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FULL PAPER

Cationic linear triphos, L [$PhP(CH_2CH_2PPh_2)_2$], alkyne complexes of molybdenum(II) and tungsten(II); crystal structures of [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]$_2$[W_6O_{19}], [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)][BPh_4] and [$MoBr_2$(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*P*,*P*′,*O*}]

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Equimolar quantities of [MoX(Y)(CO)(NCMe)(η^2-RC_2R)$_2$] and L [= $PhP(CH_2CH_2PPh_2)_2$] reacted in CH_2Cl_2 at room temperature to give the cationic tridentate linear triphos complexes [MoX(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]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 [WX_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] in dry acetonitrile afforded the cationic complexes, [WX(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')]X **6**–**8** (X = Br or I, R = R′ = Me; X = I, R = Me, R′ = Ph), whereas refluxing [WI_2(CO)(L-*P*,*P*′)(η^2-MeC_2Me)] in slightly wet acetonitrile yielded the unusual crystallographically characterised complex [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]$_2$[W_6O_{19}] **9**. Silver tetrafluoroborate reacted with an equimolar amount of [MI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] in acetonitrile to give the cationic complexes [MI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4] **10**–**13** (M = Mo, R = R′ = Me or Ph; M = W, R = R′ = Me, R = Me, R′ = Ph). The tetraphenylborate complexes [WI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BPh_4] (R = R′ = Me **14**, R = Me, R′ = Ph **15**) were prepared by an iodide exchange reaction of [WI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')]I with Na[BPh_4] in acetonitrile. The crystal structure for **14** has been determined. The dicationic complexes [W(CO)(NCMe)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4]$_2$ **16**–**18** (R = R′ = Me or Ph; R = Me, R′ = Ph) were prepared by treating [WI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] with 2 equivalents of Ag[BF_4] in acetonitrile. The cationic bromomolybdenum complexes [MoBr(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]Br (R = Me or Ph) rearrange in refluxing $CHCl_3$ in air to give the unusual molybdenum(IV) product [$MoBr_2$(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*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 Green[8] described the synthesis and characterisation of a series of cationic cyclopentadienyl and indenyl molybdenum(II) complexes of the type [Mo(CO)(η^2-RC_2R')$_2$(η^5-C_5H_5 or C_9H_7)][BF_4] (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 [WI_2(CO)(NCMe)(η^2-RC_2R)$_2$] (R = Me or Ph) in 1988[19] 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 1996[25] we described the reactions of [WI_2(CO)(NCMe)(η^2-RC_2R')$_2$] (R = R′ = Me or Ph; R = Me, R′ = Ph) with equimolar amounts of L {$PhP(CH_2CH_2PPh_2)_2$} in CH_2Cl_2 at room temperature which gave the bidentate linear triphos complexes, [WI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')], crystallographically characterised for R = R′ = Me and R = Me, R′ = Ph. Linear triphos, $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, means the three phosphorus atoms are in a linear mode, with two CH_2 groups separating each phosphorus atom. In this paper we describe the conversion of these [WI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] and related complexes to the cationic tridentate linear triphos complexes of the type [MX(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')]Y (M = Mo or W; X = Cl, Br or I; R = R′ = Me or Ph; R = Me, R′ = Ph; Y = Br, I, $\frac{1}{2}W_6O_{19}$, BF_4 or BPh_4) and dicationic tungsten complexes [W(CO)(NCMe)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4]$_2$ (R = R′ = Me or Ph; R = Me, R′ = Ph). The oxidative rearrangement of the cationic molybdenum bromo complexes [MoBr(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]Br (R = Me or Ph) to give the novel crystallographically characterised molybdenum(IV) complex, [$MoBr_2$(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*P*,*P*′,*O*}] is also described. The crystal structures of the complexes [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]$_2$[W_6O_{19}] and [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)][BPh_4] are also discussed.

