ELSEVIER

Journal of Organometallic Chemistry 648 (2002) 99–108

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ complexes of molybdenum(II) and tungsten(II). Reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ $(M = Mo$ or $W)$ with molybdenum(II) and tungsten(II) complexes

Paul K. Baker *, Mutlaq Al-Jahdali, Margaret M. Meehan

Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK

Received 10 July 2001; received in revised form 16 October 2001

Abstract

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ react in CH_2Cl_2 at room temperature for 5 min to give $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ (**1** and **2**) which contain one uncomplexed phosphorus donor atom capable of further coordination. Complexes **1** and **2** react in refluxing $CHCl_3$ for 15 h (M = Mo) or 72 h (M = W) to give the complexes $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$ (**3** and **4**). The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with two equivalents of **1** (L^{Mo}) and **2** (L^{W}) to yield the trimetallic complexes $[MI_2(CO)_3(L^{Mo}$ or $L^{W})_2]$ (**5**–**8**). A series of mixed-ligand seven-coordinate bimetallic complexes of the type $[MI_2(CO)_3L(L^{Mo}$ or $L^{W})]$ {M = Mo or W; L = PPh_3, $AsPh_3$, $SbPh_3$; for M = W, $P(OR)_3$ (R = Me, Et, Ph)} (**9**–**17**) have been prepared by reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L to give $[MI_2(CO)_3(NCMe)L]$, followed by an in situ reaction with L^{Mo} or L^{W}. Similarly, reactions of $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ $\{n = 1$ or $2\}$ (prepared in situ) with equimolar amounts of L^{Mo} or L^{W} affords the cationic complexes, $[MI(CO)_3(L^{Mo}$ or $L^{W})\{Ph_2P(CH_2)_nPPh_2\}]I$ (**18**–**21**). Reaction of equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and L^{Mo} (for M = Mo) or L^{W} (for M = W) affords the acetonitrile displaced products, $[MI_2(CO)(L^{Mo}$ or $L^{W})(\eta^2\text{-}EtC_2Et)_2]$ (**22**) and (**23**). Treatment of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with two equivalents of L^{Mo} (for M = Mo) or L^{W} (for M = W) gives the mono(3-hexyne) trimetallic complexes $[MI_2(CO)(L^{Mo}$ or $L^{W})_2(\eta^2\text{-}EtC_2Et)]$ (**24**) and (**25**). All the new complexes described in this paper have been characterised by elemental analysis, IR, ^1H- and ^{31}P-NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Tungsten; Tripodal ligand; Triphos

1. Introduction

Although a wide variety of trimetallic complexes containing bridging phosphine ligands such as bis(diphenylphosphino)methane has been prepared and characterised [1–24], hitherto very few examples containing bridging-tridentate phosphines such as chain triphos $\{PhP(CH_2CH_2PPh_2)_2\}$ or tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ have been described. In 1994, Horng et al. [25] described the synthesis and characterisation of the chain-triphos bridged complexes $[\{M(CO)_5\}_3\{\mu^3\text{-}PhP(CH_2CH_2PPh_2)_2–P,P',P''\}]$ (M = Cr, Mo). More recently [26], the mixed-metal complexes $[(OC)_4M(\mu^2\text{-}PhP(CH_2CH_2PPh_2)_2–P,P',P''\}M'(CO)_5]$ (M = Cr, M′ = Mo, W; M = Mo, M′ = Cr, W) have been prepared by reacting $[M(CO)_4\{PhP(CH_2CH_2PPh_2)_2–P,P'\}]$ with $[M'(CO)_5(NCMe)]$.

In 1986 [27], we described the synthesis and characterisation of the highly versatile seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W). These complexes have a wide range of chemistry [28,29]. In 1994 [30], we described the reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and linear triphos $\{PhP(CH_2CH_2PPh_2)_2\}$, to initially yield $[MI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2–P,P'\}]$, which eventually react intramolecularly to give, $[MI_2(CO)_2\{PhP(CH_2CH_2PPh_2)_2–P,P',P''\}]$. Preliminary studies of the reactions of $[WI_2(CO)_3\{PhP(CH_2CH_2PPh_2)_2–P,P'\}]$ as a monodentate phosphine ligand have been described [30]. More recently [31,32], we have described the synthesis and crystallographic characterisation of the monophosphine alkyne complexes, $[WX_2(CO)\{PhP(CH_2CH_2PPh_2)_2–P,P'\}(\eta^2\text{-}RC_2R')]$ (X = I, R = R′ = Me [31],

---

* Corresponding author. Tel.: +44-1248-351151; fax: +44-1248-370528.

E-mail address: chs018@bangor.ac.uk (P.K. Baker).

PII: S0022-328X(01)01367-5

Ph [32]; R = Me, R′ = Ph [31]; X = Br, R = R′ = Ph [32]). The reactions of the diiodo complexes as monodentate phosphines with molybdenum(II) and tungsten(II) complexes [31], molybdenum(II) π-allyl complexes [33] and iron carbonyl complexes[34] have been described.

In this paper, we describe the synthesis and characterisation of the seven-coordinate tripodal triphos organometallic phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ (M = Mo or W) and their intramolecular rearrangement to the dicarbonyl complexes, $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$. We also report the reactions of the monodentate phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ with a range of molybdenum(II) and tungsten(II) complexes to give a series of bi- and trimetallic tripodal triphos-bridged complexes.

2. Results and discussion

2.1. Synthesis and characterisation of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ (1 and 2) and $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$ (3 and 4)

The starting materials used in this research, namely $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) have been prepared by reacting the zero-valent complexes, *fac*-$[M(CO)_3(NCMe)_3]$ (prepared in situ) with an equimolar quantity of I_2 at 0 °C [27]. Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ and tripodal triphos, $\{MeC(CH_2PPh_2)_3\}$ react in CH_2Cl_2 at room temperature for 5 min, to give the new complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ (**1** and **2**), which have the tripodal triphos ligand attached in a bidentate manner. Complexes **1** and **2** have been fully characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy (Tables 3 and 4). The complexes are air-sensitive in solution, but can be stored for several months in the solid state under nitrogen in the absence of light. They are soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but only slightly soluble in hydrocarbon solvents and diethyl ether.

