ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 622 (2001) 228–241

Journal of Organo metallic Chemistry

3-Hexyne complexes of molybdenum(II) and tungsten(II) containing phosphite ligands: X-ray crystal structures of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ and $[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (M = Mo and W)

Mutlaq Al-Jahdali [a], Paul K. Baker [a,*], Michael G.B. Drew [b]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW, UK*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK*

Received 7 August 2000; received in revised form 27 November 2000; accepted 27 November 2000

Abstract

Equimolar quantities of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Ph, ^{i}Pr) gave the 3-hexyne displaced products, $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) and (**2**), which was crystallographically characterised for R = Ph. By contrast, reaction of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Me, ^{i}Pr, Ph) afforded the acetonitrile displaced products, $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**3** to **5**). The reactions of the mono(triphenylphosphite)molybdenum complex, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) with a series of neutral mono, bidentate and anionic dithiocarbamate ligands have been investigated to give a variety of reaction products, including $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ (**12**), which has been structurally characterised. Reaction of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with two equivalents of $P(OR)_3$ gave the mono(3-hexyne) complexes, $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ {M = Mo or W; R = Me, Et, ^{i}Pr, ^{n}Bu, Ph(for M = W only)} (**15** to **23**), which were crystallographically characterised for M = Mo and W, R = ^{i}Pr **19** and **20**, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 3-Hexyne; Phosphites; Molybdenum(II); Tungsten(II); Diiodo; Carbonyl; Crystal structures

---

1. Introduction

Halocarbonyl alkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention over the years, and two extensive review articles have been published on this area [1,2]. Although many halocarbonyl alkyne complexes containing two phosphine or phosphite ligands of the type $[MXY(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo, W; X = Cl, Br, I; R′ ,R′ = alkyl, aryl etc) have been described [3–30], few examples containing one phosphine or phosphite ligand have been reported. Some early examples are the mono(ligand) complexes, $[WI_2(CO)_2L(\eta^2\text{-}HC_2Bu^t)]$ (L = CN^{t}Bu, PMe_3, $AsMe_3$) described by Umland and Vahrenkamp in 1982 [3].

In 1999 [30], we described the preparation of the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W), and their reactions with phosphine donor ligands to give a series of bis(phosphine) complexes, including the crystallographically characterised complexes, $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$. In 1989 [31], we reported the preparation of the bis(phosphite) complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R')]$ (R = Me, Et, ^{i}Pr and ^{n}Bu; R′ = Me or Ph), which was structurally characterised for R = R′ = Me. Very recently [32], we have described the synthesis and crystallographic characterisation of 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), and also extended the series of bis(phosphite) complexes

---

* Corresponding author. Fax: +44-1248-370528.
E-mail address: chs018@bangor.ac.uk (P.K. Baker).

PII: S0022-328X(00)00926-8

$[MI_2(CO)\{P(OR)_3\}_2\eta^2\text{-}R'C_2R'')]$, including six which were crystallographically characterised. In this paper, we describe the synthesis and structural characterisation (R = Ph) for the mono(3-hexyne) complexes $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$ (R = ^{i}Pr, Ph). We also describe the chemistry of the structurally characterised complex $[MoI_2(CO(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$, to give a variety of products including the crystallographically characterised product, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$. The new 3-hexyne bis (phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (M = Mo, W; R = Me, Et, ^{i}Pr, ^{n}Bu , Ph (for M = W only)}, including M = Mo or W, R = ^{i}Pr, which were structurally characterised are also discussed.

2. Results and discussion

*2.1. The synthesis and X-ray crystal structure (R = Ph) of $[MoI_2(CO)(NCMe)(P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$ (R = Ph or ^{i}Pr) (**1**) and (**2**)*

The starting materials used in this research, $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W) were prepared by reacting the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ with 3-hexyne [30]. Reaction of equimolar quantities of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Ph or ^{i}Pr) in diethyl ether at room temperature gave the new mixed ligand complexes, $[MoI_2(CO)(NCMe)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1** and **2**) in high yield, via displacement of one of the 3-hexyne ligands. Complexes **1** and **2** have been fully characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^{1}H-, $^{13}C\{^1H\}$-NMR spectroscopy (Tables 3 and 4) and ^{31}P-NMR for complex **1** only (Table 5), and X-ray crystallography for R = Ph (complex **1**). Both complexes **1** and **2** are very soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, and also soluble in diethyl ether. The complexes are very air-sensitive in solution, but can be stored under dinitrogen for several months (−17°C) without any significant decomposition.

The IR spectra ($CHCl_3$) (Table 2) for both complexes have, as expected single carbonyl bands at 1983 and 1986 cm^{-1}, respectively. These are similar to the three closely related crystallographically characterised complexes, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}RC_2R')]$, {R = R′ = Me, $\nu(CO) = 1995\ cm^{-1}$; Ph, $\nu(CO) = 2013\ cm^{-1}$; R = Me, R′ = Ph, $\nu(CO) = 2000\ cm^{-1}$ [32]. The IR spectra of **1** and **2** also show weak nitrile bands at 2286 cm^{-1}, and alkyne stretching bands at 1646 and 1616 cm^{-1}, respectively. These alkyne stretching bands are at lower wavenumber compared to the uncoordinated 3-hexyne ligand, due to the back-donation of electron density from the filled d-orbitals to empty π^*-antibonding orbitals on the 3-hexyne ligand, which lowers the bond order and hence the alkyne stretching frequency.

A suitable single crystal of the triphenylphosphite complex, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) was grown by cooling (−17°C) a concentrated diethyl ether solution of **1** for 24 h. The structure of **1** is shown in Fig. 1. The crystal data and structure refinement for **1** are given in Table 6 and bond lengths and angles are given in Table 7. The metal environment is best considered as a distorted octahedron with the hexyne moiety occupying one site. The molybdenum atom is bonded to a carbonyl group {Mo(1)–C(200), 1.948(14) Å}, *trans* to an acetonitrile {Mo(1)–N(300), 2.212(13) Å}, and a phosphite ligand {Mo(1)–P(4), 2.485(4) Å}, *trans* to an iodide {Mo–I(2), 2.799(3) Å}. The coordination sphere is completed by the hexyne Mo(1)–C(5) 2.007(12), Mo(1)–C(4) 2.040(13) Å, *trans* to iodide {I(3) at 2.862(3) Å}. The bond from the iodide *trans* to phosphite is significantly shorter than the bond from the iodide *trans* to the hexyne, presumably because the latter bond is weakened by the trans effect.

It is probable that the reaction of the complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W) with $P(OR)_3$ proceed via an associative mechanism, as the 3-hexyne ligand can change its bonding mode from being a 4-electron to a 2-electron donor, upon addition of $P(OR)_3$. This type of associative mechanism has been previously described for this type of substitution reaction in molybdenum(II) and tungsten(II) alkyne complexes [33,34]. The $^{31}P\{^1H\}$-NMR ($CDCl_3$, +25°C) spectrum of **1** has a single resonance at $\delta = 114.44$ ppm (Table 5). The ^{1}H-NMR ($CDCl_3$, +25°C) spectrum shows the expected resonances for **1** and **2**, which is confirmed by the crystal structure that there is NCMe in the complexes at $\delta = 2.20$ and 2.05 ppm, respectively. The $^3C\{^1H\}$-NMR spectra for the complexes **1** and **2** show alkyne contact carbon resonances at $\delta = 193.0$ and 196.85 ppm, respectively, which from Templeton and Ward's [35] correlation of the alkyne contact carbon resonances to the number of electrons donated by the 3-hexyne is acting as a 4-electron donor to the molybdenum centre. This also conforms with complexes **1** and **2** obeying the effective atomic number rule.

*2.2. The synthesis and characterisation of the bis(3-hexyne) tungsten complexes $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (R = Me, ^{i}Pr and Ph) (**3**–**5**)*

Treatment of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $P(OR)_3$ (R = Me, ^{i}Pr or Ph) in diethyl ether at r.t. gave the acetonitrile replaced bis(3-hexyne) complexes, $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**3**–**5**) in high yield. Complexes **3**–**5** have been fully characterised by elemental analysis (Table 1), IR (Table 2), ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy (Tables 3 and 5). Complex **4** was also characterised by $^{13}C\{^1H\}$-NMR spectroscopy (Table 4).

The solubilities and air stabilities of **3**–**5** are similar to complexes **1** and **2**. They are slightly more soluble and stable than **1** and **2**. This differing reactivity of the molybdenum and tungsten complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $P(OR)_3$ is not unexpected, as we have previously observed similar differences. For example, reaction of equimolar amounts of $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and 2,2′-bipy(bipy) gave the neutral molybdenum mono-

Table 1
Physical and analytical data [a] for the complexes (**1**–**23**)

