

New Synthesis of Seven-coordinate Complexes of Molybdenum(II) and Tungsten(II) Containing Bidentate Phosphorus Ligands, $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 1-6$)

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Abstract

A new high yielding synthesis of the seven-coordinate complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($\text{M} = \text{Mo}$ and W ; $n = 1-6$) is described. The procedure involves reacting the complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ in CH_2Cl_2 with an equimolar amount of the bidentate phosphorus ligand. The low temperature (-70°C) ^{13}C NMR spectra of the complexes $[\text{Wl}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 3$ and 5) indicates that the geometry is capped octahedral with a carbonyl ligand in the unique capping position.

Introduction

Although a wide variety of $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ and W ; $\text{X} = \text{Cl}$ and Br ; $\text{L} = \text{phosphines}$) complexes have been reported [1], far fewer diiodo compounds have been prepared, mainly due to the difficulty [1] in synthesising $[\text{M}(\mu\text{-I})\text{I}(\text{CO})_4]_2$. There is considerable interest in seven-coordinate complexes of molybdenum(II) and tungsten(II). For example, the compounds $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ and W ; $\text{X} = \text{Cl}$ and Br ; $\text{L} = \text{PPh}_3$ and AsPh_3) are catalysts in the ring-opening polymerisation of norbornene and norbornadiene [2, 3]. We wish to report a new high-yielding synthesis of the diiodide complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($\text{M} = \text{Mo}$ and W ; $n = 1-6$).

Experimental

$[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ were prepared according to literature methods [4] and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-6$) were purchased from commercial sources. CH_2Cl_2 was dried and distilled before use.

^1H NMR spectra were recorded on a Jeol FX60 NMR spectrometer. Low temperature ^{13}C NMR spectra were recorded on a Bruker WH-400 NMR spectrometer at the University of Warwick. Infrared

spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium carrier gas).

$\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}$ (7)

To $\text{MoI}_2(\text{CO})_3(\text{NCMe})_2$ (0.23 g, 0.446 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (0.19 g, 0.446 mmol), and the mixture was stirred for 5 min. After filtration, removal of the solvent *in vacuo* gave brown crystals of $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ (yield = 0.29 g, 65%), which were recrystallised from CH_2Cl_2 .

$\text{Wl}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}$ (8)

To $\text{Wl}_2(\text{CO})_3(\text{NCMe})_2$ (0.25 g, 0.414 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (0.177 g, 0.415 mmol), and the mixture was stirred for 8 min. After filtration, removal of the solvent *in vacuo* gave green crystals of $[\text{Wl}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$ (yield = 0.25 g, 64%), which were recrystallised from CH_2Cl_2 .

In similar reactions of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, 5$ and 6) afforded the complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$.

Results and Discussion

The complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ and W) react in CH_2Cl_2 with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-6$) to afford high yields of the new seven-coordinate complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 3, 4, 5$ and 6) and the previously reported [1, 5, 6] compounds $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ ($n = 1$ and 2) via displacement of two acetonitrile ligands. The complexes have been fully characterised by elemental analyses (C, H, and N) (Table I), infrared and ^1H NMR spectroscopy (Table II). The complex $[\text{Wl}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}]$ was confirmed as a CH_2Cl_2 solvate from repeated elemental analyses

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TABLE I. Physical and Analytical Data for the Complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$

Complex	Colour	Yield (%)	Analysis (%) ^a	
			C	H
1 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}]$	brown	77	40.6(41.1)	2.6(2.7)
2 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}]$	orange	62	37.5(37.1)	2.6(2.5)
3 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$	brown	80	41.9(41.9)	3.2(2.9)
4 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$	green	68	37.7(37.9)	2.9(2.6)
5 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}]$	yellow	78	41.9(42.6)	3.2(3.1)
6 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}]$	yellow	66	38.7(38.6)	2.8(2.8)
7 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$	brown	76	43.1(43.3)	3.6(3.3)
8 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}]$	green	64	39.0(39.3)	3.1(3.0)
9 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2\}]$	brown	82	43.9(44.0)	3.6(3.5)
10 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2\}]$	green	70	39.9(40.0)	3.3(3.1)
11 $[\text{MoI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}]$	green	75	45.4(44.6)	3.9(3.6)
12 $[\text{WI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2\}] \cdot \text{CH}_2\text{Cl}_2$	yellow	66	38.7(38.5)	3.2(3.2)

