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1,4,7-Trithiacyclononane ([9]aneS_3) and 2,5,8-trithia[9]orthocyclophane complexes of molybdenum(II) and tungsten(II): crystal structures of $[WI(CO)_3([9]aneS_3)][BPh_4]$ and $[WI_2(CO)_3(NCMe)(PPh_3)]$

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Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of 1,4,7-trithiacyclononane ([9]aneS_3) in CH_2Cl_2 at room temperature gave the cationic complexes $[MI(CO)_3([9]aneS_3)]I$ **1** and **2** in high yield. Treatment of **1** and **2** with an excess of Na$[BPh_4]$ in methanol gave $[MI(CO)_3([9]aneS_3)][BPh_4]$ **3** and **4**. The molecular structure of $[WI(CO)_3([9]aneS_3)][BPh_4]$ **4** has been determined by X-ray crystallography. It shows that the geometry around the tungsten centre is distorted capped octahedral with a capping carbonyl ligand. Room-temperature ^{13}C NMR studies on complexes **1** and **2** indicate a unique CO ligand, demonstrating that their structures in solution are similar to that found for **4** in the solid state. Reaction of $[MI_2(CO)_3(NCMe)L]$ [M = Mo or W, L = PPh_3; M = W, L = $P(OPh)_3$] with an equimolar quantity of [9]aneS_3 gave the seven-co-ordinate cation/anion complexes $[MI(CO)_2L([9]aneS_3)][MI_3(CO)_4]$ **5**–**7**. Treatment of $[MI_2(CO)_3(NCMe)_2]$ with 1 equivalent of 2,5,8-trithia[9]orthocyclophane (ttoc) in CH_2Cl_2 at room temperature gave the dicarbonylmolybdenum complex $[MoI_2(CO)_2(ttoc)]$ **8** or the seven-co-ordinate cation/anion tungsten complex $[WI(CO)_3(ttoc)][WI_3(CO)_4]$ **9**. Reaction of $[MI_2(CO)_3(NCMe)L]$ with an equimolar amount of ttoc gave $[MI(CO)_2L(ttoc)][MI_3(CO)_4]$ **10**–**12**. The complex $[WI_2(CO)_3(NCMe)(PPh_3)]$ was also shown to have a distorted capped-octahedral geometry by X-ray crystallography.

The importance of thiolate-, thioether- or sulfide-ligated molybdenum complexes as models for the molybdenum centre in nitrogenase has been enhanced by the recently described[1–3] crystal structure of the active site of nitrogenase. It has been observed for molybdenum that zerovalent complexes containing sulfur-donor ligands bind dinitrogen,[4,5] however such co-ordination has not been reported for sulfur-ligated complexes in the higher oxidation states. In this paper we describe chemistry in which the nitrogenase inhibitor carbon monoxide is co-ordinated in macrocyclic trithioether complexes of molybdenum(II) and tungsten(II).

Although a wide range of transition-metal complexes containing the trithia macrocyclic ligands 1,4,7-trithiacyclononane ([9]aneS_3) and 2,5,8-trithia[9]orthocyclophane (ttoc) are known,[6–14] hitherto no examples of carbonyl halide complexes of molybdenum(II) and tungsten(II) have been reported. Some previously reported examples of relevance include the zerovalent molybdenum complexes *fac*-$[Mo(CO)_3([9]aneS_3)]$,[15] and *fac*-$[Mo(CO)_3(ttoc)]$,[16] the molybdenum(II) complex $[([9]aneS_3)Mo(O_2CMe)_2Mo(NCMe)_3]^{2+}$ (ref. 17) and the molybdenum(III) complex $[MoCl_3([9]aneS_3)]$.[18] Herein, we describe the reactions of the seven-co-ordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $[MI_2(CO)_3(NCMe)L]$ [M = Mo or W, L = PPh_3; M = W, L = $P(OPh)_3$] with [9]aneS_3 and ttoc. The molecular structures of $[WI(CO)_3([9]aneS_3)][BPh_4]$ and $[WI_2(CO)_3(NCMe)(PPh_3)]$ are also described.

Results and Discussion

[9]aneS_3 complexes

The starting materials $[MI_2(CO)_3(NCMe)_2]$[19] were prepared by treating the zerovalent complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared *in situ*) with an equimolar amount of I_2 at 0 °C. The reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of [9]aneS_3 in CH_2Cl_2 at room temperature gave the seven-co-ordinate cationic complexes $[MI(CO)_3([9]aneS_3)]I$ (M = Mo **1** or W **2**) in good yield. These complexes have been characterised by elemental analyses and IR spectroscopy (Table 1) and ^1H and ^{13}C NMR spectroscopies (Tables 2 and 3). Complexes **1** and **2** are both soluble in dimethyl formamide (dmf) and dimethyl sulfoxide (dmso), fairly soluble in methanol and tetrahydrofuran (thf) and insoluble in chlorinated solvents, acetone and diethyl ether. They are moderately air-sensitive both in the solid state and in solution but can be stored under dinitrogen in the dark for several days without significant decomposition, and as expected the tungsten complex is more stable than its molybdenum analogue. Conductivity measurements in dmf showed the complexes to be 1 : 1 electrolytes.

The IR spectra of complexes **1** and **2** as KBr discs both showed three broad carbonyl bands in the region expected for such complexes[19,20] (Table 1): 2056, 1938 and 1848 and 2038, 1936 and 1830 cm^{-1}. The ^1H NMR spectra of these complexes in $(CD_3)_2SO$ (Table 2) showed resonances for the co-ordinated crown thioether ligand shifted slightly downfield relative to free [9]aneS_3. Also, the resonance had changed from a singlet to a second-order multiplet, due to the conformational rigidity of the CH_2 linkages imposed by co-ordination. The room-temperature ^{13}C NMR spectra in $(CD_3)_2SO$ showed three carbonyl resonances for each complex (Table 3). Attempts were made to grow single crystals of these complexes for structural characterisation, but were unsuccessful due to their low solubilities. It should be noted, however, that the cation $[WI(CO)_3([9]aneS_3)]^+$ in the complex $[WI(CO)_3([9]aneS_3)][BPh_4]$ **4** has been structurally characterised, as described

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Table 1 Analytical,[a] conductivity and infrared spectral[b] data for seven-co-ordinate trithiacrown ether complexes of molybdenum(II) and tungsten(II)