Number	Complex	Colour	Yield (%)	Analysis (%)		
				C	H	N
1	$[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	84	40.0 (39.9)	3.5 (3.5)	1.7 (1.7)
2	$[MoI_2(CO)(NCMe)\{P(O^iPr)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	76	30.1 (30.5)	4.7 (4.8)	2.0 (2.0)
3	$[WI_2(CO)\{P(OMe)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	79	24.1 (24.3)	4.2 (3.9)	
4	$[WI_2(CO)\{P(O^iPr)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	85	31.2 (31.5)	5.4 (4.9)	
5	$[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)_2]$	Green	80	38.2 (38.8)	3.5 (3.8)	
6	$[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$	Brown	42	40.3 (39.1)	4.9 (3.2)	
7	$[MoI_2(CO)(PPh_3)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$	Brown	57	46.8 (47.3)	3.9 (3.8)	
8	$[MoI_2(CO)\{P(O^iPr)_3\}\{P(O(Ph)_3\}(\eta^2\text{-}EtC_2Et)]\cdot Et_2O$	Brown	43	42.9 (43.3)	5.5 (5.4)	
9	$[MoI_2(CO)(L^{Mo})\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ $\{L^{Mo} = [MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\}$	Brown	62	44.5 (45.3)	3.6 (3.5)	
10	$[MoI_2(CO)(L^W)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ $\{L^W = [WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]\}$	Brown	36	42.5 (43.2)	3.4 (3.4)	
11	$[MoI_2(CO)(2,2'\text{-bipy})(\eta^2\text{-}EtC_2Et)]$	Brown		45.4 (45.4)	3.7 (3.6)	3.2 (3.0)
12	$[MoI_2(CO)\{PPh_2(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)]$	Green	92	46.2 (46.2)	4.0 (4.0)	
13	$[MoI(CO)(S_2CNMe_2)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]CH_2Cl_2$	Brown	36	40.3 (40.2)	4.1 (4.0)	1.9 (1.7)
14	$[MoI(CO)(S_2CNEt_2)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$	Brown	53	42.5 (42.5)	4.5 (4.3)	1.7 (1.6)
15	$[MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	78	22.1 (22.1)	4.0 (4.0)	
16	$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EC_2Et)]$	Green	57	19.2 (19.6)	3.5 (3.5)	
17	$[MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	41	28.6 (28.8)	5.2 (5.1)	
18	$[WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]\cdot Et_2O$	Green	49	27.8 (28.9)	5.0 (5.2)	
19	$[MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	77	33.9 (34.3)	5.9 (6.0)	
20	$[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Green	91	31.4 (31.1)	5.6 (5.4)	
21	$[MoI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}EtC_2Et)]$	Brown	56	38.5 (38.8)	6.7 (6.7)	
22	$[WI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}EtC_2Et)]\cdot Et_2O$	Green	54	38.0 (37.5)	6.6 (6.6)	
23	$[WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}EtC_2Et))$	Green	80	43.5 (44.2)	3.9 (3.5)	

[a] Calculated values in parentheses.

Table 2
Infrared data for the phosphite complexes **1**–**23**

Complex	ν(C≡O) (cm^{-1})	ν(C≡C) (cm^{-1})	ν(C≡N) (cm^{-1})
1	1983(s)	1646(w)	2286(vw)
2	1986(s)	1616(w)	2286(vw)
3	2044(s)	1653(w)	
4	2046(s)	1636(w)	
5	2064(s)	1636(w)	
6	2040(s)	1641(w)	
7	1963(s)	1590(w)	
8	1967(s)	1594(w)	
9	2042(s); 1971(s); 1938(s); 1859(s)	1648(w)	
10	2037(s); 1962(s); 1904(s); 1852(s)	1636(w)	
11	1949(s)	1638(w)	
12	1941(s)	1656(w)	
13	2039(s)	1590(w)	
14	2034(s)	1736(w)	
15	2004(s); 1989(sh)	1636(w)	
16	1988(s); 1953(sh)	1654(w)	
17	1986 [a](s); 1956 [a](sh); 1995 [b](s); 1967 [b](sh)	1630(w); 1626(w)	
18	1981 [a](s); 1956 [a](sh); 1938 [b]($_{s}$); 1987 [b](sh)	1636(w); 1625(w)	
19	1966(s)	1602(w)	
20	1950(s)	1727(w)	
21	1968(s); 1996(sh)	1636(w)	
22	1951(s); 2002(sh)	1602(w)	
23	1976(s)	1631(w)	

[a] Spectra recorded in $CHCl_3$ as thin films between NaC1 plates; s = strong, sh = shoulder, w = weak, vw = very weak.

[b] Spectra recorded in the solid state as KBr discs.

(2-butyne) complex [MoI_2(CO)(bipy)(η^2-MeC_2Me)] [29], whereas, the reaction of equimolar amounts of [WI_2(CO)(NCMe)(η^2-MeC_2Me)$_2$] and bipy gave the cationic complex, [WI(CO)(bipy)(η^2-MeC_2Me)$_2$]I, which was crystallographically characterised as its [BPh_4]$^-$ salt [37].

The IR spectra (Table 2) of **3**–**5**, all have carbonyl bands above 2000 wavenumbers, which would be expected for complexes of the type, [WI_2(CO)L(η^2-RC_2R')$_2$]. They also have, as expected, alkyne stretching bands at lower wavenumber compared to the uncoordinated 3-hexyne. Several unsuccessful attempts were made to grow single crystals for X-ray crystallography of **3**–**5**, however, since the reactions of [WI_2(CO)(NCMe)(η^2-RC_2R)$_2$] (R = Me or Ph) with a range of monodentate neutral donor ligands always go with retention of configuration, it is very likely the reactions of equimolar amounts of [WI_2(CO)(NCMe)(η^2-EtC_2Et)$_2$] and P(OR)$_3$ will also proceed in the same way. The most likely structure for **3**–**5** is shown in Fig. 2, since the crystal structures of a range of complexes, [MI_2(CO)(NCMe)(η^2-RC_2R')$_2$] have this geometry [1,2,36–40].

The ^{13}C{^{1}H}-NMR spectrum for complex **4** shows alkyne contact carbon resonances at $\delta = 166.8$ and 169.5 ppm, which suggests [35] that the two 3-hexyne ligands are donating an average of 3 electrons each to the tungsten centre, which also enables this complex to obey the effective atomic number rule. This is very typical for other bis(alkyne) complexes of this type previously described [1,2,38].

*2.3. Reactions of [MoI_2(CO)(NCMe){P(OPh)$_3$}(η^2-EtC_2Et)] (**1**)*

In a recent study [32], the reactions of [MoI_2(CO)(NCMe)(η^2-RC_2R')$_2$] with one equivalent of P(OPh)$_3$ to give the three crystallographically characterised complexes, [MoI_2(CO)(NCMe){P(OPh)$_3$}(η^2-RC_2R')] (R = R′ = Me or Ph; R = Me, R′ = Ph), were described. However, no reactions were attempted with these new mono(phosphite) complexes. In this section, the chemistry of the crystallographically characterised complex, [MoI_2(CO)(NCMe){P(OPh)$_3$}(η^2-EtC_2Et)] (**1**) is discussed. The first simple reaction was carried out by bubbling carbon monoxide through an Et_2O solution of **1**, which gives the acetonitrile replaced product, [MoI_2(CO)$_2${P(OPh)$_3$}(η^2-EtC_2Et)] (**6**), which has been characterised in the normal manner (see Tables 1–5). However, after a number of attempts it was not possible to obtain a satisfactory elemental analysis of this complex, due to its instability. The IR spectrum ($CHCl_3$) for [MoI_2(CO)$_2${P(OPh)$_3$}(η^2-EtC_2Et)] has a single carbonyl band at 2040 cm^{-1}, which is as expected much higher than for **1**, which has ν(CO) = 1983 cm^{-1}. The molybdenum(II) complex will likely have two *trans* strong π-accepting CO groups, an electron deficient phosphite, P(OPh)$_3$ and 3-hexyne ligand,

Table 3
^{1}H-NMR data for the complexes **1**–**23** [a]

Complex	^{1}H-NMR (δ ppm)
1	7.25–7.5 (m, 15H, 3*Ph*), 3.4–3.6 (q, 4H, $2CH_2$), 2.20 (s, 3H, NC*Me*), 1.25 (t, 6H, $2CH_3$)
2	4.2–4.8 (m, 3H, OC*H*), 3.4 (q, 4H, $2CH_2$), 2.05 (s, 3H, NC*Me*), 1.9 {d, 9H, $J_{H–H} = 6.76$ Hz, $3OCH(CH_3)_2$}, 1.3 (d, 9H, $J_{H–H} = 6.1$ Hz, $3OCH(CH_3)_2$}, 1.2 (s, 6H, $2CH_3$)
3	3.7 (d, 3H, $J_{H–H} = 7.35$, CH_3), 3.5 (d, 6H, $J_{H–H} = 5.34$, $2CH_3$), 3.6 (q, 4H, $2CH_2$ hexyne), 1.1 (t, 6H, $2CH_3$ hexyne)
4	4.6–4.4 (m, 3H phosphite, 3C*H*), 3.6–3.4 (q, 8H hexyne, $4CH_2$), 1.35 (t, 12H hexyne, $4CH_3$), 1.15 (t, 18H, $6CH_3$ phosphite)
5	7.5–7.1 (vbr, 15H, 3*Ph*), 3.6–3.1 (q, 8H, $4CH_2$), 1.4–1.0 (t, 12H, $4CH_3$)
6	7.5–6.8 (m, 15H, 3*Ph*), 3.4 (m, 4H, $2CH_2$ hexyne), 1.4 (t, 6H, $2CH_3$ hexyne)
7	7.6–7.0 (vbr, 30H, 6*Ph*), 5.2 (s, 2H, CH_2Cl_2), 3.3–2.8 (q, 4H, $2CH_2$), 1.0–0.8 (t, 6H, $2CH_3$)
8	7.6–6.9 (m, 15H, 3*Ph*) 4.7 (m, 3H, $3CH^iPr$), 4.8 (q, 4H, $2CH_2$ hexyne), 3.4 (q, 4H, $2CH_2$ ether), 1.4 (d, 18H, $J_{H–H} = 5.60$, $6CH_3$ of ^iPr), 1.1 (t, 6H, $2CH_3$), 0.9 (t, 6H, $2CH_3$ ether)
9	7.8–7.0 (vbr, 30H, 6*Ph*), 3.5–3.2 (q, 4H, $2CH_2$), 2.4–2.1 (m, 6H, $2CH_2$), 1.3 (s, 3H, $1CH_3$), 1.2 (t, 6H, $2CH_3$)
10	7.7–6.7 (vbr, 30H, 6*Ph*), 3.6–3.1 (q, 4H, $2CH_2$), 2.4–2.1 (m, 6H, $2CH_2$), 1.4–1.15 (t, 6H, $2CH_3$), 0.8 (s, 3H, $1CH_3$)
12	7.3–7.1 (vbr, 24H, 4*Ph*), 4.0 (s, 4H, $2CH_2$), 3.5 (q, 4H, $2CH_2$), 0.85 (t, 6H, $2CH_3$)
13	7.4–7.1 (m, 15H, 3*Ph*), 5.3 (s, 2H, CH_2Cl_2), 3.8 (q, 4H, $2CH_2$ hexyne), 3.5 {q, 6H, $2CH_3$ of $(CH_3)_2NCS_2$}, 1.4 (t, 6H, $2CH_3$ hexyne)
14	7.5–7.1 (m, 15H, 3*Ph*), 5.3 (s, 2H, CH_2Cl_2), 4.1–3.8 (m, 4H $2CH_2(CH_3CH_2)_2NCS_2$), 3.8–3.6 (q, 4H, $2CH_2$ of hexyne), 1.5 {t, 6H, $2CH_3$ of $(CH_3CH_2)_2NCS_2$), 1.1 (t, 6H, $2CH_3$ hexyne)
15	3.95 (br,m, 9H, OMe), 3.65 (br,m, 4H, $2CH_2$), 3.6 (br, m, 9H, O*Me*), 1.35 (br,m, 6H, $2CH_3$)
16	3.95 (br,m, 6H, O*Me*), 3.75 (br,m, 3H, O*Me*), 3.6 (br, m, 4H, $2CH_2$), 3.3 (br,m, 9H O*Me*), 1.2 (br,m, 6H, $2CH_3$)
17	3.9–4.2 (m, 12H, OCH_2CH_3), 3.1 (m, 4H, $2CH_2$), 1.0–1.25 (m, 18H, OCH_2CH_3), 0.9 (m, 6H, CH_3)
18	4.75 (m, 12H, $6CH_2$), 3.1 (m, 4H, $2CH_2$), 1.4 (m, 18H, OCH_2CH_3), 1.1 (m, 6H, $2CH_3$ of hexyne)
19	4.75 (m, 6H, OCH_2), 3.65 (q, 4H, $2CH_2$), 1.3 (t, 6H, $2CH_3$ of hexyne), 1.2 {d, 36H, $J_{H–H} = 1.21$ Hz, $6OCH(CH_3)_2$}
20	4.5–4.8 (m, 6H, OC*H*), 3.5 (q, 4H, $2CH_2$ of hexyne), 1.36 {d, 18H, $J_{H–H} = 6.08$ Hz, $3OCH(CH_3)_2$}, 1.2 (d, 18H, $J_{H–H} = 6.15$ Hz, $3OCH(CH_3)_2$), 0.85 (t, 6H, CH_3 of hexyne)
21	3.85 (m, 12H, $2OCH_2$), 1.15–1.70 (m, 36H $OCH_2CH_2CH_2CH_3$), 0.7–0.9 (m, 18H, $OCH_2CH_2CH_2CH_3$), 0.7–0.9 (m, 6H, $2CH_3$ of hexyne)
22	3.9 (md, 12H, $6OCH_2$, OCH_2CH_3), 3.65 (m, 4H, $2CH_2CH_2CH_2CH_3$), 1.80–1.20 (m, 24H, $OCH_2CH_2CH_3$), 0.85 (m, 18H, $6CH_3$), 0.85 (m, 6H, $2CH_3$)
23	7.3–6.6 (vbr, 30H, 6*Ph*), 3.5–3.1 (mq, 4H, $2CH_2$), 1.3–1.1 (t, 6H, $2CH_3$)

