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Preparation and spectroscopic properties of a series of new bimetallic phosphine-bridged seven-coordinate complexes of the type $[M_2I_4(CO)_6L_2(\mu-\overline{L L})]$ {M = Mo or W; L = PPh₃, AsPh₃ or SbPh₃; $\overline{L L} = Ph_2P(CH_2)_n PPh_2$ ($n = 1, 2$ or 4); $\overline{L L} = [Fe(\eta^5-C_5H_4PPh_2)_2]$ }

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Abstract

Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with one equivalent of L (L = PPh₃, AsPh₃ or SbPh₃) in CH₂Cl₂ at room temperature gives $[MI_2(CO)_3(NCMe)L]$, which when treated *in situ* with half an equivalent of $\overline{L L}$ ($\overline{L L} = Ph_2P(CH_2)_n PPh_2$, $n = 1, 2$ or 4 ; $\overline{L L} = [Fe(\eta^5-C_5H_4PPh_2)_2]$) affords the new bimetallic seven-coordinate complexes $[M_2I_4(CO)_6L_2(\mu-\overline{L L})]$ in high yield. ³¹P NMR studies suggest that reaction of $[WI_2(CO)_3(NCMe)(AsPh_3)]$ with an equimolar amount of $Ph_2P(CH_2)_4PPh_2$ gives a mixture of $[W_2I_4(CO)_6(AsPh_3)_2(\mu-Ph_2P(CH_2)_4PPh_2)]$, $[WI_2(CO)_3(AsPh_3)(\eta^1-Ph_2P(CH_2)_4PPh_2)]$ and unchanged $Ph_2P(CH_2)_4PPh_2$.

Introduction

Bimetallic complexes containing bridging bidentate phosphine donor ligands have received considerable attention in recent years [1–5]. Although, for example, Hor [6] has described the synthesis of the zero-valent six-coordinate complexes $[Mo_2(CO)_{10}(\mu-Ph_2P(CH_2)_n PPh_2)]$ ($n = 2$ or 3) by oxidative decarbonylation of $[Mo(CO)_6]$ with ONMe₃ in the presence of $Ph_2P(CH_2)_n PPh_2$, there has been little work carried out on bimetallic seven-coordinate complexes of molybdenum(II) or tungsten(II). We describe below a simple stepwise synthesis of the new bimetallic phosphine-bridged seven-coordinate complexes $[M_2I_4(CO)_6L_2(\mu-\overline{L L})]$ {M = Mo or W; L = PPh₃, AsPh₃ or SbPh₃; $\overline{L L} = Ph_2P(CH_2)_n PPh_2$, $n = 1, 2$ or 4 , or $[Fe(\eta^5-C_5H_4PPh_2)_2]$ }.

Results and discussion

The starting materials for this research, the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) [7] were prepared by reaction of the trisacetonitrile complexes

$[\text{M}(\text{CO})_3(\text{NCMe})_3]$ [8] *in situ* with an equimolar amount of I_2 . Equimolar quantities of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) and L ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3) react in CH_2Cl_2 at room temperature to give $[\text{MI}_2(\text{CO})_3(\text{NCMe})\text{L}]$ which have been isolated and fully characterised [9]. These $[\text{MI}_2(\text{CO})_3(\text{NCMe})\text{L}]$ complexes react *in situ* with half an equivalent of $\overline{\text{L}}\text{L}$ ($\overline{\text{L}}\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1, 2$ or 4 ; $\overline{\text{L}}\text{L} = [\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$) to give high yields of the bimetallic complexes **1–24**. The new bimetallic complexes **1–24** are stable in the solid state when stored under nitrogen and have been fully characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (Tables 1–3). The complexes **1**, **4**, **11**, **14**, **15**, **19** and **20** were confirmed as either CH_2Cl_2 or $2\text{CH}_2\text{Cl}_2$ solvates by repeated elemental analyses and ^1H NMR spectroscopy. The dinuclear nature of these compounds is suggested by molecular weight measurements on several complexes by the Rast method [10] (see Experimental section). Magnetic susceptibility measurements on compounds **1–24** show them to be diamagnetic. This was expected since the seven-coordinate molybdenum(II) and tungsten(II) complexes $[\text{M}_2\text{I}_4(\text{CO})_6\text{L}_2(\mu\text{-}\overline{\text{L}}\text{L})]$ (**1–24**) obey the effective atomic number rule. Compounds **1–24** are moderately soluble in CH_2Cl_2 and CHCl_3 , and slightly soluble in Et_2O .

