms, which suggests from Templeton and Ward's⁶ correlation that the but-2-yne ligand is donating four electrons to the tungsten which enables it to obey the effective atomic number rule.

Treatment of $[\text{W}_2(\text{CO})(\text{L}-P,P')(\eta^2\text{-RC}_2\text{R}')]]$ with 2 equivalents of $\text{Ag}[\text{BF}_4]$ in acetonitrile at room temperature gives moderate yields of the dicationic complexes $[\text{W}(\text{CO})(\text{NCMe})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R}')] [\text{BF}_4]_2$ **16–18** ($\text{R} = \text{R}' = \text{Me}$ or Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$). Complexes **16–18** were characterised as before. They all have strong bands at $\nu(\text{BF})(\text{CHCl}_3)$ 1060 cm^{-1} in their IR spectra confirming the presence of the $[\text{BF}_4]^-$ anions, and weak nitrile stretching bands at $\nu(\text{N}\equiv\text{C})(\text{CHCl}_3)$ 2282 (for **16**), 2285 and 2273 (for **17**), and 2285 and 2261 cm^{-1} (for **18**). They are slightly more soluble and stable than their monocationic analogues. It should be noted that, although the reaction of $[\text{W}_2(\text{CO})(\text{L}-P,P')(\eta^2\text{-PhC}_2\text{Ph})]$ with 1 equivalent of $\text{Ag}[\text{BF}_4]$ in acetonitrile did not after several attempts give the expected cationic complex $[\text{W}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-PhC}_2\text{Ph})] [\text{BF}_4]$, the reaction with 2 equivalents of $\text{Ag}[\text{BF}_4]$ proceeded to the dication **18** in 34% yield. This is a very surprising result which is very difficult to explain, but the reactions of $[\text{W}_2(\text{CO})(\text{L}-P,P')(\eta^2\text{-PhC}_2\text{Ph})]$ with 1 and 2 equivalents of $\text{Ag}[\text{BF}_4]$ in acetonitrile were repeated several times with similar results. The ^{31}P NMR spectra for **16** to **18** each have two resonances, in accord with a structure whereby the second iodide is replaced by the acetonitrile ligand from the structures shown in Figs. 1 and 3, to give the proposed structures for the dications shown in Fig. 4. A number of unsuccessful attempts were made to grow suitable single crystals for X-ray crystallography of

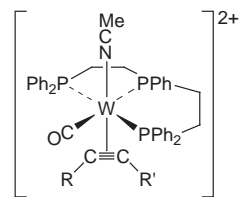


Fig. 4 Proposed structure of the dicationic complexes $[\text{W}(\text{CO})(\text{NCMe})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R}')] [\text{BF}_4]_2$ **16–18**.

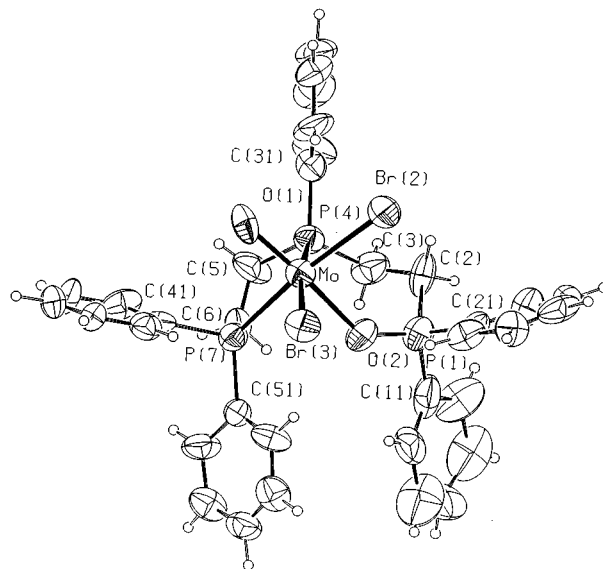


Fig. 5 Crystal structure of $[\text{MoBr}_2(\text{O})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{POPh}_2\text{-}P,P',O\}]$ **19**. Ellipsoids shown at 30% probability.

complexes **16** to **18**. Also, several unsuccessful attempts were made to obtain suitable ^{13}C NMR spectra for them.