[a] Spectra recorded in $CDCl_3$ (+25^{0}C) and referenced to $SiMe_4$; s = singlet, br = broad, d = doublet, m = multiplet, q = quartet, t = triplet.

which leaves little excess electron density on the metal to back-donate into the empty π*-orbitals of the carbon monoxide ligands. The $^{13}C\{^1H\}$-NMR spectrum of **6** has a single alkyne, (C≡C) resonance at $\delta = 198.74$ ppm, which indicates [35] that the 3-hexyne is utilizing both of its filled π-orbitals and donating 4-electrons to the molybdenum in this complex.

Equimolar quantities of **1** and L {L = PPh_3, $P(O^iPr)_3$, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo, W)} I react in CH_2CI_2 at r.t. to give the acetonitrile replaced products, $[MoI_2(CO)L\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**7**–**10**). Complexes **7**–**10** have been fully characterised (see Tables 1–3 and 5 except complexes (**7**) and (**10**), and as expected are generally less soluble (L = PPh_3, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$) than **1**–**6**, but more stable than these complexes. It should be noted that the organometallic phosphines, $[MI_2(CO)_3\text{-}\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (M = Mo or W) have been prepared by reacting equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and $MeC(CH_2PPh_2)_3$ in CH_2Cl_2 at r.t. [41].

The complexes (L = PPh_3) (**7**) and {L = $P(O^iPr)_3$} (**8**) were confirmed as CH_2Cl_2 and Et_2O solvates respectively, by repeated elemental analyses and ^{1}H-NMR spectroscopy. From the reaction of **1** with CO described above, it is very likely the structure of **7**–**10** will be with the acetonitrile replaced by L in **1**, which is likely to undergo a trigonal twist to give the geometry with the two phosphorus donor ligands *trans* to each other as shown in Fig. 3. This was observed for the bis(PPh_3) complex, $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ [30] and other related bis(phosphite) complexes [31,32]. The IR spectra (Table 2) for **7** and **8** show as expected single carbonyl bands at 1963 and 1967 cm^{-1} respectively, whereas the IR spectra for the complexes **9** and **10** have bands at 1971 and 1962 cm^{-1} due to the carbonyl group on the molybdenum 3-hexyne centre, and three other bands due to the $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ units. The IR spectra for the complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ have bands at $v(CO) = 2042$, 1938 and 1859 (for M = Mo) and at 2037, 1904 and 1852 cm^{-1} (for M = W) [41].

Reaction of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) with an equimolar amount of L^L (L^L = bipy or dppe) afforded the new complexes $[MoI_2(CO)(L\wedge L)(\eta^2\text{-}EtC_2Et)]$ (**11** or **12**) in high yield, via displacement of the acetonitrile and triphenylphosphite ligands. Complexes **11** and **12** were characterised by elemental analysis (Table 1), IR (Table 2), ^{1}H-NMR spectroscopy (Table 3) and by ^{31}P-NMR spectroscopy (Table 5), and X-ray crystallography for the bis(diphenylphosphino)ethane complex, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ (**12**). Complexes **11** and **12** are considerably less soluble than **1**–**10** as they do not contain a solubilising phosphite ligand. They are both more air-stable in both the solid state and solution com-

Table 4
$^{13}C\{^1H\}$-NMR data (5 ppm) for selected complexes [a]

Complex	^{13}C (δ ppm)
1	5.40 (s, NC*Me*), 14.36, 15.26 (2s, 2*C*H_3), 32.80 (s, 2*C*H_3), 115.45, 120.41, 121.04, 121.11, 130.16 (s, O*Ph*), 149.62, 149.77 (s, *C*≡N), 193.0 (s, *C*≡*C*), 208.40(s, *C*≡O)
2	5.7 (s, NC*Me*), 14.40, 15.02, 15.34 (3s, 2*C*H_3), 31.30 (s, 2*C*H_2), 65.93, 66.31(2s, O*C*H$(CH_3)_2$), 135.0 (s, *C*≡N), 196.85 (s, *C*≡*C*), 233.90 (s, *C*≡O)
4	12.70,13.03, 15.25 (3s, 4*C*H_3 of hexyne), 23.81, 23.87 (2s, 6CH_3 phosphite), 31.18,31.41(2s, 4*C*H_2 hexyne), 65.81 (s, 3*C*H phosphite), 166.8, 169.5 (s, *C*≡*C*), 202.27, 204.39 (s, *C*≡O)
6	24.95(s, 2*C*H_3 of hexyne), 32.84, 34.27 (s, 2*C*H_2 hexyne), 115.44, 120.178,121.18,125.80, 126.62, 129.55, 129.97, 130.20 (s, 3*Ph*), 198.74 (s, *C*≡*C*), 204.18 (s, *C*≡O)
15	14.36 (br,s, 2*C*H_3), 32.55 (br,s, 2*C*H_2), 53.95 (br,s, O*C*H_3), 235.0 (br,s, *C*≡*C*)
16	12.62, 20.28 (br,s, 2*C*H_3), 31.45 (br,s, 2*C*H_2), 52.12, 54.27 (br,s 2OCH_3), 207.5 (br,s, *C*≡*C*), 222.5 (br,s, *C*≡O)
17	18.68, 23.60 (br,s, 2*C*H_3), 32.32, 32.41, 35.47 (br,s, 2*C*H_2), 65.44, 65.52, 67.38 (br,s, O*C*H_2CH_3), 195.0 (br,s, *C*≡*C*), 200.99 (s, *C*≡O)
18	15.78, 15.89, 16.60 (br,s, 2*C*H_3), 31.41, 33.61 (br,s, 2*C*H_2), 61.74, 61.82, 62.62,63.29, 63.40, 63.50 (br,s, O*C*H_2CH_3), 203.0, 205.0 (br,s, *C*≡*C*), 227.7 (s, *C*≡O)
19	21.93, 22.85, 24.02 (s, 2*C*H_3), 30.51, 30.98, 31.34, 32.20, 34.59 (s, 2*C*H_2), 65.79, 67.39, 69.57, 70.59, 70.72, 71.772 (s, O*C*H$(CH_3)_2$), 207.82, 208.01 (2s, *C*≡*C*), 236.21 (s, *C*≡O)
20	23.58, 23.65, 23.94 (s, 2*C*H_3), 31.15, 31.38 (s, 2*C*H_2), 65.78, 67.35, 68.50 (s, OCH(*C*$H_3)_2$), 205.30 (s, *C*≡*C*), 236.12 (s, *C*≡O)
21	13.51,13.68, 13.82 (3s, 2*C*H_3), 32.33, 32.58, 32.67 (3s, 2*C*H_2), 65.42, 65.51,66.12, 66.39, 66.73,66.86 (s, O*C*$H_2CCH_2CH_2CH_3$), 203.40 (s, *C*≡*C*), 236.29 (s, *C*≡O)
23	12.56,13.31, 14.22, 14.45 (s, 2*C*H_3), 29.13, 29.31, 29.76, 31.97 (s, 2*C*H_2), 115.50, 117.38, 121.04, 121.12, 128.69, 129.50 (s, 6Ph), 204.69 (s, *C*≡*C*), 219.81(s, *C*≡O)

[a] Spectra recorded in $CDCl_3$(+25°C) and referenced to $SiMe_4$; s = singlet, br = broad, d = doublet, m = multiplet, q = quartet, t = triplet.

pared to complexes **1**–**10.** There are many complexes known of the general formula $[MI_2(CO)(L^\wedge L)(\eta^2\text{-}RC_2R')]$, including the following complexes $[MoI_2(CO)(5,6\text{-}Me_2\text{-}1,10\text{-}Phen)(\eta^2\text{-}PhC_2Ph)]$ [29], $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2R)]$ (R = Me [10], R = Ph [27]) and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ [30], which have been structurally characterised. Suitable single crystals for X-ray crystallography of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ (**12**) were grown by cooling (−17°C) a CH_2Cl_2–Et_2O (80:20) solution of **12**. The structure of **12** is shown in Fig. 4, together with the atom numbering scheme.