Many unsuccessful attempts were made to grow single crystals for X-ray crystallography in order to elucidate the solid state structure of these complexes. The most likely structure for these seven-coordinate complexes is capped octahedral, since the vast majority of seven-coordinate mononuclear complexes of molybdenum(II) and tungsten(II) have this geometry [11] including $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ [12]. The $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR spectrum of $[\text{W}_2\text{I}_4(\text{CO})_6(\text{AsPh}_3)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ (**17**) (CDCl_3 , -25°C) showed a single resonance at $\delta = 0.1$ ppm due to the bimetallically coordinated $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$. The IR $\{\nu(\text{CO})\}$ pattern closely resembles those found in mononuclear bisphosphine complexes of the type $[\text{MX}_2(\text{CO})_3\text{L}_2]$ which generally have been found to have capped octahedral geometry [11,12].

It is noteworthy that reaction of $[\text{WI}_2(\text{CO})_3(\text{NCMe})(\text{AsPh}_3)]$ (prepared *in situ*) with one equivalent of $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ gave a mixture of $[\text{W}_2\text{I}_4(\text{CO})_6(\text{AsPh}_3)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ (**17**), $[\text{WI}_2(\text{CO})_3(\text{AsPh}_3)\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ and unreacted $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$. The $^{31}\text{P}\text{-}\{^1\text{H}\}$ (CDCl_3 , $+25^\circ\text{C}$) NMR spectrum of this mixture showed resonances at $\delta = 0.1$ ppm due to $[\text{W}_2\text{I}_4(\text{CO})_6(\text{AsPh}_3)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ (**17**), $\delta = -1.1$ and -11.1 ppm due to $[\text{WI}_2(\text{CO})_3(\text{AsPh}_3)\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ and $\delta = -17.1$ ppm due to unreacted $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$.

Experimental

The preparation and purification of the complexes described were carried out under nitrogen by standard Schlenk line techniques. The complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) were prepared by the published method [7]. All chemicals used were obtained from commercial sources. Dichloromethane was dried and distilled before use. Elemental analyses (C, H and N) were carried out with a Carlo Erba elemental analyser MOD 1106 (with helium as a carrier gas) by Mr. E. Lewis of this Department. IR spectra were recorded on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer, with tetramethylsilane as

Table 1

Physical and analytical data for the complexes $[M_2I_4(CO)_6L_2(\mu-L)_2]$

Complexes	Colour	Yield (%)	Analysis (Found (calc.) (%))	
			C	H
1 $[Mo_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}] \cdot CH_2Cl_2$	Beige	84	43.9 (43.9)	3.1 (3.0)
2 $[Mo_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}]$	Light brown	79	42.5 (43.2)	3.1 (2.8)
3 $[Mo_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}]$	Brown	79	40.6 (41.1)	3.0 (2.7)
4 $[W_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}] \cdot CH_2Cl_2$	Yellow beige	61	39.8 (39.5)	2.5 (2.6)
5 $[W_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}]$	Orange	59	39.5 (39.4)	2.9 (2.6)
6 $[W_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)PPh_2\}]$	Orange	50	37.6 (37.7)	2.8 (2.5)
7 $[Mo_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}]$	Dark green	86	45.6 (45.6)	3.1 (3.0)
8 $[Mo_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}]$	Beige	54	42.8 (43.5)	3.1 (2.9)
9 $[Mo_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}]$	Brown	75	41.7 (41.4)	2.9 (2.8)
10 $[W_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}]$	Light green	98	41.2 (41.5)	3.0 (2.8)
11 $[W_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}] \cdot CH_2Cl_2$	Yellow	52	38.5 (38.8)	2.9 (2.6)
12 $[W_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)_2PPh_2\}]$	Dark orange	96	38.2 (37.8)	2.6 (2.5)
13 $[Mo_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}]$	Dark green	84	45.9 (46.2)	3.6 (3.2)
14 $[Mo_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}] \cdot CH_2Cl_2$	Green	86	42.8 (42.8)	3.3 (3.0)
15 $[Mo_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}] \cdot 2CH_2Cl_2$	Brown	60	39.5 (39.9)	2.8 (2.9)
16 $[W_2I_4(CO)_6(PPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}]$	Yellow green	80	41.6 (42.2)	3.1 (2.9)
17 $[W_2I_4(CO)_6(AsPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}]$	Yellow orange	86	39.7 (40.4)	3.1 (2.8)
18 $[W_2I_4(CO)_6(SbPh_3)_2\{\mu-Ph_2P(CH_2)_4PPh_2\}]$	Orange	89	38.8 (38.6)	2.8 (2.7)
19 $[Mo_2I_4(CO)_6(PPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}] \cdot CH_2Cl_2$	Dark green	91	45.7 (45.5)	3.1 (3.0)
20 $[Mo_2I_4(CO)_6(AsPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}] \cdot CH_2Cl_2$	Brown	61	43.4 (43.4)	3.3 (3.4)
21 $[Mo_2I_4(CO)_6(SbPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}]$	Dark brown	84	42.9 (42.9)	2.7 (2.8)
22 $[W_2I_4(CO)_6(PPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}]$	Dark green	88	42.4 (43.0)	2.9 (2.8)
23 $[W_2I_4(CO)_6(AsPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}]$	Orange brown	94	41.1 (41.3)	2.9 (2.7)
24 $[W_2I_4(CO)_6(SbPh_3)_2\{\mu-[Fe(\eta^5-C_5H_4PPh_2)_2]\}]$	Orange	82	39.5 (39.6)	2.7 (2.5)