The bidentate coordination mode of the tripodal triphos ligand in complexes **1** and **2** is confirmed by both the IR (Table 2) and $^{31}P\{^1H\}$-NMR spectral data (Table 4). The IR spectra of **1** and **2** show three carbonyl bands in their spectra (Table 2), with the apparent absence of any isomers in solution. This is by contrast to the analogous linear triphos tungsten com-

Table 1
Physical and analytical data[a] for the tripodal triphos $\{MeC(CH_2PPh_2)_3\}$ complexes of molybdenum(II) and tungsten(II) **1**–**25**

Complex	Colour	Yield (%)	Analysis (%)	
			C	H
$[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$, (**1**)	Brown	80	49.7 (49.9)	3.6 (3.7)
$[WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$, (**2**)	Orange	91	46.4 (46.1)	3.5 (3.4)
$[MoI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$, (**3**)	Brown	66	50.1 50.0)	3.8 (3.8)
$[WI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$, (**4**)	Orange	86	46.5 (46.2)	3.4 (3.5)
$[MoI_2(CO)_3[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2]\cdot 2Et_2O$, (**5**)	Brown	87	44.7 (44.1)	3.6 (3.7)
$[WI_2(CO)_3[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2]$, (**6**)	Brown	78	41.1 (41.4)	3.0 (3.0)
$[MoI_2(CO)_3[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2]$, (**7**)	Yellow	20	40.2 (40.0)	3.2 (2.9)
$[WI_2(CO)_3[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2]$, (**8**)	Orange	85	38.6 (38.8)	3.1 (2.8)
$[MoI_2(CO)_3(PPh_3)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]\cdot Et_2O$, (**9**)	Brown	90	46.2 (46.0)	3.5 (3.9)
$[MoI_2(CO)_3(AsPh_3)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**10**)	Brown	81	43.0 (43.4)	3.2 (3.0)
$[MoI_2(CO)_3(SbPh_3)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**11**)	Brown	70	42.0 (42.2)	3.2 (3.0)
$[WI_2(CO)_3(PPh_3)[\mu–WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**12**)	Orange	85	40.1 (40.4)	3.0 (2.8)
$[WI_2(CO)_3(AsPh_3)[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**13**)	Yellow	27	40.1 (39.5)	3.0 (2.8)
$[WI_2(CO)_3(SbPh_3)[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**14**)	Orange	89	38.9 (38.6)	2.8 (2.7)
$[WI_2(CO)_3\{P(OMe)_3\}[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**15**)	Yellow	58	34.0 (33.5)	2.9 (2.7)
$[WI_2(CO)_3\{P(OEt)_3\}[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**16**)	Orange	62	35.4 (34.7)	3.0 (3.0)
$[WI_2(CO)_3\{P(OPh)_3\}[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]$, (**17**)	Yellow	59	39.5 (39.5)	2.8 (2.8)
$[MoI(CO)_3\{Ph_2P(CH_2)PPh_2\}[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]I$, (**18**)	Brown	64	45.6 (45.9)	3.4 (3.3)
$[WI(CO)_3\{Ph_2P(CH_2)PPh_2\}[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]I$, (**19**)	Orange	71	42.4 (42.1)	2.9 (3.0)
$[MoI(CO)_3\{Ph_2P(CH_2)_2PPh_2\}[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]I$, (**20**)	Brown	74	45.8 (46.2)	3.3 (3.3)
$[WI(CO)_3\{Ph_2P(CH_2)_2PPh_2\}[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]]I$, (**21**)	Yellow	66	42.4 (42.4)	3.1 (2.9)
$[MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}](\eta^2\text{-}EtC_2Et)_2]$, (**22**)	Brown	65	42.3 (42.7)	3.6 (3.7)
$[WI_2(CO)[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}](\eta^2\text{-}EtC_2Et)_2]$, (**23**)	Yellow	56	38.5 (38.5)	3.4 (3.4)
$[MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2(\eta^2\text{-}EtC_2Et)]$, (**24**)	Brown	73	44.5 (44.2)	3.9 (3.4)
$[WI_2(CO)[\mu\text{-}WI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]_2(\eta^2\text{-}EtC_2Et)]$, (**25**)	Orange	73	40.3 (40.1)	3.5 (3.1)

[a] Calculated values in parenthesis.

Table 2
Infrared data for the tripodal triphos {MeC(CH$_2$PPh$_2$)$_3$} complexes of molybdenum(II) and tungsten(II) **1**–**25**

Complex	ν(C≡O) (cm^{-1})	ν(C≡C) (cm^{-1})
1	2041s, 1938s, 1917s	–
2	2036s, 1958s, 1904s	–
3	1936s, 1836s	–
4	1971s, 1857s	–
5	2042s, 1971br, 1938s, 1845br	–
6	2074s, 2044s, 2005br, 1939s, 1844br	–
7	2074s, 2037s, 1963s, 1935s, 1908s, 1842br	–
8	2072s, 2035s, 2009s, 1959s, 1908s, 1838br	–
9	2074s, 2044s, 2023s, 1939vs, 1848br	–
10	2044s, 2027vs, 1966vs, 1937br, 1848br	–
11	2072s, 2028vs, 1967vs, 1940vs, 1899s, 1860s	–
12	2072s, 2036vs, 2019br, 1961br, 1910br, 1844s	–
13	2072vs, 2037s, 2017s, 1933br, 1910s, 1839br	–
14	2012s, 1934s, 1833br	–
15	2072s, 2037s, 1935s, 1839br	–
16	2072s, 2037s, 2007s, 1935s, 1840br	–
17	2035s, 1965s, 1939s, 1915s, 1840s	–
18	2044s, 1972m, 1940s, 1866br	–
19	2036vs, 1960vs, 1907vs, 1855s	–
20	2041s, 1973s, 1937s, 1861br	–
21	2037s, 1962s, 1907s	–
22	2046s, 2034s, 1980s, 1938s	1619w
23	2037s, 1960s, 1905s	1619w
24	2029s, 1977s, 1937br,s	1654w
25	2038s, 1961s, 1907br,s	1618w

Spectra recorded in CHCl$_3$ as thin films between NaCl plates; br, broad; s, strong; m, medium; vs, very strong; w, weak.

plex, [WI$_2$(CO)$_3${PhP(CH$_2$CH$_2$PPh$_2$)$_2$–*P*,*P*′}], which has five carbonyl bands in its IR spectrum [30].

The ^{31}P{^{1}H}-NMR (CDCl$_3$) spectra for the molybdenum complex **1** at − 50, 25 and 50 °C have been investigated. At − 50 °C, the spectrum shows a resonance at − 29.51 ppm due to the uncoordinated phosphorus atom, a single resonance at 16.67 ppm due to the fluxional seven-coordinate unit, [MoI$_2$(CO)$_3$-{MeC(CH$_2$PPh$_2$)$_3$–*P*,*P*′}]. At 25 °C, the ^{31}P{^{1}H}-NMR (CDCl$_3$) spectrum is similar, but the resonance for the coordinated phosphorus atoms appears at $\delta = 12.63$ ppm. It should be noted that the free ligand, MeC(CH$_2$PPh$_2$)$_3$, has a single resonance at $\delta = -26.32$ ppm in CDCl$_3$ at 25 °C, and the resonance at $\delta = -29.51$ ppm for the free phosphorus on **1** is, as expected, close to this value. Variable temperature ^{31}P{^{1}H}-NMR spectra in CDCl$_3$ for complex **2** have also been studied. At − 50 °C there are two doublets at $\delta = -14.55$ ppm and $\delta = -25.21$ ppm, ($J_{PP} = 38.42$

Table 3
^{1}H-NMR spectral data for the tripodal triphos {MeC(CH$_2$PPh$_2$)$_3$} complexes of molybdenum(II) and tungsten(II) **1**–**25**