It is interesting that when the complexes $[\text{MoBr}(\text{CO})(\text{L}-P,P',P'')(\eta^2\text{-RC}_2\text{R})] \text{Br}$ ($\text{R} = \text{Me}$ or Ph) are refluxed in CHCl_3 for 2 h in air the unusual oxidised molybdenum(IV) product $[\text{MoBr}_2(\text{O})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{POPh}_2\text{-}P,P',O\}]$ **19** is obtained. One of the terminal phosphorus atoms of the linear triphos ligand has been oxidised in the tridentate ligand. It should be noted that this is the only isolated organometallic product in this reaction. Complex **19** has been characterised by elemental analysis (Table 1), and suitable single crystals of it were grown from a concentrated CHCl_3 solution at room temperature for 24 h. It is only slightly soluble in typical NMR solvents such as CDCl_3 , CD_2Cl_2 and $(\text{CD}_3)_2\text{CO}$, hence it was not possible to obtain satisfactory ^1H and ^{31}P NMR spectra. The structure of **19** is shown in Fig. 5, together with the atomic numbering scheme. The co-ordination of the molybdenum atom is distorted octahedral. The metal is bonded to this tridentate ligand in a *fac* arrangement *via* two phosphorus atoms P(4) and P(7) and the oxygen atom O(2) which is bonded to the third phosphorus atom P(1). The two phosphorus atoms are *trans* to the two bromine atoms and both sets of bond lengths are equivalent and have expected values [$\text{Mo}-\text{P}$ 2.459(6), 2.477(5); $\text{Mo}-\text{Br}$ 2.587(3), 2.608(3) Å]. The ligand oxygen atom O(2) [$\text{Mo}-\text{O}(2)$ 2.164(12) Å] is *trans* to a terminal oxygen atom O(1) [$\text{Mo}-\text{O}(1)$ 1.775(16) Å]. Both bonds are slightly longer than might be expected and this is possibly due to a mutual *trans* effect. The ligand $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{POPh}_2$ has only been found once before attached to a transition-metal centre, in the crystallographically characterised complex, *fac*- $[\text{MoO}\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2\text{-}P,P',O\}(\text{SeC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2]$.³⁵ It is interesting that Park *et al.*³⁶ have shown that the molybdenum(II) complex *cis,cis,cis*- $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ can be oxidised in air to give the molybdenum(VI) complex *cis,cis,trans*- $[\text{MoBr}_2(\text{O})_2(\text{OPPh}_3)_2]$. Similarly, Woodward and co-workers³⁷, in an attempt to synthesize

