

Synthesis and spectroscopic properties of some new bi-, tri- and tetrametallic complexes of the type $[M(\text{CO})_5\text{L}]$, $[M(\text{CO})_4\text{L}_2]$ and $[M(\text{CO})_3\text{L}_3]$ $\{M = \text{Cr, Mo, W};$
 $\text{L} = [\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]$
 $(\text{R} = \text{R}' = \text{Me, Ph}; \text{R} = \text{Me, R}' = \text{Ph})\}$

Paul K. Baker^{*}, Margaret M. Meehan

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

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Abstract

Reaction of L $\{\text{L} = [\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]\}$ ($\text{R} = \text{R}' = \text{Me, Ph}; \text{R} = \text{Me, R}' = \text{Ph}$) with an equimolar quantity of $[\text{M}(\text{CO})_5(\text{NCMe})]$ ($\text{M} = \text{Cr, Mo, W}$) (prepared in situ) gives high yields of the bimetallic complexes $[\text{M}(\text{CO})_5\text{L}]$ $\{\text{L} = [\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]\}$ ($\text{M} = \text{Cr, W, R} = \text{R}' = \text{Me}; \text{M} = \text{Cr, Mo, R} = \text{Me, R}' = \text{Ph}; \text{M} = \text{Mo, W; R} = \text{R}' = \text{Ph}$) (**1** → **6**). Treatment of *cis*- $[\text{M}(\text{CO})_4(\text{piperidine})_2]$ ($\text{M} = \text{Mo, W}$) with two equivalents of L (as above) in refluxing CH_2Cl_2 affords the trimetallic complexes $[\text{M}(\text{CO})_4\text{L}_2]$ $\{\text{L} = [\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]\}$ ($\text{M} = \text{Mo, W, R} = \text{R}' = \text{Me}; \text{M} = \text{W, R} = \text{Me, R}' = \text{Ph}$) (**7** → **9**). The *cis-trans* isomerism of complexes **7** and **8** has been investigated by infrared spectroscopy. Reaction of *fac*- $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ (prepared in situ) with three equivalents of L in refluxing acetonitrile yields the tetrametallic complexes $[\text{Mo}(\text{CO})_3\text{L}_3]$ $\{\text{L} = [\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]\}$ ($\text{R} = \text{R}' = \text{Me, Ph}; \text{R} = \text{Me, R}' = \text{Ph}$) (**10** → **12**). All the new complexes have been characterised by elemental analysis (C, H and N), infrared, ¹H NMR spectroscopy and in selected cases by ³¹P NMR spectroscopy. © 1997 Elsevier Science S.A.

Keywords: Triphos; Chromium; Molybdenum; Tungsten; Alkyne

1. Introduction

Although many bimetallic complexes containing a bridging bidentate phosphine such as bis(diphenylphosphino)methane have been prepared [1–12], very few examples of potentially tridentate phosphine ligands have been used to prepare bimetallic or multimetallic complexes. A recent example [13] is the use of the tripodal phosphine ligand complex $[\text{RuCl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\text{-P, P'}\}\text{Cp}]$ to form a range of multimetallic complexes such as $[\text{RuCl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\text{-P, P', P''}\}\text{Fe}(\text{CO})_4]$, which use the uncoordinated phosphine group.

In this paper, we describe the reactions of the organometallic monodentate phosphine ligands $[\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{Me, Ph}; \text{R} = \text{Me, R}' = \text{Ph}$) with a

series of substituted zero-valent carbonyls of chromium, molybdenum and tungsten to give new bi-, tri- and tetrametallic complexes.

2. Results and discussion

The starting materials for this research, namely $[\overline{\text{WI}}_2(\text{CO})\{\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2\text{-P, P'}\}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{Me, Ph}; \text{R} = \text{Me, R}' = \text{Ph}$) are prepared by reacting the bis(alkyne) complexes $[\overline{\text{WI}}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}')_2]$ with an equimolar amount of triphos {triphos = $\text{Ph}_2\overline{\text{P}}(\text{CH}_2)_2\overline{\text{P}}\text{Ph}(\text{CH}_2)_2\text{PPh}_2$ } in CH_2Cl_2 at room temperature [14]. An acetonitrile solution of $[\text{M}(\text{CO})_5(\text{NCMe})]$ ($\text{M} = \text{Cr, Mo, W}$), prepared in situ by reacting $[\text{M}(\text{CO})_6]$ with one equivalent of TMNO (TMNO = $\text{ONMe}_3 \cdot 2\text{H}_2\text{O}$) as previously described by

^{*} Corresponding author.