Complex	Analysis (%) C	H	S	Λ/S cm^2 mol^{-1}	$\tilde{\nu}$(CO)/cm^{-1}
1 [MoI(CO)$_3$([9]aneS$_3$)]I	17.2	1.9	16.0	65[c]	2056 (br), 1938 (br), 1848 (br)
	(17.6)	(2.0)	(15.7)		
2 [WI(CO)$_3$([9]aneS$_3$)]I	15.4	1.7	13.4	68[c]	2038 (br), 1936 (br), 1830 (sh)
	(15.4)	(1.7)	(13.7)		
3 [MoI(CO)$_3$([9]aneS$_3$)][BPh$_4$]	48.6	3.8	11.2	78[d]	2053 (br), 1939 (br), 1843 (br)
	(49.2)	(4.0)	(11.9)		
4 [WI(CO)$_3$([9]aneS$_3$)][BPh$_4$]	44.0	3.6	10.4	80[d]	2043 (br), 1934 (br), 1835 (sh)
	(44.3)	(3.6)	(10.8)		
5 [WI(CO)$_2$(PPh$_3$)([9]aneS$_3$)][WI$_3$(CO)$_4$]	23.9	1.9	7.0	80[d]	2047s, 2012m, 1975s, 1932s, 1906s, 1801 (sh)
	(24.3)	(1.8)	(6.5)		
6 [MoI(CO)$_2$(PPh$_3$)([9]aneS$_3$)][MoI$_3$(CO)$_4$]	28.0	2.5	7.8	77[d]	2054s, 2020m, 1980m, 1930s, 1910s, 1810 (sh)
	(27.5)	(2.1)	(7.3)		
7 [WI(CO)$_2${P(OPh)$_3$}([9]aneS$_3$)][WI$_3$(CO)$_4$]	23.7	2.0	6.0	74[d]	2038 (br), 1984s, 1922s, 1908s, 1805 (sh)
	(24.0)	(1.8)	(6.4)		
8 [MoI$_2$(CO)$_2$(ttoc)]	25.1	2.4	14.0	15[c]	1940s, 1873s
	(25.4)	(2.4)	(14.5)		
9 [WI(CO)$_3$(ttoc)][WI$_3$(CO)$_4$]	16.8	1.4	7.8	75[d]	2066m, 2053m, 2002 (sh), 1984s, 1953m, 1938 (br)
	(17.2)	(1.2)	(7.2)		
10 [MoI(CO)$_2$(PPh$_3$)(ttoc)][MoI$_3$(CO)$_4$]	30.9	2.1	—	—	2055s, 2015m, 1985m, 1935s, 1912m, 1815 (sh)
	(31.2)	(2.3)			
11 [WI(CO)$_2$(PPh$_3$)(ttoc)][WI$_3$(CO)$_4$]	27.4	1.7	5.7	—	2050s, 2016m, 1980m, 1930s, 1910s, 1820 (sh)
	(27.7)	(2.0)	(6.2)		
12 [WI(CO)$_2${P(OPh)$_3$}(ttoc)][WI$_3$(CO)$_4$]	26.7	1.6	—	—	2040s, 1980m, 1930m, 1920m, 1905s, 1810 (sh)
	(26.9)	(1.9)			

[a] Calculated values in parentheses. [b] Recorded as KBr discs; br = broad, sh = shoulder, s = strong, m = medium and w = weak. [c] In dimethylformamide. [d] In nitromethane

Table 2 Proton NMR data for the trithiacrown ether complexes at 25 °C referenced to SiMe$_4$

Complex	δ (J/Hz)
1[a]	3.3 (m, 12 H, SCH$_2$CH$_2$S)
2[a]	3.4 (m, 12 H, SCH$_2$CH$_2$S)
3[b]	7.5–6.9 (m, 20 H, Ph), 3.5–3.3 (m, 12 H, SCH$_2$CH$_2$S)
4[b]	7.45–6.9 (m, 20 H, Ph), 3.6–3.4 (m, 12 H, SCH$_2$CH$_2$S)
5[c]	7.6–7.4 (m, 15 H, Ph), 3.3 (m, 12 H, SCH$_2$CH$_2$S)
6[c]	7.5–7.3 (m, 15 H, Ph), 3.25 (m, 12 H, SCH$_2$CH$_2$S)
7[d]	7.5–7.4 (m, 15 H, Ph), 3.6 (m, 12 H, SCH$_2$CH$_2$S)
8[a]	7.4 (s, 4 H, C$_6$H$_4$), 4.50, 4.20 (2 d, 4 H, C$_6$H$_4$CH$_2$S, J_{HH} = 13), 2.9 (m, 8 H, SCH$_2$CH$_2$S)
9[b]	7.52 (s, 4 H, C$_6$H$_4$), 5.08, 4.86 (2 d, 4 H, C$_6$H$_4$CH$_2$S, J_{HH} = 14), 3.08 (m, 8 H, SCH$_2$CH$_2$S)
10[c]	7.7–7.4 (m, 19 H, Ph), 5.1, 4.6 (2 d, 4 H, C$_6$H$_4$CH$_2$S, J_{HH} = 14), 2.9–2.7 (m, 8 H, SCH$_2$CH$_2$S)
11[c]	7.7–7.3 (m, 19 H, Ph), 5.0, 4.6 (2 d, 4 H, C$_6$H$_4$CH$_2$S, J_{HH} = 14), 2.8–2.6 (m, 8 H, SCH$_2$CH$_2$S)
12[d]	7.8–7.4 (m, 19 H, Ph), 4.9, 4.5 (2 d, 4 H, C$_6$H$_4$CH$_2$S, J_{HH} = 13), 2.7–2.5 (m, 8 H, SCH$_2$CH$_2$S)

s = singlet, d = doublet and m = multiplet. [a] Spectrum recorded in (CD$_3$)$_2$SO. [b] Spectrum recorded in CD$_3$NO$_2$. [c] Spectrum recorded in CD$_3$CN. [d] Spectrum recorded in CDCl$_3$.

Table 3 Carbon-13 NMR data for selected trithiacrown ether complexes at 25 °C referenced to SiMe$_4$

Complex	δ (J/Hz)
1[a]	240.2, 218.4, 216.1 (3s, $C\equiv O$), 36.9, 34.1, 32.4 (3s, SCH$_2$CH$_2$S)
2[a]	231.1 (s, $C\equiv O$, J_{WC} = 58.5), 216.3, 215.0 (2s, $C\equiv O$), 38.2, 34.0, 32.8 (3s, SCH$_2$CH$_2$S)
5[b]	235.2, 200.1 (2s, $C\equiv O$), 131.2–128.6 (m, Ph), 39.0, 38.7, 38.5 (3s, SCH$_2$CH$_2$S)
8[a]	205 (s, $C\equiv O$), 142.1, 135.3, 132.0 (3s, C$_6$H$_4$), 36.0 (s, C$_6$H$_4$CH$_2$S), 34.1, 32.2 (2s, SCH$_2$CH$_2$S)

[a] Spectrum recorded in (CD$_3$)$_2$SO. [b] Spectrum recorded in CD$_3$CN.

in the next section. It is likely that the cations in **1** and **2** also have the same geometry, as their spectral properties are very similar.

The reaction of complexes **1** and **2** with an excess of Na[BPh$_4$] in methanol at room temperature gave the anion-exchanged products [MI(CO)$_3$([9]aneS$_3$)][BPh$_4$] (M = Mo **3** or W **4**). Physical data for these compounds are in Tables 1 and 2. Complex **4** has also been characterised by ^{11}B NMR spectroscopy and X-ray crystallography.

