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New Synthesis of Seven-coordinate Complexes of Molybdenum(II) and Tungsten(II) Containing Bidentate Phosphorus Ligands, $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1–6)

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Abstract

A new high yielding synthesis of the seven-coordinate complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo and W; n = 1–6) is described. The procedure involves reacting the complexes $[MI_2(CO)_3(NCMe)_2]$ 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 $[WI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (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 $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = phosphines) complexes have been reported [1], far fewer diiodo compounds have been prepared, mainly due to the difficulty [1] in synthesising $[M(\mu\text{-}I)I(CO)_4]_2$. There is considerable interest in seven-coordinate complexes of molybdenum(II) and tungsten(II). For example, the compounds $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = 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 $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo and W; n = 1–6).

Experimental

$[MI_2(CO)_3(NCMe)_2]$ were prepared according to literature methods [4] and $Ph_2P(CH_2)_nPPh_2$ (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).

$MoI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}$ *(7)*

To $MoI_2(CO)_3(NCMe)_2$ (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 $Ph_2P(CH_2)_4PPh_2$ (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 $[MoI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}]$ (yield = 0.29 g, 65%), which were recrystallised from CH_2Cl_2.

$WI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}$*(8)*

To $WI_2(CO)_3(NCMe)_2$ (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 $Ph_2P(CH_2)_4PPh_2$ (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 $[WI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}]$ (yield = 0.25 g, 64%), which were recrystallised from CH_2Cl_2.

In similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3, 5 and 6) afforded the complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$.

Results and Discussion

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) react in CH_2Cl_2 with $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) to afford high yields of the new seven-coordinate complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 3, 4, 5 and 6) and the previously reported [1, 5, 6] compounds $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (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 $[WI_2(CO)_3\{Ph_2P(CH_2)_6PPh_2\}]$ 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 $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$

Complex	Colour	Yield (%)	Analysis (%)[a]	
			C	H
1 $[MoI_2(CO)_3\{Ph_2P(CH_2)PPh_2\}]$	brown	77	40.6(41.1)	2.6(2.7)
2 $[WI_2(CO)_3\{Ph_2P(CH_2)PPh_2\}]$	orange	62	37.5(37.1)	2.6(2.5)
3 $[MoI_2(CO)_3\{Ph_2P(CH_2)_2PPh_2\}]$	brown	80	41.9(41.9)	3.2(2.9)
4 $[WI_2(CO)_3\{Ph_2P(CH_2)_2PPh_2\}]$	green	68	37.7(37.9)	2.9(2.6)
5 $[MoI_2(CO)_3\{Ph_2P(CH_2)_3PPh_2\}]$	yellow	78	41.9(42.6)	3.2(3.1)
6 $[WI_2(CO)_3\{Ph_2P(CH_2)_3PPh_2\}]$	yellow	66	38.7(38.6)	2.8(2.8)
7 $[MoI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}]$	brown	76	43.1(43.3)	3.6(3.3)
8 $[WI_2(CO)_3\{Ph_2P(CH_2)_4PPh_2\}]$	green	64	39.0(39.3)	3.1(3.0)
9 $[MoI_2(CO)_3\{Ph_2P(CH_2)_5PPh_2\}]$	brown	82	43.9(44.0)	3.6(3.5)
10 $[WI_2(CO)_3\{Ph_2P(CH_2)_5PPh_2\}]$	green	70	39.9(40.0)	3.3(3.1)
11 $[MoI_2(CO)_3\{Ph_2P(CH_2)_6PPh_2\}]$	green	75	45.4(44.6)	3.9(3.6)
12 $[WI_2(CO)_3\{Ph_2P(CH_2)_6PPh_2\}]\cdot CH_2Cl_2$	yellow	66	38.7(38.5)	3.2(3.2)

[a] Calculated values in parenthesis.

