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Synthesis, molecular structures, fluxional properties and catalytic activity of a series of alkyne complexes of molybdenum(II) and tungsten(II) containing phosphite donor ligands

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Treatment of $[MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ with one equivalent of $P(OPh)_3$ in diethyl ether at room temperature afforded the crystallographically characterised complexes $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')]$ ($R' = R'' = Me$ or Ph; $R' = Me$, $R'' = Ph$) which have five different ligands attached in a pseudo-octahedral arrangement. Reaction of $[MI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ with two equivalents of $P(OR)_3$ in diethyl ether at room temperature gave high yields of the bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$ {R = Ph, R′ = Me, R″ = Ph (M = Mo only); M = Mo or W, R = Me, R′ = R″ = Me or Ph (M = Mo only), R′ = Me, R″ = Ph (M = W only); R′ = Me, R″ = Ph (M = W only); R = Et, R′ = R″ = Me or Ph (M = Mo only), R′ = Me, R″ = Ph (M = W only); R = ^{i}Pr, R′ = R″ = Me or Ph (M = Mo only), R′ = Me, R″ = Ph (M = W only); R = ^{n}Bu, R′ = R″ = Me, Ph (M = Mo only for both complexes)}. The crystal structures for $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$ {M = Mo, R = Me, ^{i}Pr; R′ = R″ = Me; M = Mo, R = Ph, R′ = Me, R″ = Ph; M = W, R = Et or ^{i}Pr; R′ = R″ = Me; R′ = Me, R″ = Ph (R = ^{i}Pr only)} have been determined, and all have *trans*-phosphite ligands except for M = Mo, R = R′ = R″ = Me which has *cis*-phosphite groups. The trimerisation of MeC_2Ph by the reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]$ with $P(O^iPr)_3$ to give the crystallographically characterised trimer of MeC_2Ph, 1,2,4-trimethyl-3,5,6-triphenylbenzene, is also described. The fluxional properties of selected complexes have been investigated.

In molybdenum(II) and tungsten(II) complexes containing alkyne ligands the alkyne can act as either a two- or a four-electron donor.[1–3] The importance of this type of complex has been highlighted by two extensive review articles.[4,5] Although a wide range of halogenocarbonyl alkyne complexes of the types $[MoX_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ and $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo or W; X = Cl, Br, I; R, R′ = alkyl, aryl, *etc.*) have been prepared,[6–14] until our work described herein there are very few examples containing one phosphine or phosphite ligand. Umland and Vahrenkamp[6] have described the synthesis of the mono (L) complexes $[WI_2(CO)_2L(\eta^2\text{-}HC_2Bu^t)]$ ($L = PMe_3$, $AsMe_3$ or $CNBu^t$).

In 1988[15] we described the synthesis and crystal structures of the bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph). These have an extensive range of chemistry,[5,16] including reactions with phosphite donor ligands. In 1989[17] we described the synthesis and crystal structure (for R = R′ = Me) of the bis(phosphite) complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R')]$ (R = Me, Et, ^{i}Pr or ^{n}Bu; R′ = Me or Ph). In this paper we report the reactions of equimolar quantities of $[MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ and $P(OPh)_3$ to give the first mono(phosphite) complexes of the type $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')]$ (R′ = R″ = Me or Ph; R′ = Me, R″ = Ph) which have all been crystallographically characterised. We also considerably extend the series of bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$, including six which have been crystallographically characterised. The trimerisation of MeC_2Ph from the reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]$ with $P(O^iPr)_3$ to give the crystallographically characterised arene 1,2,4-trimethyl-3,5,6-triphenylbenzene is also briefly discussed.

Results and discussion

Equimolar quantities of $[MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]$ (R′ = R″ = Me or Ph; R′ = Me, R″ = Ph) and $P(OPh)_3$ react in diethyl ether at room temperature to give the alkyne displaced products $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}R'C_2R'')]$ **1–3** in good yield. Complexes **1–3** have been fully characterised by elemental analysis (Table 1), IR (Table 2), ^{1}H and ^{31}P NMR spectroscopy (Tables 3 and 4). All three complexes have also been crystallographically characterised. The complexes are all very air-sensitive in solution, but can be stored in the solid state under an inert atmosphere for several months at −17 °C without significant decomposition. Their IR spectra all show weak nitrile bands and alkyne stretching bands in the expected positions for these ligands when they are co-ordinated to a transition-metal centre. The more electron rich alkyne 2-butyne has the lowest carbonyl stretching band (1995 cm^{-1}), whereas the least electron rich alkyne diphenylacetylene has ν(CO) at 2013 cm^{-1} (see Table 2).

Suitable single crystals for X-ray analysis were grown by cooling (−17 °C) concentrated diethyl ether solutions of complexes **1–3** for 24 h. The structures are shown in Figs. 1, 2 and 3 respectively and their dimensions are compared in Table 5. Crystal data are given in Table 6. The differences between the molecules are in the nature of the alkyne being 2-butyne in **1**, diphenylacetylene in **2** and 1-phenyl-1-propyne in **3**. These changes have made little difference to the geometry of the metal co-ordination sphere. Each contains a molybdenum atom in a distorted octahedral environment assuming that the alkyne occupies one site. There are five different groups bonded to the metal with the only duplication being two iodides. The carbonyl

Table 1 Physical and analytical data[a] for the phosphite alkyne complexes of molybdenum(II) and tungsten(II) **1**–**18**

Complex	Colour	Yield (%)	Analysis (%) C	H	N
1 $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Me)}]$	Brown	89	39.2 (38.2)	3.2 (3.1)	1.7 (1.8)
2 $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MePhC_2Ph)}]$	Light brown	82	46.4 (46.2)	3.3 (3.3)	1.8 (1.5)
3 $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Ph)}]$	Brown	65	42.6 (42.6)	3.4 (3.1)	1.5 (1.7)
4 $[\mathrm{MoI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}MeC_2Ph)}]$	Brown	61	50.2 (49.6)	3.6 (4.3)	—
5 $[\mathrm{MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Green	81	19.8 (19.4)	3.5 (3.5)	—
6 $[\mathrm{WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Purple-green	92	17.4 (17.2)	3.2 (3.3)	—
7 $[\mathrm{MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}PhC_2Ph)}]$	Green	92	30.8 (31.3)	5.4 (3.5)	—
8 $[\mathrm{WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Ph)}]$	Green	66	23.6 (23.2)	3.0 (3.2)	—
9 $[\mathrm{MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Green	90	26.6 (26.6)	4.6 (4.7)	—
10 $[\mathrm{MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}PhC_2Ph)}]$	Dark-brown	87	35.5 (36.4)	3.7 (4.5)	—
11 $[\mathrm{WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Green	83	24.2 (24.0)	4.0 (4.3)	—
12 $[\mathrm{WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Ph)}]$	Green	82	29.2 (28.9)	3.9 (4.2)	—
13 $[\mathrm{MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Green	85	32.6 (32.5)	5.8 (5.7)	—
14 $[\mathrm{MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}PhC_2Ph)}]$	Brown	84	40.2 (40.6)	5.0 (5.4)	—
15 $[\mathrm{WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Green	90	29.7 (29.5)	5.3 (5.2)	—
16 $[\mathrm{WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Ph)}]$	Green	98	34.1 (33.7)	5.8 (5.1)	—
17 $[\mathrm{MoI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}MeC_2Me)}]$	Brown	66	37.9 (37.3)	6.8 (6.4)	—
18 $[\mathrm{MoI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}PhC_2Ph)}]$	Brown	79	43.9 (44.2)	5.8 (6.1)	—

[a] Calculated values in parentheses.

Table 2 IR Data[a] ($\mathrm{cm^{-1}}$), for the phosphite alkyne complexes of molybdenum(II) and tungsten(II) **1**–**18**

Complex	ν(C≡N)	ν(C≡O)	ν(C≡C)
1	2314w, 2287w	1995s	1591w
2	2360w, 2341w	2013s	1643w
3	2319w, 2225w	2000s	1653w
4		1994s	1637w
5		2001s, 1943 (sh)	1676w
6		1989s (br)	1665w
7		2014s, 1968 (sh)	1654w, 1601w
8		1992s, 1960 (sh) s	1656vw
9		1998s, 1970s	1668w
10		2004s, 1979s	1608w
11		1981 (br) s, 1961 (sh)	1655w
12		1986, 1962s (br)	1625vw
13		1969s	1677w
14		1970s	1601w
15		1955s (br)	1654w
16		1959s	1619w
17		1962s	1618w
18		1964s	1601w

[a] Spectra recorded in $\mathrm{CHCl_3}$ as thin films between NaCl plates; br = broad, s = strong, w = weak.

group is *trans* to the acetonitrile, the phosphite ligand P(4) is *trans* to one iodide I(3), and the alkyne is *trans* to the other iodide I(2). It is interesting that in all four cases {two molecules of **1**, together with **2** and **3**} the Mo–I(2) bond length is greater than the Mo–I(3) bond length, no doubt because of the *trans* effect of the alkyne. It is possible to conclude that this effect is greater in the case of the diphenylacetylene in **2**, where the difference is 0.059 Å than in **1** and **3** where the differences are 0.033, 0.032 and 0.027 Å respectively. The position of the two carbon atoms *trans* to I(2) are slightly different with C(21) more closely *trans* than C(11) by between 4 and 8°. Bond lengths in the three structures are otherwise unremarkable.