Table 3 Distances (Å) and angles (°) in complexes **9**, **14** and **19**

	9	14	
W(1)–C(100)	1.98(6)	2.020(14)	
W(1)–C(63)	1.97(4)	1.983(12)	
W(1)–C(62)	2.05(3)	2.050(15)	
W(1)–P(7)	2.544(10)	2.534(4)	
W(1)–P(1)	2.558(11)	2.520(4)	
W(1)–P(4)	2.569(9)	2.526(4)	
W(1)–I(1)	2.864(4)	2.861(2)	
C(100)–W(1)–C(63)	112.6(19)	111.4(5)	
C(100)–W(1)–C(62)	72.9(18)	75.0(6)	
C(63)–W(1)–C(62)	39.8(14)	36.6(5)	
C(100)–W(1)–P(7)	94.4(17)	93.4(4)	
C(63)–W(1)–P(7)	104.8(12)	107.6(4)	
C(62)–W(1)–P(7)	106.5(10)	106.8(4)	
C(100)–W(1)–P(1)	100.8(17)	101.8(4)	
C(63)–W(1)–P(1)	90.2(12)	87.9(4)	
C(62)–W(1)–P(1)	99.6(10)	99.1(4)	
P(7)–W(1)–P(1)	152.7(3)	152.6(1)	
C(100)–W(1)–P(4)	161.4(16)	159.5(3)	
C(63)–W(1)–P(4)	86.0(11)	89.0(4)	
C(62)–W(1)–P(4)	125.6(9)	125.3(5)	
P(7)–W(1)–P(4)	78.6(3)	78.2(1)	
P(1)–W(1)–P(4)	79.9(3)	79.7(1)	
C(100)–W(1)–I(1)	80.4(16)	78.5(3)	
C(63)–W(1)–I(1)	166.0(11)	166.9(3)	
C(62)–W(1)–I(1)	153.0(9)	153.0(5)	
P(7)–W(1)–I(1)	78.4(2)	79.5(1)	
P(1)–W(1)–I(1)	82.0(2)	81.4(1)	
P(4)–W(1)–I(1)	81.3(2)	81.6(1)	
19			
Mo–O(1)	1.775(16)	Mo–P(7)	2.477(5)
Mo–O(2)	2.164(12)	Mo–Br(2)	2.587(3)
Mo–P(4)	2.459(6)	Mo–Br(3)	2.608(3)
O(1)–Mo–O(2)	167.6(5)	P(4)–Mo–Br(2)	93.14(14)
O(1)–Mo–P(4)	86.6(5)	P(7)–Mo–Br(2)	169.79(14)
O(2)–Mo–P(4)	83.3(4)	O(1)–Mo–Br(3)	104.0(4)
O(1)–Mo–P(7)	88.5(4)	O(2)–Mo–Br(3)	85.8(4)
O(2)–Mo–P(7)	82.8(4)	P(4)–Mo–Br(3)	168.94(16)
P(4)–Mo–P(7)	80.23(18)	P(7)–Mo–Br(3)	96.57(15)
O(1)–Mo–Br(2)	99.0(4)	Br(2)–Mo–Br(3)	88.49(9)
O(2)–Mo–Br(2)	88.7(4)		
The [W ₆ O ₁₉] ²⁻ anion in 9			
W(2)–O(2)	1.69(3)	W(3)–O(8)	1.95(2)
W(2)–O(6)	1.95(3)	W(3)–O(4)	1.98(3)
W(2)–O(5')	1.94(2)	W(3)–O(10)	2.350(3)
W(2)–O(4)	1.95(2)	W(4)–O(3)	1.71(3)
W(2)–O(7)	2.04(2)	W(4)–O(8)	1.84(2)
W(2)–O(10)	2.358(3)	W(4)–O(7')	1.94(3)
W(3)–O(1)	1.64(3)	W(4)–O(6)	1.98(3)
W(3)–O(9)	1.84(3)	W(4)–O(9')	1.99(3)
W(3)–O(5)	1.92(3)	W(4)–O(10)	2.347(3)
O(6)–W(2)–O(5')	88.0(11)	O(3)–W(4)–O(7')	102.0(13)
O(2)–W(2)–O(4)	102.5(13)	O(8)–W(4)–O(7')	85.8(11)
O(6)–W(2)–O(4)	88.2(10)	O(3)–W(4)–O(6)	101.5(13)
O(2)–W(2)–O(6)	103.9(12)	O(8)–W(4)–O(6)	87.9(11)
O(2)–W(2)–O(5')	104.8(12)	O(7')–W(4)–O(6)	156.5(10)
O(5')–W(2)–O(4)	152.5(11)	O(3)–W(4)–O(9')	104.1(13)
O(2)–W(2)–O(7)	101.4(12)	O(8)–W(4)–O(9')	148.5(11)
O(6)–W(2)–O(7)	154.7(11)	O(7')–W(4)–O(9')	89.6(11)
O(5')–W(2)–O(7)	84.3(10)	O(6)–W(4)–O(9')	84.0(11)
O(4)–W(2)–O(7)	87.6(10)	O(3)–W(4)–O(10)	177.2(10)
O(2)–W(2)–O(10)	178.8(10)	O(8)–W(4)–O(10)	75.0(7)
O(6)–W(2)–O(10)	77.3(8)	O(7')–W(4)–O(10)	79.6(7)
O(5')–W(2)–O(10)	75.3(8)	O(6)–W(4)–O(10)	76.9(7)
O(4)–W(2)–O(10)	77.3(8)	O(9')–W(4)–O(10)	73.6(8)
O(7)–W(2)–O(10)	77.4(7)	W(2)–O(4)–W(3)	115.8(13)
O(1)–W(3)–O(9)	101.3(14)	W(3)–O(5)–W(2')	118.8(13)
O(1)–W(3)–O(5)	104.6(14)	W(2)–O(6)–W(4)	115.8(13)
O(9)–W(3)–O(5)	86.6(12)	W(4')–O(7)–W(2)	113.1(12)
O(1)–W(3)–O(8)	109.5(13)	W(4)–O(8)–W(3)	122.0(12)
O(9)–W(3)–O(8)	149.1(11)	W(3)–O(9)–W(4')	120.2(14)
O(5)–W(3)–O(8)	83.4(10)	W(4')–O(10)–W(3)	90.03(7)
O(1)–W(3)–O(4)	102.6(14)	W(4)–O(10)–W(3)	89.97(7)
O(9)–W(3)–O(4)	88.3(11)	W(4')–O(10)–W(2')	90.07(6)
O(5)–W(3)–O(4)	152.7(11)	W(4)–O(10)–W(2')	89.93(6)
O(8)–W(3)–O(4)	87.4(10)	W(3)–O(10)–W(2')	90.02(6)
O(1)–W(3)–O(10)	177.4(11)	W(3')–O(10)–W(2')	89.98(6)
O(9)–W(3)–O(10)	76.1(9)	W(4')–O(10)–W(2)	89.93(6)
O(5)–W(3)–O(10)	75.8(7)	W(4)–O(10)–W(2)	90.07(6)
O(8)–W(3)–O(10)	73.1(7)	W(3)–O(10)–W(2)	89.98(6)
O(4)–W(3)–O(10)	76.9(7)	W(3')–O(10)–W(2)	90.02(6)
O(3)–W(4)–O(8)	107.3(12)		