Results and discussion

Reaction of equimolar quantities of [MoX(Y)(CO)(NCMe)(η^2-RC_2R)$_2$][19,26] and L {= $PhP(CH_2CH_2PPh_2)_2$} in CH_2Cl_2 at room temperature for 24 h gives the tridentate linear triphos complexes [MoX(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]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 ^{1}H and ^{31}P NMR spectroscopy (Table 2). The complex [MoCl(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]I·CH_2Cl_2 **3** was confirmed as a CH_2Cl_2 solvate by repeated elemental analyses and ^{1}H NMR spectroscopy. They are all soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, 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 shown[27] that reaction of the mixed halide tungsten complex [WCl(I)(CO)(NCMe)(η^2-MeC_2Me)$_2$] 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 (%) C	H	N	$\tilde{\nu}(C\equiv O)/cm^{-1}$	$\tilde{\nu}(C\equiv C)/cm^{-1}$
1 $[MoBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]Br$	Brown	90	53.8 (53.7)	4.3 (4.5)	—	1960s	1601w
2 $[MoBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}PhC_2Ph)]Br$	Orange-brown	83	59.6 (59.0)	4.1 (4.3)	—	1966s	1590w
3 $[MoCl(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]I\cdot CH_2Cl_2$	Brown	82	49.7 (49.4)	4.0 (4.0)	—	1974s	1666w
4 $[MoCl(CO)(L\text{-}P,P',P'')(\eta^2\text{-}PhC_2Ph)]I$	Brown	85	59.0 (58.8)	4.2 (4.3)	—	1979s	1671w
5 $[MoBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]I$	Red-brown	87	51.2 (50.9)	4.6 (4.3)	—	1976s	1665w
6 $[WBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]Br$	Purple	61	48.2 (48.9)	4.4 (4.1)	—	1967s	1601w
7 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]I$	Brown	66	44.8 (44.4)	3.8 (3.0)	—	1961s	1585w
8 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Ph)]I$	Brown	87	47.7 (47.7)	4.3 (3.7)	—	1969s	1587w
9 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]_2[W_6O_{19}]$	Brown	18	29.5 (28.7)	2.1 (2.4)	—	1969s	1522w
10 $[MoI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BF_4]$	Brown	53	50.2 (50.3)	4.1 (4.2)	—	1963s	1600w
11 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BF_4]$	Purple	66	45.1 (45.6)	4.1 (4.1)	—	1967s	1601w
12 $[MoI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}PhC_2Ph)][BF_4]$	Brown	62	55.4 (55.9)	3.6 (4.1)	—	1965s	1590w
13 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Ph)][BF_4]$	Purple	45	48.6 (49.0)	4.7 (4.8)	—	1968s	1570w
14 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot 0.5CH_2Cl_2$	Red-purple	67	59.6 (59.1)	4.7 (4.7)	—	1970s	1579w
15 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Ph)][BPh_4]$	Red-purple	73	61.8 (62.3)	5.3 (4.8)	—	1971s	1579w
16 $[W(CO)(NCMe)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BF_4]_2$	Red	36	48.3 (48.5)	4.2 (4.2)	1.3 (1.4)	1959s	1600w
17 $[W(CO)(NCMe)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Ph)][BF_4]_2$	Red	39	51.0 (51.2)	4.1 (4.2)	1.6 (1.3)	1966s	1629w
18 $[W(CO)(NCMe)(L\text{-}P,P',P'')(\eta^2\text{-}PhC_2Ph)][BF_4]_2$	Red-brown	34	53.0 (53.7)	3.8 (4.1)	1.2 (1.3)	1973s	1601w
19 $[MoBr_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]$	Green	62	49.6 (49.6)	4.4 (4.1)	—		

[a] Calculated values in parentheses. [b] Spectra recorded as thin films in $CHCl_3$ between NaCl plates; s = strong, w = weak.