Complex	^{1}H-NMR data (δ (ppm))
1	7.65–7.15 (v.br, 30H, Ph); 2.55–2.1 (v.br,m, 6H, CH$_2$); 1.35 (s, 3H, CH$_3$)
2	7.8–7.1 (v.br, 30H, Ph); 2.5–2.1 (v.br, 6H, CH$_2$); 1.4 (s, 3H, CH$_3$)
3	7.65–7.05 (v.br,m, 30H, Ph); 2.3–1.9 (br, 6H, CH$_2$); 1.1 (s, 3H, CH$_3$)
4	7.7–7.3 (br, 30H, Ph); 2.5–2.2 (br, m, 6H, CH$_2$); 1.2 (s, 3H, CH$_3$)
5	7.9–7.0 (v.br,m, 60H, Ph); 3.5 (q, 8H, CH$_2$, diethyl ether); 2.5 (t, 12H, CH$_3$, diethyl ether); 2.4–2.0 (br, 6H, CH$_2$); 1.3 (s, 3H, CH$_3$)
6	7.5–7.1 (br,m, 60H, Ph); 2.2 (br, 12H, CH$_2$); 1.2 (br,s, 6H, CH$_3$)
7	7.65–7.2 (v.br,m 60H, Ph); 2.25 (br,m, 12H, CH$_2$); 1.3 (s, 6H, CH$_3$)
8	7.7–7.1 (v.br,m, 60H, Ph); 2.45–2.1 (br,m, 12H, CH$_2$); 1.3 (s, 6H,CH$_3$)
9	7.9–7.1 (v.br,m, 45H, Ph); 3.5 (q, 4H, CH$_2$, diethyl ether); 2.5 (t, 6H, CH$_3$, diethyl ether); 2.3–1.9 (br,m, 6H, CH$_2$); 1.1 (br,s, 3H, CH$_3$)
10	7.7–7.25 (v.br,m, 45H, Ph); 2.15 (br,m, 6H, CH$_2$); 1.2 (s, 3H, CH$_3$)
11	7.8–7.0 (v.br,m, 45H, Ph); 2.4–1.9 (br,m, 6H, CH$_2$); 1.35 (s, 3H, CH$_3$)
12	7.25 (v.br,m, 45H, Ph); 2.6 (br,m, 6H, CH$_2$); 1.38 (br,s, 3H, CH$_3$)
13	7.7–7.1 (v.br,m, 45H, Ph); 2.65–2.2 (br,m, 6H, CH$_2$); 1.6 (br,s, 3H, CH$_3$)
14	7.7–7.1 (v.br,m, 45H, Ph); 2.5–1.9 (br,m, 6H, CH$_2$); 1.25 (s, 3H, CH$_3$)
15	8.0–6.9 (v.br,m, 30H, Ph); 3.8–3.5 (m, 6H, CH$_2$); 1.3 (s, 9H, OCH$_3$, phosphite); 1.1 (s, 3H, CH$_3$)
16	7.7–7.0 (v.br,m, 30H, Ph); 4.2–4.0 (br,m, 6H, OCH$_2$, phosphite); 2.4–2.0 (v.br, 6H, CH$_2$); 1.3 (t, 9H, CH$_3$, phosphite); 1.2 (s, 3H, CH$_3$)
17	7.8–6.7 (v.br,m, 45H, Ph); 2.4–1.9 (br,m, 6H, CH$_2$); 1.1 (s, 3H, CH$_3$)
18	7.6–6.8 (v.br,m, 50H, Ph); 4.6 (br,m, 2H, CH$_2$, dppm); 2.3–1.9 (br,m, 6H, CH$_2$); 1.25 (br,s, 3H, CH$_3$)
19	7.6–7.1 (v.br,m, 50H, Ph); 4.6 (br,m, 2H, CH$_2$, dppm); 2.2 (br,m, 6H, CH$_2$); 1.1 (s, 3H, CH$_3$)
20	7.0–6.9 (br,m, 50H, Ph); 2.9–2.6 (br,m, 4H, CH$_2$, dppe); 2.1 (br,m, 6H, CH$_2$); 1.25 (br,s, 3H, CH$_3$)
21	7.7–7.1 (br,m, 50H, Ph); 2.9–2.1 (br,m, 4H, CH$_2$, dppe); 2.2 (br,m, 6H, CH$_2$); 1.1 (s, 3H, CH$_3$)
22	7.7–7.0 (v.br,m, 30H, Ph); 3.25 (q, 8H, hexyne); 2.4–2.0 (v.br,m, 6H, CH$_2$, tripodal triphos); 1.25 (t, 6H, CH$_3$, hexyne); 1.1 (s, 3H, CH$_3$, tripodal triphos)
23	7.9–7.1 (v.br,m, 30H, Ph); 3.5–3.2 (q, 8H, CH$_2$, hexyne); 3.1–2.5 (v.br,m, 6H, CH$_2$, tripodal triphos); 1.2 (t, 12H, CH$_3$, hexyne); 1.1 (s, 3H, CH$_3$, tripodal triphos)
24	7.8–7.2 (v.br,m, 60H, Ph); 3.4 (q, 4H, CH$_2$, hexyne); 2.4–2.1 (m, 12H, CH$_2$, tripodal triphos); 1.2 (t, 6H, CH$_3$, hexyne); 1.1 (s, 6H, CH$_3$, tripodal triphos)
25	7.8 (v.br,m, 60H, Ph); 3.5-3.1 (dq, 4H, CH$_2$, hexyne); 2.5-2.1 (m, 12H, CH$_2$, tripodal triphos); 1.25 (t, 6H, CH$_3$, hexyne), 1.1 (s, 6H, CH$_3$, tripodal triphos)

Spectra recorded in CDCl$_3$ (25 °C) and referenced to Me$_4$Si; s, singlet; br, broad; d, doublet; m, multiplet; t, triplet; q, quartet.

Table 4
^{31}P-NMR data (δ)^{a} for selected tripodal triphos {$MeC(CH_2PPh_2)_3$} complexes of molybdenum(II) and tungsten(II)