It is likely that the reactions of $[\mathrm{MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2}]$ with $\mathrm{P(OPh)_3}$ go *via* an associative mechanism, since the alkyne can alter its mode of bonding from being a 4- to a 2-electron donor, upon addition of $\mathrm{P(OPh)_3}$. Associative mechanisms have been previously suggested for this type of substitution reaction in molybdenum(II) and tungsten(II) alkyne complexes.[19,20] It is interesting, that in our previous studies[17] refluxing equimolar amounts of $[\mathrm{WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2}]$ and $\mathrm{P(OPh)_3}$ in $\mathrm{CHCl_3}$ for 48 h afforded the proposed mono(triphenyl phosphite) complex $[\mathrm{WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}PhC_2Ph)_2}]$ {ν(CO) 2030 $\mathrm{cm^{-1}}$}, $[\mathrm{WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}PhC_2Ph)}]$ {ν(CO) 1990 $\mathrm{cm^{-1}}$} and the starting complex $[\mathrm{WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2}]$ {ν(CO) 2090 $\mathrm{cm^{-1}}$}. It was also reported that there was extensive decomposition in these reactions. By contrast, the reactions described herein using molybdenum instead of tungsten proceed smoothly to the alkyne substituted product in an apparently stereoselective manner. Addition of a second equivalent of $\mathrm{P(OPh)_3}$ to $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Ph)}]$ **3** in diethyl ether eventually gives the crystallographically characterised (Fig. 4) *trans*-bis(triphenyl phosphite) complex $[\mathrm{MoI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}MeC_2Ph)}]$ **4**. It is very likely this reaction goes *via* initial formation of the *cis*-complex (see structures of *cis*-$[\mathrm{MI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)}]$ {M = Mo (this work);

Table 3 Proton NMR data (δ, J/Hz)[a] for the phosphite alkyne complexes of molybdenum(II) and tungsten(II) **1**–**18**

Complex	
1	7.5–7.2 {m, 15 H, $\mathrm{P(OPh)_3}$}; 2.9 (s, 6 H, $\mathrm{C_2CH_3}$); 2.1 (s, 3 H, NCMe)
2	7.7–7.4 {m, 25 H, $\mathrm{P(OPh)_3}$}; 2.1 (s, 3 H, NCMe)
3	7.2 {m, 15 H, $\mathrm{P(OPh)_3}$}; 7.0 (m, 5 H, $\mathit{Ph}\mathrm{C_2CH_3}$); 3.0 (s, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$); 2.1 (s, 3 H, $\mathrm{NCCH_3}$)
4	7.25 {m, 30 H, $\mathrm{P(OPh)_3}$}; 6.9 (m, 5 H, $\mathit{Ph}\mathrm{C_2CH_3}$); 3.0 (br s, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$)
5	3.9 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$); 3.5 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$); 3.0 (s, 6 H, $\mathrm{C_2CH_3}$), *cis*; 3.6 (t, $J_{P\text{-}H}$ = 5.2, 18 H, $\mathrm{OCH_3}$); 3.1 (m, 6 H, $\mathrm{C_2CH_3}$), *trans*
6	4.0 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$); 3.5 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$); 2.9 (s, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2C}\mathit{H}_3$), *cis*; 3.6 (t, $J_{P\text{-}H}$ = 5.4, 18 H, $\mathrm{OCH_3}$); 3.1 (s, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2C}\mathit{H}_3$), *trans*
7	7.8–7.6 (m, 10 H, Ph); 3.9 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$); 3.7 (d, $J_{P\text{-}H}$ = 10.0, 9 H, $\mathrm{OCH_3}$), *cis*; 7.6–7.4 (m, 10 H, Ph); 3.6 (t, $J_{P\text{-}H}$ = 5.4, 18 H, $\mathrm{OCH_3}$), *trans*
8	7.5 (m, 5 H, $\mathrm{CH_3C_2}\mathit{Ph}$); 3.7 (d, $J_{P\text{-}H}$ = 11.9, 9 H, $\mathrm{OCH_3}$); 3.4 (d, $J_{P\text{-}H}$ = 9.3, 9 H, $\mathrm{OCH_3}$); 3.2 (s, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$), *cis*; 7.4 (m, 5 H, $\mathrm{CH_3C_2}\mathit{Ph}$); 3.5 (m, 18 H, $\mathrm{OCH_3}$); 3.0 (s, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$), *trans*
9	3.95 (m, 12 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$); 3.1 (t, $J_{H\text{-}H}$ = 1.0, 6 H, $\mathrm{C_2C}\mathit{H}_3$); 1.35 (m, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *cis*; 3.85 (m, 12 H, $\mathrm{OCH_2C}\mathit{H}_3$); 2.9 (s, 6 H, $\mathrm{C_2CH_3}$); 1.15 (t, $J_{H\text{-}H}$ = 5.4, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *trans*
10	7.6–7.3 (m, 10 H, Ph); 4.15 (m, 12 H, $\mathrm{OCH_2}$); 1.3 (m, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *cis*; 7.3–6.9 (m, 10 H, Ph); 3.95 (m, 12 H, $\mathrm{OCH_2}$); 1.15 (m, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *trans*
11	4.3 (m, 12 H, $\mathrm{OCH_2C}\mathit{H}_3$); 2.9 (s, 6 H, $\mathrm{C_2C}\mathit{H}_3$); 1.4 (t, $J_{P\text{-}H}$ = 7.0, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *cis*; 4.0 (m, 12 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$); 3.1 (t, $J_{H\text{-}H}$ = 2.1, 6 H, $\mathrm{C_2CH_3}$); 1.2 (t, $J_{P\text{-}H}$ = 7.0, 18 H, $\mathrm{OCH_2CH_3}$), *trans*
12	7.6–7.4 (m, 5 H, $\mathrm{CH_3C_2}\mathit{Ph}$); 4.0 (m, 12 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$); 3.3 (m, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$); 1.4 (m, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *cis*; 7.4–7.2 (m, 5 H, $\mathrm{CH_3C_2}\mathit{Ph}$); 3.9 (m, 12 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$); 3.2 (m, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$); 1.2 (m, 18 H, $\mathrm{OCH_2C}\mathit{H}_3$), *trans*
13	4.4–4.2 {m, 6 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$}; 3.0 (s, 6 H, $\mathrm{C_2CH_3}$); 1.9 {m, $J_{P\text{-}H}$ = 6.4, 36 H, $\mathrm{OCH(C}\mathit{H}_3)_2$}
14	7.5–6.8 (m, 10 H, Ph); 4.7–4.5 {m, 6 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$}; 1.3–1.1 (m, 36 H, $\mathrm{OCH(C}\mathit{H}_3)_2$)
15	4.7 {m, 6 H, $\mathrm{OC}\mathit{H}(\mathrm{C}\mathit{H}_3)_2$}; 3.1 (s, 6 H, $\mathrm{C_2CH_3}$); 1.2 {d, $J_{P\text{-}H}$ = 7.7, 36 H, $\mathrm{OCH(C}\mathit{H}_3)_2$}
16	7.4 (m, 5 H, $\mathrm{CH_3C_2}\mathit{Ph}$); 4.7 {m, 6 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$}; 3.2 (s, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{C_2Ph}$); 1.2 {m, 36 H, $\mathrm{OCH(C}\mathit{H}_3)_2$}
17	4.2 (m, 12 H, $\mathrm{OCH_2}$); 2.9 (s, 6 H, $\mathrm{C_2CH_3}$); 1.5–1.3 (m, 24 H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$); 0.95 (m, 18 H, $\mathrm{CH_3}$)
18	7.7–7.4 (m, 10 H, Ph); 4.1 (m, 12 H, $\mathrm{OCH_2}$); 1.5 (m, 24 H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$); 0.9 (m, 18 H, $\mathrm{CH_3}$)

[a] Spectra recorded in $\mathrm{CDCl_3}$ (+25 °C) and referenced to $\mathrm{SiMe_4}$; br = broad, d = doublet, m = multiplet, s = singlet.