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

Complex	^1H (δ)	^{31}P (δ, J/Hz)
1	7.8–7.5 (m, 25 H, Ph), 3.0 (s, 6 H, C_2Me), 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_2Cl_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_2Me), 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_2Me), 2.8–2.6 (m, 8 H, CH_2)	70.3 (s, 1P, J_{WP} = N.O.), 39.9 (s, 2P, J_{WP} = N.O.)
7	7.7–7.4 (m, 25 H, Ph), 3.1 (s, 6 H, C_2Me), 2.8–2.6 (m, 8 H, CH_2)	67.7 (s, 1P, J_{WP} = N.O.), 33.2 (s, 2P, J_{WP} = 261.9)
8	7.8–7.4 (m, 35 H, Ph), 3.1 (s, 3 H, C_2Me), 2.6–2.4 (m, 8 H, CH_2)	67.7 (s, 1P, J_{WP} = N.O.), 33.2 (s, 2P, J_{WP} = N.O.)
9	7.8–7.4 (m, 25 H, Ph), 3.1 (s, 6 H, C_2Me), 2.6–2.4 (m, 8 H, CH_2)	68.0 (s, 1P, J_{WP} = 262.1), 33.3 (s, 2P, J_{WP} = N.O.)
10	7.9–7.6 (m, 25 H, Ph), 3.1 (s, 6 H, C_2Me), 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_2Me), 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, J_{WP} = 228.5), 42.8 (s, 2P, J_{WP} = 266.6)
14	7.6–7.1 (m, 45 H, Ph), 5.3 (s, H, CH_2Cl_2), 3.1 (s, 6 H, C_2Me), 2.8–2.7 (m, 8 H, CH_2)	66.8 (s, 1P, J_{WP} = 263.1), 32.5 (s, 2P, J_{WP} = 276.8)
15	7.6–7.9 (m, 50 H, Ph), 3.1 (s, 3 H, C_2Me), 2.9–2.7 (m, 8 H, CH_2)	66.8 (s, 1P, J_{WP} = N.O.), 32.3 (s, 2P, J_{WP} = 254.6)
16	7.8–7.3 (m, 25 H, Ph), 3.1 (s, 6 H, C_2Me), 2.9–2.7 (m, 8 H, CH_2), 2.1 (s, 3 H, NCMe)	58.5 (s, 1P, J_{WP} = N.O.), 42.0 (s, 2P, J_{WP} = 260.3)
17	7.6–7.2 (m, 30 H, Ph), 3.0 (s, 3 H, C_2Me), 2.8–2.6 (m, 8 H, CH_2), 2.1 (s, 3 H, NCMe)	59.8 (s, 1P, J_{WP} = N.O.), 42.9 (s, 2P, J_{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, J_{WP} = N.O.), 42.9 (s, 2P, J_{WP} = 234.2)

[a] Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; m = multiplet, s = singlet. [b] Spectra recorded in $CDCl_3$ and referenced to 85% H_3PO_4; N.O. = not observed.

the crystallographically characterised chloro-co-ordinated cation $[WCl(CO)(2,2'\text{-}bipy)(\eta^2\text{-}MeC_2Me)_2]I$, 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 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]_2[W_6O_{19}]$ **9** and $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BPh_4]$ **14** (see Figs. 1

and 3), which are discussed later. The $^{31}P-\{^1H\}$ NMR spectra ($CDCl_3$, +25 °C) of complexes **1**–**5** (see Table 2) also show two resonances with an intensity ratio of 1:2. For example, $[MoBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]Br$ **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, $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ (R = R′ = Me, R = Me, R′ = Ph)[25] do not rearrange at room temperature in CH_2Cl_2 for 48 h to give the cationic complexes $[WX(CO)(L\text{-}P,P',P'')(\eta^2\text{-}RC_2R')]X$, only the neutral bidentate linear triphos starting materials are isolated. However, refluxing the complexes $[WX_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ in dry acetonitrile for 24 h gives the cationic complexes $[WX(CO)(L\text{-}P,P',P'')(\eta^2\text{-}RC_2R')]X$ **6**–**8** (X = Br, R = R′ = Me; X = I, R = R′ = Me, R = Me, R′ = 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 $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ in slightly wet acetonitrile gives the unusual $[W_6O_{19}]^{2-}$ dianion complex $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]_2[W_6O_{19}]$ **9** which has been crystallographically characterised. Complex **9** has been fully characterised (see Tables 1 and 2). The $[W_6O_{19}]^{2-}$ dianion is apparently very stable and has been crystallographically characterised in association with a variety of different cations.[28–33] The rearrangement/oxidation of $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]^+$ to its $[W_6O_{19}]^{2-}$ salt is strange, and very difficult to explain, except that the dianion $[W_6O_{19}]^{2-}$ is in a potential well and occurs in many structures.[28–33] In 1993, McCann and co-workers[34] also found that addition of $[NBu^n_4][ClO_4]$ to the filtrate which remains after the synthesis of $[Mo_2(\mu\text{-}O_2CMe)_4]$ {from $[Mo(CO)_6]$, $MeCO_2H$ and $(MeCO)_2O$} followed by exposure to air affords $[NBu^n_4]_2[W_6O_{19}]$.