Complex	^{31}P-NMR data (δ (ppm))
1	at −50 °C (tricarbonyl complex); 16.67 due to two coordinated P in $MeC(CH_2PPh_2)_3$ atoms; −29.51 due to free P in $MeC(CH_2PPh_2)_3$, at 25 °C (tricarbonyl complex); 12.63 due to two coordinated P, $MeC(CH_2PPh_2)_3$ atom and −29.51 due to free P in $MeC(CH_2PPh_2)_3$
2	at −50 °C (tricarbonyl complex); −14.55 (J_{wp} = 219.7 Hz) and −25.21 (d, J_{PP} = 38.42 Hz) *cis*, due to the coordinated P in $MeC(CH_2PPh_2)_3$; −31.25 due to free uncoordinated P in $MeC(CH_2PPh_2)_3$
3	17.82 {s, $MeC(CH_2PPh_2)_3$ coordinated}
4	15.72 {s, $MeC(CH_2PPh_2)_3$ (J_{PW} = 222.46 Hz)}
5	19.36 {s, 4P, $MeC(CH_2PPh_2)_3$}; 24.99 {s, 2P, $MeC(CH_2PPh_2)_3$}
6	17.45 {s, 4P, $MeC(CH_2PPh_2)_3$}; 35.19 {s, 2P, $MeC(CH_2PPh_2)_3$}
7	−12.38 {brs, 4P, $MeC(CH_2PPh_2)_3$}; 32.61 {brs, 2P, $MeC(CH2PPh_2)_3$}
8	−15.83 {brs, 4P, $MeC(CH_2PPh_2)_3$}; 28.77 {brs, 2P, $MeC(CH_2PPh_2)_3$}
9	17.51 {s, 2P, $MeC(CH_2PPh_2)_3$}; 29.85 {s, 1P, $MeC(CH_2PPh_2)_3$}; 71.45 (s, 1P, PPh_3)
10	17.51 {brs, 2P, $MeC(CH_2PPh_2)_3$}; 41.14 {brs, 1P, $MeC(CH_2PPh_2)_3$};
11	17.55 {brs, 2P, $MeC(CH_2PPh_2)_3$}; 25.94 {brs, 1P, $MeC(CH_2PPh_2)_3$}
12	−13.76 {brs, 2P, $MeC(CH_2PPh_2)_3$}; 25.16 {brs, 1P, $MeC(CH_2PPh_2)_3$}; 35.47 (s, PPh_3)
13	−14.32 {br, 2P, $MeC(CH_2PPh_2)_3$}; 34.20 {br, 1P, $MeC(CH_2PPh_2)_3$}
18	−22.50 and −29.75 (s, dppm); 17.45 {s, 2P, $MeC(CH_2PPh_2)_3$}; 39.45 {s, 1P, $MeC(CH_2PPh_2)_3$
19	−29.62 and −36.19 {d, (J_{PP} = 53.56 Hz) dppm}; −14.41 {s, 2P, $MeC(CH_2PPh_2)_3$}; 24.97 {s, 1P, $MeC(CH_2PPh_2)_3$}
20	−15.93 and −30.64 {d, (J_{PP} = 51.87 Hz) dppe}; 17.52 {s, 2P, $MeC(CH_2PPh_2)_3$}, (J_{PP} = 229.329 Hz); 25.63 {s, 1P, $MeC(CH_2PPh_2)_3$}
21	−13.16 {s, 2P, $MeC(CH_2PPh_2)_3$}; 25.17 {s, 1P, $MeC(CH_2PPh_2)_3$, ($\mathrm{J_{PW}}$ = 201.11 Hz)}; −17.16 and −29.50 (s, dppe)
22	17.56 {s, 2P, $MeC(CH_2PPh_2)_3$}; 38.95 {s, 1P, $MeC(CH_2PPh_2)_3$}
23	−12.63 {s, 2P, $MeC(CH_2PPh_2)_3$}; 49.80 {s, 1P, $MeC(CH_2PPh_2)_3$}
24	19.78 {s, 2P, $MeC(CH_2PPh_2)_3$}; 25.34 {s, 1P, $MeC(CH_2PPh_2)_3$}
25	−12.76 {s, 2P, $MeC(CH_2PPh_2)_3$}; 46.68 {s, 1P, $MeC(CH_2PPh_2)_3$}

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

Hz), which can be assigned to the two coordinated phosphorus atoms in different environments, with perhaps one phosphorus atom *trans* to a carbonyl ligand, and one *trans* to an iodide atom. The coupling J_{PP} = 38.42 Hz, can be assigned to the coordinated *cis*-phosphorus atoms, and J_{WP} coupling for the resonance at $\delta = -14.55$ ppm is 219.7 Hz. The resonance at $\delta = -31.25$ ppm at −50 °C is likely to be due to the uncoordinated phosphorus atom. Since the structure of a wide range of seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ have capped octahedral geometry [28,29,35–37], it may be that the structure of **1** and **2** have the structure as shown in Fig. 1, in view of the different environment of the phosphorus atoms observed in the −50 °C $^{31}P\{^1H\}$-NMR spectrum of **2**. Many unsuccessful attempts were made to grow suitable single crystals for X-ray analysis of **1** and **2**.

The intramolecular reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3$-*P*,*P'*}] (**1** and **2**) in $CHCl_3$ to give $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3$-*P*,*P'*,*P''*}] (**3** and **4**) were followed by IR spectroscopy. The reactions of **1** and **2** in refluxing $CHCl_3$ at 60 °C takes 15 h for **1** (M = Mo), and 72 h for **2** (M = W) gives the dicarbonyl complexes **3** and mainly **4**, respectively. The greater lability of molybdenum complexes compared with their tungsten analogues has been previously observed. Complexes **3** and **4** both have, as expected, two carbonyl bands in their IR spectra, which suggests that the carbonyl groups are *cis* to each other (see Table 2). Larger scale reactions of **1** and **2** in $CHCl_3$ at 60 °C to give the dicarbonyl complexes **3** and **4** are described in the Section 3. It is interesting to note the reaction of chain triphos {$PhP(CH_2CH_2PPh_2)_2$} [30], with $[MI_2(CO)_3(NCMe)_2]$ is much faster than with tripodal triphos to eventually give the dicarbonyl complexes, $[MI_2(CO)_2\{PhP(CH_2CH_2PPh_2)_2$-*P*,*P'*,*P''*}] and $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3$-*P*,*P'*,*P''*}] (**3** and **4**), respectively. This may be due to the ease of coordination of the third phosphorus atom in chain triphos compared with the more restricted tripodal triphos ligand. For complex **3**, the reaction was totally completed in refluxing in $CHCl_3$ for 15 h. Whereas, complex **4** gave the dicarbonyl complex as a green powder, and very little of the tricarbonyl complex after 72 h reflux. The dicarbonyl

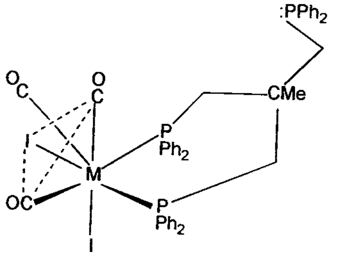


Fig. 1. The proposed structure of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3$-*P*,*P'*}] (**1** and **2**).

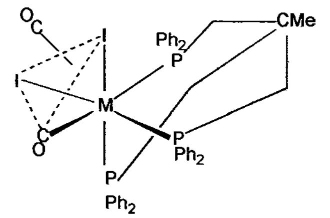


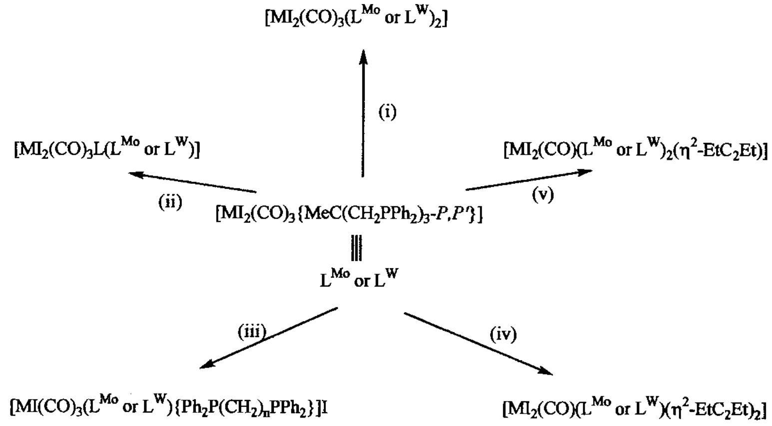
Fig. 2. The proposed structure of $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3–P,P',P''\}]$ (**3** and **4**).

complexes **3** and **4** are considerably less soluble in CH_2Cl_2 and $CHCl_3$ than the tricarbonyl complexes **1** and **2**. This may be due to the symmetrical nature of **3** and **4**, which may pack well in the crystal lattice, whereas the uncoordinated CH_2PPh_2 groups in **1** and **2** may inhibit symmetrical packing of the molecules in the crystal lattice. The structure shows that all three phosphorus atoms of tripodal triphos in **3** and **4** are bonded to the tungsten centre to give them greater stability compared with **1** and **2**. A proposed capped octahedral structure [28,29,35–37], of **3** and **4** is shown in Fig. 2, which conforms with the IR data (Table 2) and $^{31}P\{^1H\}$-NMR data (Table 4).