The tetraphenylborate complexes **3** and **4** are more soluble in common solvents than their iodide analogues **1** and **2**; they are soluble in acetone, acetonitrile, nitromethane and are slightly soluble in chlorinated solvents. They are stable when stored under dinitrogen, but readily decompose on exposure to air, both in the solid state and in solution. Conductivity measurements in nitromethane show them to be 1 : 1 electrolytes. The IR spectra of complexes **3** and **4** both have three carbonyl stretching bands in similar positions to those of their iodide analogues **1** and **2** (Table 1). Their ^{1}H NMR spectra in CD$_3$NO$_2$ (Table 2), show multiplets at around δ 3.5, which are due to the CH$_2$ groups in co-ordinated [9]aneS$_3$. The aromatic protons in the [BPh$_4$]$^-$ anion resonate as a multiplet between δ 6.9 and 7.5. The ^{11}B NMR spectrum of **4** in CD$_3$NO$_2$ showed a broad singlet at δ −4.1, which is slightly shifted from that of Na[BPh$_4$] (δ −4.0, s).

Single crystals of complex **4** suitable for X-ray crystallography were grown from an acetonitrile solution at −17 °C. The molecular structure of the cation [WI(CO)$_3$([9]aneS$_3$)]$^+$ is shown in Fig. 1. Selected bond lengths and angles are in Table 4. The tungsten is seven-co-ordinate and may be described as having a 4 : 3 piano-stool type geometry (Fig. 1), which consists of three S atoms forming a triangular plane on one side of the metal and three carbonyl ligands and the iodide in a tetragonal group opposite. An example of a tetrathiamacrocyclic complex [WI(CO)$_2$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$](Me$_8$[16]aneS$_4$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane)

Table 4 Selected molecular dimensions (bond lengths in Å, angles in °) in $[WI(CO)_3([9]aneS_3)][BPh_4]$ **4** with estimated standard deviations (e.s.d.s) in parentheses

(*a*) About the tungsten atom			
W–I	2.8179(5)	W–S(5)	2.511(1)
W–C(2)	2.001(6)	W–S(6)	2.547(1)
W–C(3)	1.971(5)	W–S(7)	2.553(1)
W–C(4)	1.993(5)		
I–W–C(2)	78.2(2)	C(2)–W–S(6)	161.6(2)
I–W–C(3)	129.8(2)	C(3)–W–S(6)	123.9(2)
C(2)–W–C(3)	74.5(2)	C(4)–W–S(6)	82.4(2)
I–W–C(4)	75.6(2)	S(5)–W–S(6)	80.1 *
C(2)–W–C(4)	105.4(2)	I–W–S(7)	80.2 *
C(3)–W–C(4)	72.3(2)	C(2)–W–S(7)	82.9(2)
I–W–S(5)	158.5 *	C(3)–W–S(7)	135.4(2)
C(2)–W–S(5)	108.8(2)	C(4)–W–S(7)	152.0(2)
C(3)–W–S(5)	71.5(2)	S(5)–W–S(7)	80.5 *
C(4)–W–S(5)	119.9(2)	S(6)–W–S(7)	82.8 *
I–W–S(6)	88.0 *		
(*b*) In the cation ligands			
C(2)–O(2)	1.134(6)	W–C(2)–O(2)	177.8(5)
C(3)–O(3)	1.144(6)	W–C(3)–O(3)	178.1(5)
C(4)–O(4)	1.137(6)	W–C(4)–O(4)	178.8(5)
S(5)–C(56)	1.809(5)	C(67)–C(76)	1.486(9)
S(5)–C(57)	1.815(5)	C(76)–S(7)	1.817(6)
C(56)–C(65)	1.491(7)	S(7)–C(75)	1.820(6)
C(65)–S(6)	1.820(5)	C(75)–C(57)	1.469(7)
S(6)–C(67)	1.840(6)		
W–S(5)–C(56)	109.3(2)	S(6)–C(67)–C(76)	116.0(5)
W–S(5)–C(57)	103.4(2)	C(67)–C(76)–S(7)	117.0(4)
C(56)–S(5)–C(57)	102.5(3)	W–S(7)–C(76)	102.1(2)
S(5)–C(56)–C(65)	112.1(4)	W–S(7)–C(75)	107.0(2)
C(56)–C(65)–S(6)	114.5(4)	C(76)–S(7)–C(75)	102.5(3)
W–S(6)–C(65)	103.5(2)	S(7)–C(75)–C(57)	114.4(4)
W–S(6)–C(67)	105.3(2)	S(5)–C(57)–C(75)	115.2(4)
C(65)–S(6)–C(67)	100.3(3)		
(*c*) Torsion angles in the thioether ring			
S(5)–C(56)–C(65)–S(6)	−50.7(5)		
C(56)–C(65)–S(6)–C(67)	−61.8(5)		
C(65)–S(6)–C(67)–C(76)	129.6(5)		
S(6)–C(67)–C(76)–S(7)	−46.5(7)		
C(67)–C(76)–S(7)–C(75)	−67.2(5)		
C(76)–S(7)–C(75)–C(57)	128.0(4)		
S(7)–C(75)–C(57)–S(5)	−47.5(5)		
C(75)–C(57)–S(5)–C(56)	−65.3(5)		
C(57)–S(5)–C(56)–C(65)	136.8(4)		

* e.s.d. is less than 0.05°.

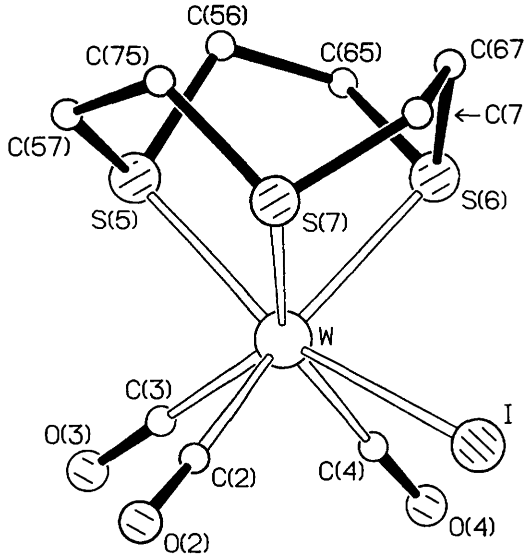

Fig. 1 Molecular structure of the cation $[WI(CO)_3([9]aneS_3)]^+$ in complex 4

with 4:3 geometry in the cation has been described previously.[20] Alternatively, the cation is better described as having a distorted capped-octahedral geometry, in which the carbonyl of C(3) is the capping ligand, C(2), C(4) and S(5) form the capped face and S(6), S(7) and I are on the opposite face of the octahedron. This is essentially the same arrangement as found[20] in the cation $[WI(CO)_3(Me_8[16]aneS_4)]^+$ and similar to those in the neutral molecules $[WI_2(CO)_3(4\text{-}MeC_6H_4SCH_2CH_2SC_6H_4Me\text{-}4)]$[21] and $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\}]$[21] and in the anion $[WI_3(CO)_4]^-$;[20] in each there is a capping carbonyl group and the largest ligands are preferred in the face of the octahedron opposite the capping ligand.