The crystal data and structural refinement are given in Table 6. Selected bond lengths (Å) and angles (°) are given in Table 7. The structure consists of discrete molecules of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ (**12**). Although the structure is disordered over a crystallographic mirror plane, the structure of an individual molecule has been unequivocally established. Each metal atom occupies an octahedral environment with the hexyne ligand occupying one site.

The dppe ligand {Mo–P(2) 2.545(4) Å} together with an iodide {Mo(1)–I(1) 2.759(3) Å}, and a carbonyl group {Mo(1)–C(l00) 2.00(4) Å} occupying an equatorial plane, and the hexyne {Mo(1)–C(3) 2.01(2) and Mo(1)–C(4) 2.08(3) Å} together with the second iodide {Mo(1)–I(2) 2.853(4) Å} occupying the axial site. In this coordination sphere C(l00), I(1) and (4) are disordered over two sites related by the mirror plane, and are given 50% occupancy in the refinement. As in **1**, the Mo–I bond *trans* to the hexyne is significantly longer than the bond *trans* to phosphorus.

This arrangement in the coordination sphere contrasts with that observed in $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Ph)]$ [27] and $[WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)]$ [10], where the two phosphorus atoms are *trans* to an iodide and the 3-hexyne, with the second iodide *trans* to the carbonyl. The difference in the structure of **12** may be due to the increased bite of dppe compared to dppm,

Table 5
$^{31}P\{^1H\}$-NMR data δ (ppm) for complexes **1**–**23** [a]

Complex	$^{31}P\{^1H\}$ δ (ppm)
1	114.44 {s, $P(OPh)_3$}
3	104.98 {s, $J_{w\text{–}p} = 205.53$ Hz, $P(O^iPr)_3$}
4	94.76 {s, $J_{w\text{–}p} = 211.6$ Hz, $P(O^iPr)_3$}
5	92.26 {s, $P(OPh)_3$}
6	111.22 {s,$P(OPh)_3$}
8	127.33 {s, $P(OPh)_3$}; 110.88 {s, $P(O^iPr)_3$}
9	(17.58, 2P of L^{Mo} and 32.17, 1P of L^{Mo}); 114.50 {s, $P(OPh)_3$}
12	31.35 (s,dppe)
13	128.01 {s, $P(OPh)_3$}
14	127.26 {s, $P(OPh)_3$}
16	105.06 {s, *trans*, $J_{P\text{–}W} = 259.14$ Hz, $P(OMe)_3$}; 98.0 (d, *cis*, $J_{P\text{–}W} = 97$ Hz, $P(OMe)_3$}; 109.25 {d, *cis*, $J_{P\text{–}P} = 61.97$ Hz, $P(OMe)_3$}
18	100.3 {s, *trans*, $J_{W\text{–}P} = 273.36$ Hz, $P(OEt)_3$}; 107.40 {d, *cis*, $J_{P\text{–}P} = 20.24$ Hz, $P(OEt)_3$}; 92.50 {d, cis, $J_{P\text{–}P} = 20.24$ Hz, $P(OEt)_3$}
19	105.49 {s, *trans*, $P(O^iPr)_3$}
20	94.74 {s, *trans*, $J_{W\text{–}P} = 227.73$ Hz, $P(O^iPr)_3$}
21	109.38 {s, *trans*, $P(O^nBu)_3$}; 127.28 {d, *cis*, $J_{P\text{–}P} = 35.44$ Hz, $(P(O^nBu)_3$}; 117.75 {d, *cis*, $J_{P\text{–}P} = 35.44$Hz, $P(O^nBu)_3$}
22	99.38 {s, *trans*, $J_{W\text{–}P} = 211.21$ Hz, $P(O^nBu)_3$}; 107.08 {d, $J_{P\text{–}P} = 29.97$ Hz, $P(O^nBu)_3$}; 100.74 {d, *cis*, $J_{P\text{–}P} = 29.97$ Hz, $P(O^nBu)_3$}
23	92.45 {s, *trans*, $J_{P\text{–}P} = 207.58$ Hz, $P(OPh)_3$}

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to H_3PO_4.

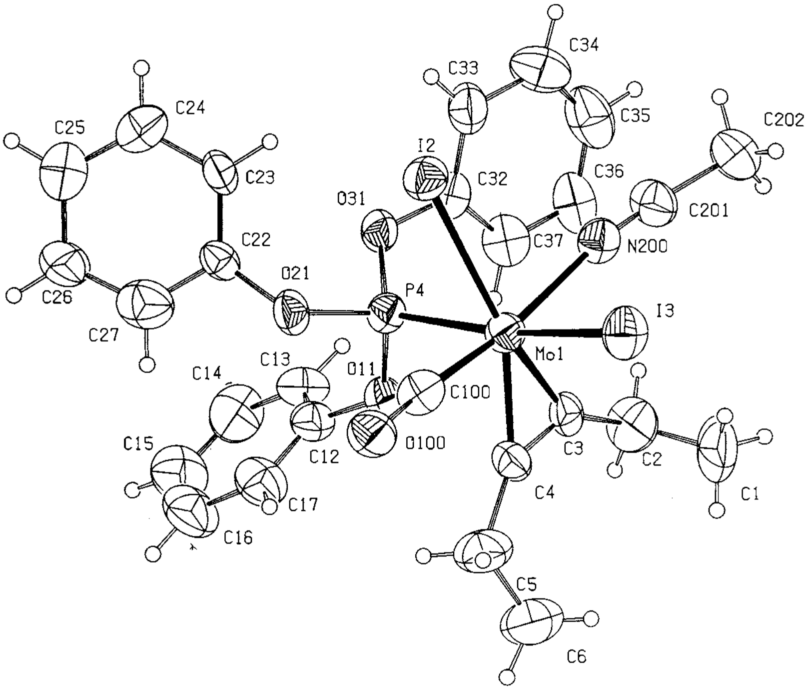


Fig. 1. The structure of **1** with ellipsoids shown at 30% probability.

Table 6
Crystal data and structure refinement for **1**, **12**, **19** and **20**

Compound	**1**	**12**	**19**	**20**
Empirical formula	$C_{27}H_{28}I_2MoNO_4P$	$C_{33}H_{34}MoOP_2$	$C_{25}H_{52}I_2O_7P_2Mo$	$C_{25}H_{52}I_2O_7P_2W$
Molecular weight	811.21	858.28	876.35	964.26
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/a$	*Pnam*(No 62)	$P22_12_1$	$P22_12_1$
Unit cell dimensions				
a (Å)	16.36(2)	15.555(17)	9.628(9)	9.689(9)
b (Å)	12.484(14)	10.058(12)	14.087(17)	13.983(17)
c (Å)	16.604(17)	21.59(2)	14.073(17)	14.015(17)
β (°)	113.78(1)	(90)	(90)	(90)
V (Å^3)	3102	3378	1909	1899
Z	4	4	2	2
D_{calc} (Mg m^{-3})	1.737	1.688	1.525	1.687
Absorption coefficient (mm^{-1})	2.495	2.334	2.078	4.785
F(000)	1568	1672	872	936
Crystal size (mm^3)	$0.25\times0.25\times0.10$	$0.25\times0.17\times0.10$	$0.25\times0.25\times0.10$	$0.25\times0.20\times0.05$
Theta range for data collection (°)	2.11–26.01	2.41–25.91	2.94–26.04	2.10–26.08
Index ranges	$-20\leq h\leq 20$ $0\leq k\leq 15$ $-20\leq l\leq 20$	$-16\leq h\leq 16$ $0\leq k\leq 12$ $-26\leq l\leq 26$	$0\leq h\leq 10$ $-17\leq k\leq 17$ $-17\leq l\leq 17$	$0\leq h\leq 11$ $-16\leq k\leq 17$ $-17\leq l\leq 17$
Reflections measured	10520	7369	6568	6083
Independent reflections [R_{int}]	5631/0.0845	2375/0.0701	3472/0.0719	3581/0.1118
Data/restraints/parameters	5631/0/328	2375/0/118	3472/45/117	3581/46/117
R indices ($I>2\sigma$(I))				
R_1	0.0728	0.0806	0.0743	0.0797
wR_2	0.1845	0.2205	0.2020	0.2162
R indices (all data)				
R_1	0 1834	0.1262	0.1496	0.1620
wR_2	0.2286	0.2494	0.2390	0.2607
Largest diff. peak and hole (e A^{-3})	1.495, −0.790	1.365, −0.856	0.847, −0.593	1.297, −0.904

Table 7
Bond lengths (Å) and angles (°) in the metal coordination spheres for **1**, **12**, **19** and **20**