Hor and coworkers [15] was added to an equimolar amount of $[\overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P'\}(\eta^2\text{-RC}_2\text{R}')]$ in CH_2Cl_2 at room temperature to give the bimetallic complexes $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{-}PPh_2\text{-}P,P',P''\}(\eta^2\text{-RC}_2\text{R}')\rangle M(\text{CO})_5]$ ($M = \text{Cr}, \text{W}, \text{R} = \text{R}' = \text{Me}; M = \text{Cr}, \text{Mo}, \text{R} = \text{Me}, \text{R}' = \text{Ph}; M = \text{Mo}, \text{W}, \text{R} = \text{R}' = \text{Ph}$) (**1** → **6**) in high yield. The complexes have been characterised by elemental analysis (C, H and N) (Table 1), infrared spectroscopy (Table 2), ^1H NMR spectroscopy (Table 3) and for complexes **1**, **2** and **5** by ^{31}P NMR spectroscopy (Table 4).

The pentacarbonyl complexes **1** → **6** were stable in the solid state for several months when stored under nitrogen, but were less stable in solution. All complexes **1** → **6** were soluble in dichloromethane, and only sparingly soluble in chloroform and diethyl ether with the exception of **6** which was not soluble in diethyl ether.

The infrared spectra for complexes **1** → **4** all show three carbonyl stretching bands as expected for an $[\text{M}(\text{CO})_5\text{L}]$ phosphine complex [16], where the $A_1^{(2)}$ and E modes exhibit an accidental or near degeneracy in the region of 1944 cm^{-1} , the $A_1^{(1)}$ band absorbing at 2070 cm^{-1} , and the B_1 band at 1989 cm^{-1} as for

$[\text{M}(\text{CO})_5(\text{PPh}_3)]$. However, complexes **5** and **6** show four stretching bands indicating a lifting of the degeneracy of the E mode which is therefore split [17]. The carbonyl stretching bands of the monodentate phosphine ligands $[\overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P'\}(\eta^2\text{-RC}_2\text{R}')]$ occurring at 1959 cm^{-1} for $\text{R} = \text{R}' = \text{Me}$; 1969 cm^{-1} for $\text{R} = \text{R}' = \text{Ph}$ and 1968 cm^{-1} for $\text{R} = \text{Me}, \text{R}' = \text{Ph}$ respectively are masked by the broad absorption in the region of $1935\text{--}1975\text{ cm}^{-1}$ for complexes **1** → **6**.

The ^{31}P NMR spectra of complexes **1** and **2** showed six resonances indicating the presence of two isomers in solution. This result could be predicted as the crystal structure of the monodentate phosphine ligand $[\overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P'\}(\eta^2\text{-MeC}_2\text{Me}) \cdot 0.75\text{CH}_2\text{Cl}_2]$ shows two independent diastereoisomers in the asymmetric unit, the free phosphine in each occupying a different orientation [14]. Therefore the ^{31}P NMR spectra of the three new phosphines, namely $[\overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P'\}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{Me}, \text{Ph}; \text{R} = \text{Me}, \text{R}' = \text{Ph}$) show five resonances consistent with two isomers in solution. The ^{31}P NMR spectrum of complex **5** showed only five