The dimensions in complex 4 are very similar to those in the cation $[WI(CO)_3(Me_8[16]aneS_4)]^+$ with W–I at 2.8179(5) Å in 4 and 2.806(1) Å in the other cation. The W–$C_{capping}$ distances are identical at 1.971 Å in each; this distance is slightly shorter than the other W–C lengths by *ca.* 0.02–0.05 Å. The W–S distances vary principally according to the ligand opposite (in the approximately octahedral pattern), and those in 4 (with the nine-membered ring) are slightly shorter than those involving the larger, more cumbersome, substituted 16-membered ring; hence we find, respectively, W–S distances of 2.511(1) and 2.549(3) Å for the S *trans* to the iodide in the two complexes, and mean values of 2.550(3) and 2.605(15) Å for the S opposite a carbonyl group.

The $[9]aneS_3$ ligand in complex 4 has virtually the same conformation as that in the six-co-ordinate complexes $[M(CO)_3([9]aneS_3)]$ (M = Mo[15] or W[22]). These latter are isostructural and their mean torsion angles around the nine-membered ring are shown in Table 5. In these structures, and in complex 4, there is pseudo-three-fold symmetry in the $[9]aneS_3$ ligand, whereas in the unco-ordinated molecule of $[9]aneS_3$[23] (Table 5) the three-fold symmetry is precise. As previously noted,[6–14] only small changes in the conformation of the free molecule are required to co-ordinate the metal atom to all three S atoms of the ligand; the resulting conformation is remarkably consistent in the six- and seven-co-ordinate species described here.

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of PPh_3, followed by an *in situ* reaction with 1 equivalent of $[9]aneS_3$ in CH_2Cl_2 at room temperature, afforded a mixture of products. The first to be isolated was a yellow precipitate, which was shown to be the unusual complex $[WI(CO)_2(PPh_3)([9]aneS_3)][WI_3(CO)_4]$ **5**. The second was isolated from the orange supernatant by reducing the volume and allowing the solution to crystallise at −17 °C. It was found to be the previously reported complex $[WI_2(CO)_3(NCMe)(PPh_3)]$.[24] Both complexes have been characterised by elemental analysis and IR spectroscopy (Table 1 and Experimental section) and ^1H NMR spectroscopy (Table 2 and Experimental section).

The structure of the complex $[WI_2(CO)_3(NCMe)(PPh_3)]$ was also determined by X-ray crystallography. Single crystals were grown from a solution in CH_2Cl_2 cooled to −17 °C. The molecular structure is shown in Fig. 2, selected bond lengths and angles in Table 6. The tungsten centre has a distorted capped-octahedral co-ordination geometry, very similar to that of 4 and the other complexes described above. The structure is also very similar to those of the complexes $[WI_2(CO)_3(NCEt)(AsPh_3)]$ and $[WI_2(CO)_3(NCPh)(AsPh_3)]$,[25] which have been described as having distorted capped trigonal-prismatic co-ordination. In these latter structures one of the iodides was considered to be the capping ligand, with two carbonyls, the nitrile (N) and the second iodide forming the capped, approximately rectangular face, and the arsine and the third carbonyl forming the opposite edge. Our phos-

Table 5 Conformation of the [9]aneS_3 ring in the unco-ordinated molecule and as a ligand in some six- and seven-co-ordinate complexes of Mo and W. Torsion angles (°) are, for the ligands, mean values with their standard errors in parentheses

Compound	S–C–C–S	C–C–S–C	C–S–C–C	Ref.
[9]aneS_3	58.5	55.1	−131.1	23
4 [WI(CO)$_3$([9]aneS_3)][BPh_4]	−48.6(13)	−64.8(16)	131.7(28)	This work
[W(CO)$_3$([9]aneS_3)]	−48.1(6)	−65.2(3)	131.5(7)	22
[Mo(CO)$_3$([9]aneS_3)]	48.8(11)	64.5(4)	−131.4(11)	15

Table 6 Selected molecular dimensions (bond lengths in Å, angles in °) for [WI$_2$(CO)$_3$(NCMe)(PPh$_3$)] with e.s.d.s in parentheses

(*a*) About the tungsten atom			
W–I(1)	2.8577(10)	W–C(1)	1.972(9)
W–I(2)	2.8518(9)	W–C(2)	2.009(11)
W–P	2.565(3)	W–C(3)	2.002(10)
W–N	2.171(7)		
I(2)–W–I(1)	88.44(3)	N–W–P	78.7(2)
P–W–I(1)	161.98(5)	C(1)–W–P	70.6(3)
N–W–I(1)	84.4(2)	C(2)–W–P	108.1(3)
C(1)–W–I(1)	126.9(3)	C(3)–W–P	119.2(3)
C(2)–W–I(1)	76.2(3)	C(1)–W–N	134.9(3)
C(3)–W–I(1)	74.5(3)	C(2)–W–N	84.9(3)
P–W–I(2)	83.64(6)	C(3)–W–N	152.2(3)
N–W–I(2)	83.8(2)	C(2)–W–C(1)	74.7(4)
C(1)–W–I(2)	123.2(3)	C(3)–W–C(1)	72.9(4)
C(2)–W–I(2)	161.7(3)	C(3)–W–C(2)	106.8(4)
C(3)–W–I(2)	77.9(3)		
(*b*) In the ligands			
P–C(6)	1.823(9)	C(6)–P–W	118.4(3)
P–C(12)	1.839(9)	C(12)–P–W	117.8(3)
P–C(18)	1.825(9)	C(18)–P–W	107.5(3)
		C(12)–P–C(6)	101.9(4)
		C(18)–P–C(6)	106.6(4)
		C(18)–P–C(12)	103.3(4)
O(1)–C(1)	1.140(10)	O(1)–C(1)–W	177.4(8)
O(2)–C(2)	1.145(12)	O(2)–C(2)–W	177.4(8)
O(3)–C(3)	1.131(11)	O(3)–C(3)–W	177.5(8)
N–C(4)	1.146(11)	C(4)–N–W	166.1(7)
C(4)–C(5)	1.438(13)	N–C(4)–C(5)	175.7(10)

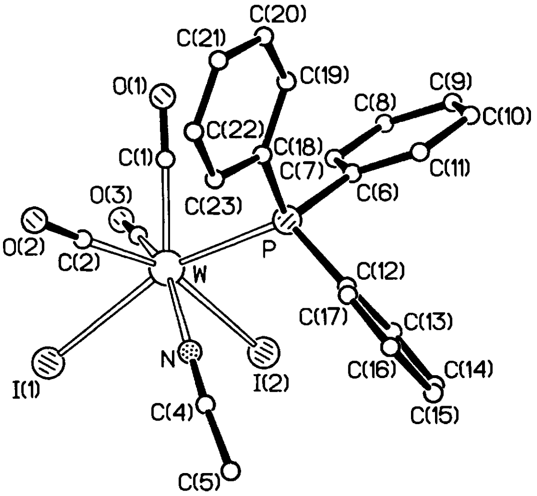

Fig. 2 Molecular structure of [WI$_2$(CO)$_3$(NCMe)(PPh$_3$)]

phine complex can be aligned similarly, but in the three structures the capping iodide occupies a rather off-centre capping position.

