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Tricyclohexylphosphinecarbondisulphide seven-coordinate complexes of molybdenum(II) and tungsten(II)

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Abstract

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with one equivalent of S_2CPCy_3 in CH_2Cl_2 to afford the new seven-coordinate complexes $[MI_2(CO)_3(S_2CPCy_3)]$. Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), with two equivalents of S_2CPCy_3 afford the new dicationic complexes $[M(CO)_3(S_2CPCy_3)_2]2I$ in good yield. The dicationic nature of $[W(CO)_3(S_2CPCy_3)_2]2I$ was confirmed by the formation of the complex $[W(CO)_3(S_2CPCy_3)_2][BPh_4]_2$ by iodide exchange with $Na[BPh_4]$. Further reaction *in situ* of $[M(CO)_3(S_2CPCy_3)_2]2I$ with one equivalent of S_2CPCy_3 afforded the tris ligand complex $[W(CO)_3(S_2CPCy_3)_3]2I$. The reaction of $[W(CO)_3(S_2CPCy_3)_3]2I$ with $Na[BPh_4]$ in acetonitrile gave $[W(CO)_3(S_2CPCy_3)_3][BPh_4]_2$, which confirmed the dicationic nature of $[W(CO)_3(S_2CPCy_3)_3]2I$. The mixed ligand complexes $[MI(CO)_3(PPh_3)(S_2CPCy_3)]I$ (M = Mo or W) and $[WI(CO)_3L(S_2CPCy_3)]I$ (L = $P(OPh)_3$, $AsPh_3$ or $SbPh_3$) were synthesised by reaction of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L in CH_2Cl_2 followed by an *in situ* reaction with one equivalent of S_2CPCy_3. The cationic nature of $[MI(CO)_3(PPh_3)(S_2CPCy_3)]I$ was confirmed by iodide exchange with $Na[BF_4]$ to afford the complexes $[MI(CO)_3(PPh_3)(S_2CPCy_3)][BF_4]$. The reaction of two equivalents of $[WI_2(CO)_3(NCMe)(PPh_3)]$ with S_2CPCy_3 afforded the ligand-bridged complex $[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)]$. Treatment of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of PPh_3 followed by an *in situ* reaction with one equivalent of S_2CPCy_3 afforded the dicationic complex $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I$. The ionic nature of the complex was confirmed by iodide exchange with $Na[BPh_4]$ to give $[W(CO)_3(PPh_3)_2(S_2CPCy_3)][BPh_4]_2$. Treatment of $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I$ with one further equivalent of S_2CPCy_3 afforded the complex $[W(CO)_3(PPh_3)_2(S_2CPCy_3)_2]2I$. The low temperature ^{13}C NMR spectra (carbonyl region) of several seven-coordinate complexes are interpreted to suggest likely structures for these compounds.

Introduction

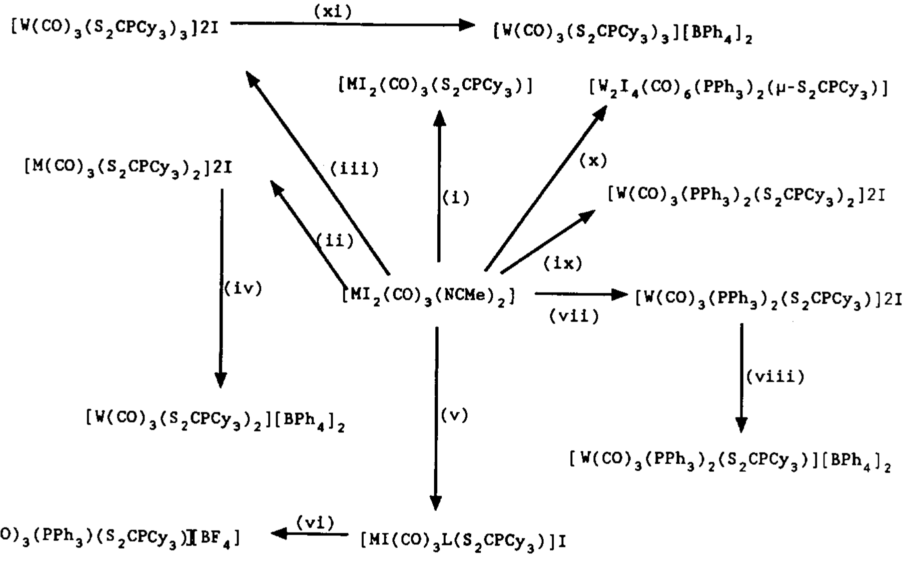
Over the last 30 years there has been much interest in seven-coordinate complexes of molybdenum(II) and tungsten(II). Many examples of seven-coordinate complexes containing anionic group 6B donor ligands such as dithiocarbamates, xanthates and piconalines have been reported [1–7]. However, comparatively few examples of seven-coordinate molybdenum(II) and tungsten(II) complexes containing neutral 6B donor ligands have been reported. Examples include $[MX_2(CO)_3(dth)]$ (M = Mo or W; X = Br or I; dth = 2,5-dithiahexane) reported by Mannerskantz and Wilkinson in 1962 [8], and the first selenium seven-coordinate complexes