Table 2

Infrared data ^a for the complexes [M₂I₄(CO)₆L₂(μ-L)]

Complex	ν(CO) (cm ⁻¹)		
1	2040s	1938s	1860s
2	2005s	1964s	1930s
3	2004s	1938s	1858s
4	1998s	1920s	1900s
5	2000s	1948s	1900s
6	2000s	1938s	1902s
7	2020s	1958br	1920br
8	2009s	1958s	1920br
9	2008s	1955s	1892s
10	2008s	1942s	1910s
11	2020s	1945s	1915s
12	2009s	1944s	1912s
13	2008s	1960s	1921s
14	2020s	1958s	1922s
15	2010s	1956s	1918s
16	2002s	1939s	1904s
17	2005s	1939s	1910s
18	2004s	1938s	1905s
19	2010s	1932s	1898s
20	2005s	1959s	1896s
21	2004s	1958s	1890s
22	2006s	1942s	1910s
23	2004s	1944s	1908s
24	2002s	1943s	1904s

^a Spectra recorded in CHCl₃ as thin films between NaCl plates; s, strong; br, broad.

reference. ³¹P-{¹H} NMR spectra were also recorded on a Bruker AC 250 CP/MAS NMR spectrometer, with 85% H₃PO₄ as reference. Molecular weights of selected complexes were determined by the Rast method [10]. Magnetic susceptibility measurements were determined with a Johnson–Matthey magnetic susceptibility balance.

[Mo₂I₄(CO)₆(PPh₃)₂{μ-Ph₂P(CH₂)PPh₂}] · CH₂Cl₂ (1)

To a stirred solution of [MoI₂(CO)₃(NCMe)₂] (0.500 g, 0.969 mmol) in CH₂Cl₂ (20 cm³) under a stream of nitrogen was added PPh₃ (0.254 g, 0.969 mmol). The solution was stirred for 1 min and Ph₂P(CH₂)PPh₂ (0.186 g, 0.485 mmol) then added and the mixture stirred for a further 3 h. Filtration, followed by removal of the solvent *in vacuo* gave beige crystals of [Mo₂I₄(CO)₆(PPh₃)₂(μ-Ph₂P(CH₂)PPh₂)] · CH₂Cl₂ (1) (yield = 0.76 g, 84%), which were recrystallised from CH₂Cl₂/Et₂O. Molecular weight for [Mo₂I₄(CO)₆(PPh₃)₂{μ-Ph₂P(CH₂)PPh₂}] · CH₂Cl₂ (1), found: 1767; C₆₈H₅₄I₄Mo₂O₆P₄Cl₂ calc.: 1861.

Similar reactions of [MI₂(CO)₃(NCMe)₂] (M = Mo or W) with an equimolar quantity of L (L = PPh₃, AsPh₃ or SbPh₃) to give [MI₂(CO)₃(NCMe)L], followed by reactions with half an equivalent of Ph₂P(CH₂)_nPPh₂ (n = 1, 2 or 4) or [Fe(η⁵-C₅H₄PPh₂)₂] afforded the phosphine-bridged complexes [M₂I₄(CO)₆L₂{μ-Ph₂P(CH₂)PPh₂}] (2–18) or [M₂I₄(CO)₆L₂{μ-[Fe(η⁵-C₅H₄PPh₂)₂]}] (19–24). Reaction times for 2[MI₂(CO)₃(NCMe)₂] + 2L → 2[MI₂(CO)₃(NCMe)L] + 2NCMe

Table 3

¹H NMR data ^a for the complexes [M₂I₄(CO)₆L₂(μ-L₂)]