The room temperature $^{31}P\{^1H\}$-NMR spectra ($CDCl_3$) of **3** and **4** both show one resonance for the phosphorus atoms at $\delta = 17.82$ and 15.72 ppm, respectively. This suggests that the complexes are fluxional in solution. It is much more likely they are fluxional, but also due to poor solubility it was not possible to obtain good low temperature NMR spectra, as the complexes crystallised out of solution very rapidly in NMR solvents such as $CDCl_3$ and CD_2Cl_2 at low temperature. The rest of this paper describes the reactions of the complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ (**1** and **2**) as monodentate phosphine ligands, and are designated as L^{Mo} (complex **1**) and L^{W} (complex **2**). A summary of the reactions described is given in Scheme 1.

2.2. Reactions of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3–P,P'\}]$ *(1 and 2) with a series of molybdenum(II) and tungsten(II) complexes*

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with two equivalents of L^{Mo} or L^{W} in CH_2Cl_2 at room temperature yields the acetonitrile displaced trimetallic complexes $[MI_2(CO)_3(L^{Mo}$ or $L^{W})_2]$ (**5**–**8**). Complexes **5**–**8** have been fully characterised (see Tables 1–4). Complex **5** (M = Mo, L^{Mo}) was confirmed as a bis(diethyl ether) solvate by repeated elemental analyses and ^1H-NMR spectroscopy. Attempts to obtain suitable FAB mass spectra for **5**–**8** were unsuccessful, as no parent ions were obtained, however, molecular weight measurements by Rast's method [38] (see Section 3) give an indication that the complexes are trimetallic in nature. The solubility of complexes **5**–**8** is less than **1** and **2**, and the complexes are only moderately soluble in CH_2Cl_2. They are of similar stability to **1** and **2**, and can be stored under nitrogen in the solid state for several weeks without decomposition.



M = Mo or W

(i) $0.5[MI_2(CO)_3(NCMe)_2]$

(ii) $[MI_2(CO)_3(NCMe)L]$

(iii) $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1 or 2)

(iv) $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$

(v) $0.5[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$

Scheme 1.

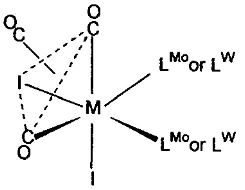


Fig. 3. Proposed structure of $[MI_2(CO)_3(L^{Mo}$ or $L^{W})_2]$ (**5**–**8**).

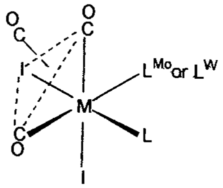


Fig. 4. Proposed structure of $[MI_2(CO)_3L$ (L^{Mo} or L^{W})] {M = Mo or W; L = PPh_3, $AsPh_3$, $SbPh_3$, {for M = W only, $P(OR)_3$ (R = Me, Et or Ph)}} (**9**–**17**).

The IR spectra of **5**–**8** all show a number of carbonyl bands, which are overlapping due to both the tricarbonyl centres, $[MI_2(CO)_3L_2]$, and the tricarbonyl complexes, **1** and **2** attached to the central molybdenum or tungsten centres. For example, complex **6** has five carbonyl bands at, $\nu(CO) = 2074$, 2044, 2005, 1939 and 1844 cm^{-1}. A number of unsuccessful attempts were made to grow suitable single crystals of **5**–**8**, however, since the structure of $[WI_2(CO)_3(NCMe)_2]$ has been crystallographically determined, and a structure of the units of $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ have been proposed (see Fig. 1), a possible structure for **5**–**8** is shown in Fig. 3. The $^{31}P\{^1H\}$-NMR (25 °C, $CDCl_3$) spectra for **5**–**8** show two resonances; one of them for the two phosphorus atoms on one metal, and the other resonance for the third phosphorus atom on the other metal. Due to poor solubility of **5**–**8**, it was difficult to observe coupling constants in their $^{31}P\{^1H\}$-NMR spectra. For example, complex **5** has two resonances, one at $\delta = 19.36$ ppm, which is due to the same sets of two phosphorus atoms on the fluxional Mo unit of $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ {see complex **1**, $\delta = 16.67$ ppm}, and at $\delta = 24.99$ ppm, which is due to the phosphorus atoms bonded to the $[MoI_2(CO)_3(L^{Mo})_2]$ centre. The resonance intensities for **5** at 19.36 and 24.99 ppm are in an ca. 2:1 ratio, which is in accord with the structure of the complexes shown in Fig. 3.

Treatment of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L {L = PPh_3, $AsPh_3$, $SbPh_3$; for M = W only, $P(OR)_3$ (R = Me, Et or Ph)} in CH_2Cl_2 at room temperature gives the mono(acetonitrile) complexes $[MI_2(CO)_3(NCMe)L]$ [39], which react in situ with equimolar amounts of L^{Mo} or L^{W} to afford the new mixed-ligand bimetallic complexes $[MI_2(CO)_3L(L^{Mo}$ or $L^{W})]$ (M = Mo or W) (**9**–**17**). Complexes **9**–**17** have been characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^1H-NMR (Table 3) and in selected cases by $^{31}P\{^1H\}$-NMR spectroscopy (Table 4). Complex **9** (M = Mo, L = PPh_3, L^{Mo}) was confirmed as a diethyl ether solvate by repeated elemental analyses and ^1H-NMR spectroscopy. Molecular weight measurements by Rast's method [38] (see Section 3) of selected complexes suggest the bimetallic nature of these complexes. The stability and solubility of complexes **9**–**17** are similar to the trimetallic complexes **5**–**8**, with the exception of the phosphite complexes **15**–**17**, which are considerably more soluble than **9**–**14**, and slightly less stable. The mechanism of these ligand displacement reactions are likely to be dissociative, since both $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ complexes obey the effective atomic number rule.

The IR spectra of **9**–**17** show a number of overlapping bands, as for complexes **5**–**8** described above. For example, complex **12** has bands at $\nu(CO) = 2036$, 1961 and 1910 cm^{-1}, which are likely to be due to the L^{W}, and bands at $\nu(CO) = 2072$, 2019 and 1844 cm^{-1}, which may be due to the $[WI_2(CO)_3(PPh_3)\ldots]$ unit. The $^{31}P\{^1H\}$-NMR spectra of the $AsPh_3$ and $SbPh_3$ complexes show two different resonances due to tripodal triphos ligand. For example, complex **13** has two resonances; one at $\delta = -14.32$ ppm, which is due to the two phosphorus atoms on the fluxional $[WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ unit, and one at $\delta = 34.20$ ppm for the third phosphorus atom, which is attached to the $[WI_2(CO)_3(AsPh_3)]$ unit. The resonances at $\delta = -14.32$ and 34.20 ppm are in an ca. 2:1 intensity ratio. A possible structure for complexes **9**–**17** is shown in Fig. 4.

Reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) in CH_2Cl_2 at room temperature affords the previously described [40] complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$, which react in situ with one equivalent of L^{Mo} or L^{W} to produce the cationic complexes $[MI(CO)_3(L^{Mo}$ or $L^{W})\{Ph_2P(CH_2)_nPPh_2\}]I$ (**18**–**21**) in high yield, which were characterised (Tables 1–4) in the normal manner. Molecular weight studies by Rast's method [38], suggest the bimetallic nature of these complexes. The IR spectrum of, for example, complex **18**, has bands at 2044, 1972, 1940 and 1866 cm^{-1}. It may be that the bands at 1972, 1940 and 1866 cm^{-1} are due to the $[MoI(CO)_3\ldots]$ unit, and bands at 1972 and 1940 including another band at 2044 cm^{-1}, are due to L^{Mo}. The $^{31}P\{^1H\}$-NMR spectra have, as expected, four different resonances (see Table 4). For example, complex **19** has a resonance at $\delta = -14.41$ ppm, which is due to the two phosphorus atoms on the fluxional L^{W} unit, and at $\delta = 24.97$ ppm due to the third phosphorus atom attached to the $[WI(CO)_3(L^{W})\{Ph_2P(CH_2)PPh_2\}]I$ centre. Also complex **19** has two doublets at $\delta = -29.62$ and -36.19 ppm, due to the coordinated dppm ligand. J_{PP} coupling was often not observed in the spectra due to poor solubility of the complexes in $CDCl_3$ and CD_2Cl_2. A possible structure for this complex is shown in Fig. 5.

The bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo or W) [41] were prepared by reacting the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of 3-hexyne. Equimolar quantities of L^{Mo} or L^{W} and $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ react in CH_2Cl_2 at room temperature to give the bis(3-hexyne) complexes, $[MI_2(CO)(L^{Mo}$ or $L^{W})(\eta^2\text{-}EtC_2Et)_2]$ {M = Mo, L^{Mo} (**22**); M = W, L^{W} (**23**)}. Whereas, two equivalents of L^{Mo} or L^{W} react in CH_2Cl_2 at room temperature with one equivalent of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ to give the mono(3-hexyne) complexes, $[MI_2(CO)(L^{Mo}$ or $L^{W})_2(\eta^2\text{-}EtC_2Et)]$ {M = Mo, L^{Mo} (**24**); M = W, L^{W} (**25**)} in high yield. Complexes **22**–**25** have been fully characterised in the normal manner (see Tables 1–4).

The IR spectrum of, for example, complex **22** shows four carbonyl bands; three of them at $\nu(CO)(CHCl_3) = 2034$, 1980 and 1938 cm^{-1}, for the L^{Mo} unit, and one band at $\nu(CO)(CHCl_3) = 2046$ cm^{-1} for the $[MoI_2(CO)(\eta^2\text{-}EtC_2Et)_2]$ part of the molecule. The IR spectrum of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ has $\nu(CO) = 2056$ cm^{-1} in $CHCl_3$ [41]. Since the structure of the acetonitrile bis(alkyne) complexes, $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) has *cis* and parallel alkyne molecules [42], then it is likely that the structure of **22** and **23** will have the acetonitrile replaced by L^{Mo} (**22**) or L^{W} (**23**), with retention of configuration as shown in Fig. 6. The spectroscopic data for **22** and **23** conform with this structure. The $^{31}P\{^1H\}$-NMR spectrum of **22** has resonances at $\delta = 17.56$ and 38.95 ppm due to the $[MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ unit, and the $[MoI_2(CO)L^{Mo}(\eta^2\text{-}EtC_2Et)_2]$ unit, respectively, in an ca. 2:1 intensity ratio. However, complexes **24** and **25** have carbonyl bands due to L^{Mo} or L^{W}, and bands due to the $[MI_2(CO)(\eta^2\text{-}EtC_2Et)]$ unit. For example, the IR spectrum of complex **24** has bands at $\nu(CO) = 2029$, 1977 and 1937 cm^{-1}, due to the L^{Mo} unit, and the broad band at 1937 cm^{-1} due to the $[MoI_2(CO)(\eta^2\text{-}EtC_2Et)]$ unit. The IR spectrum of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ has $\nu(CO) = 1942$ cm^{-1} in $CHCl_3$ [41].

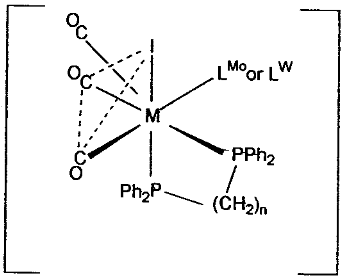


Fig. 5. Proposed structure of $[MI(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]I$ (L^{Mo} or L^{W}) (**18**–**21**).

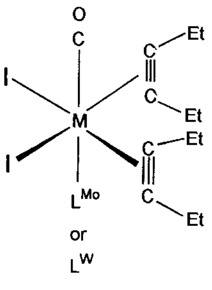


Fig. 6. Proposed structure of $[MI_2(CO)(L^{Mo}$ or $L^{W})(\eta^2\text{-}EtC_2Et)_2]$ (**22** and **23**).

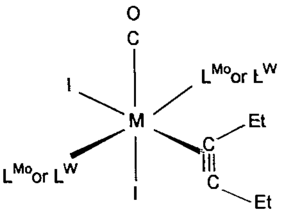


Fig. 7. Proposed structure of $[MI_2(CO)(L^{Mo}$ or $L^{W})_2(\eta^2\text{-}EtC_2Et)]$ (**24** and **25**).

The room temperature $^{31}P\{^1H\}$-NMR spectra for complexes **24** and **25** show two resonances for the tripodal phosphorus coordinated to L^{Mo} or L^{W}. For example, complex **24** has a resonance at $\delta = 19.78$ ppm due to the two phosphorus atoms on the fluxional L^{Mo} centre, and at $\delta = 25.34$ ppm for the third phosphorus atom coordinated to the $[MoI_2(CO)(\eta^2\text{-}EtC_2Et)]$ unit in an ca. 2:1 intensity ratio. It is very likely that the structures of **24** and **25** have *trans* L^{Mo} and L^{W} ligands in their respective complexes as shown in Fig. 7. This conforms with the spectroscopic properties of these complexes. The 3-hexyne ligand makes these complexes more soluble than their starting materials, **1** and **2**. Several unsuccessful attempts were made to grow single crystals for X-ray analysis of **22**–**25**.

In conclusion, tripodal triphos $\{MeC(CH_2PPh_2)_3\}$, reacts with the seven-coordinate complexes, $[MI_2(CO)_3(NCMe)_2]$ to give $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**1** and **2**). The tricarbonyl complexes $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**1**) and (**2**) eventually react intramolecularly to give the dicarbonyl complexes, $[MI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}]$ (**3**) and (**4**), respectively. The monodentate phosphine ligands, $[MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$ (**1**) and (**2**) react with a wide range of complexes of molybdenum(II) and tungsten(II) to give a number of new, fully characterised multimetallic complexes as shown in Scheme 1.