$[MX_2(CO)_3(LL')]$ ($M = Mo$ or W; $X = Cl$ or Br; $LL' = Ph_2P(CH_2)P(Se)Ph_2$) and $[MoX_2(CO)_2(LL')_2]$ ($X = Cl$ or Br; $LL' = Ph_2P(CH_2)P(Se)Ph_2$) or $[MoX_2(CO)_3\{Ph_2As(CH_2)P(Se)Ph_2\}]$ ($X = Cl$ or Br) reported by Colton and Panagiotidou in 1987 [9]. Hitherto no examples of seven-coordinate complexes containing tricyclohexylphosphinecarbondisulphide have been reported.

In recent years, we have been studying the chemistry of the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) which are synthesised in quantitative yield by reaction of the zero-valent complexes $[M(CO)_3(NCMe)_3]$ with an equimolar quantity of I_2 at 0 °C [10]. The bis-acetonitrile compounds $[MI_2(CO)_3(NCMe)_2]$ have been found to react readily with a range of neutral monodentate oxygen and sulphur donor ligands (see, for example Ref. 11,12). In this paper, we describe the preparation of some new seven-coordinate complexes containing the neutral sulphur donor ligand S_2CPCy_3.

Results and discussion

The neutral sulphur donor ligand tricyclohexylphosphinecarbondisulphide reacts with the complexes $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W), $[MI_2(CO)_3(NCMe)(PPh_3)]$, $[WI_2(CO)_3(NCMe)L]$ ($L = P(OPh)_3$, $AsPh_3$ or $SbPh_3$) or $[WI_2(CO)_3(PPh_3)_2]$ to give a range of new seven-coordinate complexes. The reactions described in this paper are summarised in Scheme 1. All the new seven-coordinate complexes have been characterised by elemental analysis (C, H and N) (Table 1), IR



Scheme 1. All reactions carried out in CH_2Cl_2 at room temperature except (iv), (viii) and (xi) which were carried out in NCMe. Reagents: (i) $M = Mo$ or W, S_2CPCy_3 for 5 min. (ii) $M = Mo$ or W, $2S_2CPCy_3$ for 5 min. (iii) $M = W$, $3S_2CPCy_3$ for 30 min. (iv) $M = W$, $2Na[BPh_4]$ for 18 h. (v) $M = Mo$ or W, $L = PPh_3$ (1 min), S_2CPCy_3 for 5 min; $M = W$, $L = P(OPh)_3$ (5 min), $AsPh_3$ (3 min), $SbPh_3$ (5 min). (vi) $M = Mo$ or W, $L = PPh_3$, $Na[BF_4]$ for 18 h. (vii) $M = W$, $2PPh_3$ (5 min), S_2CPCy_3 (5 min). (viii) $M = W$, $2Na[BPh_4]$ for 18 h. (ix) $M = W$, $2PPh_3$ (5 min), $2S_2CPCy_3$ (5 min). (x) $M = W$, PPh_3 (1 min), $\frac{1}{2}S_2CPCy_3$ (30 min). (xi) $M = W$, $2Na[BPh_4]$ for 18 h.