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 $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)][BPh_4]$ **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) and 152.6(1)° 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 $[W_6O_{19}]^{2-}$ 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.

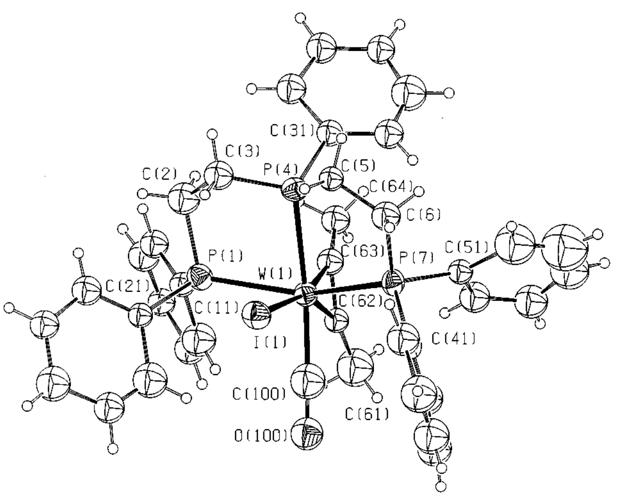

Fig. 1 Cation in complex **9** together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

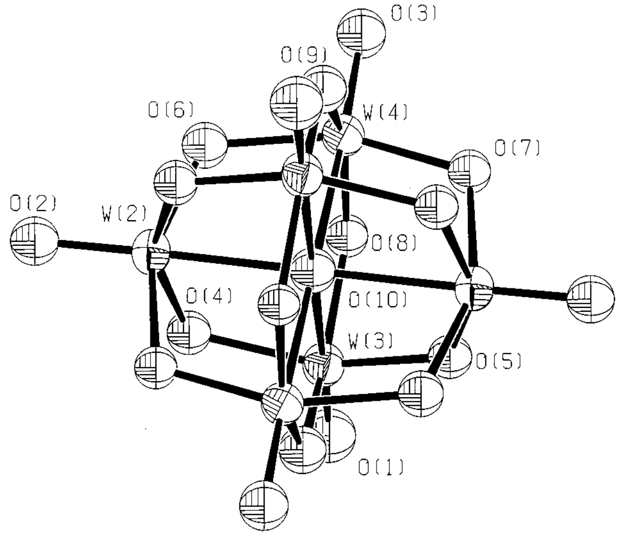

Fig. 2 Structure of the $[W_6O_{19}]^{2-}$ dianion in complex **9**. Ellipsoids shown at 30% probability.

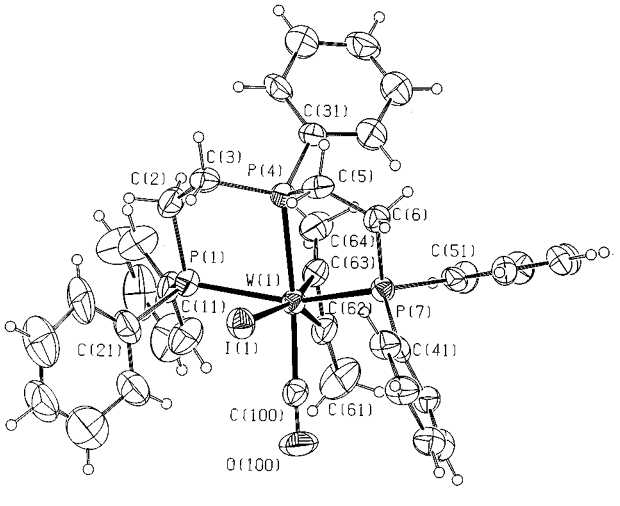

Fig. 3 Crystal structure of the $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]^+$ in complex **14**, together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