Table 4 ^{31}P NMR Data (δ, J/Hz)[a] for the phosphite alkyne complexes of molybdenum(II) and tungsten(II) **1**–**18**

Complex	
1	134.0 {s, $\mathrm{P(OPh)_3}$}
2	84.1 {s, $\mathrm{P(OPh)_3}$}
3	111.70 {s, $\mathrm{P(OPh)_3}$}
4	127.3 {s, $\mathrm{P(OPh_3)}$}, *trans*
5	131.4 {d, $J_{P\text{-}P}$ = 46.5, $\mathrm{P(OMe)_3}$}, *cis*; 121.6 {d, $J_{P\text{-}P}$ = 46.5, $\mathrm{P(OMe)_3}$}, *cis*; 117.1 {s, $\mathrm{P(OMe)_3}$}, *trans*
6	110.7 {d, $J_{P\text{-}P}$ = 29.4, $\mathrm{P(OMe)_3}$}, *cis*; 104.1 {d, $J_{P\text{-}P}$ = 29.4, $\mathrm{P(OMe)_3}$}, *cis*; 105.5 {s, $\mathrm{P(OMe)_3}$}, *trans*
7	126.5 {d, $J_{P\text{-}P}$ = 42.2, $\mathrm{P(OMe)_3}$}, *cis*; 118.7 {d, $J_{P\text{-}P}$ = 42.2, $\mathrm{P(OMe)_3}$}; *cis*; 114.9 {s, $\mathrm{P(OMe)_3}$}, *trans*
8	110.3 {d, $J_{P\text{-}P}$ = 28.9, $\mathrm{P(OMe)_3}$}, *cis*; 102.2 {d, $J_{P\text{-}P}$ = 28.9, $\mathrm{P(OMe)_3}$}, *cis*; 104.1 {s, $\mathrm{P(OMe)_3}$}; *trans*
9	129.2 {d, $J_{P\text{-}P}$ = 47.7, $\mathrm{P(OEt)_3}$}, *cis*; 116.4 {d, $J_{P\text{-}P}$ = 47.7, $\mathrm{P(OEt)_3}$}, *cis*; 111.0 {s, $\mathrm{P(OEt)_3}$}, *trans*
10	123.4 {d, $J_{P\text{-}P}$ = 44.0, $\mathrm{P(OEt)_3}$}, *cis*; 114.0 {d, $J_{P\text{-}P}$ = 44.0, $\mathrm{P(OEt)_3}$}, *cis*; 110.3 {s, $\mathrm{P(OEt)_3}$}, *trans*
11	109.4 {d, $J_{P\text{-}P}$ = 30.4, $\mathrm{P(OEt)_3}$}, *cis*; 98.7 {d, $J_{P\text{-}P}$ = 30.4, $\mathrm{P(OEt)_3}$}, *cis*; 100.5 {s, $\mathrm{P(OEt)_3}$}, *trans*
12	108.6 {d, $J_{P\text{-}P}$ = 34.4, $\mathrm{P(OEt)_3}$}, *cis*; 97.3 {d, $J_{P\text{-}P}$ = 34.4, $\mathrm{P(OEt)_3}$}, *cis*; 99.5 {s, $\mathrm{P(OEt)_3}$}, *trans*
13	109.0 {s, $\mathrm{P(O^iPr)_3}$}, *trans*
14	105.5 {s, $\mathrm{P(O^iPr)_3}$}, *trans*
15	94.8 {s, $J_{W\text{-}P}$ = 211.0, $\mathrm{P(O^iPr)_3}$}, *trans*
16	94.4 {s, $J_{W\text{-}P}$ = 208.2, $\mathrm{P(O^iPr)_3}$}, *trans*
17	127.4 {s, $\mathrm{P(O^nBu)_3}$}, *trans*
18	78.6 {s, $\mathrm{P(O^nBu)_3}$}, *trans*

[a] Spectra recorded in $\mathrm{CDCl_3}$ at +25 °C, referenced to 85% $\mathrm{H_3PO_4}$.

M = W (ref. 17)}), which due to the larger "cone angle"[21] of $\mathrm{P(OPh)_3}$ rapidly rearranges *via* a trigonal twist mechanism to the thermodynamically more stable *trans* isomer (Fig. 4). The proposed mechanism for these steps in the addition of 1 and 2 equivalents of $\mathrm{P(OPh)_3}$ to $\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ is shown in Scheme 1. The mechanism for the reaction of the tungsten complexes $\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]}$ with $\mathrm{P(OR')_3}$ is different, and most likely goes *via* the bis(alkyne) intermediates $\mathrm{[WI_2(CO)\{P(OR')_3\}(\eta^2\text{-}RC_2R)_2]}$.[17] The ^{1}H and ^{31}P NMR spectra of **1**–**3** all conform with the structures shown in Figs. 1–3.

Reaction of $\mathrm{[MI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2]}$ with two equivalents of $\mathrm{P(OR)_3}$ in diethyl ether at room temperature affords high yields of the bis(phosphite) complexes $\mathrm{[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]}$ **4**–**18** {M = Mo, R = Ph, R′ = Me, R″ = Ph; M = Mo or W, R = Me, R′ = R″ = Me or Ph (M = Mo only); R′ = Me, R″ = Ph (M = W only); R = Et, R′ = R″ = Me or Ph (M = Mo only); R′ = Me, R″ = Ph (M = W only); R = ^{i}Pr, R′ = R″ = Me or Ph (M = Mo only), R′ = Me, R″ = Ph (M = W only); M = Mo, R = ^{n}Bu, R′ = R″ = Me or Ph} in high yield. All complexes have been fully characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy (Table 2), ^{1}H and ^{31}P NMR spectroscopy (Tables 3 and 4) and in selected cases by ^{13}C NMR spectroscopy (Table 7). The crystal structures of six of the complexes $\mathrm{[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]}$ {M = Mo, R = Me or ^{i}Pr, R′ = R″ = Me; R = Ph, R′ = Me, R″ = Ph; M = W, R = Et or ^{i}Pr, R′ = R″ = Me; R′ = Me, R″ = Ph} have been determined. The complexes are all air-sensitive in solution, but can be stored under an inert $\mathrm{N_2}$ atmosphere for several months at −17 °C. They are extremely soluble in $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$, and soluble in diethyl ether. The preparations in this paper differ from the closely related synthesis of $\mathrm{[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R')]}$ (R = Me, Et, ^{i}Pr or ^{n}Bu; R′ = Me, Ph)[17] in that the previous syntheses were carried out in $\mathrm{CH_2Cl_2}$, whereas here they are carried out in diethyl ether. This procedure enabled growth of suitable single crystals for X-ray analysis.

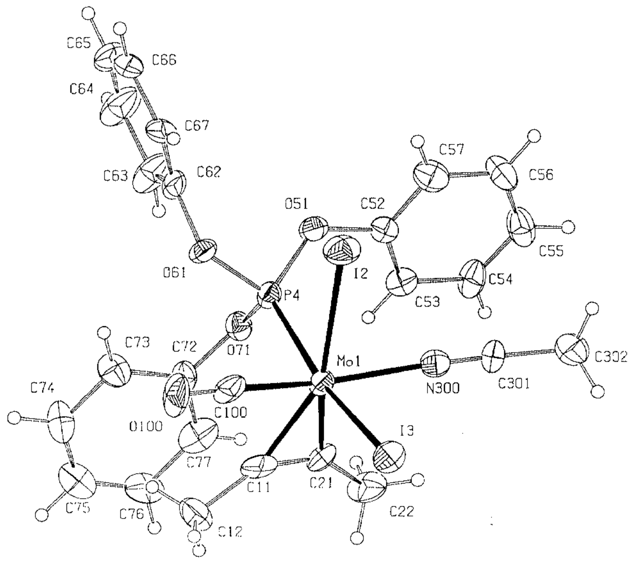


Fig. 1 An ORTEP[18] diagram showing the structure of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Me)]$ **1** and the atom numbering scheme.