For ***1***		
Mo(1)–C(100)	1.948(14)	
Mo(1)–C(3)	2.007(12)	
Mo(1)–C(4)	2.040(13)	
Mo(1)–N(200)	2.212(13)	
Mo(1)–P(4)	2.485(4)	
Mo(1)–I(3)	2.799(3)	
Mo(1)–I(2)	2.862(3)	
C(100)–Mo(1)–C(3)	112.5(5)	
C(100)–Mo(1)–C(4)	74.0(5)	
C(3)–Mo(1)–C(4)	38.5(5)	
C(100)–Mo(1)–N(200)	166.0(5)	
C(3)–Mo(1)–N(200)	80.6(5)	
C(4)–Mo(1)–N(200)	118.8(5)	
C(100)–Mo(1)–p(4)	87.1(4)	
C(3)–Mo(1)–P(4)	90.3(3)	
C(4)–Mo(1)–P(4)	89.0(4)	
N(200)–Mo(1)–P(4)	98.2(3)	
C(100)–Mo(1)–I(3)	90.4(4)	
C(3)–Mo(1)–I(3)	99.1(3)	
C(4)–Mo(1)–I(3)	99.0(4)	
N(200)–Mo(1)–I(3)	82.3(3)	
P(4)–Mo(1)–I(3)	170.6(1)	
C(100)–Mo(1)–I(2)	83.9(4)	
C(3)–Mo(1)–I(2)	160.7(4)	
C(4)–Mo(1)–I(2)	155.8(4)	
N(200)–Mo(1)–I(2)	84.3(3)	
P(4)–Mo(1)–I(2)	80.0(1)	
I(3)–Mo(1)–I(2)	90.7(1)	
For ***12***		
Mo(1)–C(100)	2.00(4)	
Mo(1)–C(3)	2.01(2)	
Mo(1)–C4)	2.08(3)	
Mo(1)–P(2)	2.545(4)	
Mo(1)–I(1)	2.759(3)	
Mo(1)–I(2)	2.853(4)	
C(100)–Mo(1)–C(3)	112.4(10)	
C(100)–Mo(1)–C(4)	70.9(12)	
C(3)–Mo(1)–C(4)	41.7(8)	
C(100)–Mo(1)–P(2) [a]	160.1(10)	
C(3)–Mo(1)–P(2) [a]	85.6(5)	
C(4)–Mo(1)–P(2) [a]	127.2(4)	
C(100)–Mo(1)–P(2)	92.7(9)	
C(3)–Mo(1)–P(2)	85.6(5)	
C(4)–Mo(1)–P(2)	91.0(7)	
P(2) [a]–Mo(1)–P(2)	80.0(2)	
C(100)–Mo(1)–I(1)	88.3(9)	
C(3)–Mo(1)–I(1)	101.4(4)	
C(4)–Mo(1)–I(1)	96.9(7)	
P(2) [a]–Mo(1)–I(1)	96.4(1)	
P(2)–Mo(1)–I(1)	171.9(1)	
C(100)–Mo(1)–I(2)	79.2(1)	
C(3)–Mo(1)–I(2)	163.1(6)	
C(4)–Mo(1)–I(2)	148.8(7)	
P(2)–Mo(1)–I(2)	81.5(1)	
I(1)–Mo(1)–I(2)	90.8(1)	
For ***19*** *and* ***20***		
	19 M = Mo	**20** M = W
M(1)–C(11)	1.93(2)	1.92(2)
M(1)–C(21)	1.95(2)	1.95(2)
M(1)–C(100)	2.09(3)	2.02(3)
M(1)–P(4)	2.565(5)	2.541(8)
M(1)–I(2)	2.872(2)	2.853(3)
C(11)–M(1)–C(21)	40.3(6)	40.0(5)
C(11)–M(1)–C(100)	105.1(12)	107.1(14)
C(21)–M(1)–C(100)	65.0(9)	67.2(11)
C(11)–M(1)–P(4)	87.0(13)	89(2)
C(21)–M(1)–P(4)	92.2(1)	92.2(2)
C(100)–M(1)–P(4)	92.0(4)	91(3)
C(11)–M(1)–P(4) [b]	96.7(13)	94(2)
C(21)–M(1)–P(4) [b]	92.6(2)	92.3(2)
C(100)–M(1)–P(4) [b]	90.0(4)	91(3)
P(4)–M(1)–P(4) [b]	175.2(3)	175.6(4)
C(100)–M(1)–I(2)	160.1(9)	157.5(11)
C(11)–M(1)–I(2)	94.7(6)	95.4(5)
C(21)–M(1)–I(2)	134.8(1)	135.3(1)
P(4)–M(1)–I(2)	88.1(3)	89.6(6)
P(4) [b]2–M(1)–I(2)	87.9(3)	87.3(6)
C(11)–M(1)–I(2) [b]	172.9(10)	174.4(13)
C(21)–M(1)–I(2) [b]	134.8(5)	135.6(1)
C(100)–M(1)–I(2) [b]	69.9(9)	68.5(11)
P(4)–M(1)–I(2) [b]	88.7(3)	87.3(6)
I(2)–M(1)–I(2) [b]	90.3(1)	89.0(1)

[a] Symmetry element *x*, *y*,.5−*z* for **20**
[b] Symmetry element *x*, 5−*y*, 1−*z* for **19** and **20**.

but may also be due to stabilising packing effects in the disordered structure. It is interesting to note that the bidentate ligands, bipy and dppe in these reactions displace both a nitrile and a $P(OPh)_3$ ligand. Triphenylphosphite is the most weakly bonding of the series $P(OR)_3$ (R = Me, Et, Pr, Ph), and might be expected to be displaced in this type of reaction rather than an iodo or a carbonyl ligand. Complexes **11** and **12** have single carbonyl bands at 1949 and 1941 cm^{-1} respectively, in the expected position for this type of complex. The ^{1}H-NMR spectra for **12** conform with the $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ formulation. The $^{31}P\{^1H\}$-NMR spectrum ($CDCl_3$, +25°C) for **12** has a single resonance at $\delta = 31.35$ ppm, which suggests that the complex is fluxional at r.t.

Equimolar quantities of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) and $NaS_2CNR_2 \cdot nH_2O$ (R = Me or Et) react in CH_2Cl_2 at r.t. to give the dithiocarbamate complexes, $[MoI(CO)\{P(OPh)_3\}(S_2CNR_2\text{-}S,S')(\eta^2\text{-}EtC_2Et)] \cdot CH_2Cl_2$ (**13** and **14**) in good yield, via displacement of the acetonitrile and an iodo ligand. The new complexes have been characterised in the normal manner (see Tables 1–3 and 5), and are confirmed as CH_2CI_2 solvates by repeated elemental analyses and ^{1}H-NMR spectroscopy. They are both very soluble in chlorinated solvents, CH_2Cl_2 and $CHCl_3$, but much less soluble in diethyl ether. The complexes are air-sensitive in both the solid state and solution. A number of dithiocarbamate alkyne complexes of molybdenum(II) and tungsten(II) have been previously characterised [42–44], including the crystallographically characterised complex $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ [44]. It is

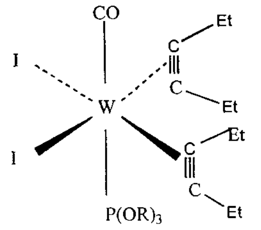


Fig. 2. Proposed structure of $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**3**–**5**).

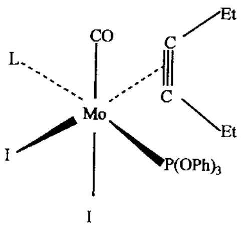


Fig. 3. Proposed structure of $[MoI_2(CO)L\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**7**–**10**).

likely **13** and **14** will have a similar structure, except the 2-butyne ligand is replaced by a $P(OPh)_3$ ligand, and is shown in Fig. 5. The IR spectra of **13** and **14** have single carbonyl bands at 2039s and 2034s cm^{-1} respectively. The $^{31}P\{^1H\}$-NMR spectra of **13** and **14** have single resonances at 128.01 and 127.26 ppm respectively, due to the triphenylphosphite ligand.

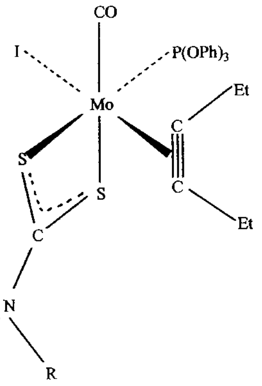


Fig. 5. Proposed structure of $[MoI(CO)\{P(OPh)_3\}(S_2CNR)_2(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$ (**13** and **14**).

It should be noted that a number of other reactions of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) with a variety of neutral and anionic ligands, such as 1,10-phenanthroline, $AsPh_3$, $SbPh_3$ were carried out, and although reactions occurred, no pure products could be isolated from these reactions.

2.4. Synthesis and characterisation of the bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**15**–**23**)

The complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ were reacted with two equivalents of $P(OR)_3$ in diethyl ether at r.t. to give the bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ {M = Mo or W; R = Me, Et, ^{i}Pr, ^{n}Bu, Ph (for M = W only)} (**15-23**) in high yield, via displacement of an acetonitrile and a 3-hexyne ligand.

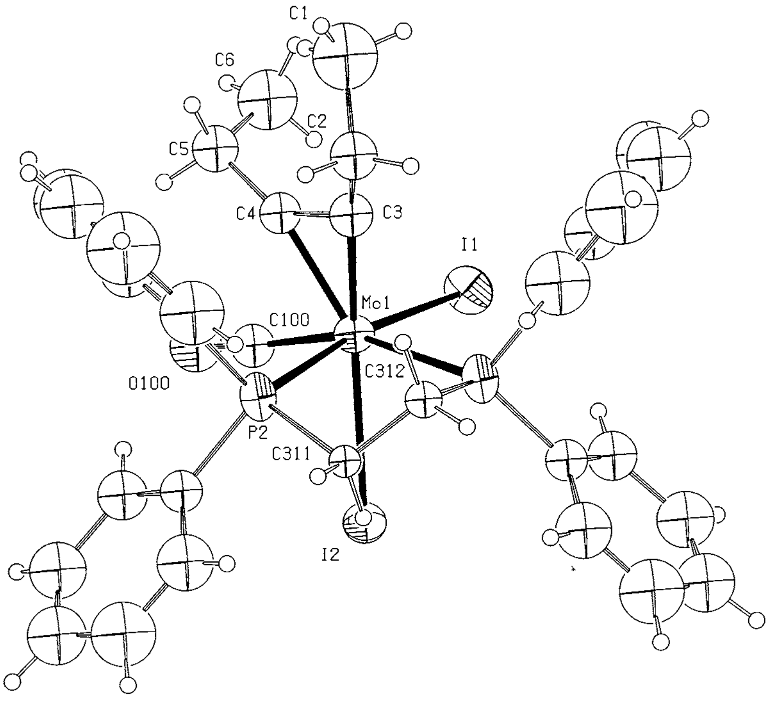


Fig. 4. The structure of $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$ (**12**) with ellipsoids at 30% probability. The structure is disordered over a crystallographic mirror plane through atoms Mo(1), I(2), C(3), C(2) and C(1). Only one discrete molecule is shown.