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 $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ displace the iodide *trans* to the carbonyl to give the stereochemistry of the cation, $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]^+$, shown in Fig. 1. For example, the $^{31}P-\{^1H\}$ NMR ($CDCl_3$, +25 °C) of $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]_2[W_6O_{19}]$ **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 of the but-2-yne cation $[WI(CO)(L\text{-}P,P',P'')(\eta^2\text{-}MeC_2Me)]^+$, whereby the two terminal phosphorus atoms are equivalent. It is interesting that refluxing the diphenylacetylene complexes $[WX_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (X = 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 [MI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] and Ag[BF_4] react in acetonitrile at room temperature to afford the cationic tridentate triphos complexes [WI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4] **10**–**13** (M = Mo or W, R = R′ = Me; M = Mo, R = R′ = Ph; M = W, R = Me, R′ = Ph) in good yield. Complexes **10**–**13** have been fully characterised (see Tables 1 and 2). Treatment of [WI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')]I with 1 equivalent of Na[BPh_4] in acetonitrile gives the iodide exchanged products [WI(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BPh_4] (R = R′ = Me **14**; R = Me, R′ = Ph **15**) in good yield. The complex [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)][BPh_4]·0.5CH_2Cl_2 **14** was confirmed as an 0.5CH_2Cl_2 solvate by repeated elemental analyses and ^1H NMR spectroscopy. The IR spectra of complexes **10**–**13** all show ν(BF)($CHCl_3$) broad bands at ≈1060 cm^{-1}. The ^{11}B-{F} NMR ($CDCl_3$, +25 °C) of **11** has a resonance at δ −1.2. The ^{11}B NMR spectrum ($CDCl_3$, +25 °C) for **14** has a single resonance at δ −6.9. By this approach we have been able to prepare the only monocationic diphenylacetylene complex [MoI(CO)(L-*P*,*P*′,*P*″)(η^2-PhC_2Ph)][BF_4] **12**. However, treatment of the tungsten diphenylacetylene complex [WI_2(CO)(L-*P*,*P*′)(η^2-PhC_2Ph)] with either an equimolar amount of Ag[BF_4] or Na[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 [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)][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 [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 [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]X (X = I **7**, $\frac{1}{2}W_6O_{19}$ **9** or BPh_4 **14**) have two resonances in very similar positions. The ^{13}C-{^1H} NMR spectrum (25 °C, CD_2Cl_2) of **14** (see Experimental section) shows a resonance at δ 216.9 due to the alkyne (C≡C) atoms, which suggests from Templeton and Ward's[6] 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 [WI_2(CO)(L-*P*,*P*′)(η^2-RC_2R')] with 2 equivalents of Ag[BF_4] in acetonitrile at room temperature gives moderate yields of the dicationic complexes [W(CO)(NCMe)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4]$_2$ **16**–**18** (R = R′ = Me or Ph; R = Me, R′ = Ph). Complexes **16**–**18** were characterised as before. They all have strong bands at ν(BF)($CHCl_3$) 1060 cm^{-1} in their IR spectra confirming the presence of the [BF_4]$^-$ anions, and weak nitrile stretching bands at ν(N≡C)($CHCl_3$) 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 [WI_2(CO)(L-*P*,*P*′)(η^2-PhC_2Ph)] with 1 equivalent of Ag[BF_4] in acetonitrile did not after several attempts give the expected cationic complex [WI(CO)(L-*P*,*P*′,*P*″)(η^2-PhC_2Ph)][BF_4], the reaction with 2 equivalents of Ag[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 [WI_2(CO)(L-*P*,*P*′)(η^2-PhC_2Ph)] with 1 and 2 equivalents of Ag[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 complexes **16** to **18**. Also, several unsuccessful attempts were made to obtain suitable ^{13}C NMR spectra for them.

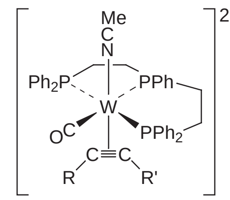

Fig. 4 Proposed structure of the dicationic complexes [W(CO)(NCMe)(L-*P*,*P*′,*P*″)(η^2-RC_2R')][BF_4]$_2$ **16**–**18**.