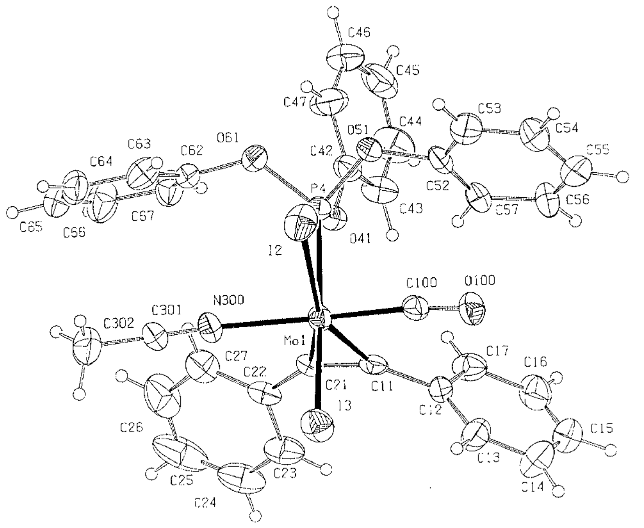


Fig. 2 An ORTEP diagram showing the structure of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}PhC_2Ph)]$ **2** and the atom numbering scheme.

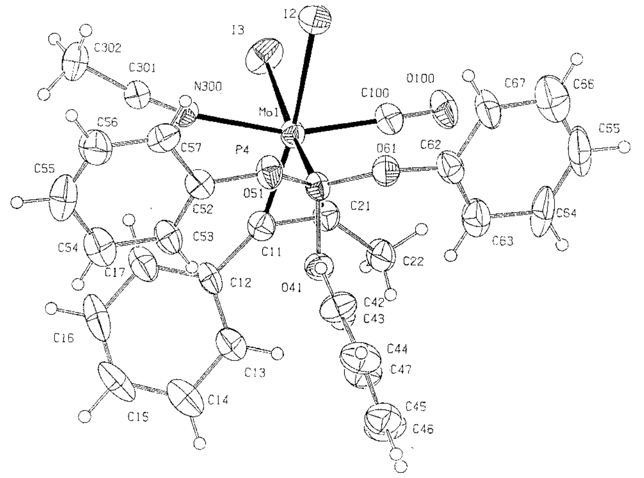


Fig. 3 An ORTEP diagram showing the structure of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Ph)]$ **3** and the atom numbering scheme.

Suitable single crystals for X-ray crystallography were generally grown by cooling (−17 °C) concentrated diethyl ether solutions of **4**, **5**, **11**, **13**, **15** and **16** for 24 h. The molecular structures of **4**, **5**, **11**, **13** (which is equivalent to the structure of **15** not shown) and **16** are shown in Figs. 4–8, together with their atom numbering schemes. The structure of *cis*-$[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ **5** is similar to the previously reported[17] structure of the exact tungsten analogue, *cis*-$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$. It is interesting that once the mother-liquor was removed from the green crystals of **5** small brown crystals not good enough for X-ray crystallography were grown, which are very likely to be the *trans* isomer. This also occurs with the tungsten analogue:[17] a green solution from purple *cis* gives small green crystals which were unsuitable for X-ray crystallography.

Dimensions in the structures of complexes **4**, **11**, **13**, **15**, **16**, and **5** are listed in Table 5. In **4**, **11**, **13**, **15** and **16** the two phosphite ligands are mutually *trans*, while in **5** they are mutually *cis*. The five structures with *trans*-phosphites are all similar with an alkyne *trans* to one iodide and the carbonyl groups *trans* to the other iodide. However, in all these examples the structures of the molecules are compatible with C_2 symmetry, apart from the substituted alkyne, and the carbonyl group. In **13** and **15** this symmetry is imposed crystallographically. However in **4**, **11** and **16** this is not the case. In **11** there was positional disorder, but this was not apparent in **4** or **16**. The disorder proved difficult to treat because of overlapping atoms and the dimensions obtained are somewhat more inaccurate than is desirable. When the dimensions in Table 5 are compared, it should be noted that for the molecules without crystallographically imposed symmetry there are two alternative ways of numbering, and the comparison of dimensions may reflect these differences.

Owing to the disorder it is difficult to draw any detailed conclusions from these structures, other than to confirm the connectivity and the relative positions of the donor atoms. However, it is clear from the dimensions that the disposition of the alkyne group relative to the *trans* atom I(2) is not symmetrical. Thus the difference between C(11)–M–I(2) and C(11)–M–I(3) ranges from 15 to 36°. The angles subtended at the metal by the two phosphorus atoms in all structures are within 10.5° of 180°, while the angle between the carbonyl group and I(2) ranges from 158(2) to 168(2)°. It is significant that the disorder between carbonyl groups and alkyne occurs for both 2-butyne and 1-phenyl-1-propyne indicating that the phenyl group has little effect on the geometry of the coordination sphere. However, we did not determine a structure containing diphenylacetylene and the bulk of this ligand may well have produced a more ordered structure.

In these examples there was no discernible difference in structure between examples when R = Et, ^{i}Pr or Ph. However, with R = Me as in **5**, a different configuration was found with the phosphite ligands mutually *cis* and this is shown in Fig. 5. One phosphorus atom P(4) is *trans* to an iodide I(2), and forms a shorter bond to the metal, 2.469(3) Å, than the phosphorus atom P(7) *trans* to carbonyl, 2.516(3) Å. The iodide I(3) *trans* to the alkyne group forms a longer bond than I(2) *trans* to phosphorus {2.849(2), 2.823(2) Å}. The dimensions are generally as expected. Unlike the *trans* examples, there is no sign of disorder in this structure. It is interesting that this compound is isomorphous with the tungsten analogue,[17] but it is not apparent why the phosphite with R = methyl has a different structure from R = ethyl, isopropyl or phenyl in which the phosphite groups are *trans*. It may be that the "cone angle"[21] of R = Et, ^{i}Pr or Ph is larger compared to R = Me in these complexes.

The IR spectra of complexes **5**, **7**, **8**, **9**, **10**, **11** and **12** all showed two carbonyl stretching bands, and it is very likely the higher wavenumber band will be due to that of the *cis* isomer. In this case the carbonyl ligand is *trans* to a strong π-acceptor phosphite ligand, whereas in the *trans*-phosphite complexes the carbonyl group is *trans* to an iodo-group. The rapidly obtained IR spectrum ($CHCl_3$) of single crystals of the complex *cis*-$[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ **5** displayed a single band at 2001 cm^{-1}, due to the *cis* isomer, whereas a rapidly obtained

Table 5 Dimensions (bond lengths in Å angles in °) in the co-ordination spheres of the metal complexes

	1a	**1b**	**2**	**3**
Mo(1)–C(100)	1.979(15)	2.025(14)	1.988(13)	1.983(13)
Mo(1)–C(21)	2.019(12)	2.026(14)	2.046(10)	2.026(13)
Mo(1)–C(11)	2.074(13)	2.032(11)	2.052(11)	1.989(13)
Mo(1)–N(300)	2.218(11)	2.191(11)	2.193(10)	2.223(11)
Mo(1)–P(4)	2.477(4)	2.472(4)	2.471(4)	2.471(4)
Mo(1)–I(3)	2.818(3)	2.821(3)	2.794(3)	2.811(3)
Mo(1)–I(2)	2.851(3)	2.853(3)	2.853(3)	2.839(2)
C(100)–Mo(1)–C(21)	110.6(6)	110.7(5)	112.6(4)	111.7(5)
C(100)–Mo(1)–C(11)	71.6(6)	73.9(7)	75.1(5)	72.5(5)
C(21)–Mo(1)–C(11)	38.4(5)	37.0(5)	37.6(4)	39.2(5)
C(100)–Mo(1)–N(300)	166.0(5)	167.6(5)	160.7(4)	160.9(5)
C(21)–Mo(1)–N(300)	83.0(4)	81.3(5)	85.0(4)	86.7(4)
C(11)–Mo(1)–N(300)	121.0(5)	117.9(5)	121.7(4)	125.6(4)
C(100)–Mo(1)–P(4)	91.8(4)	89.3(4)	93.4(4)	94.5(4)
C(21)–Mo(1)–P(4)	89.3(4)	92.2(4)	88.4(3)	84.5(3)
C(11)–Mo(1)–P(4)	91.8(3)	95.5(3)	93.2(3)	88.6(4)
N(300)–Mo(1)–P(4)	93.8(3)	92.9(3)	94.8(3)	92.2(3)
C(100)–Mo(1)–I(3)	87.9(4)	90.3(4)	84.8(4)	85.4(4)
C(21)–Mo(1)–I(3)	102.2(3)	97.7(4)	103.3(3)	103.4(3)
C(11)–Mo(1)–I(3)	99.6(3)	94.6(3)	97.9(3)	99.3(4)
N(300)–Mo(1)–I(3)	83.9(3)	85.3(3)	83.5(3)	85.3(3)
P(4)–Mo(1)–I(3)	167.83(9)	169.52(9)	167.92(8)	171.68(8)
C(100)–Mo(1)–I(2)	84.3(4)	85.2(4)	82.0(3)	82.2(4)
C(21)–Mo(1)–I(2)	161.5(4)	162.0(4)	160.1(3)	159.0(3)
C(11)–M(1)–I(2)	153.7(4)	158.5(4)	154.5(3)	150.7(4)
N(300)–Mo(1)–I(2)	84.2(3)	85.3(3)	83.0(3)	81.6(3)
P(4)–Mo(1)–I(2)	78.22(9)	79.21(9)	76.83(9)	78.62(11)
I(3)–Mo(1)–I(2)	89.66(6)	90.32(5)	91.10(6)	93.10(9)