3. Experimental

3.1. Reagents and general techniques

All reactions were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. The starting materials [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) [27], [$MI_2(CO)_3(NCMe)L$] [39], [$MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}$] ($n = 1$ or 2) [40], [$MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2$] [41] were prepared by published methods. CH_2Cl_2 and Et_2O were dried and distilled before use. All chemicals were obtained from commercial sources.

Elemental analyses (carbon, hydrogen and nitrogen) were determined using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). IR spectra were recorded as $CHCl_3$ films between NaCl plates on a Perkin–Elmer 1600 series FTIR spectrophotometer, ^1H- (referenced to $SiMe_4$) and $^{31}P\{^1H\}$- (referenced to 85% H_3PO_4) NMR spectra on a Bruker AC 250 MHz NMR spectrometer. Molecular weights were determined using Rast's method [38] using camphor as the standard.

3.2. Preparation of [$MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (1)

To a stirred solution of [$MoI_2(CO)_3(NCMe)_2$] (0.50 g, 0.97 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C was added 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$ (0.607 g, 0.97 mmol). After stirring for 5 min, filtration and removal of solvent in vacuo, gave the brown crystalline powder of [$MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (**1**), which was recrystallised from CH_2Cl_2–Et_2O at −17 °C. Yield of pure product 0.82 g (80%). Molecular weight: Complex **1** requires, 1058; found, 1142.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with one equivalent of L {L = $MeC(CH_2PPh_2)_3$} in CH_2Cl_2 at room temperature (r.t.) for 5 min gave the complex, [$WI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (**2**). Molecular weight: Complex **2** requires, 1146; found, 1330. For physical and analytical data see Table 1.

3.3. Preparation of [$MoI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}$] (3)

To a stirred solution of [$MoI_2(CO)_3(NCMe)_2$] (0.25 g, 0.48 mmol) in refluxing $CHCl_3$ (20 cm^3) at 60 °C was added $MeC(CH_2PPh_2)_3$ (0.30 g, 0.48 mmol). After refluxing for 15 h, filtration and removal of solvent in vacuo, gave the brown crystalline powder, [$MoI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}$] (**3**), which was recrystallised from $CHCl_3$–Et_2O at −17 °C. Yield of pure product 0.33 g (66%). Molecular weight: Complex **3** requires, 1030; found, 1143.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with one equivalent of L {L = $MeC(CH_2PPh_2)_3$} in refluxing $CHCl_3$ at 60 °C, for 72 h gave mainly the dicarbonyl complex, [$WI_2(CO)_2\{MeC(CH_2PPh_2)_3\text{-}P,P',P''\}$] (**4**). For physical and analytical data see Table 1.

3.4. Preparation of [$MoI_2(CO)_3\{\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\}\text{-}P,P'\}_2$] (5)

To a stirred solution of [$MoI_2(CO)_3(NCMe)_2$] (0.15 g, 0.26 mmol) in CH_2Cl_2 (20 cm^3) was added [$MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (**1**) (0.54 g, 0.51 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the brown crystalline powder, [$MoI_2(CO)_3[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]_2$] (**5**), which was recrystallised from CH_2Cl_2–Et_2O at −17 °C. Yield of pure product 0.65 g (87%). Molecular weight: Complex **5** requires, 2550; found, 2667.

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with two equivalents of L {L = [$MI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] {M = W, L = L^{Mo} or L^W}; {M = Mo, L = L^W} in CH_2Cl_2 at r.t., after 24 h gave the complexes, [$MI_2(CO)_2(L^{Mo}$ or $L^W)_2$] (**6**–**8**). For physical and analytical data see Table 1. Molecular weights: Complex **6** requires, 2638; found, 2220. Complex **7** requires, 2726; found, 2667.

3.5. Preparation of [$MoI_2(CO)_3(PPh_3)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]I$ (9)

To a stirred solution of [$MoI_2(CO)_3(NCMe)_2$] (0.3 g, 0.58 mmol) in CH_2Cl_2 (20 cm^3) at r.t. was added PPh_3 (0.15 g, 0.57 mmol), and left to stir for 1 min. To this was added [$MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (0.62 g, 0.58 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the brown crystalline powder of [$MoI_2(CO)_3(PPh_3)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]$] (**9**), which was recrystallised from CH_2Cl_2–Et_2O at −17 °C. Yield of pure product 0.92 g (90%).

Similar reactions of [$MI_2(CO)_3(NCMe)_2$] with one equivalent of L {L = PPh_3 (1 min), $AsPh_3$ (3 min), $SbPh_3$ (5 min), $P(OR)_3$ (1 min)}, in CH_2Cl_2 at r.t., and then followed by L^W or L^{Mo} {M = Mo, L′ = L^{Mo}), L = $AsPh_3$ (**10**), L = $SbPh_3$ (**11**), {M = W, L^W, L = PPh_3 (**12**), L = $AsPh_3$ (**13**), L = $SbPh_3$ (**14**), L = $P(OMe)_3$ (**15**), R = $P(OMe)_3$ (**16**), R = $P(OPh)_3$ (**17**)}, gave the complexes, [$MI_2(CO)_3(L)(L^{Mo}$ or $L^W)$] (**10**–**17**). For physical and analytical data see Table 1. Molecular weights: Complex **10** requires, 1796; found, 1330. Complex **11** requires, 1845; found, 1429. Complex **12** requires, 1930; found, 2000. Complex **16** requires,1834; found, 2010.

3.6. Preparation of [$MoI(CO)_3\{Ph_2P(CH_2)PPh_2\}[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}]I$ (18)

To a stirred solution of [$MoI_2(CO)_3(NCMe)_2$] (0.2 g, 0.39 mmol) in CH_2Cl_2 (20 cm^3) at r.t. was added dppm (0.15 g, 0.39 mmol), and stirred for 20 min. To this solution was added [$MoI_2(CO)_3\{MeC(CH_2PPh_2)_3\text{-}P,P'\}$] (0.41 g, 0.38 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the brown crystalline powder of $[\mathrm{MoI(CO)_3\{Ph_2P(CH_2)PPh_2\}[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}]]\mathrm{I}$ (**18**), which was recrystallised from $\mathrm{CH_2Cl_2\text{–}Et_2O}$ at −17 °C. Yield of pure product 0.47 g (64%).

Similar reactions of $[\mathrm{MI_2(CO)_3(NCMe)_2}]$ with one equivalent of $\mathrm{Ph_2P(CH_2)_nPPh_2}$, followed by ($\mathrm{L = L^W}$ or $\mathrm{L^{Mo}}$) {$\mathrm{M = W,\ L = L^W}$}, $n = 1$ (**19**), $n = 2$ (**20**); {$\mathrm{M = Mo,\ L = L^{Mo}}$, $n = 2$ (**21**)} in $\mathrm{CH_2Cl_2}$ at r.t. gave the complexes, $[\mathrm{MI(CO)_3\{Ph_2P(CH_2)_{\mathit{n}}PPh_2\}\ (L^{Mo}\ or\ L^W)]I}$ ($n = 1$ or 2) (**19**–**21**). For physical and analytical data see Table 1. Molecular weight: Complex **21** requires, 2193; found, 2000.