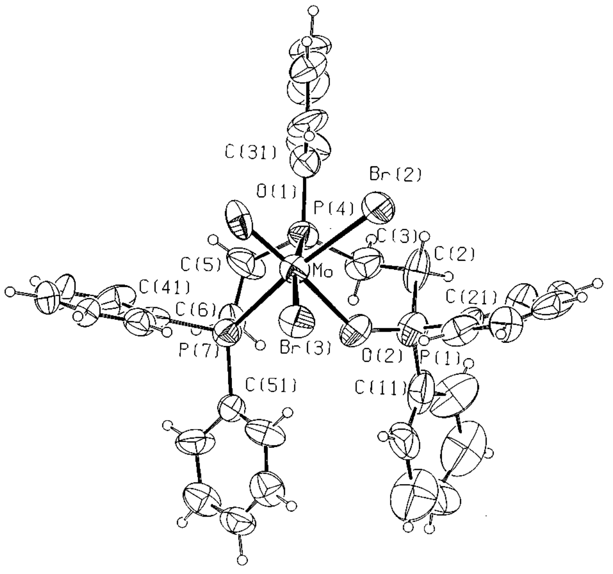

Fig. 5 Crystal structure of [$MoBr_2$(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*P*,*P*′,*O*}] **19**. Ellipsoids shown at 30% probability.

It is interesting that when the complexes [MoBr(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]Br (R = Me or Ph) are refluxed in $CHCl_3$ for 2 h in air the unusual oxidised molybdenum(IV) product [$MoBr_2$(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*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 $(CD_3)_2CO$, 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 [Mo–P 2.459(6), 2.477(5); Mo–Br 2.587(3), 2.608(3) Å]. The ligand oxygen atom O(2) [Mo–O(2) 2.164(12) Å] is *trans* to a terminal oxygen atom O(1) [Mo–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 $Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$ has only been found once before attached to a transition-metal centre, in the crystallographically characterised complex, *fac*-[MoO{$Ph_2P(O)CH_2CH_2P(Ph)CH_2CH_2PPh_2$-*P*,*P*′,*O*}($SeC_6H_2Me_3$-2,4,6)$_2$].[35] It is interesting that Park *et al.*[36] have shown that the molybdenum(II) complex *trans*,*cis*,*cis*-[$MoBr_2(CO)_2(PPh_3)_2$] can be oxidised in air to give the molybdenum(VI) complex *cis*,*cis*,*trans*-[$MoBr_2(O)_2(OPPh_3)_2$]. Similarly, Woodward and co-workers[37], 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 $[W_6O_{19}]^{2-}$ 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: ′ $1 - x, 1 - y, 1 - z$.

$[MoBr_2(CO)_2\{P(C_6H_{11})_3\}_2]$, by bromine addition to *cis*- or *trans*-$[Mo(CO)_4\{P(C_6H_{11})_3\}_2]$ obtained the oxidised product $[HP(C_6H_{11})_3][MoBr_4(O)L]$ [L = OH_2 or $OP(C_6H_{11})_3$]. The most likely reason why our oxidation reactions of [MoBr(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]Br (R = Me **1** or Ph **2**) stop at the molybdenum(IV) complex $[MoBr_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*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*″)(η^2-RC_2R')]Y and [W(CO)(NCMe)(L-*P*,*P*′,*P*″)(η^2-RC_2R')]$[BF_4]_2$ were prepared and characterised, including [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]$_2$$[W_6O_{19}]$ and [WI(CO)(L-*P*,*P*′,*P*″)(η^2-MeC_2Me)]$[BPh_4]$, which have been crystallographically characterised. The unusual formation of the $[W_6O_{19}]^{2-}$ 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*″)(η^2-PhC_2Ph)]$[BF_4]_2$ was simply prepared. Refluxing $CHCl_3$ solutions of [MoBr(CO)(L-*P*,*P*′,*P*″)(η^2-RC_2R)]Br (R = Me or Ph) in air gave the unusual molybdenum(IV) product $[MoBr_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-*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)(η^2-RC_2R')$_2$] (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′ = Ph[19]) 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, ^{11}B, ^{13}C and ^{31}P NMR spectra on a Bruker AC 250 MHz spectrometer. The ^1H and ^{13}C spectra were referenced to $SiMe_4$, ^{31}P spectra to 85% H_3PO_4 and ^{11}B spectra to boronic acid.