Complex	¹ H NMR δ (ppm)
1	7.6–7.1 (brm, 50H, Ph); 5.3 (s, 2H, CH ₂ Cl ₂); 4.9 (brm, 2H, PCH ₂ P)
2	7.7–7.1 (brm, 50H, Ph); 4.9 (brm, 2H, PCH ₂ P)
3	8.1–7.2 (brm, 50H, Ph); 5.3 (brm, 2H, PCH ₂ P)
4	7.7–7.3 (brm, 50H, Ph); 5.31 (s, 2H, CH ₂ Cl ₂); 5.1 (brm, 2H, PCH ₂ P)
5	7.7–7.3 (brm, 50H, Ph); 5.35 (brm, 2H, PCH ₂ P)
6	7.7–7.4 (brm, 50H, Ph); 5.35 (brm, 2H, PCH ₂ P)
7	7.9–7.3 (brm, 50H, Ph); 2.9 (brm, 4H, PCH ₂ CH ₂ P)
8	7.9–7.3 (brm, 50H, Ph); 2.9 (brm, 4H, PCH ₂ CH ₂ P)
9	8.1–7.4 (brm, 50H, Ph); 2.8 (brm, 4H, PCH ₂ CH ₂ P)
10	7.9–7.3 (brm, 50H, Ph); 2.8 (brm, 4H, PCH ₂ CH ₂ P)
11	7.8–7.3 (brm, 50H, Ph); 5.3 (s, 2H, CH ₂ Cl ₂); 2.8 (brm, 4H, PCH ₂ CH ₂ P)
12	7.9–7.3 (brm, 50H, Ph); 2.9 (brm, 4H, PCH ₂ CH ₂ P)
13	8.1–7.3 (brm, 50H, Ph); 5.32 (s, 2H, CH ₂ Cl ₂); 3.2 (brm, 4H, PCH ₂); 2.2 (brm, 4H, PCH ₂ CH ₂)
14	7.9–7.3 (brm, 50H, Ph); 5.3 (s, 2H, CH ₂ Cl ₂); 3.1 (brm, 4H, PCH ₂); 2.1 (brm, 4H, PCH ₂ CH ₂)
15	8.1–7.7 (brm, 50H, Ph); 5.32 (s, 4H, CH ₂ Cl ₂); 3.15 (brm, 4H, PCH ₂); 2.05 (brm, 4H, PCH ₂ CH ₂)
16	7.7–7.3 (brm, 50H, Ph); 3.25 (brm, 4H, PCH ₂); 2.0 (brm, 4H, PCH ₂ CH ₂)
17	7.7–7.3 (brm, 50H, Ph); 3.2 (brm, 4H, PCH ₂); 1.8 (brm, 4H, PCH ₂ CH ₂)
18	7.8–7.3 (brm, 50H, Ph); 3.1 (brm, 4H, PCH ₂); 1.9 (brm, 4H, PCH ₂ CH ₂)
19	7.95–7.35 (brm, 50H, Ph); 5.3 (s, 2H, CH ₂ Cl ₂); 4.78, 4.7, 4.32, 4.24 (4xs, 8H, C ₅ H ₄)
20	7.7–7.3 (brm, 50H, Ph); 5.31 (s, 2H, CH ₂ Cl ₂); 5.0, 4.8, 4.38, 4.32 (4xs, 8H, C ₅ H ₄)
21	7.8–7.3 (brm, 50H, Ph); 4.9, 4.7 (2xs, 8H, C ₅ H ₄)
22	7.9–7.35 (brm, 50H, Ph); 4.7, 4.35 (2xs, 8H, C ₅ H ₄)
23	7.85–7.1 (brm, 50H, Ph); 4.72, 4.38 (2xs, 8H, C ₅ H ₄)
24	7.75–7.24 (brm, 50H, Ph); 4.7, 4.35 (2xs, 8H, C ₅ H ₄)

^a Spectra recorded in CDCl₃ (+25 °C) referenced to SiMe₄; s, singlet; brm, broad multiplet.

and 2[MI₂(CO)₃(NCMe)L] + Ph₂P(CH₂)PPh₂ → [M₂I₄(CO)₆L₂(μ-Ph₂P(CH₂)PPh₂)] + 2NCMe at 25 °C are: (2) M = Mo, L = AsPh₃, 3 min, Ph₂P(CH₂)PPh₂, 3 h. (3) M = Mo, L = SbPh₃, 5 min, Ph₂P(CH₂)PPh₂, 3 h. Similar reaction times were used for the complexes 4–24. Molecular weight for [W₂I₄(CO)₆(PPh₃)₂(μ-Ph₂P(CH₂)PPh₂)] (10), found: 1823. C₆₈H₅₄I₄O₆P₄W₂ calc.: 1976. Molecular weight for [Mo₂I₄(CO)₆(AsPh₃)₂(μ-Ph₂P(CH₂)₄PPh₂)] · CH₂Cl₂ (14), found: 1986. C₇₁H₆₀I₄Mo₂O₆P₂As₂Cl₂ calc.: 1991. Molecular weight for [W₂I₄(CO)₆(SbPh₃)₂(μ-[Fe(η⁵-C₅H₄)PPh₂])] (24), found: 1953. C₇₆H₅₈FeI₄O₆P₂W₂Sb₂ calc.: 2248. For physical and analytical data, see Table 1.

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