Complexes **15**–**23** were characterised by elemental analysis (Table 1), IR (Table 2), ^{1}H (Table 3), $^{31}P\{^1H\}$ (Table 5 except complex **17**), and in selected cases $^{13}C\{^1H\}$-NMR spectroscopy (Table 4, except complex **22**), and for the complexes where M = Mo and W, R = ^{i}Pr (**19**) and (**20**) by X-ray crystallography. All the bis(phosphite) complexes were extremely soluble in polar solvents, such as CH_2Cl_2 and $CHCl_3$, and also in diethyl ether. They are very air-sensitive in solution, but can be stored under nitrogen in the solid state at − 17°C for several days.

The tungsten complexes $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ {R = Et (**18**) and ^{n}Bu (**22**)} were confirmed as Et_2O solvates by repeated elemental analysis and ^{1}H-NMR spectroscopy. These bis(phosphite)-3-hexyne complexes are closely related to the complexes, $[WI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R')]$ (R = Me, Et, ^{i}Pr, ^{n}Bu; R′ = Me or Ph) (structurally characterised for R = R′ = Me) [31] and the large series of 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, Ph (M = Mo only); R′ = Me, R″ = Ph (M = W only); R = Et, R′ = R″ = Me, Ph (M = Mo only); R′ = Me, R″ = Ph (M = W only); R = ^{i}Pr, R = R″ = Me, Ph (M = Mo only); R = ^{n}Bu, R′ = R″ = Me, Ph (M = Mo only for both complexes)} {structurally characterised for 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)} very recently reported [32].

Suitable single crystals for X-ray analysis of $[MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**19**) and (**20**) were grown by cooling (− 17°C) concentrated diethyl ether solutions of **19** and **20** for 24 h. The structure of **20** (M = W) is shown in Fig. 6 together with the atomic numbering scheme. Crystal data and structure refinement for **19** and **20** are given in Table 6 and selected bond lengths (Å) and angles (°) are given in Table 7. The structure consists of discrete molecules of $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**20**). The structure of **19** with M = Mo is isostructural with **20**, M = W. In both structures the metal atom has a distorted octahedral environment, with the hexyne ligand occupying one site. The two phosphite ligands are mutually *trans* to each other {W(1)–P(4) 2.541 (8) 2 Å, Mo(1)–P(4) 2.565(5) Å}. The carbonyl and hexyne groups are mutually *cis*, and each is *trans* to an iodide. The W–I(2) and Mo–I(2) distances are 2.853(3) and 2.872(2) Å respectively. This *trans* configuration around the metal has been observed previously [32].

The IR spectra of complexes **15**–**18**, $\{P(OMe)_3\}$ and $\{P(OEt)_3\}$, and **21** and **22** $\{P(O^nBu)_3\}$ complexes, have two carbonyl stretching bands in both their solution ($CHCl_3$) and solid state (KBr disc) spectra, and it is very likely the carbonyl bands at higher wavenumber will be due to the *cis*-isomer. For example, for the complex $[MoI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**17**) has carbonyl bands $\nu(C\equiv O)$ at 1956 and 1986 cm^{-1} in liquid state and 1967 and 1995 cm^{-1} in the solid state. For the *cis*-phosphite isomers, the carbonyl group with the higher stretching frequencies will be *trans* to the

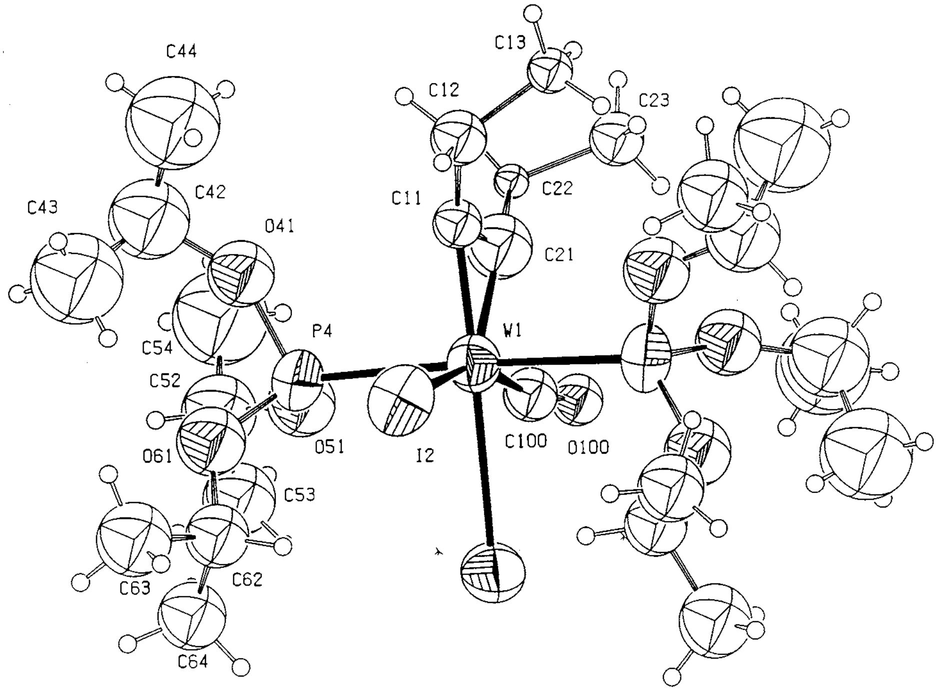
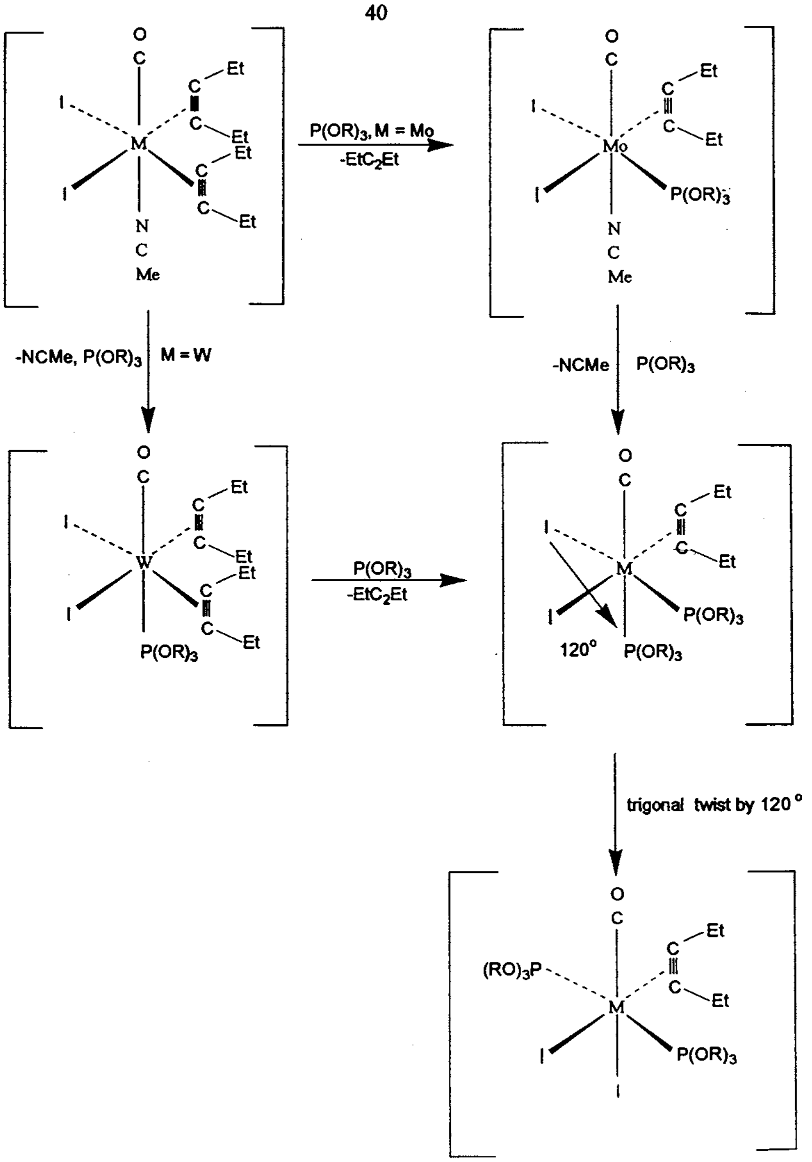


Fig. 6. The structure of $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (**20**) with ellipsoids at 30% probability. The structure is disordered over a crystallographic two-fold axis through the metal atom. Only one discrete molecule is shown. The structure of (**19**) is isostructural.



Scheme 1. Proposed mechanism for the stepwise reactions of two equivalents of phosphite ligands with $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$.

strong π-accepting phosphite group [32], whereas in the trans-isomer the carbonyl is *trans* to an iodo group (see Fig. 6), which could conform with the lower carbonyl stretching bands in both the solid and solution state.