		11[a] (M = W)					
	4 (M = Mo)	a	b	c	**13**[b] (M = Mo)	**15**[b] (M = W)	**16** (M = W)
M(1)–C(21)	1.92(4)	1.987(18)	2.009(18)	1.99(3)	1.941(19)	1.929(16)	1.961(19)
M(1)–C(100)	1.96(3)	2.027(17)	2.018(17)	2.019(17)	2.030(13)	2.079(13)	1.932(19)
M(1)–C(11)	1.85(5)	2.021(18)	2.023(18)	1.999(19)	1.991(16)	1.959(12)	2.091(18)
M(11)–P(4)	2.505(8)	2.497(11)	2.495(12)	2.496(15)	2.545(4)	2.528(2)	2.511(7)
M(1)–P(4′)[c]	2.523(8)	2.570(11)	2.545(11)	2.545(16)	2.545(4)	2.528(2)	2.569(6)
M(1)–I(2)	2.833(5)	2.831(4)	2.842(4)	2.836(5)	2.891(2)	2.875(1)	2.847(3)
M(1)–I(2′)[d]	2.844(4)	2.883(4)	2.873(4)	2.891(5)	2.891(2)	2.875(1)	2.890(4)
C(21)–M(1)–C(100)	115.0(14)	109.2(16)	106.6(18)	106(3)	105.1(11)	108.0(9)	110.1(8)
C(21)–M(1)–C(11)	43.0(9)	38.1(6)	37.8(7)	38.6(7)	38.9(7)	38.1(5)	38.7(7)
C(100)–M(1)–C(11)	72.2(15)	71.3(16)	68.8(11)	68(3)	66.9(10)	69.9(8)	71.9(7)
C(21)–M(1)–P(4)	98.5(12)	101.4(16)	95.7(14)	94(3)	100.8(8)	94(2)	85.4(7)
C(100)–M(1)–P(4)	88.1(9)	85.0(16)	88.1(15)	86(3)	93(2)	96.5(9)	92.6(7)
C(11)–M(1)–P(4)	94.9(15)	94.4(16)	93.2(17)	91(2)	96(2)	95.9(15)	93.3(6)
C(21)–M(1)–P(4′)	85.2(12)	81.7(16)	87.5(14)	90(3)	83.7(8)	90(2)	105.0(7)
C(100)–M(1)–P(4′)	95.5(9)	96.2(16)	92.5(15)	96(3)	90(2)	86.3(9)	85.8(7)
C(11)–M(1)–P(4′)	91.7(15)	89.6(16)	90.2(17)	94(2)	91(2)	90.3(15)	96.1(6)
P(4)–M(1)–P(4′)	173.2(3)	176.1(2)	176.5(3)	174.5(7)	173.7(2)	173.7(1)	169.43(18)
C(21)–M(1)–I(2)	165.5(11)	168.5(15)	172.2(13)	170.9(15)	171.1(8)	178(2)	165.3(6)
C(100)–M(1)–I(2)	76.7(9)	72.9(14)	76.8(15)	82(2)	72.8(6)	71.9(6)	80.1(5)
C(11)–M(1)–I(2)	148.2(13)	143.3(10)	143.1(10)	149.2(14)	139.6(7)	141.8(5)	151.7(5)
P(4)–M(1)–I(2)	90.2(2)	89.9(2)	91.4(2)	90.4(3)	87.9(2)	87.7(2)	83.61(14)
P(4′)–M(1)–I(2)	85.1(2)	86.9(2)	85.4(2)	84.9(4)	87.7(2)	87.9(2)	85.82(14)
C(21)–M(1)–I(2′)	83.5(11)	92.6(9)	90.4(9)	86.9(13)	91.2(6)	90.6(5)	84.4(6)
C(100)–M(1)–I(2′)	160.9(8)	157.7(14)	162.9(13)	165(2)	163.2(6)	160.5(6)	164.6(5)
C(11)–M(1)–I(2′)	126.0(13)	130.0(9)	128.1(9)	125.0(14)	129.8(7)	128.7(5)	121.5(5)
P(4)–M(1)–I(2′)	84.8(2)	91.0(2)	88.1(2)	86.0(4)	87.7(2)	87.9(2)	94.03(16)
P(4′)–M(1)–I(2′)	90.0(2)	86.5(2)	90.3(2)	90.4(3)	87.9(2)	87.7(2)	85.12(14)
I(2)–M(1)–I(2′)	85.65(16)	86.6(1)	86.6(1)	85.8(2)	90.4(1)	89.38(4)	86.74(6)

5

Mo(1)–C(100)	2.010(10)	C(100)–Mo(1)–C(21)	111.7(5)	C(21)–Mo(1)–P(7)	78.9(3)	P(7)–Mo(1)–I(2)	88.43(6)
Mo(1)–C(21)	2.022(9)	C(100)–Mo(1)–C(11)	73.6(5)	C(11)–Mo(1)–P(7)	117.1(4)	C(100)–Mo(1)–I(3)	82.2(4)
Mo(1)–C(11)	2.027(10)	C(21)–Mo(1)–C(11)	38.2(4)	P(4)–Mo(1)–P(7)	90.27(8)	C(21)–Mo(1)–I(3)	161.5(3)
Mo(1)–P(4)	2.469(3)	C(100)–Mo(1)–P(4)	93.9(3)	C(100)–Mo(1)–I(2)	85.2(3)	C(11)–Mo(1)–I(3)	151.2(3)
Mo(1)–P(7)	2.516(3)	C(21)–Mo(1)–P(4)	88.8(3)	C(21)–Mo(1)–I(2)	103.6(3)	P(4)–Mo(1)–I(3)	77.79(10)
Mo(1)–I(2)	2.823(2)	C(11)–Mo(1)–P(4)	88.4(3)	C(11)–Mo(1)–I(2)	103.7(3)	P(7)–Mo(1)–I(3)	88.40(8)
Mo(1)–I(3)	2.849(2)	C(100)–Mo(1)–P(7)	168.7(4)	P(4)–Mo(1)–I(2)	167.03(7)	I(2)–Mo(1)–I(3)	89.27(9)

[a] Disordered without crystallographic symmetry. Dimensions of one structure only are given. [b] Disordered with crystallographic symmetry. [c] P(7) in complexes **4** and **16**. [d] I(3) in complexes **4** and **16**.

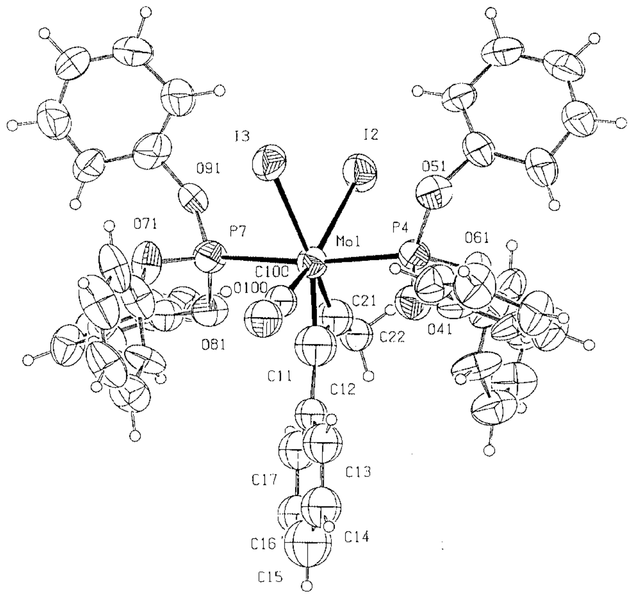
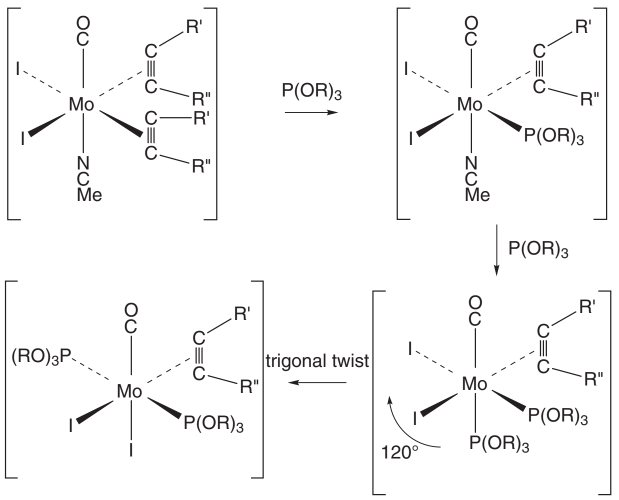


Fig. 4 An ORTEP diagram showing the structure of *trans*-[$MoI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}MeC_2Ph)$] **4** and the atom numbering scheme.