Symmetry element: ' 1 – x, 1 – y, 1 – z.

[MoBr₂(CO)₂{P(C₆H₁₁)₃}₂], by bromine addition to *cis*- or *trans*-[Mo(CO)₄{P(C₆H₁₁)₃}₂] obtained the oxidised product [HP(C₆H₁₁)₃][MoBr₄(O)L] [L = OH₂ or OP(C₆H₁₁)₃]. The most likely reason why our oxidation reactions of [MoBr(CO)-(L-P,P',P'')(η²-RC₂R)]Br (R = Me **1** or Ph **2**) stop at the molybdenum(IV) complex [MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-P,P',O}] **19** is probably due to the fact that two of the phosphorus atoms of linear triphos are attached to the molybdenum in **1** and **2** and the chelate effect is only allowing one unattached terminal phosphorus atom to be oxidised.

Conclusion

A series of monocationic and dicationic complexes of the types [MX(CO)(L-P,P',P'')(η²-RC₂R')Y] and [W(CO)(NCMe)-(L-P,P',P'')(η²-RC₂R')][BF₄]₂ were prepared and characterised, including [W(CO)(L-P,P',P'')(η²-MeC₂Me)]₂[W₆O₁₉]²⁻ and [W(CO)(L-P,P',P'')(η²-MeC₂Me)][BPh₄], which have been crystallographically characterised. The unusual formation of the [W₆O₁₉]²⁻ dianion is very difficult to explain, and is one of the unexpected results that often occurs in organometallic chemistry. It was also surprising that it was generally not possible to prepare the tungsten diphenylacetylene monocations, whereas the dication [W(CO)(NCMe)(L-P,P',P'')(η²-PhC₂Ph)]₂[BF₄]₂ was simply prepared. Refluxing CHCl₃ solutions of [MoBr(CO)(L-P,P',P'')(η²-RC₂R)]Br (R = Me or Ph) in air gave the unusual molybdenum(IV) product [MoBr₂(O){Ph₂-P(CH₂)₂PPh(CH₂)₂POPh₂-P,P',O}] which was structurally characterised.