3.7. Preparation of $[\mathrm{MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}](\eta^2\text{-}\mathrm{EtC_2Et})_2]$ (22)

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ (0.25 g, 0.43 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at r.t. was added $[\mathrm{MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}]$ (0.45 g, 0.42 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the brown crystalline powder $[\mathrm{MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}](\eta^2\text{-}\mathrm{EtC_2Et})_2]$ (**22**), which was recrystallised from $\mathrm{CH_2Cl_2\text{–}Et_2O}$ at −17 °C. Yield of pure product 0.42 g (65%). Molecular weight: Complex **22** requires, 1600; found, 1600.

A similar reaction of $[\mathrm{WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ with one equivalent of $\mathrm{L^W}$ in $\mathrm{CH_2Cl_2}$ gave $[\mathrm{WI_2(CO)(L^W)(\eta^2\text{-}EtC_2Et)_2}]$ (**23**). For physical and analytical data see Table 1.

3.8. Preparation of $[\mathrm{MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}]_2(\eta^2\text{-}\mathrm{EtC_2Et})]$ (24)

To a stirred solution of $[\mathrm{MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ (0.125 g, 0.21 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at r.t. was added $[\mathrm{MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}]$ (0.45 g, 0.42 mmol). Filtration and removal of solvent in vacuo after 24 h, gave the brown crystalline powder $[\mathrm{MoI_2(CO)[\mu\text{-}MoI_2(CO)_3\{MeC(CH_2PPh_2)_3}\text{–}P,P'\}]_2(\eta^2\text{-}\mathrm{EtC_2Et})]$ (**24**), which was recrystallised from $\mathrm{CH_2Cl_2\text{–}Et_2O}$ at −17 °C. Yield of pure product 0.45g (73%).

A similar reaction of $[\mathrm{WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2}]$ with two equivalents of $\mathrm{L^W}$ in $\mathrm{CH_2Cl_2}$ gave $[\mathrm{WI_2(CO)(L^W)_2(\eta^2\text{-}EtC_2Et)}]$ (**25**). For physical and analytical data see Table 1. Molecular weight: Complex **25** requires, 2840; found, 2650.

Acknowledgements

M.M.M. thanks the E.P.S.R.C. for a studentship. M.Al-J. thanks the Saudi Arabian Government for supporting him on a Ph.D. studentship.

References

[1] B.F. Hoskins, R.J. Steen, T.W. Turney, Inorg. Chim. Acta 77 (1983) L69.

[2] J.G. Toerien, P.H. van Rooyen, J. Chem. Soc. Dalton Trans. (1991) 2693.

[3] F.S. Hassan, D.P. Markham, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 279.

[4] H.-K. Yip, T.-F. Lai, C.-M. Che, J. Chem. Soc. Dalton Trans. (1991) 1639.

[5] R.J. Puddephatt, M.A. Thomson, L. Manojlović-Muir, K.W. Muir, A.A. Frew, M.P. Brown, J. Chem. Soc. Chem. Commun. (1981) 805.

[6] C.-S. Chin, M.S. Sennett, P.J. Weir, L. Vaska, Inorg. Chim. Acta 31 (1978) L443.

[7] E.W. Stern, P.K. Maples, J. Catal. 27 (1972) 120.

[8] L. Manojlović-Muir, K.W. Muir, M.C. Grossel, M.P. Brown, C.D. Nelson, A. Yavari, E. Kallas, R.P. Moulding, K.R. Seddon, J. Chem. Soc. Dalton Trans. (1986) 1955.

[9] L. Manojlović-Muir, K.W. Muir, J. Chem. Soc. Chem. Commun. (1982) 1155.

[10] C.T. Hunt, A.L. Balch, Inorg. Chem. 20 (1981) 2267.

[11] A.L. Balch, C.T. Hunt, C.-L. Lee, M.M. Olmstead, J.P. Farr, J. Am. Chem. Soc. 103 (1981) 3764.

[12] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1982) 1313.

[13] F.S.M. Hassan, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 1501.

[14] A.T. Hutton, P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1985) 1677.

[15] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Chem. Commun. (1982) 956.

[16] B. Mohr, E.E. Brooks, N. Rath, E. Deutsch, Inorg. Chem. 30 (1991) 4541.

[17] N. Marsich, A. Camus, G. Nardin, J. Organomet. Chem. 239 (1982) 429.

[18] A.M.M. Lanfredi, F. Ugozzoli, A. Camus, N. Marsich, R. Capelletti, Inorg. Chim. Acta 206 (1993) 173.

[19] J.T. Mague, Inorg. Chem. 33 (1994) 4261.

[20] J. Diéz, M.P. Gamasa, J. Gimeno, A. Tiripicchio, M.T. Camellini, J. Chem. Soc. Dalton Trans. (1987) 1275.

[21] D.M. Ho, R. Bau, Inorg. Chem. 22 (1983) 4073.

[22] H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama, G. Hüttner, Chem. Ber. 110 (1977) 1748.

[23] X. Hong, K.-K. Cheung, C.-X. Guo, C.-M. Che, J. Chem. Soc. Dalton Trans. (1994) 1867.

[24] L.-K. Liu, L.-S. Luh, Y.-S. Wen, U.B. Eke, M.A. Mesubi, Organometallics 14 (1995) 4474.

[25] D.-N. Horng, S.-T. Jeng, C.-H. Ueng, J. Chin. Chem. Soc. 41 (1994) 539.

[26] D.-N. Horng, C.-H. Ueng, Inorg. Chim. Acta 232 (1995) 175.

[27] P.K. Baker, S.G. Fraser, E.M. Keys, J. Organomet. Chem. 309 (1986) 319.

[28] P.K. Baker, Adv. Organomet. Chem. 40 (1996) 45, and refs. therein.

[29] P.K. Baker, Chem. Soc. Rev. 27 (1998) 125, and refs. therein.

[30] P.K. Baker, D. Sherlock, Polyhedron 13 (1994) 525.

[31] P.K. Baker, S.J. Coles, D.E. Hibbs, M.M. Meehan, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1996) 3995.

[32] P.K. Baker, M.G.B. Drew, M.M. Meehan, J. Szewczyk, J. Organomet. Chem. 580 (1999) 265.

[33] P.K. Baker, M.M. Meehan, J. Organomet. Chem. 582 (1999) 259.

[34] P.K. Baker, M.M. Meehan, Inorg. Chim. Acta 303 (2000) 17.

[35] M.G.B. Drew, Prog. Inorg. Chem. 23 (1977) 67, and refs. therein.

[36] M. Melńik, P. Sharrock, Coord. Chem. Rev. 65 (1985) 49, and refs. therein.
[37] C.W. Haigh, P.K. Baker, Polyhedron 13 (1994) 417, and refs. therein.
[38] F.G. Mann, B.L. Saunders, Practical Organic Chemistry, Longman's Green, London, 1954, pp. 342–344.
[39] P.K. Baker, S.G. Fraser, Transition-Met. Chem. 12 (1987) 560.
[40] P.K. Baker, S.G. Fraser, Inorg. Chim. Acta 130 (1987) 61.
[41] M. Al-Jahdali, P.K. Baker, M.G.B. Drew, Z. Naturforsch. Sect. B 54 (1999) 171.
[42] E.M. Armstrong, P.K. Baker, M.G.B. Drew, Organometallics 7 (1988) 319.