Table 1
Physical and analytical data for complexes **1**–**12**^a

Complex	Colour	Yield (%)	C (%)	H (%)
1 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{Cr}(\text{CO})_5]$	Green	73	42.6 (42.4)	3.1 (3.1)
2 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{W}(\text{CO})_5]$	Green	80	38.0 (38.3)	2.7 (2.8)
3 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{Cr}(\text{CO})_5]$	Green	78	45.3 (45.0)	3.6 (3.2)
4 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{Mo}(\text{CO})_5]$	Green	80	43.7 (43.4)	3.9 (3.1)
5 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{Mo}(\text{CO})_5]$	Green	80	45.3 (45.7)	3.4 (3.1)
6 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle \text{W}(\text{CO})_5]$	Green	73	43.1 (43.1)	3.1 (2.9)
7 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_2 \text{Mo}(\text{CO})_4]$	Green	90	42.5 (42.5)	3.9 (3.4)
8 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_2 \text{W}(\text{CO})_4]$	Green	91	41.0 (40.9)	3.7 (3.3)
9 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_2 \text{W}(\text{CO})_4]$	Green	85	44.1 (43.7)	3.9 (3.3)
10 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_3 \text{Mo}(\text{CO})_3]$	Green	87	42.5 (43.0)	4.0 (3.5)
11 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_3 \text{Mo}(\text{CO})_3]$	Green	85	45.9 (45.9)	4.1 (3.5)
12 $[\langle \overline{WI}_2(CO)\{\text{Ph}_2\overline{P}(\text{CH}_2)_2\overline{P}Ph(\text{CH}_2)_2\text{PPh}_2\text{-}P,P',P''\}(\eta^2\text{-MeC}_2\text{Me})\rangle_3 \text{Mo}(\text{CO})_3]$	Green	86	48.4 (48.0)	4.1 (3.5)

^a Calculated values in parentheses.

Table 2
Infrared data for complexes 1–12^a

Complex	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})
1	2062s, 1935br, 1889sh	1656w
2	2125w, 2010w, 1959br	1675w
3	2063s, 1974sh, 1936br	1654w
4	2060w, 1990sh, 1974br	1589w
5	2072s, 1989sh, 1947hr, 1860sh	1573w
6	2066s, 1975br, 1921sh, 1852sh	1591w
7	2015s, 1950s, 1903br, 1841sh	1657w
8	2010s, 1960sh, 1891br, 1837sh	1588w
9	2010s, 1971sh, 1893br, 1841sh	1590w
10	1971br, 1957sh, 1938sh, 1893sh, 1855sh	1588w
11	1967br, 1903sh, 1850sh, 1830sh, 1814sh	1590w
12	1968br, 1942sh, 1904sh, 1836sh, 1814sh	1588w

^a Spectra recorded in CHCl_3 as thin films between NaCl plates. s = strong, m = medium, w = weak, sh = shoulder, br = broad.

resonances, but the signal at $\delta = -3.4$ ppm is a broad multiplet possibly formed by overlapping doublets due to the terminal phosphorus atom of each isomer coordinated to the tungsten metal centre of the pentacarbonyl complex. It is interesting to note that the chemical shifts of the pentacarbonyl phosphine complexes are comparable to those found by Grim et al. [17]. The ^1H NMR spectra are consistent with the proposed structure of these complexes (Fig. 1).

Reaction of $cis\text{-}[\text{M}(\text{CO})_4(\text{piperidine})_2]$ ($\text{M} = \text{Mo}, \text{W}$) [18] with two equivalents of $[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-}P, P'\}(\eta^2\text{-RC}_2\text{R}')]]$ in refluxing CH_2Cl_2 (15 min) gives good yields of the trimetallic complexes $[\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{-}P, P', P''\}(\eta^2\text{-RC}_2\text{R}')]\text{M}(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$, $\text{R} = \text{R}' = \text{Me}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) (7–9). Complexes 7–9 have been characterised by elemental analysis (C, H and N) (Table 1), infrared spectroscopy (Table 2), ^1H

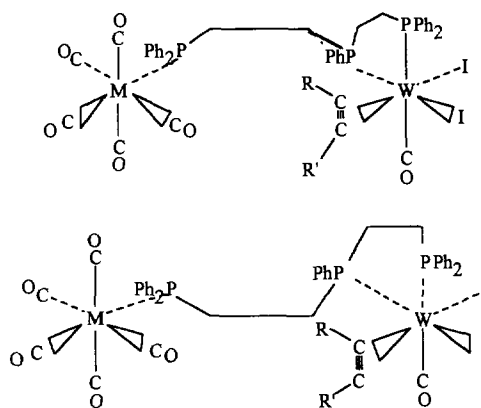


Fig. 1. Two possible isomers for complexes $[\text{M}(\text{CO})_5\text{L}]$ [$\text{L} = [\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-}P, P'\}(\eta^2\text{-RC}_2\text{R}')]]$ ($\text{M} = \text{Cr}, \text{W}$, $\text{R} = \text{R}' = \text{Me}$; $\text{M} = \text{Cr}, \text{Mo}$, $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; $\text{M} = \text{Mo}, \text{W}$, $\text{R} = \text{R}' = \text{Ph}$) (1–6).