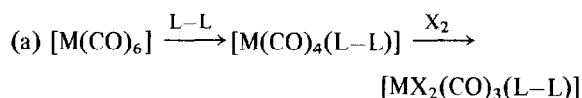
^aCalculated values in parenthesis.TABLE II. Infrared^a and ¹H NMR^b Data for the Complexes $[\text{MI}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$

Complex	$\nu(\text{CO}) (\text{cm}^{-1})$	¹ H NMR Data (δ)
1	2035(m), 1967(s), 1915(m)	7.26 (m, 20H, Ph), 1.63 (s, 2H, PCH ₂)
2	2035(m), 1940(s), 1920(m)	7.45 (m, 20H, Ph) 2.72 (brs, 2H, PCH ₂)
3	2035(m), 1966(s), 1915(s)	7.48 (m, 20H, Ph) 2.85 (d, $J^{31}\text{P}-^1\text{H} = 16.1 \text{ Hz}$, 4H, PCH ₂)
4	2015(s), 1934(s), 1900(s)	7.45 (m, 20H, Ph), 2.83 (d, $J^{31}\text{P}-^1\text{H} = 16.4 \text{ Hz}$, 4H, PCH ₂)
5	2035(s), 1960(s), 1919(s)	7.42 (m, 20H, Ph), 3.33 (m, 4H, PCH ₂) 1.96 (brs, 2H, P-CH ₂ CH ₂)
6	2010(s), 1940(s), 1904(s)	7.26 (m, 20H, Ph), 3.32 (m, 2H, PCH ₂), 2.78 (m, 2H, PCH ₂), 2.17 (s, 2H, PCH ₂ CH ₂)
7	2020(s), 1950(s), 1912(s)	7.43 (m, 20H, Ph), 3.11 (m, 4H, PCH ₂), 2.0 (m, 4H, PCH ₂ CH ₂)
8	2010(s), 1937(s), 1902(s)	7.41 (m, 20H, Ph), 3.13 (m, 4H, PCH ₂), 1.99 (m, 4H, PCH ₂ CH ₂)
9	2025(s), 1958(s), 1920(s)	7.49 (m, 20H, Ph), 2.07 (m, 4H, PCH ₂), 1.58 (m, 4H, PCH ₂ CH ₂), 1.25 (s, 2H, PCH ₂ CH ₂ CH ₂)
10	2025(s), 1946(s), 1910(s)	7.41 (m, 20H, Ph), 3.13 (m, 4H, PCH ₂), 2.18 (m, 4H, PCH ₂ CH ₂), 1.25 (brs, 2H, PCH ₂ CH ₂ CH ₂)
11	2020(s), 1955(s), 1916(s)	7.41 (m, 20H, Ph), 3.07 (m, 4H, PCH ₂), 1.58 (brs, 4H, PCH ₂ CH ₂), 1.14 (brs, 4H, PCH ₂ CH ₂ CH ₂)
12	2015(s), 1935(s), 1904(s)	7.42 (m, 20H, Ph), 5.30 (s, 2H, CH ₂ Cl ₂), 3.12 (brs, 4H, PCH ₂), 2.59 (m, 4H, PCH ₂ CH ₂), 1.25 (m, 4H, PCH ₂ CH ₂ CH ₂)