Table 1

Physical and analytical data for $[MI_2(CO)_3(S_2CPCy_3)]$ and derivatives

Complex	Colour	Yield (%)	Analysis (Found (calcd) (%))	
			C	H
$[MoI_2(CO)_3(S_2CPCy_3)] \cdot CH_2Cl_2$ **(1)**	Dark purple	66	31.6 (31.6)	4.5 (4.0)
$[WI_2(CO)_3(S_2CPCy_3)]$ **(2)**	Dark purple	74	30.3 (30.1)	3.6 (3.8)
$[Mo(CO)_3(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ **(3)**	Dark purple	70	40.1 (40.1)	5.8 (5.4)
$[W(CO)_3(S_2CPCy_3)_2]2I$ **(4)**	Dark purple	76	39.7 (39.9)	5.7 (5.4)
$[W(CO)_3(S_2CPCy_3)_2][BPh_4]_2$ **(5)**	Dark red	61	65.4 (66.0)	6.7 (6.6)
$[W(CO)_3(S_2CPCy_3)_3]2I$ **(6)**	Dark purple	83	44.8 (44.3)	6.5 (6.3)
$[W(CO)_3(S_2CPCy_3)_3][BPh_4]_2$ **(7)**	Dark brown	69	65.2 (65.6)	7.8 (7.1)
$[MoI(CO)_3(PPh_3)(S_2CPCy_3)]I$ **(8)**	Dark green	80	45.6 (45.6)	4.6 (4.6)
$[MoI(CO)_3(PPh_3)(S_2CPCy_3)][BF_4]$ **(9)**	Green	71	48.0 (47.5)	4.5 (4.8)
$[WI(CO)_3(PPh_3)(S_2CPCy_3)]I$ **(10)**	Dark purple	71	42.1 (42.1)	4.6 (4.2)
$[WI(CO)_3(PPh_3)(S_2CPCy_3)][BF_4] \cdot CH_2Cl_2$ **(11)**	Green	60	42.0 (41.6)	4.1 (4.4)
$[WI(CO)_3\{P(OPh)_3\}(S_2CPCy_3)]I$ **(12)**	Dark purple	87	41.0 (40.4)	4.0 (4.1)
$[WI(CO)_3(AsPh_3)(S_2CPCy_3)]I$ **(13)**	Dark purple	70	40.5 (40.6)	3.6 (4.1)
$[WI(CO)_3(SbPh_3)(S_2CPCy_3)]I$ **(14)**	Dark purple	87	41.0 (40.4)	4.0 (4.1)
$[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I \cdot 1\frac{1}{2}CH_2Cl_2$ **(15)**	Dark purple	74	46.6 (46.7)	4.4 (4.3)
$[W(CO)_3(PPh_3)_2(S_2CPCy_3)][BPh_4]_2$ **(16)**	Green	71	70.8 (71.2)	5.7 (5.8)
$[W(CO)_3(PPh_3)_2(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ **(17)**	Dark purple	76	50.0 (50.0)	5.3 (5.3)
$[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)] \cdot CH_2Cl_2$ **(18)**	Dark brown	82	37.1 (37.1)	3.3 (3.3)

spectroscopy (Table 2) and selected complexes by ^1H NMR spectroscopy (Table 3). The complexes **1**, **3**, **11**, **15**, **17** and **18** were confirmed as 1/2 CH_2Cl_2, CH_2Cl_2 or 1 1/2 CH_2Cl_2 solvates by repeated elemental analyses and ^1H NMR spectroscopy. Magnetic susceptibility measurements of the seven-coordinate complexes showed them to be diamagnetic, which was expected, since complexes **1–18** obey the 18-electron rule. The complexes described in this paper are moderately air-stable in the solid state if stored under a nitrogen atmosphere, but are much more air-sensitive in solution. The seven-coordinate complexes **1–18** described in this paper are soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but are insoluble in diethylether and hydrocarbon solvents.