NMR spectroscopy (Table 3) and for complex 7 by ^{31}P NMR spectroscopy (Table 4). The tetracarbonyl complexes (7–9) are stable in the solid state for several months when stored under nitrogen and are stable for only two or three weeks in solution at -17°C . All complexes 7–9 are soluble in dichloromethane and insoluble in diethyl ether. Complex 7 was only sparingly soluble in chloroform whereas complexes 8 and 9 were completely soluble in chloroform. This suggests that the trimetallic complexes 8–9 are surprisingly more soluble in chloroform than the bimetallic, pentacarbonyl analogues. As might be predicted all the complexes 7–9 are less soluble than complexes 1–6 in diethyl ether.

The IR spectra of complexes of the type $trans\text{-}[\text{M}(\text{CO})_4(\text{PR}_3)_2]$ generally have three carbonyl stretching bands [16]; for example, $trans\text{-}[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$ has carbonyl bands at 2005 cm^{-1} (vw), 1957 cm^{-1} (w), and 1900 cm^{-1} (vs), whereas $cis\text{-}[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$ has

Table 3
Proton NMR data (δ) for complexes 1–12^a

Complex	$^1\text{H}(\delta)$ ppm
1	7.9–7.4 (br, 25H, Ph); 3.1, 3.0 (2s, 6H, C_2Me); 2.4–2.1 (m, 8H, PhPC_2H_2)
2	7.9–7.4 (br, 25H, Ph); 3.1, 2.9 (2s, 6H, C_2Me); 2.7–2.6 (m, 8H, PhPC_2H_2)
3	7.9–7.4 (br, 30H, Ph); 3.1, 2.9 (2s, 3H, C_2Me); 2.6–2.4 (m, 8H, PhPC_2H_2)
4	7.9–7.4 (br, 30H, Ph); 3.1, 3.0 (2s, 3H, C_2Me); 2.8–2.6 (m, 8H, PhPC_2H_2)
5	7.9–7.4 (br, 35H, Ph); 2.9–2.7 (m, 8H, PhPC_2H_2)
6	7.9–7.4 (br, 35H, Ph); 2.9–2.2 (m, 8H, PhPC_2H_2)
7	7.9–7.3 (br, 50H, Ph); 3.15, 3.1 (2s, 12H, C_2Me); 2.9–2.7 (m, 16H, PhPC_2H_2)
8	7.9–7.4 (br, 50H, Ph); 3.1, 2.9 (2s, 12H, C_2Me); 2.9–2.8 (m, 16H, PhPC_2H_2)
9	7.9–7.4 (br, 60H, Ph); 3.1, 3.0 (2s, 6H, C_2Me); 2.8–2.6 (m, 16H, PhPC_2H_2)
10	7.9–7.4 (br, 75H, Ph); 3.1, 3.0 (2s, 18H, C_2Me); 2.9–2.7 (m, 24H, PhPC_2H_2)
11	7.9–7.4 (br, 90H, Ph); 3.1, 3.0 (2s, 9H, C_2Me); 2.9–2.6 (m, 24H, PhPC_2H_2)
12	7.9–7.4 (br, 105H, Ph); 2.9–2.2 (m, 24H, PhPC_2H_2)

^a Spectra recorded in CDCl_3 (+25°C) and referenced to SiMe_4 . s = singlet; br = broad; d = doublet; m = multiplet.

Table 4

³¹P NMR data (δ) for selected complexes ^a

Complex	³¹ P δ (ppm)
1	49.5 → 48.2 brm, 1P, Cr(CO) ₅ -PPh ₂ , 34.5 → 30.9 brm, 1P, Cr-PPh ₂ , 21.7, 1P, W-PPh, 19.7 m, 1P, W-PPh, 4.1 m, 1P, W-PPh ₂ , -4.0 m, 1P, W-PPh ₂
2	21.7 m, 1P, W-PPh, 19.1 m, 1P, W-PPh, 11.8 m, 1P, W(CO) ₅ -PPh ₂ , 9.7 m, 1P, W-PPh ₂ , 4.0 m, 1P, W-PPh ₂ , -4.1 m, 1P, W-PPh ₂
5	30.8 m, 1P, Mo-PPh ₂ , 28.4 m, 1P, Mo(CO) ₅ -PPh ₂ , 25.2 m, 1P, W-PPh, 19.9 brm, 1P, W-PPh, -3.4 brm, 1P, W-PPh ₂
7	32.1 → 28.8 brm, Mo-PPh ₂ , 22.6 → 19.6 brm, W-PPh, 19.7 m, W-PPh, 4.2 m, W-PPh ₂ , -2.2 → -4.1 brm, W-PPh ₂
12	39.2 s, Mo-PPh ₂ , 31.7 → 30.0 brm, Mo-PPh ₂ , 22.2 → 18.4 m, W-PPh, 7.1 m, W-PPh ₂ , -0.02 m, W-PPh ₂