Preparations

[MoBr(CO)(L-*P*,*P*′,*P*″)(η²-MeC₂Me)]Br 1. To a solution of $[MoBr_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.2 g, 0.46 mmol) in CH_2Cl_2 (30 cm^3), L $[Ph_2P(CH_2CH_2PPh_2)_2]$ (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*″)(η^2-MeC_2Me)]Br **1**, which was recrystallised from a solution in chloroform. Yield = 0.36 g, 90%.

Similar reactions of [MoX(Y)(CO)(NCMe)(η^2-RC_2R)$_2$] (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*″)(η^2-RC_2R)]Y **2**–**5**. See Table 1 for physical and analytical data.

[WI(CO)(L-*P*,*P*′,*P*″)(η²-MeC₂Me)]I 7. A suspension of $[WI_2(CO)$(L-*P*,*P*′)$(\eta^2\text{-}MeC_2Me)]$ (0.2 g, 0.19 mmol) in dry acetonitrile (30 cm^3) 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	$C_{39.5}H_{41}ClIO_{11}P_3W_4$	$C_{64}H_{61}BCl_2IOP_3W$	$C_{34}H_{29}Br_2MoO_2P_3$
Formula weight	1682.38	1331.50	818.24
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a/Å	11.759(14)	16.76(2)	12.630(19)
b/Å	14.428(16)	18.88(2)	14.308(14)
c/Å	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)		
V/Å^3	2460	2656	1624
Z, D_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
F(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 (R_{int})	6165	12735/8386 (0.0437)	8359/5202 (0.0813)
Data/restraints/parameters	6165/0/294	8386/0/669	5302/0/379
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	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 Å^{-3}	2.925, −3.419	3.666, −1.432	2.476, −0.729

brown crystalline powder of $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})]\mathrm{I}$ **7** which was recrystallised from dichloromethane. Yield = 0.13 g, 66%.

Similar 24 h acetonitrile reflux reactions of $[\mathrm{WX_2(CO)}(\mathrm{L}\text{-}P,P')(\eta^2\text{-}\mathrm{RC_2R'})]$ (X = Br, R = R′ = Me; X = I, R = Me, R′ = Ph) gave the cationic complexes $[\mathrm{WX(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{RC_2R'})]\mathrm{X}$ **6** and **8**. See Table 1 for physical and analytical data.

$[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})]_2[\mathrm{W_6O_{19}}]$ 9. A suspension of $[\mathrm{WI_2(CO)}(\mathrm{L}\text{-}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$ (1.0 g, 0.95 mmol) in wet acetonitrile (30 cm^3) was refluxed for 24 h. After cooling to room temperature, the solvent was removed *in vacuo* to give a brown crystalline powder $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})]_2[\mathrm{W_6O_{19}}]$ **9**. Suitable crystals for X-ray crystallography were grown from a room temperature solution of **9** in dichloromethane. Yield = 0.04 g, 18%.

$[\mathrm{MoI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BF_4}]$ 10. To a solution of $[\mathrm{MoI_2(CO)}(\mathrm{L}\text{-}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$ (0.2 g, 0.22 mmol) dissolved in acetonitrile (30 cm^3) in a foil covered Schlenk tube at room temperature, $\mathrm{Ag[BF_4]}$ (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 $\mathrm{CH_2Cl_2}$ and filtered through Celite, the solvent was reduced in volume to 4 cm^3 *in vacuo* and dropwise addition of diethyl ether precipitated the brown complex $[\mathrm{MoI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BF_4}]$ **10**, which was recrystallised from a solution in 80:20 $\mathrm{CH_2Cl_2\text{–}Et_2O}$. Yield = 0.11 g, 53%.