Scheme 1 Proposed mechanism for the stepwise reaction of two equivalents of $P(OR)_3$ with [$MoI_2(CO)(NCMe)(\eta^2\text{-}R'C_2R'')_2$] (R = Ph, R′ = Me, R″ = Ph).

IR ($CHCl_3$) of single crystals of *trans*-[$MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)$] **9** showed a single band at 1970 cm^{-1} due to the *trans* isomer. The complexes with the larger phosphite {$P(OR)_3$} ligands, R =^{i}Pr, ^{n}Bu or Ph, all showed only one carbonyl band in their spectra (Table 2) due to the *trans* isomer. This was confirmed by the ^{31}P NMR studies discussed later.

The ^1H NMR data (Table 3) of complexes **4**–**18** generally conform with the structures of selected complexes shown. In order to investigate the barrier to 2-butyne rotation of [$MoI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}MeC_2Me)$] {R = Me **5**, or Et **9**} variable temperature ^1H NMR studies were carried out. The ^1H NMR spectra were obtained from single crystals of the *cis* isomers of complexes **5** and **9** dissolved in $CDCl_3$, soon after dissolution. The ^1H NMR spectra of the 2-butyne methyl groups at different temperatures of **9** are shown in Fig. 9. The barriers to 2-butyne rotation of **5** and **9** were calculated,[22–24] to be $\Delta G^{\ddagger} = 54.7$ ($T_c = 263$ K, $\Delta\nu = 34.5$ Hz) and 56.9 ($T_c = 274$ K, $\Delta\nu = 33.6$ Hz) kJ mol^{-1} respectively. These values are similar as expected, to that of the previously reported[17] crystallographically characterised tungsten complex, *cis*-[$WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)$] which has $\Delta G^{\ddagger} = 55.3$ kJ mol^{-1}. Since the ligand cone angles[21] of $P(OR)_3$ are 107° for R = Me, and 109° for R = Et, very similar, it would not be expected that these values would differ significantly.

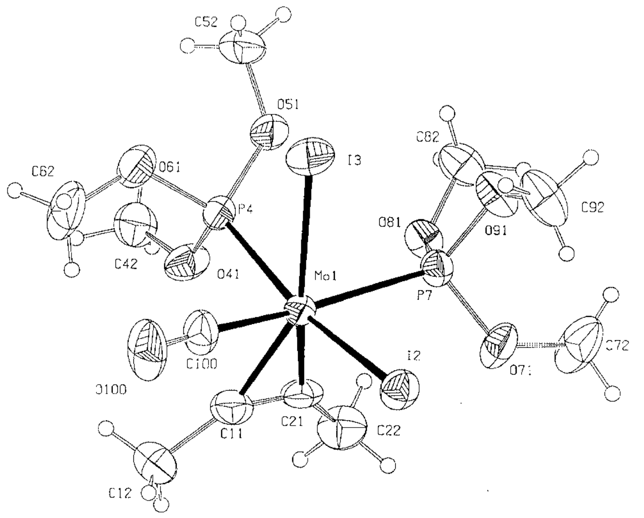


Fig. 5 An ORTEP diagram showing the structure of *cis*-[$MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)$] **5** and the atom numbering scheme.

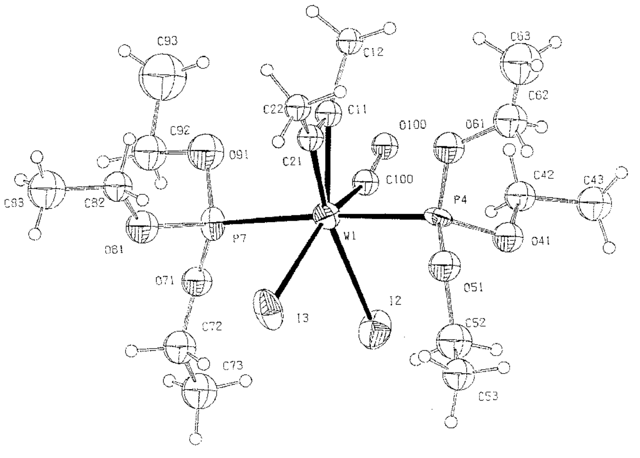


Fig. 6 An ORTEP diagram showing the structure of *trans*-[$WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)$] **11** and the atom numbering scheme.

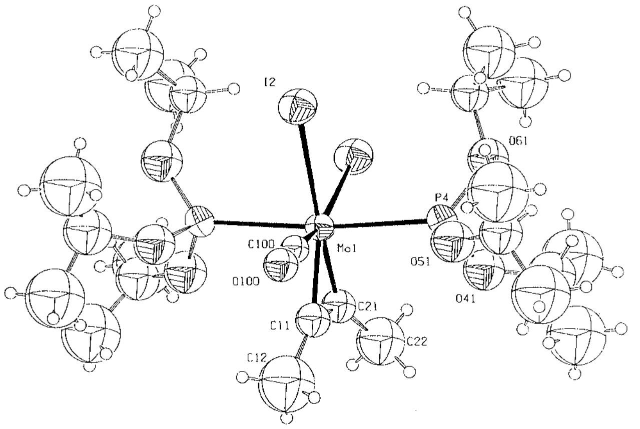


Fig. 7 An ORTEP diagram showing the structure of *trans*-[$MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)$] **13** and the atom numbering scheme. This structure is equivalent to that of *trans*-[$WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)$] **15**.

We have also used the integral ratios in the ^1H NMR spectra of three series of complexes described here to give the *cis*:*trans* isomer ratio of the phosphites in [$MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')$]. For the series of 2-butyne complexes, [$MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}MeC_2Me)$], the *cis*:*trans* isomer ratios are, 80:20 (R = Me), 40:60 (R = Et) and 0:100 (R = ^{i}Pr). The values for the analogous molybdenum and tungsten complexes are as expected very similar. For the 1-phenyl-1-propyne complexes, [$WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}MeC_2Ph)$], ratios are 75:25

Table 6 Crystal data and structure refinement for the complexes

	1	**2**	**3**	**4**	**5**	**11**	**13**	**15**	**16**	
Empirical formula	$C_{25}H_{24}I_2MoN_3O_4P$	$C_{35}H_{28}I_2MoNO_4P$	$C_{32.5}H_{34}I_2MoNO_{5.5}P$	$C_{46}H_{36}I_2MoO_7P_2$	$C_{11}H_{24}I_2MoNO_7P_2$	$C_{17}H_{36}I_2WO_7P_2$	$C_{23}H_{48}I_2MoO_7P_2$	$C_{23}H_{48}I_2O_7P_2W$	$C_{29}H_{44}I_2O_6P_2W$	$C_{27}H_{24}$
Formula weight	784.16	907.13	893.31	1111.42	679.98	852.48	848.29	936.20	988.23	348.46
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, Cc	Orthorhombic, $Pbcn$	Monoclinic, Cc	Orthorhombic, $P2_12_12$	Orthorhombic, $P2_12_12$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a/Å	14.738(16)	10.439(12)	12.121(13)	18.08(2)	20.52(2)	11.133(12)	14.116(15)	14.079(15)	12.498(14)	11.631(14)
b/Å	13.392(15)	11.186(14)	15.702(17)	11.581(17)	15.400(17)	40.22(5)	14.142(15)	14.072(15)	16.916(17)	11.290(14)
c/Å	14.581(17)	16.110(17)	20.38(2)	23.65(3)	14.286(16)	19.49(2)	9.143(12)	9.146(12)	18.95(2)	15.645(17)
α/°		89.76(1)								
β/°	92.07(1)	73.93(1)	106.26(1)	112.47(1)		93.81(1)			97.94(1)	99.64(1)
γ/°		77.10(1)								
V/Å^3	1506	1759	3723	4575	4514	8710	1825	1812	3969	2025
Z, D_c/mg m^{-3}	4, 1.811	2, 1.713	4, 1.594	4, 1.614	8, 2.001	12, 1.949	2, 1.544	2, 1.716	4, 1.654	4, 1.143
μ/mm^{-1}	2.688	2.211	2.089	1.754	3.482	6.240	2.170	5.011	4.579	0.064
F(000)	1506	880	1744	2180	2592	4848	840	904	1904	744
Reflections collected/unique (R_{int})	9497/9360 (0.0290)	5681/5681	11072/6779 (0.0649)	5649/3702 (0.0763)	12203/4198 (0.0936)	12756/8573 (0.0762)	4922/3299 (0.0961)	5550/3325 (0.0399)	10016/6193 (0.0741)	6329/3623 (0.0502)
Data/restraints/parameters	9360/0/620	5681/0/399	6779/0/377	3702/219/446	4198/0/217	8573/65/493	3299/102/166	3335/63/166	6193/6/200	3623/0/248
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0515, 0.1375	0.0856, 0.2223	0.0926, 0.2658	0.0814, 0.2125	0.0591, 0.1749	0.1080, 0.3344	0.0651, 0.1733	0.0427, 0.1206	0.0901, 0.2215	0.0912, 0.2526
(all data)	0.0915, 0.1554	0.1155, 0.2417	0.1413, 0.2996	0.1771, 0.2693	0.0807, 0.1959	0.1602, 0.3847	0.0840, 0.1898	0.0456, 0.1258	0.1761, 0.2621	0.1713, 0.3101
Largest difference peak and hole/e Å^{-3}	0.820, −1.017	1.474, −1.232	1.618, −1.463	1.077, −0.925	1.344, −1.031	5.83, −4.51	0.672, −0.798	1.107, −1.202	2.822, −1.618	0.146, −0.164