Table 2

IR data [a] for $[MI_2(CO)_3(S_2CPCy_3)]$ and derivatives

Complex	$\nu(C\equiv O)$ (cm^{-1})
1	2000(s), 1965(s) and 1925(s)
2	2005(s), 1945(s) and 1905(s)
3	2030(s), 1975(s) and 1925(s)
4	2020(s), 1950(s) and 1915(s)
5	2025(s), 1960(s) and 1920(s)
6	2005(s), 1980(s) and 1915(s)
7	2005(s), 1970(s) and 1925(s)
8	2000(s), 1950(s) and 1915(s)
9	2005(s), 1940(s) and 1920(s)
10	2010(s), 1975(m) and 1920(s)
11	2000(m), 1940(s) and 1860(s)
12	2000(m), 1950(s) and 1920(s)
13	2000(s), 1960(s) and 1925(s)
14	2000(s), 1935(s) and 1880(m)
15	2010(s), 1945(s) and 1905(m)
16	2015(m), 1955(s) and 1885(s)
17	2000(m), 1950(s) and 1895(m)
18	2010(s), 2000(m), 1980(m), 1935(s) and 1880(m)

[a] Spectra recorded as thin films between NaCl plates in $CHCl_3$; m = medium, s = strong.

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with an equimolar quantity of S_2CPCy_3 in CH_2Cl_2 for 5 min to afford the complexes $[MI_2(CO)_3(S_2CPCy_3)]$ (**1** and **2**). Reaction of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of S_2CPCy_3, rapidly afforded the purple cationic products $[M(CO)_3(S_2CPCy_3)_2]2I$ (**3** and **4**). The dicationic nature of the complexes was confirmed by preparing the tetraphenylborate salt $[W(CO)_3(S_2CPCy_3)_2][BPh_4]_2$ (**5**) by reaction of $[W(CO)_3(S_2CPCy_3)_2]2I$ with $Na[BPh_4]$ in NCMe. Reaction of $[WI_2(CO)_3(NCMe)_2]$

Table 3

Selected ^1H HMR data [a] for $[MI_2(CO)_3(S_2CPCy_3)]$ and derivatives

Complex	δ (ppm)
1	5.3 (s, 2H, CH_2Cl_2); 1.95, 1.8, 1.7, 1.3 (m, 33H, Cy)
3	5.3 (s, 3H, CH_2Cl_2); 1.85 (m, 36H, Cy); 1.3 (m, 30H, Cy)
5	7.5 (m, 40H, Ph); 1.9 (m, 36H, Cy); 1.3 (m, 30H, Cy)
7	7.4 (m, 40H, Ph); 1.85 (m, 54H, Cy); 1.25 (m, 45H, Cy)
8	7.55 (m, 15H, Ph); 1.95, 1.75 (d, 18H, Cy); 1.35(s, 15H, Cy)
9	7.45 (m, 15H, Ph); 1.9, 1.8 (m, 18H, Cy); 1.35 (d, 15H, Cy)
10	7.65 (m, 15H, Ph); 1.95, 1.8 (d, 18H, Cy); 1.35 (m, 15H, Cy)
11	7.7 (m, 3H, Ph); 7.48 (m, 12H, Ph); 5.3 (s, 2H, CH_2Cl_2); 1.9, 1.8 (d, 18H, Cy); 1.35 (m, 15H, Cy)
12	7.35 (m, 3H, Ph); 7.2 (m, 6H, Ph); 6.8 (m, 6H, Ph); 2.0, 1.8 (d, 18H, Cy); 1.3 (d, 15H, Cy)
13	7.35 (m, 15H, Ph); 2.0, 1.8, 1.15 (m, 33H, Cy)
14	7.55 (m, 3H, Ph), 7.45 (m, 6H, Ph); 7.32 (m, 6H, Ph); 2.0, 1.8 (m, 18H, Cy); 1.38 (d, 15H, Cy)
15	7.55 (m, 30H, Ph); 5.3 (s, 3H, CH_2Cl_2); 1.85, 1.35 (m, 33H, Cy)
16	7.5 (m, 70H, Ph); 1.8 (m, Cy), 1.3 (m, Cy, 66H)
17	7.5 (m, 30H, Ph); 5.3 (s, 3H, CH_2Cl_2); 1.95, 1.8 (d, Cy), 1.35 (s, Cy, 66H)
18	7.5 (bm, 30H, Ph): 5.3 (s, 2H, CH_2Cl_2); 1.95, 1.8 (d, 18H, Cy); 1.45 (m, 15H, Cy)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to Me_4Si. b, broad; d, doublet; m, multiplet; s, singlet.