The cone angles [45] for $P(OR)_3$ are {R = Me (107°), Et $\approx$ ^{n}Bu (109°), ^{i}Pr (128°)}, and hence for the larger triisopropyl phosphite, it would be expected that a greater proportion of trans-phosphite complexes for the larger cone angle phosphite ligands. The $^{31}P\{^1H\}$-NMR data has been used to obtain the *cis*:*trans* isomer ratio of the series of phosphite ligands $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ (R = Me, Et, ^{n}Bu or ^{i}Pr) and were found to be in similar ratios to those previously observed for the closely related 2-butyne and 1-phenylpropyne complexes of the type, $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}R'C_2R'')]$ ($R' = R'' = Me$; $R' = Me$, $R'' = Ph$) [32], which was for R = Me, Et, ^{n}Bu, ^{i}Pr; 80:20, 40:60, 40:60 and 0:100 respectively. The ratio between the *cis* and *trans*-isomers for the bis$\{P(OMe)_3\}$ complex **16** is approximately 50:50. For the bis$\{P(O^{n}Bu)_3\}$complex **18**, the ratio was 10:90, and the ratios for the bis$\{P(O^{i}Pr)_3\}$complexes **19** and **20** were, as expected, 0:100. The ^{1}H-NMR spectra of **15**–**18**, **21** and **22** all have complex multiplet resonances, which conforms with the mixture of *cis*- and *trans*-isomers in solution.

The $^{13}C\{^1H)$-NMR spectra of complexes, **16**–**21** and **23** all generally show alkyne contact carbon resonances above 200 ppm, which conform with the 3-hexyne ligand donating 4 electrons to the molybdenum or tungsten in these complexes [35], which also enables the complexes to obey the effective atomic number rule.

2.5. Conclusions

In conclusion, the synthesis and characterisation of a number of new 3-hexyne phosphite complexes of molybdenum(II) and tungsten(II), including the crystallographic characterisation of the mono(phosphite) complex $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**) has been described. The chemistry of **1** has been extensively studied, and one of the reaction products, $[MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)]$, has been crystallographically characterised. The synthesis and structures (M = Mo and W; R = ^{i}Pr) of a series of bis(phosphite) complexes $[MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)]$ are also described. Finally, by considering the results of two previous papers describing the reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with phosphites [31,32] with the work described in this paper, a detailed mechanism of the reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with phosphites can be described, and is shown in Scheme 1. This shows the different pathways that when one equivalent of phosphite is added, together with the cis-trans-isomerism which occurs due to the steric effects of the phosphite ligands.

3. Experimental

All preparations described in this paper were carried out using standard vacuum/Schlenk line techniques. The starting materials, $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo, W) were prepared by the published method [30]. Diethyl ether was dried over sodium wire before use and CH_2Cl_2 over calcium hydride before use. All chemicals used were purchased from commercial sources.

Elemental analyses (C, H and N) were determined by using a Carlo Erba Elemental Analyser MOD 1108 (using helium as the carrier gas). IR spectra were recorded as thin $CHCl_3$ films between NaCl plates or in the solid state as KBr discs. ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC250 MHz NMR spectrometer. ^{1}H and $^{13}C\{^1H\}$-NMR spectra were referenced to $SiMe_4$ and $^{31}P\{^1H\}$-NMR spectra were referenced to 85% H_3PO_4.

3.1. Syntheses

3.1.1. $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (1)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25 g, 0.43 mmol) in diethyl ether (20 cm^3) was added $P(OPh)_3$ (0.13 g, 0.42 mmol, 0.11 ml). After 24 h, filtration and removal of solvent in vacuo gave the brown product, $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**1**), which was dissolved in the minimum quantity of CH_2Cl_2–Et_2O and cooled to − 17°C for 24 h to give small crystals of the product, suitable for X-ray crystallography. (Yield of pure product = 0.29 g, 84%).

A similar reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $P(O^iPr)_3$ in diethyl ether at r.t. gave the complex, $[MoI_2(CO)(NCMe)\{P(O^iPr)_3\}(\eta^2\text{-}EC_2Et)]$ (**2**). For physical and analytical data see Table 1.

3.1.2. Preparation of $[WI_2(CO)\{P(OMe)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (3)

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25 g, 0.37 mmol) in diethyl ether (20 cm^3) was added $P(OMe)_3$ (0.046 g, 0.37 mmol, 0.044 ml). After 24 h, filtration and removal of solvent in vacuo, gave an oily green product, $[WI_2(CO)\{P(OMe)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**3**), which was dissolved in the minimum quantity of CH_2Cl_2–Et_2O and cooled to − 17°C for 24 h to give small crystals of the pure product. (Yield of pure product = 0.22 g, 79%).

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with one equivalent of $P(OR)_3$ {R = ^{i}Pr (**4**) and Ph (**5**)} in diethyl ether at r.t. gave the complexes $[WI_2(CO)\{P(OR)_3\}(\eta^2\text{-}EtC_2Et)_2]$ (**4**) and (**5**). For physical and analytical data see Table 1.

3.1.3. Preparation of $[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (6)

To a stirred solution of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.25 g, 0.43 mmol) in CH_2Cl_2 (20 cm^3) was added $P(OPh)_3$ (0.13 g, 0.11 ml, 0.43 mmol), and CO was bubbled through the solution for 30 min. After 24 h, filtration and removal of solvent in vacuo gave an oily brown product of $[MoI_2(CO)_2\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (**6**), and after repeated recrystallisation it was not possible to obtain satisfactory elemental analysis data for the product, which was dissolved in the minimum quantity of CH_2Cl_2–Et_2O and cooled to − 17°C for 24 h to give small crystals of the product. (Yield of product = 0.16 g, 42%).

3.1.4. Preparation of $[MoI_2(CO)(PPh_3)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$ (7)

To a stirred solution of $[MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ (0.25 g, 0.30 mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.08 g, 0.31 mmol). After 24 h, filtration and removal of solvent in vacuo gave the brown product, $[MoI_2(CO)(PPh_3)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]\cdot CH_2Cl_2$ (**7**), which was dissolved in the minimum quantity of CH_2Cl_2–Et_2O and cooled to − 17°C for 24 h to give small crystals of the product. (Yield of pure product = 0.18 g, 57%).

A similar reaction of $[MoI_2(CO)(NCMe)\text{-}\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]$ with one equivalent of $P(O^iPr)_3$ in CH_2Cl_2 at r.t. and recrystallisation from CH_2Cl_2–Et_2O gave the complex $[MoI_2(CO)\{P(O^iPr)_3\}\text{-}\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]\cdot Et_2O$ (**8**). For physical and analytical data see Table 1.

3.1.5. *Preparation of* $[\mathrm{MoI_2(CO)L^{Mo}\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ *(**9**)* $\{\mathrm{L^{Mo}} = [\mathrm{MoI_2(CO)_3[MeC(CH_2PPh_2)_3}$ *- P,P′]}*

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ (0.18 g, 0.25 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) was added at 0°C, $[\mathrm{MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}$-*P,P′*}] (0.23 g, 0.22 mmol). After 48 h, filtration and removal of solvent in vacuo gave the brown product, $[\mathrm{MoI_2(CO)(L^{Mo})\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ (**9**), which was dissolved in the minimum quantity of $\mathrm{CH_2Cl_2{-}Et_2O}$ and cooled to − 17°C for 24 h to give small crystals of the product. (Yield of pure product = 0.25 g, 62%).

A similar reaction of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ with one equivalent of L $\{\mathrm{L^W} = [\mathrm{WI_2(CO)_3\{MeC(CH_2PPh_2)_3}$-*P,P′*}] in $\mathrm{CH_2Cl_2}$ at r.t. gave the complex, $[\mathrm{MoI_2(CO)(L^W)\{P(OPh)\}(\eta^2\text{-}EtC_2Et)}]$ (**10**). For physical and analytical data see Table 1.

3.1.6. *Preparation of* $[\mathrm{MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)}]$ *(**12**)*

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ (0.25 g, 0.31 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) was added dppe (0.12 g, 0.30 mmol). After 3 h, filtration and removal of solvent in vacuo gave the green product, $[\mathrm{MoI_2(CO)(dppe)(\eta^2\text{-}EtC_2Et)}]$ (**12**), which was dissolved in the minimum quantity of $\mathrm{CH_2Cl_2{-}Et_2O}$ and cooled to − 17°C for 24 h to give small crystals of the product, suitable for X-ray crystallography. (Yield of pure product = 0.24 g, 92%).

In a similar reaction of equimolar quantities of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)\}(\eta^2\text{-}EtC_2Et)}]$ and 2,2′-bipyridyl in $\mathrm{CH_2Cl_2}$ gave the complex, $[\mathrm{MoI_2(CO)(2,2'\text{-}bipy)(\eta^2\text{-}EtC_2Et)}]$ (**11**). See Table 1 for physical and analytical data.

3.1.7. *Preparation of* $[\mathrm{MoI(CO)\{P(OPh)_3\}(S_2CNMe_2)(\eta^2\text{-}EtC_2Et)}]$ *(**13**)*

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ (0.3 g, 0.37 mmol) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) at r.t. was added of $\mathrm{NaS_2CNMe_2{\cdot}2H_2O}$ (0.07 g, 0.39 mmol). After 24 h, filtration and removal of solvent in vacuo gave the oily brown product of $[\mathrm{Mo\{(CO)(S_2CNMe_2)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)]{\cdot}CH_2Cl_2}$ (**13**), which was dissolved in the minimum quantity of $\mathrm{CH_2Cl_2{-}Et_2O}$ and cooled to − 17°C for 24 h to give small crystals of the product. (Yield of pure product = 0.1 g, 36%).

A similar reaction of $[\mathrm{MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}EtC_2Et)}]$ with one equivalent of $\mathrm{NaS_2CNEt_2}$ in $\mathrm{CH_2Cl_2}$ at r.t. gave the complex $[\mathrm{MoI(CO)(S_2CNEt_2)\{P(OPh_3)\}(\eta^2\text{-}EtC_2Et)].CH_2Cl_2}$ (**14**). See Table 1 for physical and analytical data.

3.1.8. *Preparation of* $[\mathrm{MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)}]$ *(**15**)*

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ (0.25 g, 0.43 mmol) in diethyl ether (20 $\mathrm{cm^3}$) at r.t. was added $\mathrm{P(OMe)_3}$ (0.11 g, 0.86 mmol, 0.11 ml). After 24 h, filtration and removal of solvent in vacuo gave the oily brown product of $[\mathrm{MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}EtC_2Et)}]$ (**15**), which was dissolved in the minimum quantity of $\mathrm{CH_2Cl_2{-}Et_2O}$ and cooled to − 17°C for 24 h to give small crystals of the product. (Yield of pure product = 0.24 g, 78%).