^a Spectra recorded in CDCl₃ (+25 °C) and referenced to H₃PO₄.

s = singlet; br = broad; d = doublet; m = multiplet.

four strong sharp carbonyl bands at 2023, 1927, 1908 and 1897 cm⁻¹. For complex 7, the *cis*-isomer might be assigned the carbonyl bands at 2015, 1902 and 1841 cm⁻¹ with a fourth band expected in the region of 1930 cm⁻¹ being masked by the broad absorption at 1950 cm⁻¹, due to [W₁₂(CO){Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂-P,P'}(η²-MeC₂Me)]. Cotton et al. [19] found that in the isomerisation of *cis*-[M(CO)₄LL'] ⇌ *trans*-[M(CO)₄LL'], there is a preference for the *cis*- or *trans*-isomer depending on the electronic and steric properties of L and L'. When complex 7 was refluxed in chloroform for 24 h, bands at 2020 cm⁻¹ (w), 1923 cm⁻¹ (m) and 1897 cm⁻¹ (s) were observed which are likely to be due to the *trans*-isomer; a strong absorption at 1956 cm⁻¹ was also observed which can be assigned to the carbonyl of the monodentate phosphine. The IR spectrum also indicated the presence of a very small amount of the *cis*-isomer in solution. Reflux of complex 8 in chloroform for 24 h showed a similar change of the carbonyl absorption pattern, i.e. a decrease in the intensity of the band at 2010 cm⁻¹ and an increase in the intensity of the band at 1891 cm⁻¹, indicating a greater proportion of the *trans*-isomer in solution; a corresponding strong absorp-

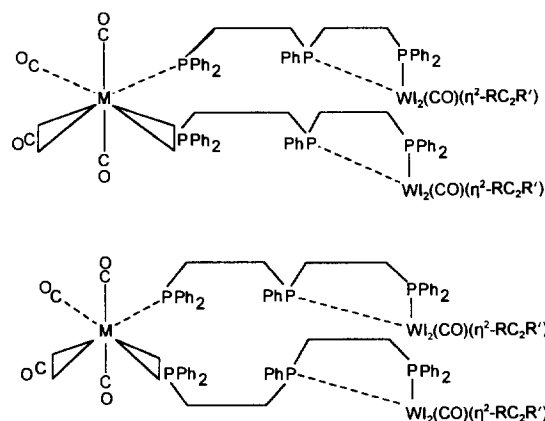


Fig. 2. Two possible isomers for the complexes *cis*-[M(CO)₄L₂] {L = [W₁₂(CO){Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂-P,P'}(η²-RC₂R')]} (M = Mo, W, R = R' = Me; M = W, R = Me, R' = Ph) (7 → 9).

tion at 1959 cm⁻¹ was observed which can be assigned to the carbonyl group of the tungsten phosphine ligand.

The ³¹P NMR spectrum of complex 7 shows five resonances, which indicate the presence of two isomers in solution. As there are two isomers of the monodentate tungsten phosphine ligand it might be expected that at least four isomers of the tetracarbonyl product would be formed as shown in Figs. 2 and 3 resulting in 24 ³¹P NMR resonances. All the ³¹P NMR resonances of complex 7 are multiplets, and could indicate the presence of overlapping resonances due to several isomers in solution. The absence of a resonance in the region of $\delta = -13$ ppm, as expected, suggests that there was no uncoordinated phosphine present. The ¹H NMR spectra of complexes 7 → 9 are consistent with the proposed structures of these complexes.