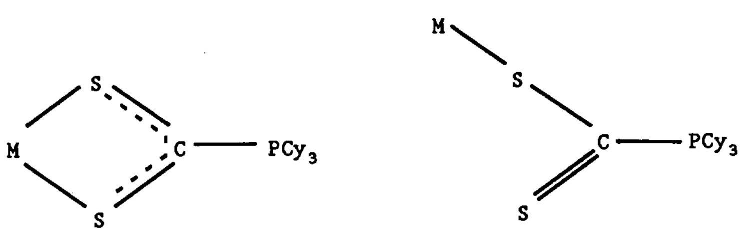


Fig. 1. Bidentate (a) and monodentate (b) coordination of a tricyclohexylphosphinecarbondisulphide ligand attached to a transition-metal centre.

with two equivalents of S_2CPCy_3, followed by addition of one further equivalent of S_2CPCy_3 *in situ* afforded the purple dicationic complex $[W(CO)_3(S_2CPCy_3)3]2I$. One of the S_2CPCy_3 ligands must coordinate to the metal in a bidentate manner, with two S_2CPCy_3 ligands bonding monodentately. It would appear, therefore, that the S_2CPCy_3 ligands prefer to bond in a monodentate fashion in preference to bonding bidentately when this would involve the loss of CO. The bidentate and monodentate coordination of a S_2CPCy_3 ligand to a transition-metal centre is shown in Fig. 1. It should be noted that Riera and co-workers [13] have prepared and structurally characterised by X-ray crystallography the manganese complex *fac*-$[Mn(CO)_3(\eta^1\text{-}S_2CPCy_3)(\eta^2\text{-}S_2CPCy_3)][ClO_4]$ which contains both mono- and bidentate coordination of the S_2CPCy_3 ligand.

The mixed ligand complexes $[MI(CO)_3L(S_2CPCy_3)]I$ (M = Mo or W, L = PPh_3; M = W, L = $P(OPh)_3$, $AsPh_3$ or $SbPh_3$) (**8**, **10**, **12–14**) were prepared by reacting $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L in CH_2Cl_2 at room temperature to give $[MI_2(CO)_3(NCMe)L]$ which have been previously described [14]. The monoacetonitrile complexes react *in situ* with one equivalent of ligand to give the new purple cationic complexes $[MI(CO)_3L(S_2CPCy_3)]I$ (**8**, **10**, **12–14**). The cationic nature was confirmed by the preparation of the complexes $[MI(CO)_3(PPh_3)(S_2CPCy_3)][BF_4]$ (M = Mo or W) (**9** and **11**) by iodide exchange with $Na[BF_4]$.

The low temperature ^{13}C NMR spectra ($-70\,°C$, CD_2Cl_2) of $[WI(CO)_3(PPh_3)(S_2CPCy_3)]I$ (**10**) and $[WI(CO)_3(AsPh_3)(S_2CPCy_3)]I$ (**13**) showed resonances at δ = 200.73 and 228.10 ppm, and 200.77 and 228.24 ppm respectively. From the work of Colton and Kevekordes [15] on the low temperature ^{13}C NMR spectra of seven-coordinate complexes of molybdenum(II) and tungsten(II) it is likely that the low field resonances at δ = 228.10 and 228.24 ppm respectively are due to a carbonyl ligand in the capping position of a capped octahedral structure. Ganscow and Vernon [16] have suggested that the low field resonances for carbonyl ligands in the capping position is due to π-backdonation and the carbonyl resonance occurs at lower field compared to an octahedral carbonyl resonance. The most likely structure of these complexes is shown in Fig. 2 with the capped face furthest away from the bulky S_2CPCy_3 ligand. The proposed capped octahedral structure is expected as most seven-coordinate complexes of molybdenum(II) and tungsten(II) have such a geometry [17–24].

The reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of triphenylphosphine give the previously reported $[WI_2(CO)_3(PPh_3)_2]$ [25]. Further reaction *in situ* with one equivalent of S_2CPCy_3 afforded the purple dicationic complex $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (**15**). The dicationic nature was confirmed by the synthesis of the complex $[W(CO)_3(PPh_3)_2(S_2CPCy_3)][BPh_4]_2$ (**16**) by

Table 4

Low temperature ^{13}C NMR data (δ ppm)[a] (carbonyl resonances) for selected seven-coordinate tricyclohexylphosphinecarbondisulphide complexes of tungsten(II)

Complex	$\delta(C{\equiv}O)$ (ppm)
10	200.73, 228.10
13	200.77, 228.24
18	200.67, 228.15

[a] Spectra recorded in CD_2Cl_2 (−70 °C) and referenced to Me_4Si.

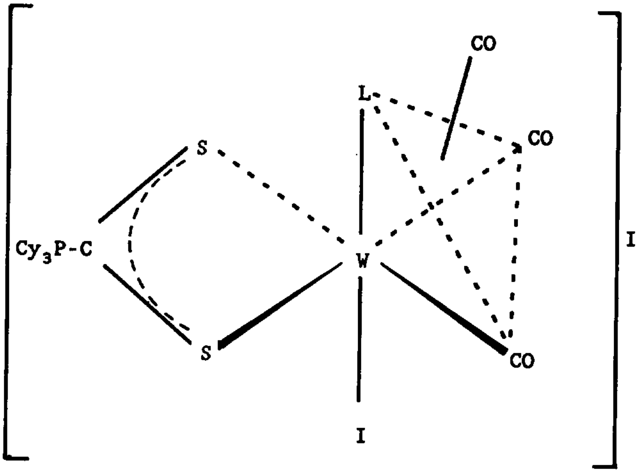


Fig. 2. Proposed structure for the complexes $[WI(CO)_3L(S_2CPCy_3)]I$ ($L = PPh_3$ and $AsPh_3$).

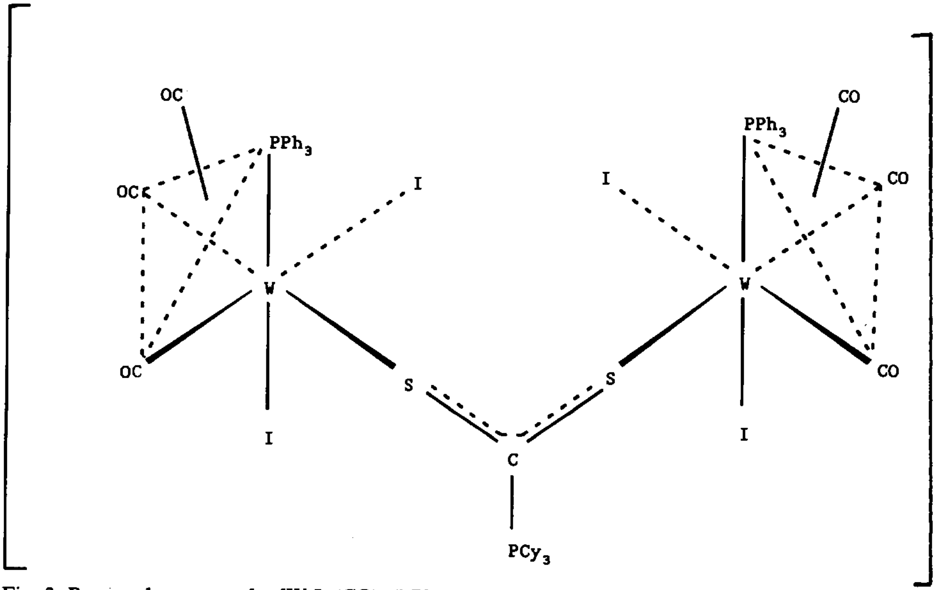


Fig. 3. Proposed structure for $[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)]$.

iodide exchange of $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I \cdot 1\frac{1}{2}CH_2Cl_2$ with $Na[BPh_4]$. Reaction *in situ* of $[WI_2(CO)_3(PPh_3)_2]$ with two equivalents of S_2CPCy_3 afforded the dicationic complex $[W(CO)_3(PPh_3)_2(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (**17**). The S_2CPCy_3 ligands bond in a monodentate manner to the central metal in preference to loss of carbonyl.