(R = Me), 33 : 67 (R = Et) and 0 : 100 (R = ^{i}Pr). The large cone angle[21] for R = ^{i}Pr is 128°, and this pushes the phosphites into a *trans* configuration. There is, as expected, an increase in the proportion of *trans* isomer in solution as we go across the series R = Me < Et < ^{i}Pr ≈ Ph. This is in accord with the IR results, and is expected on steric grounds.

The ^{31}P-{^{1}H} NMR data (CDCl$_3$, 25 °C) in Table 4 also show either a mixture of *cis* (two doublets) and *trans* (singlet) isomers in solution for the smaller cone angle[21] phosphites, P(OR)$_3$ (R = Me and Et), whereas for the larger phosphite ligands, (R = ^{i}Pr, ^{n}Bu or Ph) only a singlet due to the *trans* isomer is observed. This is in accord with the IR and ^{1}H NMR results discussed above.

The ^{13}C NMR data (Table 7) for complexes **8**, **12** and **16** all show alkyne contact carbon resonances at $\delta > 200$, which suggests from Templeton and Ward's correlation[1] of the number of electrons donated by an alkyne ligand and the alkyne contact carbon chemical shift that the alkyne is donating four electrons to the metal in these complexes. This also enables the complexes to obey the effective atomic number rule.

Finally, preliminary studies of the reaction of [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Ph)$_2$] with two equivalents of P(O^{i}Pr)$_3$ in diethyl ether at room temperature gave the trimer 1,2,4-trimethyl-3,5,6-triphenylbenzene. A suitable single crystal of the arene was grown by cooling (−17 °C) the reaction mixture for several days. The structure is shown in Fig. 10. The dimensions are as expected. The central phenyl ring is planar within experimental error with the three substituent phenyl rings making angles of 87.5, 74.3 and 76.4°. We are currently exploring the trimerisation of a wide range of alkynes by these and related complexes.

In conclusion we have observed how the reactions of [MI$_2$(CO)(NCMe)(η^2-R′C$_2$R″)$_2$] with phosphite ligands are very dependent on both the metal and the substituents on the phosphite ligands. The paper also shows the importance of solvent choice in organometallic reactions. We have also discovered a new alkyne trimerisation catalyst system, which we are continuing to study.

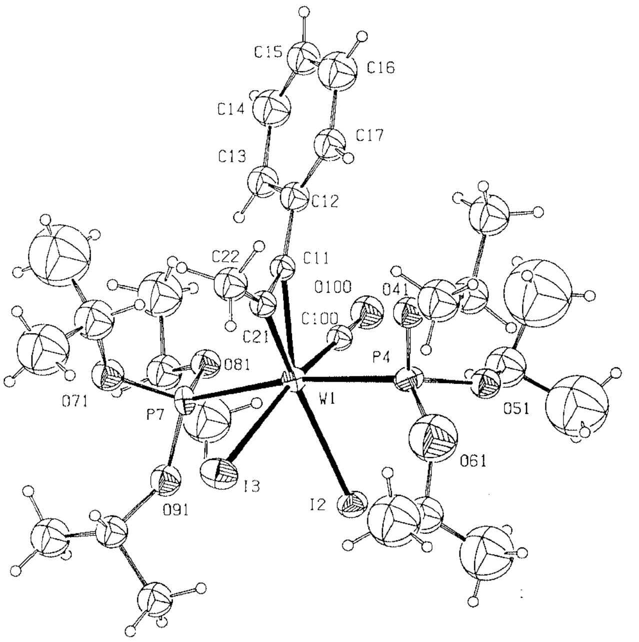


Fig. 8 An ORTEP diagram showing the structure of *trans*-[WI$_2$(CO){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Ph)] **16** and the atom numbering scheme.

Experimental

The synthesis and purification of complexes **1**–**18** were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. The starting materials [MI$_2$(CO)(NCMe)(η^2-R′C$_2$R″)$_2$] (M = W, R′ = R″ = Me or Ph; R′ = Me, R″ = Ph;[15] M = Mo, R′ = R″ = Me or Ph; R′ = Me, R″ = Ph[25]) were prepared by the published methods. All chemicals used were purchased from commercial sources. All solvents used were dried before use.

Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). The IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer, ^{1}H, ^{13}C and ^{31}P-{^{1}H} NMR spectra on a Bruker AC250 NMR spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced to SiMe$_4$, ^{31}P-{^{1}H} to 85% H$_3$PO$_4$.

Preparations

[MoI$_2$(CO)(NCMe){P(OPh)$_3$}(η^2-MeC$_2$Me)] 1. To a solution of [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (0.5 g, 0.95 mmol) in

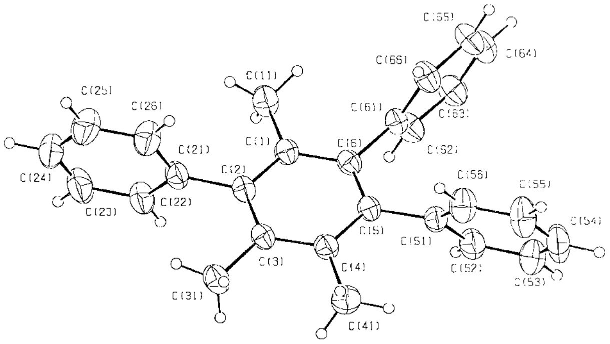


Fig. 10 An ORTEP diagram showing the structure of 1,2,4-trimethyl-3,5,6-triphenylbenzene and the atom numbering scheme.

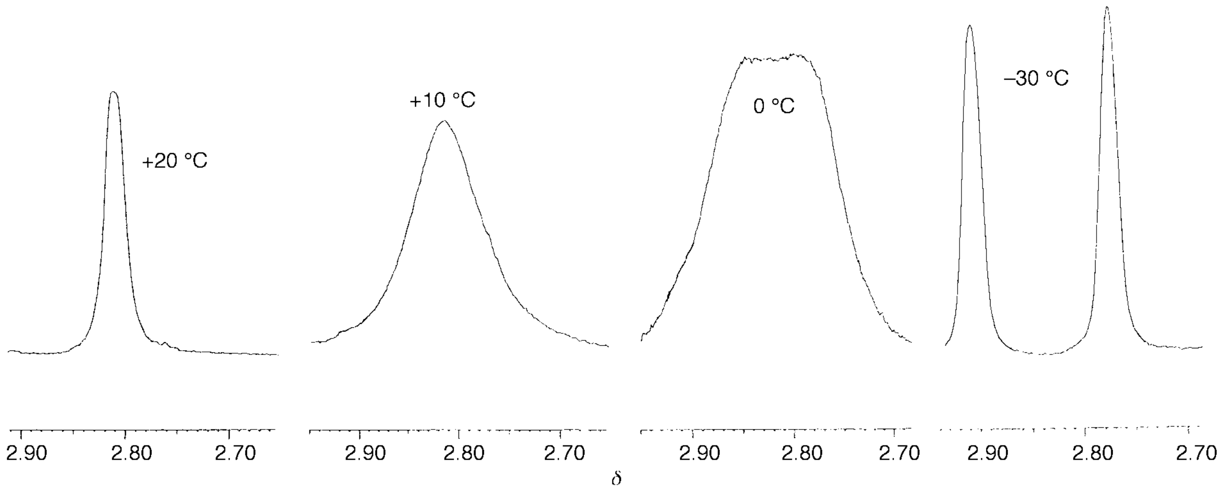


Fig. 9 The ^{1}H NMR spectra for the 2-butyne methyl groups between +20 and −30° for [MoI$_2$(CO){P(OEt)$_3$}$_2$(η^2-MeC$_2$Me)] **9**.

diethyl ether (30 cm^3) was added P(OPh)$_3$ (0.29 g, 0.25 cm^3, 0.95 mmol) and the solution stirred for 30 min. The resulting brown solution was filtered over Celite, reduced to half volume and cooled to −17 °C to yield brown crystals of [MoI$_2$(CO)(NCMe){P(OPh)$_3$}(η^2-MeC$_2$Me)] **1** suitable for X-ray crystallography. Yield = 0.68 g, 89%.