Treatment of the tris(acetonitrile) complexes *fac*-[Mo(CO)₃(NCMe)₃] (prepared in situ [20]) with three equivalents of [W₁₂(CO){Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂-P,P'}(η²-RC₂R')]} in refluxing acetonitrile for 24 h gave the tetrametallic complexes [W₁₂(CO){Ph₂P(CH₂)₂PPh(CH₂)₂-PPh₂-P,P',P''}(η²-RC₂R')]₃Mo(CO)₃] (R = R' = Me, Ph; R = Me, R' = Ph) (10 → 12). All the new complexes 10 → 12 have been characterised by elemental analysis

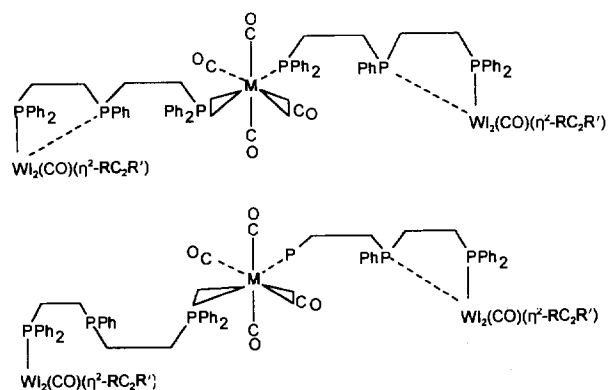


Fig. 3. Two possible isomers for the complexes *trans*-[M(CO)₄L₂] {L = [W₁₂(CO){Ph₂P(CH₂)₂PPh(CH₂)₂PPh₂-P,P'}(η²-RC₂R')]} (M = Mo, W, R = R' = Me; M = W, R = Me, R' = Ph) (7 → 9).

(C, H and N) (Table 1), infrared spectroscopy (Table 2), ^1H NMR spectroscopy (Table 3) and for complex **12** by ^{31}P NMR spectroscopy (Table 4). The tris(carbonyl) complexes **10** \rightarrow **12** were stable in the solid state for several months when stored under nitrogen but were less stable in solution. All complexes **10** \rightarrow **12** were soluble in dichloromethane and chloroform and insoluble in diethyl ether. Complexes **10** \rightarrow **12** were far less soluble in diethyl ether than complexes **1** \rightarrow **9**. It is interesting to note that these tetrametallic complexes **10** \rightarrow **12** were more soluble in chloroform than the tri- or bimetallic complexes **1** \rightarrow **9**.

The infrared spectra for complexes **11** and **12** show five carbonyl stretching bands which would be consistent with the presence of the *fac*- and *mer*-isomers being present in solution [21]. For complex **11** the bands at 1967, 1904, 1850 and 1835 cm^{-1} could be assigned to the *mer*-isomer [22] and absorptions at 1903 and 1814 cm^{-1} to the *fac*-isomer [21]. Similar assignments could be made for complex **12**, such that carbonyl stretching bands at 1968, 1942 and 1836 cm^{-1} could be assigned to the *mer*-isomer and 1904 and 1814 cm^{-1} could be assigned to the *fac*-isomer. The spectrum of complex **10** shows only four absorptions so it is possible for the fifth carbonyl absorption to be masked. The carbonyl stretching bands of the monodentate phosphine ligands [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-RC}_2\text{R}')]$ are possibly masked by the broad absorption in the region of 1968 to 1942 cm^{-1} .

The ^{31}P NMR spectrum of complex **12** showed five resonances. The resonance at $\delta = 31.7$ ppm is a broad multiplet and could be an overlapping doublet of Mo-PPh_2 (coordinated), thus indicating the presence of several isomers in solution. There was no resonance in the region of $\delta = -13$ ppm, indicating the absence of free phosphine. The ^1H NMR spectra are consistent with the proposed structures of these complexes.

3. Conclusions

In conclusion the novel tungsten monodentate phosphine ligands [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{Me, Ph}$; $\text{R} = \text{Me, R}' = \text{Ph}$) are excellent for use in the synthesis of multimetallic complexes of molybdenum and tungsten.

4. Experimental

The synthesis and purification of the new complexes **1** \rightarrow **12** were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. The complexes [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{Me, Ph}$; $\text{R} = \text{Me, R}' = \text{Ph}$) were prepared by the literature method [14]. All chemi-

cals were purchased from commercial sources. All solvents used were dried and distilled before use.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC 250 NMR spectrometer. ^1H NMR spectra were calibrated against SiMe_4 , and $^{31}\text{P}\{\text{H}\}$ NMR spectra were calibrated against 85% H_3PO_4 .