The reaction of $[WI_2(CO)_3(NCMe)_2]$ with triphenylphosphine to give $[WI_2(CO)_3(NCMe)(PPh_3)]$ followed by reaction *in situ* with a half-equivalent of S_2CPCy_3 afforded the dark brown complex $[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)] \cdot CH_2Cl_2$ (**18**) containing a bridging S_2CPCy_3 ligand. The low temperature ^{13}C (−70 °C, CD_2Cl_2) NMR spectrum of **18** showed two carbonyl resonances at $\delta = 200.67$ and 228.15 ppm. The low field resonance at $\delta = 228.15$ ppm from the observations of Colton and Kevekordes [15] is likely to be due to the carbonyl ligands in the unique capping positions of two capped octahedral structures, bridged by the S_2CPCy_3 ligand. The most likely geometry for this complex is shown in Fig. 3, with equivalent octahedral carbonyls and the triphenylphosphines furthest away from the bulky S_2CPCy_3 bridging ligand.

Experimental

The preparation and purification of the complexes described in this paper were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. Dichloromethane was dried over P_2O_5 and distilled, and all solvents were degassed before use. The compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), $[MI_2(CO)_3(NCMe)L]$ ($L = PPh_3$, $P(OPh)_3$, $AsPh_3$ or $SbPh_3$) and $[WI_2(CO)_3(PPh_3)_2]$ were synthesised by the literature methods [10,14,25], and all chemicals were purchased from commercial sources. Elemental analyses (C, H and N) were determined by using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). 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 and the low temperature ^{13}C NMR spectra were recorded on a Bruker WH 400 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Magnetic susceptibilities were determined using a Johnson–Matthey magnetic susceptibility balance.

Preparation of $[MoI_2(CO)_3(S_2CPCy_3)] \cdot CH_2Cl_2$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added S_2CPCy_3 (0.345 g, 0.969 mmol). After stirring for 5 min, the mixture was filtered, and the solvent removed *in vacuo* to give the dark purple crystalline complex $[MoI_2(CO)_3(S_2CPCy_3)] \cdot CH_2Cl_2$ (**1**) (0.56 g, 66%) which was recrystallised from CH_2Cl_2. A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of S_2CPCy_3 afforded $[WI_2(CO)_3(S_2CPCy_3)]$ (**2**) (see Table 1 for physical and analytical data).

Preparation of $[Mo(CO)_3(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (3)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added S_2CPCy_3 (0.691 g, 1.94 mmol). After stirring for 5 min, the mixture was filtered, and the solvent removed *in vacuo* to afford a dark purple crystalline complex $[Mo(CO)_3(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (**3**) (0.86 g, 70%) which was recrystallised from CH_2Cl_2.

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of S_2CPCy_3 afforded $[W(CO)_3(S_2CPCy_3)_2]2I$ (**4**).

$[W(CO)_3(S_2CPCy_3)_2]2I$ also reacts *in situ* with two equivalents of $Na[BPh_4]$ in NCMe for 18 h to afford the iodide exchange complex $[W(CO)_3(S_2CPCy_3)_2][BPh_4]_2$ (**5**) (see Table 1 for physical and analytical data).

Preparation of $[W(CO)_3(S_2CPCy_3)_3]2I$ *(6)*

To $[WI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added S_2CPCy_3 (0.886 g, 2.48 mmol). After stirring for 30 min, the mixture was filtered, and the solvent removed *in vacuo*, gave the dark purple crystalline complex $[W(CO)_3(S_2CPCy_3)_3]2I$ (**6**) (1.05 g, 83%) which was recrystallised from CH_2Cl_2.