We have compared the geometries of all these complexes to determine which might be the better description for each, following the themes of Drew[26] and Kepert[27] in their reviews. Distortions from the easily recognised, regular geometries are caused by the presence of a variety of ligands having wide ranges of steric and electronic demands. In our calculations we considered only the angles subtended by the ligands at the metal atom, and have determined the root-mean-square (r.m.s.) deviation for each structure from an ideal geometry. Our results are shown in Table 7, and suggest that for most of the complexes listed the r.m.s. deviation from the capped-octahedral pattern is much smaller than that for the capped trigonal prism; only [WI$_2$(CO)$_3${4-MeC$_6$H$_4$S(CH$_2$)$_2$SC$_6$H$_4$-Me-4}] appears closer to the capped trigonal prism, and [WI(CO)$_3$(Me$_8$[16]aneS$_4$)]$^+$ is midway between the two geometries.

Complex **5**, which has also been characterised by ^{13}C NMR spectroscopy (Table 3), is yellow and is air-sensitive, both in the solid state and in solution, but can be stored under dinitrogen in the dark for several days. It is insoluble in chlorinated solvents but soluble in acetone, acetonitrile and in nitromethane in which it is a 1 : 1 electrolyte. This complex is similar to the previously described[20] crystallographically characterised, tetrathiamacrocyclic complex [WI(CO)$_2$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$].

The IR spectrum of complex **5** showed six carbonyl stretching bands at 2047, 2012, 1975, 1932, 1906 and 1801 cm^{-1}, similar to those observed for [WI(CO)$_2$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$]. The room-temperature ^{1}H NMR spectrum in CD$_3$CN showed the expected features; a multiplet at δ 3.3 due to co-ordinated [9]aneS_3 (SCH_2CH_2S) and a multiplet at δ 7.40–7.60 due to the aromatic protons in co-ordinated PPh$_3$. The room-temperature ^{13}C NMR spectrum in CD$_3$CN showed two carbonyl resonances at δ 235.2 and 200.1. This suggests that both the anion and cation are fluxional with a rapid exchange of carbonyl ligands. This fluxionality has been previously observed for seven-co-ordinate carbonyl halide complexes of molybdenum(II) and tungsten(II).[28–31]

Several unsuccessful attempts were made to grow single crystals of complex **5** for structural analysis. However, it is likely the structure is similar to that of the previously reported[20] complex [WI(CO)$_2$(Me$_8$[16]aneS$_4$)][WI$_3$(CO)$_4$] since their spectroscopic properties are very similar.

The analogous molybdenum complex [MoI(CO)$_2$(PPh$_3$)([9]aneS_3)][MoI$_3$(CO)$_4$] **6** was also prepared in low yield by the reaction of [MoI$_2$(CO)$_3$(NCMe)$_2$] with 1 equivalent of PPh$_3$ followed by an equimolar amount of [9]aneS_3 in CH$_2$Cl$_2$ at room temperature. Its physical properties are given in Tables 1 and 2; it is brown, air-sensitive, and has very similar spectroscopic data to those for complex **5**, however it is less stable. It is insoluble in chlorinated solvents but soluble in acetone, acetonitrile and nitromethane in which it is a 1 : 1 electrolyte.

Treatment of [WI$_2$(CO)$_3$(NCMe)$_2$] with 1 equivalent of P(OPh)$_3$, followed by an equimolar amount of [9]aneS_3 *in situ*, afforded the mixed-ligand complex [WI(CO)$_2${P(OPh)$_3$}([9]aneS_3)][WI$_3$(CO)$_4$] **7** in low yield. This yellow complex is insoluble in diethyl ether, but soluble in chlorinated solvents, acetone and in nitromethane, in which it is a 1 : 1 electrolyte; its physical properties are shown in Tables 1 and 2. Complex **7** is relatively stable when stored under dinitrogen, but readily decomposes on exposure to air, both in the solid state and in solution. The IR spectrum showed only five carbonyl stretching bands at 2038, 1984, 1922, 1908 and 1805 cm^{-1}. However, the band at 2038 cm^{-1} is broad and may mask a sixth carbonyl

Table 7 Comparison of the co-ordination patterns of some seven-co-ordinate compexes of tungsten. The values quoted are r.m.s. angular deviations from the 'ideal' capped octahedral and capped trigonal-prismatic geometries[a]

	Capped octahedral		Capped trigonal prism		
Complex	Capping ligand	r.m.s. angular deviation/°	Capping ligand	r.m.s. angular deviation/°	Ref.
$[WI(CO)_3([9]aneS_3)]^+$ in **4**	C(3)	3.8	S(7)	6.0	This work
$[WI(CO)_3(Me_8[16]aneS_4)]^+$	C(17)	5.3	I(15)	5.9	20
$[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\}]$	C(4)	2.4	I(1)	6.1	21
$[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$	C(4)	7.4	S(6)	5.2	21
$[WI_3(CO)_4]^-$	C(27)	2.1	I(23)	6.8	20
$[WI_2(CO)_3(NCMe)(PPh_3)]$	C(1)	4.0	N	5.6	This work
$[WI_2(CO)_3(NCEt)(AsPh_3)]$	C(2)	3.5	N(1)	6.3	25
$[WI_2(CO)_3(NCPh)(AsPh_3)]$	C(2)	2.5	N(1)	7.0	25
$[WBr_3(CO)_4]^-$ [b]	C(2)	0.7	Br(2)	7.0	28
$[Mo(CNBu)_7]^{2+}$ [b]	C(41)	7.6	C(11)	0.7	29

[a] The 'ideal' geometries in this exercise were defined as those with *3m* (C_{3v}) (capped octahedral) and *mm2* (C_{2v}) (capped trigonal-prismatic) symmetries. For each set of 'equivalent' angles the mean value was calculated, thence the deviation, *d*, of each angle from the mean; from the sum of squares, Σd^2, over all 21 angles subtended at the metal atom the r.m.s. deviation was determined. [b] Included as example complexes having well defined geometries.

band. The analogous complexes **5** and **6** both showed six carbonyl stretching bands. The ^1H NMR spectrum of complex **7** in $CDCl_3$, showed the expected feature of a multiplet due to co-ordinated $P(OPh)_3$ at δ 7.5–7.4 and a multiplet at δ 3.6 due to co-ordinated $[9]aneS_3$.