4.1. [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{-PPh}_2\text{-P, P}', \text{P}''\}}(\eta^2\text{-MeC}_2\text{Me})\rangle\text{Cr}(\text{CO})_5]$ (**1**)

To $[\text{Cr}(\text{CO})_6]$ (0.05 g, 0.24 mmol) dissolved in NCMe (15 cm^3) was added TMNO ($\text{ONMe}_3 \cdot 2\text{H}_2\text{O}$) (0.03 g, 0.24 mmol) and the solution was stirred in vacuo for 40 min. The resulting yellow solution was added dropwise to a solution of [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-MeC}_2\text{Me})]$ (0.25 g, 0.24 mmol) in NCMe/thf (2:1) and stirred for 2 h, after which the volume was reduced to half and stirring continued for a further 24 h. The resulting green solution was filtered and the solvent removed in vacuo to give a green crystalline powder [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}', \text{P}''\}}(\eta^2\text{-MeC}_2\text{Me})\rangle\text{Cr}(\text{CO})_5]$ (**1**) (yield 0.22 g, 73%), which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 80:20 at -17°C .

Similar reactions of $[\text{M}(\text{CO})_5(\text{NCMe})]$ ($\text{M} = \text{Cr, Mo}$ or W) (prepared in situ as above) with an equimolar quantity of L [$\text{L} = [\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{-PPh}_2\text{-P, P}'\}}(\eta^2\text{-RC}_2\text{R}')]$ ($\text{M} = \text{W, R} = \text{R}' = \text{Me, Ph}$; $\text{M} = \text{Cr, R} = \text{Me, R}' = \text{Ph}$; $\text{M} = \text{Mo, R} = \text{Me, R}' = \text{Ph, R} = \text{R}' = \text{Ph}$)] gave the bimetallic complexes $[\text{M}(\text{CO})_5\text{L}]$ (**2** \rightarrow **6**).

4.2. [$\overline{\text{WI}_2(\text{CO})\{\mu^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{-PPh}_2\text{-P, P}', \text{P}''\}}(\eta^2\text{-MeC}_2\text{Me})\rangle_2\text{Mo}(\text{CO})_4]$ (**7**)

To *cis*- $[\text{Mo}(\text{CO})_4(\text{piperidine})_2]$ (0.04 g, 0.11 mmol) in CH_2Cl_2 (30 cm^3) was added [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-MeC}_2\text{Me})]$ (0.24 g, 0.22 mmol). After stirring the reaction mixture for 24 h, the solution was filtered and the solvent was removed in vacuo to give a green crystalline powder [$\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-MeC}_2\text{Me})\rangle_2\text{Mo}(\text{CO})_4]$ (**7**) (yield 0.2 g, 90%), which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 80:20 at -17°C .

Similar reactions of *cis*- $[\text{W}(\text{CO})_4(\text{piperidine})_2]$ with an equimolar quantity of L [$\text{L} = [\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P, P}'\}}(\eta^2\text{-MeC}_2\text{Me})]$ ($\text{R} = \text{R}' = \text{Me, R} = \text{Me, R}' = \text{Ph}$)] gave the trimetallic complexes $[\text{W}(\text{CO})_4\text{L}_2]$ (**8** and **9**).

4.3. [$\{\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P,P',P''}\}}(\eta^2\text{-MeC}_2\text{Me})\}_3\text{Mo}(\text{CO})_3\}$] (**10**)

A suspension of $[\text{Mo}(\text{CO})_6]$ (0.03 g, 0.09 mmol) in degassed acetonitrile (50 cm³) was refluxed for 24 h. The resulting solution of *fac*- $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ was cooled to room temperature and [$\{\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P,P',P''}\}}(\eta^2\text{-MeC}_2\text{Me})\}_3\text{Mo}(\text{CO})_3\}$] (**10**) (yield 0.28 g, 87%), which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 80:20 at -17°C .

Similar reactions of $[\text{Mo}(\text{CO})_6]$ with an equimolar quantity of L {L = [$\{\overline{\text{WI}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}(\text{CH}_2)_2\text{PPh}_2\text{-P,P',P''}\}}(\eta^2\text{-RC}_2\text{R}')\}_3\text{Mo}(\text{CO})_3\}$] (R = R' = Ph; R = Me, R' = Ph)} gave the tetrametallic complexes $[\text{Mo}(\text{CO})_3\text{L}_3]$ (**11** and **12**).

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