Similar reactions of $[\mathrm{MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ with two equivalents of $\mathrm{P(OR)_3}$ {M = Mo, R = Et (**17**), R = ^{i}Pr (**19**), R = ^{n}Bu (**21**); M = W, R = Me (**16**), R = Et (**18**), R = ^{i}Pr (**20**), R = ^{n}Bu (**22**); R = Ph (**23**)} in diethyl ether at r.t. gave the complexes, $[\mathrm{MI_2(CO)\{P(OR)_3\}_2(\eta^2\text{-}EtC_2Et)}]$ (**16**–**23**). For physical and analytical data see Table 1. Suitable single crystals of the bis$\{\mathrm{P(O^iPr)_3}\}$ complexes, $[\mathrm{MI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}EtC_2Et)}]$ (**19** and **20**) were grown by cooling concentrated diethyl ether solutions of **19** and **20** to − 17°C for 24 h.

3.2. *X-Ray crystallography-crystal structure determinations*

Crystal data are given in Table 6, together with refinement details. Data for the four crystals were collected with Mo–$\mathrm{K_\alpha}$ radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 95 Frames were measured at 20 intervals with a counting time of 4 min. Data analyses were carried out with the XDS program [46]. The structures were solved using direct methods with the SHELX 86 program [47]. In **1** all non-hydrogen atoms were refined using anisotropic thermal parameters. The structure of **12** was disordered over a crystallographic mirror plane with I(1) and the carbonyl C(100), O(100) on opposite sides. In addition three atoms of the $\mathrm{EtC_2Et}$ moiety were on the mirror plane and three atoms were on one side (or the other). The two linking carbon atoms of the dppe ligand were also disordered over 2 sites, but the $\mathrm{PPh_2}$ groups conformed to the crystallographic symmetry. All disordered atoms were given 50% occupancy. The Mo, I and P atoms were refined anisotropically and C and O atoms isotropically. The structures of **19** and **20** were isostructural and disordered over a two-fold axis and in addition the crystals were twinned. The cell dimensions {9.628, 14.087, 14.073 for **19** and 9.689, 13.983, 14.015 Å for **20**} are very similar to those found in $[\mathrm{MoI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)}]$ (9.143, 14.116, 14.142 Å) and in $[\mathrm{WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)}]$ (9.146, 14.079, 14.072 Å) [32], and indeed both **19** and **20** proved isostructural with these two structures in which the 2-butyne and carbonyl groups were disordered over the 2-fold axis. As in these two structures, **19** and **20** were refined successfully in space group $P22_12_1$ (No 18) with (010, 001) twinning. The –CO and –$\mathrm{C_6H_{10}}$ moieties were each given 50% occupancy and the structure was refined with distance constraints for these disordered groups. The twin ratios refined to 0.48 (1) in **19** and 0.50(1) in **20**. The M (M = W or Mo), I and P atoms were refined anisotropically and the C, O atoms isotropically. In all four structures, the hydrogen atoms were included in geometric positions and given thermal parameters equal to 1.2 times those of the carbon atoms to which they were bonded. All four structures were corrected for absorption using the DIFABS program [48] and then refined to convergence on F^2 using SHELXL [49]. All calculations were carried out on a Silicon Graphics INDY Workstation at the University of Reading.

4. Supplementary material

Crystallographic data for the structural analysis not included in this paper, has been deposited with the Cambridge Crystallographic Data Centre, CCDC 156368 for compound **1**, CCDC 156369 for compound **12**, CCDC 156370 for compound **19**, CCDC 156371 for compound **20**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

M. Al-Jahdali thanks the Saudi Arabian Government for supporting him on a PhD studentship. We also thank A.W. Johans for his assistance with the crystallographic investigation, and the EPSRC and the University of Reading for funds for the image plate system.

References

[1] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1 and references cited therein.
[2] P.K. Baker, Adv. Organomet. Chem. 40 (1996) 45 and references cited therein.
[3] P. Umland, H. Vahrenkamp, Chem. Ber. 115 (1982) 3580.
[4] J.L. Davidson, G. Vasapollo, J. Chem. Soc., Dalton Trans. (1985) 2239.
[5] M.A. Bennett, I.W. Boyd, J. Organomet. Chem. 290 (1985) 165.
[6] P.B. Winston, S.J.N. Burgmayer, T.L. Tonker, J.L. Templeton, Organometallics 5 (1986) 107.
[7] A.K. List, G.L. Hillhouse, A.L. Rheingold, J. Am. Chem. Soc. 110 (1988) 4855.
[8] E.M. Armstrong, P.K. Baker, S.G. Fraser, J. Chem. Res. (S) (1988) 52; J. Chem. Res. (M) 0410.
[9] E.M. Armstrong, P.K. Baker, J. Organomet. Chem. 352 (1988) 133.
[10] E.M. Armstrong, P.K. Baker, M.E. Harman, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1989) 295.
[11] B.J. Brisdon, A.G.W. Hodson, M.F. Mahon, K.C. Molloy, R.A. Walton, Inorg. Chem. 29 (1990) 2701.
[12] A. Mayr, C.M. Bastos, J. Am. Chem. Soc. 112 (1990) 7797.
[13] A. Mayr, C.M. Bastos, R.T. Chang, J.X. Haberman, K.S. Robinson, D.A. Belle-Oudry, Angew. Chem. Int. Ed. Engl. 31 (1992) 747.
[14] A. Mayr, C.M. Bastos, N. Daubenspeck, G.A. McDermott, Chem. Ber. 125 (1992) 1583.
[15] A. Mayr, T.-Y. Lee, Angew. Chem., Int. Ed. Engl. 32 (1993) 1726.
[16] T.-Y. Lee, A. Mayr, J. Am. Chem. Soc. 116 (1994) 10300.
[17] G.R. Clark, A.J. Nielson, A.D. Rae, C.E.F. Rickard, J. Chem. Soc., Dalton Trans. (1994) 1783.
[18] P.K. Baker, D. ap Kendrick, J. Chem. Soc., Dalton Trans. (1993) 1039.
[19] P.K. Baker, M.E. Harman, D. ap Kendrick, M.B. Hursthouse, Inorg. Chem. 32 (1993) 3395.
[20] P.K. Baker, P.D. Jackson, Inorg. Chim. Acta 219 (1994) 99.
[21] P.K. Baker, D.J. Muldoon, A.J. Lavery, A. Shawcross, Polyhedron 13 (1994) 2915.
[22] T. Ajayi-Obe, E.M. Armstrong, P.K. Baker, S. Prakash, J. Organomet. Chem. 468 (1994) 165.
[23] P.K. Baker, K.R. Flower, Polyhedron 13 (1994) 3265.
[24] P.K. Baker, K.R. Flower, Z. Naturforsch. Sect. B 49 (1994) 1544.
[25] P.K. Baker, S.J. Coles, D.E. Hibbs, M.M. Meehan, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1996) 3995.
[26] P.K. Baker, M.M. Meehan, J. Organomet. Chem. 535 (1997) 129.
[27] P.K. Baker, M.A. Beckett, M.G.B. Drew, S.C.M.C. Godhino, N. Robertson, A.E. Underhill, Inorg. Chim. Acta 279 (1998) 65.
[28] P.K. Baker, M.G.B. Drew, M.M. Meehan, H.K. Patel, A. White, J. Chem. Res.(S) (1998) 379; J. Chem. Res. (M) (1998) 1461.
[29] N.G. Aimeloglou, P.K. Baker, M.M. Meehan, M.G.B. Drew, Polyhedron 17 (1998) 3455.
[30] M. Al-Jahdali, P.K. Baker, M.G.B. Drew, Z. Naturforsch. Sect. B 54 (1999) 171.
[31] P.K. Baker, E.M. Armstrong, M.G.B. Drew, Inorg. Chem. 28 (1989) 2406.
[32] P.K. Baker, M.G.B. Drew, D.S. Evans, A.W. Johans, M.M. Meehan, J. Chem. Soc., Dalton Trans. (1999) 2541.
[33] S.R. Allen, P.K. Baker, S.G. Barnes, M. Green, L. Trollope, L. Manojiovic-Muir, K.W. Muir, J. Chem. Soc., Dalton Trans. (1981) 873.
[34] R.S. Herrick, D.M. Leazer, J.L. Templeton, Organometallics 2 (1983) 834.
[35] J.L. Templeton, B.C. Ward, J. Am. Chem. Soc. 102 (1980) 3288.
[36] E.M. Armstrong, P.K. Baker, M.G.B. Drew, Organometallics 7 (1988) 319.
[37] P.K. Baker, E.M. Armstrong, M.G.B. Drew, Inorg. Chem. 27 (1988) 2287.
[38] P.K. Baker, Chem. Soc. Rev. 27 (1998) 125 and references cited therein.
[39] E.M. Armstrong, P.K. Baker, M.G.B. Drew, J. Organomet. Chem. 336 (1987) 377.
[40] P.K. Baker, M.G.B. Drew, S. Edge, S.D. Ridyard, J. Organomet. Chem. 409 (1991) 207.
[41] M. Al-Jahdali, P.K. Baker, M.M. Meehan, Unpublished results.
[42] R.S. Herrick, J.L. Templeton, Organometallics 1 (1982) 842.
[43] J.R. Morrow, T.L. Tonker, J.L. Templeton, J. Am. Chem. Soc. 107 (1985) 5004.
[44] E.M. Armstrong, P.K. Baker, K.R. Flower, M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1990) 2535.
[45] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[46] W. Kabsch, J. Appl. Cryst. 21 (1988) 916.
[47] G.M. Sheldrick, Acta Cryst. A46 (1990) 467.
[48] N. Walker, D. Stuart, Acta Cryst. A39 (1983) 158.
[49] G.M. Sheldrick, SHELXL 1993 Program for Crystal Structure Refinement, University of Göttingen.