Experimental

All reactions described in this paper were carried out under a dinitrogen atmosphere except for the preparation of complex **19**, using standard vacuum/Schlenk line procedures. The starting materials, [MX(Y)(CO)(NCMe)(η²-RC₂R')]₂ (M = Mo, X = Y = Br or I, R = R' = Me or Ph,^{19,26} X = Cl or Br, Y = I, R = R' = Me or Ph;^{26,27} M = W, X = Y = Br, R = R' = Me;³⁸ M = W, X = Y = I, R = R' = Me or Ph, R = Me, R' = Ph¹⁹) were prepared by the published methods.^{19,26,27,38} All the chemicals used were purchased from commercial sources.

Elemental analyses (C, H and N) were performed by using a Carlo Erba Elemental Analyser MOD1108 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording spectrophotometer, ¹H, ¹¹B, ¹³C and ³¹P NMR spectra on a Bruker AC 250 MHz spectrometer. The ¹H and ¹³C spectra were referenced to SiMe₄, ³¹P spectra to 85% H₃PO₄ and ¹¹B spectra to boric acid.

Preparations

[MoBr(CO)(L-P,P',P'')(η²-MeC₂Me)]Br 1. To a solution of [MoBr₂(CO)(NCMe)(η²-MeC₂Me)]₂ (0.2 g, 0.46 mmol) in CH₂Cl₂ (30 cm³), L [Ph₂P(CH₂)₂PPh₂]₂ (0.25 g, 0.46 mmol) was added and the reaction mixture stirred for 24 h. The resultant brown solution was filtered through Celite and the solvent removed *in vacuo* giving a brown crystalline powder of [MoBr(CO)(L-P,P',P'')(η²-MeC₂Me)]Br **1**, which was recrystallised from a solution in chloroform. Yield = 0.36 g, 90%.

Similar reactions of [MoX(Y)(CO)(NCMe)(η²-RC₂R)]₂ (X = Y = Br, R = Ph; X = Cl, Y = I, R = Me or Ph; X = Br, Y = I, R = Me) with 1 equivalent of L afforded the complexes [MoX(CO)(L-P,P',P'')(η²-RC₂R)]Y **2–5**. See Table 1 for physical and analytical data.

[W(CO)(L-P,P',P'')(η²-MeC₂Me)]I 7. A suspension of [W(CO)(L-P,P',P'')(η²-MeC₂Me)]₂ (0.2 g, 0.19 mmol) in dry acetonitrile (30 cm³) was refluxed for 24 h. After cooling to room temperature the solvent was removed *in vacuo* to give a