ttoc Complexes

Reaction of $[MoI_2(CO)_3(NCMe)_2]$ with an equimolar amount of ttoc, in CH_2Cl_2 at room temperature for 3 h, gave the neutral dicarbonyl complex $[MoI_2(CO)_2(ttoc)]$ **8** in 65% yield, whereas treatment of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of ttoc in CH_2Cl_2 under the same conditions afforded in 40% yield a complex which we formulate as $[WI(CO)_3(ttoc)][WI_3(CO)_4]$ **9**. Complexes **8** and **9** have been characterised as shown in Tables 1 and 2. The ^{13}C NMR (Table 3) and UV spectral data of **8** are also reported. The complexes are air-sensitive, both in the solid state and in solution. The rust-brown dicarbonyl **8** is soluble in dmso and dmf in which it is non-conducting, but insoluble in acetone, acetonitrile, nitromethane and chlorinated solvents. The IR spectrum (KBr) of complex **8** showed, as expected, two carbonyl stretching bands at 1940 and 1873 cm^{-1} and its ^1H NMR spectrum in $(CD_3)_2SO$ clearly showed co-ordinated ttoc; a singlet at δ 7.4 is characteristic of the aromatic protons, there is a characteristic doublet of doublets at δ 4.50 and 4.20 due to the protons next to the ring, and a multiplet at δ 2.9 due to the protons in the linkages SCH_2CH_2S.

The room-temperature ^{13}C NMR spectrum of complex **8** in $(CD_3)_2SO$ showed a single carbonyl resonance at δ 205, which suggests that the complex is fluxional. It was not possible to record the low-temperature ^{13}C NMR spectrum, due to the low solubility. Also, no single crystals could be grown for structural characterisation. It is likely, however, that **8** has capped-octahedral geometry, as demonstrated in the structure of the analogue $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$[21] which also contains a tridentate sulfur-donor ligand, co-ordinated after the loss of CO from the starting material. The proposed structure of complex **8** is shown in Fig. 3. The capping ligand is probably a carbonyl group.

The UV/VIS spectrum of complex **8** in dmf showed a peak at 557 nm (ε = 1200 $dm^3 mol^{-1} cm^{-1}$), which is probably due to a d–d transition in the metal complex, and a band at 390 nm (ε = 8030 $dm^3 mol^{-1} cm^{-1}$) which has been assigned to a charge transfer ($S \rightarrow W$) because of its relatively high energy and intensity.

The complex $[WI(CO)_3(ttoc)][WI_3(CO)_4]$ **9**, which, like **5**–**7**, contains seven-co-ordinate anions and cations, is brown, insoluble in chlorinated solvents and diethyl ether but soluble in acetonitrile and in nitromethane in which it is a 1 : 1 electrolyte. The IR spectrum showed six carbonyl stretching bands at 2066, 2053, 2002, 1984, 1953 and 1938 cm^{-1}, not seven as expected. The band at 1938 cm^{-1}, however, is broad and could mask a seventh carbonyl band. The analogous, structurally characterised complex $[WI(CO)_3(Me_8[16]aneS_4)][WI_3(CO)_4]$[20] showed seven carbonyl stretching bands at 2068, 2036, 2010, 1992, 1967, 1944 and 1924 cm^{-1}.

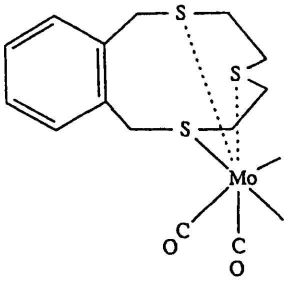

Fig. 3 Proposed structure of $[MoI_2(CO)_2(ttoc)]$ **8**

The room-temperature ^1H NMR spectrum of complex **9** in CD_3NO_2 showed the expected pattern for co-ordinated ttoc (singlet at δ 7.52 due to aromatic protons, a doublet of doublets at δ 5.08 and 4.86 due to the protons near the ring and a multiplet at δ 3.08, due to SCH_2CH_2S protons). Several unsuccessful attempts were made to grow single crystals for X-ray crystallography, however it is likely from their similarity in spectroscopic data that complexes **9** and $[WI(CO)_3(Me_8[16]aneS_4)][WI_3(CO)_4]$[20] have the same 4:3 co-ordination geometry in their cations.

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 1 equivalent of L [M = Mo or W, L = PPh_3; M = W, L = $P(OPh)_3$] in CH_2Cl_2 at room temperature, followed by an *in situ* reaction with an equimolar amount of ttoc, gave the seven-co-ordinate cation/anion complexes $[MI(CO)_2L(ttoc)][MI_3(CO)_4]$ **10**–**12** in low yield. All these complexes were very air-sensitive both in the solid state and in solution and have been characterised as shown in Tables 1 and 2. They are insoluble in chlorinated solvents, acetone and diethyl ether, but soluble in acetonitrile and in nitromethane. Their IR spectra all showed the expected six carbonyl stretching bands and the ^1H NMR spectra showed resonances due to co-ordinated ttoc and PPh_3 or $P(OPh)_3$.

Conclusion

We have investigated some new co-ordination chemistry of the

S_3 macrocycles [9]aneS_3 and ttoc at molybdenum(II) and tungsten(II) iodocarbonyl centres, prompted by the S_3 co-ordination of sulfur in the molybdenum site in the active centre of nitrogenase.[1-3] We have shown that MeCN is readily displaced from $[MI_2(CO)_3(NCMe)_2]$ by polydentate thioether ligands. For cyclic tridentate ligands [9]aneS_3 (this work) and Me_8[16]aneS_4,[20] iodide is also displaced from the metal to give cations. Where the thiolate ligand is *linear*, *e.g.* 4-$MeC_6H_4SCH_2CH_2SC_6H_4Me$-4 and $MeS(CH_2)_2S(CH_2)_2SMe$,[21] CO rather than iodide is displaced. This behaviour is presumably related to the kinetic macrocyclic effect for thiamacrocyclic ligands,[32] amongst other factors, and will be the subject of further study.

Experimental

All the reactions described were carried out under an atmosphere of dry dinitrogen using standard Schlenk-line techniques, except for the pro-ligand syntheses. The solvents were all dried and degassed before use. Dichloromethane was refluxed over phosphorus pentaoxide, diethyl ether was dried over sodium wire, and methanol was dried with magnesium activated by iodine. The starting materials $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared according to the literature method.[19] The macrocyclic sulfur-donor pro-ligands [9]aneS_3 and ttoc[13] were prepared by the variations of literature methods[33] as described below. All other chemicals used were obtained from commercial sources, and used without further purification.