Similar reactions of $[\mathrm{MI_2(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{RC_2R'})]$ (M = Mo, R = R′ = Ph; M = W, R = R′ = Me, R = Me, R′ = Ph) with 1 equivalent of $\mathrm{Ag[BF_4]}$ in acetonitrile afforded the complexes $[\mathrm{MI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{RC_2R'})][\mathrm{BF_4}]$ **11**, **12** and **13**. See Table 1 for physical and analytical data.

$[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BPh_4}]\cdot0.5\mathrm{CH_2Cl_2}$ 14. To a solution of $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})]\mathrm{I}$ (0.5 g, 0.47 mmol) in acetonitrile (30 cm^3), $\mathrm{Na[BPh_4]}$ (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 $\mathrm{CH_2Cl_2}$ and filtered through Celite, and the solvent reduced in volume to 4 cm^3 *in vacuo*. Dropwise addition of diethyl ether precipitated the red-purple complex $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BPh_4}]\cdot0.5\mathrm{CH_2Cl_2}$ **14**. Yield = 0.32 g, 67%. Suitable crystals for X-ray analysis were grown from a room temperature solution in $\mathrm{CDCl_3}$. ^{13}C NMR data (25 °C, $\mathrm{CD_2Cl_2}$): δ 20.9 (s, $\mathrm{Ph_2P}C\mathrm{H_2}$), 25.0 (s, $\mathrm{PhP}C\mathrm{H_2}$), 29.3 (s, $Me\mathrm{C_2}$), 53.8 (s, $\mathrm{CH_2Cl_2}$), 136.4–122.0 (m, $\mathrm{C_6H_5}$), 163.0, 163.8, 164.6, 165.4 [s, $\mathrm{B(C_6H_5)_4}$], 195.1 (s, CO) and 216.9 (s, $C{\equiv}C$).

A similar reaction of $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Ph})]\mathrm{I}$ with 1 equivalent of $\mathrm{Na[BPh_4]}$ in acetonitrile afforded the complex $[\mathrm{WI(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Ph})][\mathrm{BPh_4}]$ **15**. See Table 1 for physical and analytical data.

$[\mathrm{W(CO)(NCMe)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BF_4}]_2$ 16. To a solution of $[\mathrm{WI_2(CO)}(\mathrm{L}\text{-}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$ (0.33 g, 0.31 mmol) dissolved in acetonitrile (30 cm^3) in a foil covered Schlenk tube at room temperature, $\mathrm{Ag[BF_4]}$ (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 $\mathrm{CH_2Cl_2}$ and filtered through Celite, the solvent reduced in volume to 4 cm^3 *in vacuo* and dropwise addition of diethyl ether precipitated the red complex $[\mathrm{W(CO)(NCMe)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})][\mathrm{BF_4}]_2$ **16** which was recrystallised from a solution in $\mathrm{CH_2Cl_2\text{–}Et_2O}$. Yield = 0.12 g, 36%.

Similar reactions of $[\mathrm{WI_2(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{RC_2R'})]$ (R = R′ = Ph; R = Me, R′ = Ph) with 2 equivalents of $\mathrm{Ag[BF_4]}$ in acetonitrile yielded the dicationic complexes $[\mathrm{W(CO)(NCMe)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{RC_2R'})][\mathrm{BF_4}]_2$ **17** and **18**. See Table 1 for physical and analytical data.

$[\mathrm{MoBr_2(O)}\{\mathrm{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2}\text{-}P,P',O\}]$ 19. A suspension of $[\mathrm{MoBr(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{MeC_2Me})]\mathrm{Br}$ (0.2 g, 0.23 mmol) in $\mathrm{CHCl_3}$ (30 cm^3) 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 cm^3 from which green crystals of $[\mathrm{MoBr_2(O)}\{\mathrm{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2}\text{-}P,P',O\}]$ **19** were grown at room temperature. Yield = 0.12 g, 62%.

A similar reaction of $[\mathrm{MoBr(CO)}(\mathrm{L}\text{-}P,P',P'')(\eta^2\text{-}\mathrm{PhC_2Ph})]\mathrm{Br}$ in a refluxing $\mathrm{CHCl_3}$ 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-Kα 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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