TABLE II. Infrared[a] and ^1H NMR[b] Data for the Complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$

Complex	$\nu(CO)$ (cm^{-1})	^1H 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,$J^{31}P-^1H$ = 16.1 Hz, 4H, PCH_2)
4	2015(s), 1934(s), 1900(s)	7.45 (m,20H,Ph), 2.83 (d,$J^{31}P-^1H$ = 16.4 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,$P\text{-}CH_2CH_2$)
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_2CH_2)
7	2020(s), 1950(s), 1912(s)	7.43 (m,20H,Ph), 3.11 (m,4H,PCH_2), 2.0 (m,4H,PCH_2CH_2)
8	2010(s), 1937(s), 1902(s)	7.41 (m,20H,Ph), 3.13 (m,4H,PCH_2), 1.99 (m,4H,PCH_2CH_2)
9	2025(s), 1958(s), 1920(s)	7.49 (m,20H,Ph), 2.07 (m,4H,PCH_2), 1.58 (m,4H,PCH_2CH_2), 1.25 (s,2H,$PCH_2CH_2CH_2$)
10	2025(s), 1946(s), 1910(s)	7.41 (m,20H,Ph), 3.13 (m,4H,PCH_2), 2.18 (m,4H,PCH_2CH_2), 1.25 (brs,2H,$PCH_2CH_2CH_2$)
11	2020(s), 1955(s), 1916(s)	7.41 (m,20H,Ph), 3.07 (m,4H,PCH_2), 1.58 (brs,4H,PCH_2CH_2), 1.14 (brs,4H,$PCH_2CH_2CH_2$)
12	2015(s), 1935(s), 1904(s)	7.42 (m,20H,Ph), 5.30 (s,2H,CH_2Cl_2), 3.12 (brs,4H,PCH_2), 2.59 (m,4H,PCH_2CH_2), 1.25 (m,4H,$PCH_2CH_2CH_2$)

[a] Spectra recorded in $CHCl_3$; m, medium; s, strong. [b] Spectra recorded in $CDCl_3$ (+25 °C) and referenced to Me_4Si.

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 $CHCl_3$ and CH_2Cl_2 but are only slightly soluble in hexane and diethylether. Although the complexes $[MX_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (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 diiodide compounds are relatively low. Whereas the complexes $[MI_2(CO)_3(NCMe)_2]$ are prepared in quantitative yield by the reaction sequence shown in Scheme 2 [4].

$$\text{(a) } [M(CO)_6] \xrightarrow{L-L} [M(CO)_4(L-L)] \xrightarrow{X_2} [MX_2(CO)_3(L-L)]$$

M = Mo and W; X = Br and I; L–L = $PPh_2P(CH_2)_nPPh_2$ (n = 1 and 2)

$$\text{(b) } [M(CO)_6] \xrightarrow{X_2} [M(\mu\text{-}X)X(CO)_4]_2 \xrightarrow{L-L} [MX_2(CO)_3(L-L)]$$

M = Mo and W; X = Cl, Br and I; L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1 and 2)

Scheme 1.

$$[M(CO)_6] \xrightarrow[\Delta]{NCMe} [M(CO)_3(NCMe)_3] \xrightarrow[0°C]{I_2} [MI_2(CO)_3(NCMe)_2]$$

Scheme 2.

The geometry of the complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ 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 $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ 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 $[MoBr_2(CO)_3\{Ph_2P(CH_2)_2PPh_2\}]$ [17], $[WI_2(CO)_3\{Me_2P(CH_2)_2PMe_2\}]$ [18], $[WI_2(CO)_3\{Me_2AsC(CF_3){:}C(CF_3)AsMe_2\}]$ [19], $[MoI_2(CO)_3\{rac\text{-}o\text{-}C_6H_4(AsMePh)_2\}]$ [20], $[MoI_2(CO)_3\{meso\text{-}o\text{-}C_6H_4(AsMePh)_2\}]$ [20] and $[WI_2(CO)_3\{Ph_2As(CH_2)AsPh_2\}]$ [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 ^{13}C 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 ^{13}C NMR spectra of the $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ complexes were difficult to obtain due to the low solubility of these complexes at –70 °C, however, the low temperature (–70 °C) ^{13}C NMR spectra of $[WI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ for $n = 3$ showed two carbonyl resonances at δ (CD_2Cl_2) = 232.9 and 216.5 ppm and for $n = 5$ showed two carbonyl resonances at δ (CD_2Cl_2) = 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 $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ complexes since the seven-coordinate compounds $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl and Br; L = PPh_3 and $AsPh_3$) have recently been discovered to be catalysts in the ring-opening polymersiation of norbornene and norbornadiene [2, 3].

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