Proton NMR spectra were recorded on Bruker AC/250 (University of Wales, Bangor) or JEOL GSX 270 (NFL, Sussex) spectrometers, ^{13}C NMR spectra on Bruker WH400 MHz (University of Warwick) or JEOL GSX 270 (Sussex) spectrometers and the ^{11}B NMR spectrum on a Bruker AC/250 spectrometer; the ^1H and ^{13}C spectra were referenced to tetramethylsilane, the ^{11}B spectrum to $BF_3{\cdot}OEt_2$. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer and the UV/VIS spectrum on a Philips Scientific PU 800 spectrophotometer. Elemental analyses were determined using a Carlo Erba MOD 1106 instrument (helium carrier gas) for C, H, N by Mr. K. Jones at Bangor and for S by Mr. C. J. Macdonald at the Nitrogen Fixation Laboratory, Sussex. Conductivities were measured using a Portland Electronics conductivity bridge.

Preparations

1,4,7-Trithiacyclononane.[23,33] Finely powdered caesium carbonate (78.2 g, 240 mmol) and dmf (1500 cm^3) were added to a three-necked round-bottomed flask (3000 cm^3), equipped with a condenser and a mechanical stirrer. A freshly distilled solution of 2-sulfanylethyl sulfide (28 cm^3, 215 mmol), 1,2-dibromoethane (19 cm^3, 215 mmol) and dmf (900 cm^3, added in two portions) was prepared in a measuring cylinder (500 cm^3). This solution was then added dropwise, using a peristaltic pump, to the heated (100 °C), rapidly stirred mixture of Cs_2CO_3 in dmf. After 43 h, when the addition was complete, the apparatus was reassembled for distillation. The dmf was removed by distillation under vacuum, using a water condenser and an ice-cooled receiver. A mixture of CH_2Cl_2 (200 cm^3) and water (200 cm^3) was used to extract the residue thoroughly. The extraction was repeated and the combined aqueous phase extracted once with CH_2Cl_2 (50 cm^3) and discarded. The combined organic layer was washed with NaOH (250 cm^3) and twice with water (200 cm^3). Anhydrous sodium sulfate was used to filter the CH_2Cl_2 solution, which was then dried over sodium sulfate for 48 h. The drying agent was filtered off and the CH_2Cl_2 removed by rotary evaporation. The white solid product [9]aneS_3 was sublimed several times (yield = 17.5 g, 45%).

$[MoI(CO)_3([9]aneS_3)]I$ 1. To $[MoI_2(CO)_3(NCMe)_2]$ (0.573 g, 1.11 mmol), stirred in CH_2Cl_2 (25 cm^3), was added [9]aneS_3 (0.214 g, 1.19 mmol). An instant rust-brown precipitate formed and this was stirred for 1 h. The precipitate was then filtered off, washed with Et_2O and dried *in vacuo* to produce the rust-brown complex $[MoI(CO)_3([9]aneS_3)]I$ **1**, which was analytically pure (yield = 0.45 g, 66%). A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of [9]aneS_3 gave an orange precipitate, which was recrystallised from MeOH to produce the orange crystalline product $[WI(CO)_3([9]aneS_3)]I$ **2**, yield 86%.

$[WI(CO)_3([9]aneS_3)][BPh_4]$ 4. To complex **2** (0.11 g, 0.157 mmol), stirred in methanol (20 cm^3) for 30 min, was added $Na[BPh_4]$ (0.09 g, 0.263 mmol). The solution was stirred for 1 h and a yellow precipitate formed, which was filtered off and dried *in vacuo* (yield = 0.10 g, 71%). The precipitate was redissolved in NCMe and filtered to produce a yellow solution which was reduced to minimum volume and cooled at −17 °C for 24 h to give yellow single crystals of $[WI(CO)_3([9]aneS_3)][BPh_4]$ **4**, suitable for X-ray crystallography. A similar reaction of complex **1** with an excess of $Na[BPh_4]$ gave orange $[MoI(CO)_3([9]aneS_3)][BPh_4]$ **3**, yield 65%.

$[WI(CO)_2(PPh_3)([9]aneS_3)][WI_3(CO)_4]$ 5 and $[WI_2(CO)_3(NCMe)(PPh_3)]$. These complexes were both isolated from the following reaction. To $[WI_2(CO)_3(NCMe)_2]$ (0.595 g, 0.985 mmol), stirred in CH_2Cl_2 (25 cm^3), was added PPh_3 (0.27 g, 1.029 mmol), followed after 1 min by [9]aneS_3 (0.181 g, 1.004 mmol). After 30 min a yellow precipitate formed, which was filtered off, washed with CH_2Cl_2 and dried *in vacuo* to produce the complex $[WI(CO)_2(PPh_3)([9]aneS_3)][WI_3(CO)_4]$ **5**. This complex was analytically pure (yield = 0.29 g, 21%). The orange supernatant liquid was filtered, reduced in volume under vacuum and left to crystallise at −17 °C for 24 h. An orange crystalline product formed, which was filtered off and dried *in vacuo*. It was found to be $[WI_2(CO)_3(NCMe)(PPh_3)]$[24] (yield = 0.14 g, 17%), on the basis of elemental analysis, infrared and ^1H NMR data and its structure was determined by X-ray crystallography (Found: C, 33.7; H, 2.4; N, 1.7. Calc. for $C_{23}H_{18}I_2NO_3PW$: C, 33.5; H, 2.2; N, 1.5%). $\tilde{\nu}_{max}/cm^{-1}$ 2040s, 1950s and 1918s (CO). ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.52$ (m, 15 H, Ph), 1.96 (s, 3 H, Me). A similar reaction of $[MoI_2(CO)_3(NCMe)_2]$ with an equimolar amount of PPh_3 followed by 1 equivalent of [9]aneS_3 gave the brown complex $[MoI(CO)_2(PPh_3)([9]aneS_3)][MoI_3(CO)_4]$ **6**, yield 19%.

$[WI(CO)_2\{P(OPh)_3\}([9]aneS_3)][WI_3(CO)_4]$ 7. To $[WI_2(CO)_3(NCMe)_2]$ (0.60 g, 0.994 mmol) stirred in CH_2Cl_2 (30 cm^3) was added $P(OPh)_3$ (0.30 cm^3, 0.994 mmol), followed after 1 min by [9]aneS_3 (0.19 g, 1.053 mmol). The mixture was stirred for 18 h then the solvent was removed *in vacuo* to produce a yellow solid which was recrystallised from CH_2Cl_2–Et_2O as analytically pure $[WI(CO)_2\{P(OPh)_3\}([9]aneS_3)][WI_3(CO)_4]$ **7** (yield = 0.35 g, 23%).

2,5,8-Trithia[9]orthocyclophane.[13,33] A suspension of powdered caesium carbonate (21 g, 64 mmol) in dmf (1200 cm^3) was placed in a flask, and a solution of freshly distilled 2-sulfanylethyl sulfide (9.285 g, 60 mmol) and α,α′-dibromo-*o*-xylene (15.88 g, 60 mmol) in dmf (420 cm^3) was placed in the reservoir. The temperature was kept at 70–80 °C and the addition was completed in 22–25 h. The system was flushed through with neat dmf on completion of the addition, and was allowed to cool, then left stirring at room temperature overnight. The dmf was removed by distillation under vacuum, and the solid residue extracted with CH_2Cl_2 (2 × 200 cm^3). Sodium hydroxide (0.05 mol dm^{-3}, 2 × 250 cm^3) was used to wash the combined organic extract, followed by water (100 cm^3). The extract was then left standing overnight over sodium sulfate. Filtration and evaporation gave a brownish oil, which was impure. This was recrystallised from EtOH to produce colourless needles of pure ttoc (yield = 12.2 g, 80%).