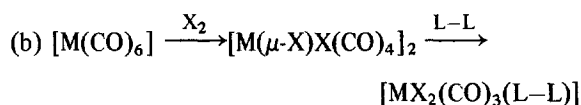
^aSpectra recorded in CHCl₃; m, medium; s, strong. ^bSpectra recorded in CDCl₃ (+25 °C) and referenced to Me₄Si.

and ¹H NMR spectroscopy. The complexes are all moderately air-stable in the solid state and can be stored under nitrogen for several days. The compounds are soluble in polar solvents such as CHCl₃ and CH₂Cl₂ but are only slightly soluble in hexane and diethylether. Although the complexes $[\text{MX}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ (M = Mo and W; X = Cl; Br and I; $n = 1$ and 2) have been made by the two routes shown in Scheme 1 [1, 5, 6], the yields obtained based on these methods for the di-

iodide compounds are relatively low. Whereas the complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ are prepared in quantitative yield by the reaction sequence shown in Scheme 2 [4].

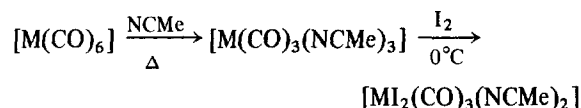


M = Mo and W; X = Br and I; L-L = PPh₂P(CH₂)_nPPh₂ ($n = 1$ and 2)



M = Mo and W; X = Cl, Br and I; L-L = Ph₂P(CH₂)_nPPh₂ (n = 1 and 2)

Scheme 1.



Scheme 2.

The geometry of the complexes [MI₂(CO)₃{Ph₂P(CH₂)_nPPh₂}] is likely to be capped octahedral in view of the previously reported X-ray crystal structures of seven-coordinate complexes, all having capped octahedral geometry. The infrared spectral properties of the [MI₂(CO)₃{Ph₂P(CH₂)_nPPh₂}] complexes are similar to analogous compounds which have been shown to have capped octahedral geometry [7–21]. The geometry of the seven-coordinate complexes containing bidentate ligands [MoBr₂(CO)₃{Ph₂P(CH₂)₂PPh₂}] [17], [Wl₂(CO)₃{Me₂P(CH₂)₂PMe₂}] [18], [Wl₂(CO)₃{Me₂-AsC(CF₃):C(CF₃)AsMe₂}] [19], [MoI₂(CO)₃{rac-o-C₆H₄(AsMePh)₂}] [20], [MoI₂(CO)₃{meso-o-C₆H₄(AsMePh)₂}] [20] and [Wl₂(CO)₃{Ph₂As(CH₂)AsPh₂}] [21] which have been determined by X-ray crystallography are all capped octahedral and have a carbonyl ligand in the unique capping position. Colton and Kevecordes [22] have recently shown how low temperature ¹³C NMR spectroscopy can be used to indicate if there is a carbonyl ligand in the capping position of a capped octahedral structure. The low temperature ¹³C NMR spectra of the [MI₂(CO)₃{Ph₂P(CH₂)_nPPh₂}] complexes were difficult to obtain due to the low solubility of these complexes at -70 °C, however, the low temperature (-70 °C) ¹³C NMR spectra of [Wl₂(CO)₃{Ph₂P(CH₂)_nPPh₂}] for n = 3 showed two carbonyl resonances at δ (CD₂Cl₂) = 232.9 and 216.5 ppm and for n = 5 showed two carbonyl resonances at δ (CD₂Cl₂) = 232.4 and 212.9 ppm and it is likely that the low field resonances at 232.9 and 232.4 are due to a carbonyl ligand in the unique capping position of the capped octahedral structure.

We are currently investigating the catalytic activity of these [MI₂(CO)₃{Ph₂P(CH₂)_nPPh₂}] complexes since the seven-coordinate compounds [MX₂-

(CO)₃L₂] (M = Mo and W; X = Cl and Br; L = PPh₃ and AsPh₃) have recently been discovered to be catalysts in the ring-opening polymerisation of norbornene and norbornadiene [2, 3].

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