Preparation of $[W(CO)_3(S_2CPCy_3)_3][BPh_4]_2$ *(7)*

To $[WI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.828 mmol) dissolved in NCMe (15 cm^3) with continuous stirring under a stream of dry nitrogen was added S_2CPCy_3 (0.886 g, 2.48 mmol). After 5 min, $Na[BPh_4]$ (0.567 g, 1.656 mmol) was added *in situ*, and the mixture stirred for 18 h; after which the solvent was removed *in vacuo*. The product was resolvated in CH_2Cl_2 (15 cm^3) and filtered to remove NaI, and the solvent was removed *in vacuo* to give the dark red anion exchanged complex $[W(CO)_3(S_2CPCy_3)_3][BPh_4]_2$ (**7**) (1.13 g, 69%), which was recrystallised from CH_2Cl_2.

Preparation of $[MoI(CO)_3(PPh_3)(S_2CPCy_3)]I$ *(8)*

To $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.969 mmol). After stirring for 1 min, S_2CPCy_3 (0.345 g, 0.969 mmol) was added and the mixture was stirred for a further 5 min. Filtration, followed by removal of the solvent *in vacuo* gave the dark green complex $[MoI(CO)_3(PPh_3)(S_2CPCy_3)]I$ (**8**) (0.82 g, 80%), which was recrystallised from CH_2Cl_2.

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L ($L = PPh_3$, $P(OPh)_3$, $AsPh_3$ or $SbPh_3$) followed by an *in situ* reaction with one equivalent of S_2CPCy_3 gave the new compounds $[WI(CO)_3L(S_2CPCy_3)]I$ (**10, 12–14**). Reaction times for $[WI_2(CO)_3(NCMe)_2] + L \rightarrow [WI_2(CO)_3(NCMe)L] + NCMe$ and $[WI_2(CO)_3(NCMe)L] + S_2CPCy_3 \rightarrow [WI(CO)_3L(S_2CPCy_3)]I + NCMe$ at 25 °C are: **10**: $L = PPh_3$, 1 min; S_2CPCy_3, 5 min; **12**: $L = P(OPh_3)_3$, 5 min; S_2CPCy_3, 5 min; **13**: $L = AsPh_3$, 3 min; S_2CPCy_3, 5 min; **14**: $L = SbPh_3$, 5 min; S_2CPCy_3, 5 min.

The complexes $[MI(CO)_3(PPh_3)(S_2CPCy_3)]I$ (**8** and **10**) also react *in situ* with one equivalent of $Na[BF_4]$ in CH_2Cl_2 to give $[MI(CO)_3(PPh_3)(S_2CPCy_3)][BF_4]$ (M = Mo or W) (**9** and **11**).

Preparation of $[W(CO)_3(PPh_3)_2(S_2CPCy_3)_n]2I \cdot 1\frac{1}{2}CH_2Cl_2$ *(n = 1 or 2) (15 and 17)*

To $[WI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.434 g, 1.656 mmol). After stirring for 5 min, S_2CPCy_3 (0.295 g, 0.828 mmol (**15**)) or S_2CPCy_3 (0.591 g, 1.65 mmol (**17**)) were added. The mixture was stirred for 5 min. Filtration, followed by removal of the solvent *in vacuo* gave the dark purple crystalline complexes $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (**15**) (0.94 g, 74%) or $[W(CO)_3(PPh_3)_2(S_2CPCy_3)_2]2I \cdot 1\frac{1}{2}CH_2Cl_2$ (**17**) (1.18 g, 76%) which were recrystallised from CH_2Cl_2. $[W(CO)_3(PPh_3)_2(S_2CPCy_3)]2I \cdot 1\frac{1}{2}CH_2Cl_2$ also reacts *in situ* with two equivalents of $Na[BPh_4]$ in NCMe to give $[W(CO)_3(PPh_3)_2(S_2CPCy_3)][BPh_4]_2$ (**16**).

Preparation of $[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)] \cdot CH_2Cl_2$ *(**18**)*

To $[WI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.217 g, 0.828 mmol). After stirring for 1 min, S_2CPCy_3 (0.147 g, 0.414 mmol) was added. The mixture was stirred for 30 min. Filtration, followed by removal of the solvent *in vacuo* gave the dark brown complex $[W_2I_4(CO)_6(PPh_3)_2(\mu\text{-}S_2CPCy_3)] \cdot CH_2Cl_2$ (**18**), (0.68 g, 82%) which was recrystallised from CH_2Cl_2.

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