Similar reactions of [MoI$_2$(CO)(NCMe)(η^2-R′C$_2$R″)$_2$] (R′ = R″ = Ph; R′ = Me, R″ = Ph) with an equimolar quantity of P(OPh)$_3$ in diethyl ether afforded the complexes [MoI$_2$(CO)(NCMe){P(OPh)$_3$}(η^2-R′C$_2$R″)] **2** and **3**, which were also crystallographically characterised. Single crystals for X-ray crystallography were grown by cooling (−17 °C) concentrated diethyl ether solutions of **2** and **3**.

[MoI$_2$(CO){P(OPh)$_3$}$_2$(η^2-MeC$_2$Ph)] 4. To a solution of [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Ph)$_2$] (0.503 g, 0.772 mmol) in diethyl ether (30 cm^3) was added P(OPh)$_3$ (0.40 cm^3, 0.479 g, 1.554 mmol), and the solution stirred for 30 min. The resulting dark brown solution was filtered over Celite, the solvent volume reduced to half volume (15 cm^3) *in vacuo* and cooled to −17 °C to yield single crystals of [MoI$_2$(CO){P(OPh)$_3$}$_2$(η^2-MeC$_2$Ph)] **4** suitable for X-ray crystallography. Yield of pure product = 0.525 g, 61%.

[WI$_2$(CO){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)] 15. To a solution of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (2.053 g, 3.339 mmol) in diethyl ether (25 cm^3) was added P(O^{i}Pr)$_3$ (1.65 cm^3, 1.391 g, 6.678 mmol) and the solution was stirred for 30 min. The resulting dark green solution was filtered over Celite, the solvent reduced to minimum volume (5 cm^3) *in vacuo* and cooled to −17 °C to yield green single crystals of [WI$_2$(CO){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)] **15** suitable for X-ray crystallography. Yield of pure product = 2.813 g, 90%.

Similar reactions of [MI$_2$(CO)(NCMe)(η^2-R′C$_2$R″)$_2$] with two mole equivalents of P(OR)$_3$ in diethyl ether at room temperature gave the complexes **5**–**14** and **16**–**18**. Suitable single crystals for X-ray analysis for **5**, **11**, **13**, **16** were grown by cooling concentrated diethyl ether solutions of them to −17 °C for 24 h.

Reaction of [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Ph)$_2$] wtih two equivalents of P(O^{i}Pr)$_3$

To a solution of [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Ph)$_2$] (0.528 g, 0.811 mmol) in diethyl ether (30 cm^3) was added P(O^{i}Pr)$_3$ (0.4 cm^3, 0.338 g, 1.621 mmol) and the solution stirred for 30 min. The resultant dark brown solution was filtered over Celite and solvent volume reduced *in vacuo* to 10 cm^3. On cooling to −17 °C for several days single crystals of 1,2,4-trimethyl-3,5,6-triphenylbenzene were formed. To date, attempts to obtain sufficient samples of the trimerised product for analyses other than the crystal structure have been unsuccessful. However, the synthesis of the mono(triisopropyl phosphite) complex [MoI$_2$(CO)(NCMe){P(O^{i}Pr)$_3$}(η^2-MeC$_2$Ph)] is under investigation, so as to determine its catalytic ability towards the trimerisation of alkynes.

X-Ray crystallography

Crystal data for complexes **1**, **2**, **3**, **4**, **5**, **11**, **13**, **15**, **16** and 1,2,4-trimethyl-3,5,6-triphenylbenzene are given in Table 6, together with refinement details. Data for all crystals were collected at 293(2) K with Mo-Kα radiation (λ 0.71073 Å) using the MAR-research Image Plate System. The default measurement and refinement procedure is presented first while variations for specific compounds are reported later. Each crystal was positioned 70 mm from the Image Plate. Ninety five frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program.[26] The structures were solved using direct methods with the SHELXS 86 program.[27] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. Absorption corrections were carried out using the DIFABS program.[28] The structures were then refined using SHELXL.[29] All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Table 7 ^{13}C NMR Data (δ)^a for selected bis(phosphite) alkyne complexes of molybdenum(II) and tungsten(II)

Complex	
8	228.39 (s, CO); 216.93 (s, *C*≡C); 216.23 (s, C≡*C*); 130.38, 129.14, 128.60, 127.72, 126.48 (m, Ph); 54.00 (s, OMe); 25.52 (s, *Me*C$_2$Ph)
12	228.26 (s, CO); 217.99 (s, *C*≡C); 216.13 (s, C≡*C*); 130.23, 130.08, 129.14, 129.07, 128.34, 127.83, 126.35 (m, *Ph*C$_2$Me); 62.65 (s, O*C*H$_2$CH$_3$); 25.28 (s, *Me*C$_2$Ph); 16.07 (s, OCH$_2$*C*H$_3$)
16	227.85 (s, CO); 218.67 (s, *C*≡C); 215.53 (s, C≡*C*); 130.25, 129.87, 129.36, 128.94, 128.13, 127.86, 127.20 (m, *Ph*C$_2$Me); 70.99 (s, O*C*HMe$_2$); 25.36 (s, *Me*C$_2$Ph); 23.87 (s, OCH*Me*$_2$)

^{a} Spectra recorded in CDCl$_3$ (+25 °C) and referenced to SiMe$_4$.

For complex **1** there were two molecules in the asymmetric unit. Alternative structures were refined with reversed co-ordinates and that with the lowest *R* value is reported. In **3** a solvent acetone molecule was located together with a water molecule. These solvent molecules were refined with 50% occupancy. In **4** the structure was disordered. All atoms apart from the carbonyl and the 1-phenyl-1-propyne were consistent with a non-crystallographic twofold axis. It was possible that these two groups were disordered over two sites but no satisfactory disordered model could be found (unlike in **11**, see below). It proved necessary however to refine the phenyl of the alkyne as a rigid group. There was high thermal motion in the structure and oxygen and carbon atoms were refined with isotropic thermal parameters. Complex **11** contained three molecules in the asymmetric unit. The structure was close to *C*2/*c* with one molecule in an eightfold general position and one in fourfold position with an imposed twofold axis but attempts to refine in this space group proved unsuccessful. A solution in *Cc* was thus sought with three independent molecules in the asymmetric unit. As in **4** the structures were consistent with twofold symmetry apart from the carbonyl and 2-butyne moieties which were each disordered over two sites. This was treated by refining two disordered overlapping positions for each moiety. Each group was given 50% occupancy in each of two positions and the distances in each co-ordinated group were constrained. The refined model therefore had approximate twofold symmetry. Only the W, I and P atoms were refined isotropically. There were several large peaks in the Fourier-difference map, but all were very close to tungsten or iodine atoms. Complexes **13** and **15** were isomorphous and treated similarly. In both cases there was considerable doubt as to the correct space group but solutions were eventually found in orthorhombic $P2_12_12$ with merohedral (h, k, l and k, h, l) twinning. The 2-butyne and the carbonyl group were disordered over two positions, but in this case, unlike **4** and **11**, the metal occupied a crystallographic twofold axis and the 2-butyne and carbonyl group occupied equivalent positions relative to this twofold axis. The superimposed carbonyl and 2-butyne were each refined with 50% occupancy with constrained dimensions and thermal parameters. The W, I and P atoms were refined anisotropically. In **16** the structure occupied a twofold axis with concomitant disorder between the carbonyl group and the 1-phenyl-1-propyne. This was treated by distance constraints and both groups were given 50% occupancy. The structure of the arene trimer was treated in the default manner, but of course no absorption correction proved necessary.

CCDC reference number 186/1509.

See http://www.rsc.org/suppdata/dt/1999/2541/ for crystallographic files in .cif format.

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