Table 4 Crystal data and structure refinement for the three structures

	9	14	19
Empirical formula	C _{39.5} H ₄₁ ClIO ₁₁ P ₃ W ₄	C ₆₄ H ₆₁ BCl ₂ IOP ₃ W	C ₃₄ H ₂₉ Br ₂ MoO ₂ P ₃
Formula weight	1682.38	1331.50	818.24
<i>T</i> /K	293(2)	293(2)	293(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / \AA	11.759(14)	16.76(2)	12.630(19)
<i>b</i> / \AA	14.428(16)	18.88(2)	14.308(14)
<i>c</i> / \AA	14.855(16)	20.21(2)	18.708(19)
α /°	78.131(10)		
β /°	88.426(10)	109.91(1)	97.02(1)
γ /°	86.037(10)		
<i>V</i> / \AA^3	2460	2656	1624
<i>Z</i> , <i>D</i> _c /Mg m ⁻³	2, 2.271	4, 1.470	4, 1.620
μ/mm^{-1}	10.151	2.642	2.945
Transmission factors	0.152, 1.000	0.507, 1.000	0.178, 1.000
<i>F</i> (000)	1554	2656	1624
Crystal size/mm	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.35 × 0.30 × 0.25
θ Range for data collection	2.22 to 25.11	2.40 to 26.05	2.33 to 25.98
Reflections collected/unique (<i>R</i> _{int})	6165	12735/8386 (0.0437)	8359/5202 (0.0813)
Data/restraints/parameters	6165/0/294	8386/0/669	5302/0/379
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)	0.0941, 0.2219	0.0704, 0.1981	0.1046, 0.2419
(all data)	0.1637, 0.2638	0.1149, 0.2271	0.2146, 0.3046
Largest difference peak and hole/e \AA^{-3}	2.925, -3.419	3.666, -1.432	2.476, -0.729

brown crystalline powder of [WI(CO)(L-*P,P',P''*)(η^2 -MeC₂-Me)]I **7** which was recrystallised from dichloromethane. Yield = 0.13 g, 66%.

Similar 24 h acetonitrile reflux reactions of [WX₂(CO)-(L-*P,P',P''*)(η^2 -RC₂R')] (X = Br, R = R' = Me; X = I, R = Me, R' = Ph) gave the cationic complexes [WX(CO)(L-*P,P',P''*)(η^2 -RC₂R')]X **6** and **8**. See Table 1 for physical and analytical data.

[WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)]₂[W₆O₁₉] **9**. A suspension of [WI₂(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)] (1.0 g, 0.95 mmol) in wet acetonitrile (30 cm³) was refluxed for 24 h. After cooling to room temperature, the solvent was removed *in vacuo* to give a brown crystalline powder [WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)]₂[W₆O₁₉] **9**. Suitable crystals for X-ray crystallography were grown from a room temperature solution of **9** in dichloromethane. Yield = 0.04 g, 18%.

[MoI(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)][BF₄] **10**. To a solution of [MoI₂(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)] (0.2 g, 0.22 mmol) dissolved in acetonitrile (30 cm³) in a foil covered Schlenk tube at room temperature, Ag[BF₄] (0.04 g, 0.22 mmol) was added and the reaction mixture was stirred for 24 h. The resulting brown solution was filtered through Celite and the solvent removed *in vacuo* to give a brown powder. The resultant brown solid was redissolved in CH₂Cl₂ and filtered through Celite, the solvent was reduced in volume to 4 cm³ *in vacuo* and dropwise addition of diethyl ether precipitated the brown complex [MoI(CO)-(L-*P,P',P''*)(η^2 -MeC₂Me)][BF₄] **10**, which was recrystallised from a solution in 80:20 CH₂Cl₂-Et₂O. Yield = 0.11 g, 53%.

Similar reactions of [MI₂(CO)(L-*P,P',P''*)(η^2 -RC₂R')] (M = Mo, R = R' = Ph; M = W, R = R' = Me, R = Me, R' = Ph) with 1 equivalent of Ag[BF₄] in acetonitrile afforded the complexes [MI(CO)(L-*P,P',P''*)(η^2 -RC₂R')][BF₄] **11**, **12** and **13**. See Table 1 for physical and analytical data.

[WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)][BPh₄].0.5CH₂Cl₂ **14**. To a solution of [WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)]I (0.5 g, 0.47 mmol) in acetonitrile (30 cm³), Na[BPh₄] (0.16 g, 0.47 mmol) was added and the reaction mixture stirred for 24 h. The resulting red solution was filtered through Celite and the solvent removed *in vacuo* to give a red powder. The resultant solid was redissolved in CH₂Cl₂ and filtered through Celite, and the solvent reduced in volume to 4 cm³ *in vacuo*. Dropwise addition of diethyl ether precipitated the red-purple complex [WI(CO)-(L-*P,P',P''*)(η^2 -MeC₂Me)][BPh₄].0.5CH₂Cl₂ **14**. Yield = 0.32 g,