[MoI$_2$(CO)$_2$(ttoc)] 8. To [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.30 g, 0.582 mmol), stirred in CH$_2$Cl$_2$ (25 cm^3), was added ttoc (0.16 g, 0.624 mmol). The mixture was stirred for 3 h and a rust-brown precipitate formed. This was filtered off, washed and dried *in vacuo* to produce the analytically pure complex [MoI$_2$(CO)$_2$(ttoc)] **8** (yield = 0.25 g, 65%). In a similar reaction between [WI$_2$(CO)$_3$(NCMe)$_2$] and 1 equivalent of ttoc under the same conditions, the brown complex [WI(CO)$_3$-(ttoc)][WI$_3$(CO)$_4$] **9** was obtained, yield 40%.

[WI(CO)$_2$(PPh$_3$)(ttoc)][WI$_3$(CO)$_4$] 11. To [WI$_2$(CO)$_3$-(NCMe)$_2$] (0.607 g, 1.01 mmol), stirred in CH$_2$Cl$_2$ (30 cm^3), was added PPh$_3$ (0.27 g, 1.03 mmol). After 1 min, ttoc (0.256 g, 0.998 mmol) was added. The mixture was stirred for 18 h forming a yellow precipitate which was filtered off, washed, then dried *in vacuo* to produce the analytically pure complex [WI(CO)$_2$(PPh$_3$)(ttoc)][WI$_3$(CO)$_4$] **11** (yield = 0.30 g, 19%). A similar reaction of [MoI$_2$(CO)$_3$(NCMe)$_2$] with 1 equivalent of PPh$_3$, followed by an equimolar amount of ttoc, under the same conditions, gave the brown complex [MoI(CO)$_2$(PPh$_3$)-(ttoc)][MoI$_3$(CO)$_4$] **10**, yield 18%.

[WI(CO)$_2${P(OPh)$_3$}(ttoc)][WI$_3$(CO)$_4$] 12. To [WI$_2$(CO)$_3$-(NCMe)$_2$] (0.60 g, 0.994 mmol), stirred in CH$_2$Cl$_2$ (30 cm^3), was added P(OPh)$_3$ (0.27 cm^3, 1.03 mmol), followed after 1 min, by ttoc (0.26 g, 1.01 mmol). The mixture was stirred for 18 h then the solvent was removed *in vacuo* to produce the orange complex [WI(CO)$_2${P(OPh)$_3$}(ttoc)][WI$_3$(CO)$_4$] **12** which was washed with Et$_2$O (yield = 0.32 g, 20%).

Crystallography

Crystal data for complex 4. C$_{33}$H$_{32}$BIO$_3$S$_3$W, M = 894.4, monoclinic, space group $P2_1/n$ (equivalent to no. 14), a = 15.398(1), b = 21.147(2), c = 9.9587(6) Å, β = 91.821(5)°, U = 3241.2(4) Å^3, Z = 4, D_c = 1.833 g cm^{-3}, F(000) = 1736, T = 293 K, μ(Mo-Kα) = 48.0 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystals are yellow rectangular prisms. One, *ca.* 0.10 × 0.12 × 0.33 mm, was mounted on a glass fibre and, after photographic examination, transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections, θ = 10–12°, each reflection centred in four orientations) and for measurement of diffraction intensities to θ_{max} = 25°.

During processing, the intensities were corrected for Lorentz-polarisation effects, crystal deterioration (*ca.* 12.5% overall), absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). Of the 5693 unique planes entered into the SHELX program system,[34] 4447 were considered 'observed', having $I > 2\sigma_I$.

The positions of the W and I atoms were determined from a Patterson synthesis, and the remainder of the non-hydrogen atoms appeared in successive Fourier-difference maps. Refinement by full-matrix least-squares methods was rapid, resulting in R and R_g[34] values of 0.041 and 0.032 for all 5693 reflections weighted $w = \sigma_F^{-2}$. All the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in idealised positions (C–H 0.98 Å) and their isotropic thermal parameters were refined freely. In a final difference map the highest peak was *ca.* 1.0 e Å^{-3} and close to the iodide ligand; there were no other peaks of significance.

Scattering factor curves for neutral atoms were taken from ref. 35. Computer programs used in this analysis have been noted above or in Table 4 of ref. 36, and were run on a DEC MicroVAX 3600 computer.

Crystal data for [WI$_2$(CO)$_3$(NCMe)(PPh$_3$)]. C$_{23}$H$_{18}$I$_2$NO$_3$-PW, M = 825.0, monoclinic, space group $P2_1/n$ (equivalent to no. 14), a = 11.456(7), b = 10.938(2), c = 20.278(2) Å, β = 104.50(2)°, U = 2460(2) Å^3, Z = 4, D_c = 2.227 g cm^{-3}, F(000) = 1528, T = 293 K, μ(Mo-Kα) = 72.9 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystals are yellow rectangular prisms; the one selected was *ca.* 0.21 × 0.21 × 0.11 mm. Intensity data for this crystal were recorded on a FAST TV area detector diffractometer, driven by MADNES software on a MicroVAX 3200 computer following previously described procedures.[37] 7111 Reflections (to θ_{max} = 24.9°) were measured, yielding 3770 independent with R_{int} = 0.064. These data were corrected for Lorentz-polarisation effects. The structure was solved *via* heavy-atom methods in SHELXS 86[38] and refinement, on F_o^2 and using all the data, was by full-matrix least-squares methods (SHELXL 93).[39] All the non-hydrogen atoms were refined anisotropically, and hydrogens were included in calculated positions with U_{iso} set to $1.5U_{eq}$ of the parent atoms. Absorption corrections were applied using DIFABS.[40] The final indices were $R1$ (on F) 0.045 and $wR2$ (on F^2) 0.112[39] for all 3770 reflections, weighted $w = \sigma^{-2}(F_o^2)$. (For the 3283 reflections with $I > 2\sigma_I$, $R1$ = 0.041 and $wR2$ = 0.107.[39]) Scattering factor data are given in ref. 39. From a final difference map, the largest peaks were *ca.* 1.4 e Å^{-3}, close to the metal atom.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/147.

Acknowledgements

We thank the EPSRC and the AFRC for a CASE award (to S. D. H.), Dr. O. W. Howarth (University of Warwick) for obtaining several ^{13}C NMR spectra on the EPSRC High-field NMR Service and the EPSRC for support of the Crystallography Service in Cardiff.

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Received 26th *February* 1996; *Paper* 6/01337F