67%. Suitable crystals for X-ray analysis were grown from a room temperature solution in CDCl₃. ¹³C NMR data (25 °C, CD₂Cl₂): δ 20.9 (s, Ph₂PCH₂), 25.0 (s, PhPCH₂), 29.3 (s, MeC₂), 53.8 (s, CH₂Cl₂), 136.4–122.0 (m, C₆H₅), 163.0, 163.8, 164.6, 165.4 [s, B(C₆H₅)₄], 195.1 (s, CO) and 216.9 (s, C \equiv C).

A similar reaction of [WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Ph)]I with 1 equivalent of Na[BPh₄] in acetonitrile afforded the complex [WI(CO)(L-*P,P',P''*)(η^2 -MeC₂Ph)][BPh₄] **15**. See Table 1 for physical and analytical data.

[W(CO)(NCMe)(L-*P,P',P''*)(η^2 -MeC₂Me)][BF₄] **16**. To a solution of [WI₂(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)] (0.33 g, 0.31 mmol) dissolved in acetonitrile (30 cm³) in a foil covered Schlenk tube at room temperature, Ag[BF₄] (0.12 g, 0.62 mmol) was added and the reaction mixture stirred for 24 h. The resulting red solution was filtered through Celite and the solvent removed *in vacuo* to give a red powder. The resultant red solid was redissolved in CH₂Cl₂ and filtered through Celite, the solvent reduced in volume to 4 cm³ *in vacuo* and dropwise addition of diethyl ether precipitated the red complex [W(CO)(NCMe)(L-*P,P',P''*)(η^2 -MeC₂Me)][BF₄] **16** which was recrystallised from a solution in CH₂Cl₂-Et₂O. Yield = 0.12 g, 36%.

Similar reactions of [WI₂(CO)(L-*P,P',P''*)(η^2 -RC₂R')] (R = R' = Ph; R = Me, R' = Ph) with 2 equivalents of Ag[BF₄] in acetonitrile yielded the dicationic complexes [W(CO)-(NCMe)(L-*P,P',P''*)(η^2 -RC₂R')][BF₄]₂ **17** and **18**. See Table 1 for physical and analytical data.

[MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-*P,P',O*}] **19**. A suspension of [MoBr(CO)(L-*P,P',P''*)(η^2 -MeC₂Me)]Br (0.2 g, 0.23 mmol) in CHCl₃ (30 cm³) open to the air was refluxed for 2 h. The resultant green-brown solution was filtered through Celite and the solution reduced *in vacuo* to 10 cm³ from which green crystals of [MoBr₂(O){Ph₂P(CH₂)₂PPh(CH₂)₂POPh₂-*P,P',O*}] **19** were grown at room temperature. Yield = 0.12 g, 62%.

A similar reaction of [MoBr(CO)(L-*P,P',P''*)(η^2 -PhC₂Ph)]Br in a refluxing CHCl₃ solution open to the air for 2 h also gave the oxidised product **19**.

X-Ray crystallography

Crystal data for complexes **9**, **14** and **19** are given in Table 4, together with refinement details. Data were collected with

Mo-K α radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program.³⁹ The structures were solved using direct methods with the SHELXS 86 program.⁴⁰ In **9** the W, I, P atoms were refined with anisotropic thermal parameters, but the O and C with isotropic thermal parameters. In **14** and **19** all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In **9** there was one molecule of solvent dichloromethane overlapping with one water molecule. Both were given 50% occupancy. In **14** there was one molecule of solvent, dichloromethane, but with four pairs of alternative positions for the chlorine atom. Each pair was refined with 25% occupancy. In **19** there was no solvent. Absorption corrections were carried out using DIFABS.⁴¹ The structures were all refined on F^2 using SHELXL.⁴² All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

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See <http://www.rsc.org/suppdata/dt/1999/765/> for crystallographic files in .cif format.

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