Synthesis and Spectroscopic Properties of the 'Mixed' Seven-co-ordinate Complexes $[MI_2(CO)_3L(L')]$ [M = Mo or W; L,L' = PPh_3, $PPh_2(C_6H_{11})$, $PPh(C_6H_{11})_2$, $AsPh_3$, or $SbPh_3$] and Rearrangement of Selected $[MI_2(CO)_3L(L')]$ to $[HL][MI_3(CO)_3L']$. *X*-Ray Crystal Structure of $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]\cdot Et_2O$†

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Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 1 equivalent of L(L = PPh_3, $AsPh_3$, or $SbPh_3$) in CH_2Cl_2 at room temperature followed by 1 equivalent of L'[L' = PPh_3, $PPh_2(C_6H_{11})$, $PPh(C_6H_{11})_2$, $AsPh_3$, or $SbPh_3$] *in situ* affords the 'mixed' seven-co-ordinate compounds $[MI_2(CO)_3L(L')]$. Low-temperature (−70 °C, CD_2Cl_2) ^{13}C n.m.r. spectra of the triphenylantimony complexes $[MI_2(CO)_3L(SbPh_3)]$ [L = PPh_3, $PPh_2(C_6H_{11})$, or $PPh(C_6H_{11})_2$] showed two carbonyl resonances. This indicated capped octahedral geometry with a carbonyl ligand in the unique capping position. Some of the neutral seven-co-ordinate complexes $[MI_2(CO)_3L(L')]$ containing phosphines disproportionated in CH_2Cl_2 to give the salts $[HL][MI_3(CO)_3L']$. ^{31}P N.m.r. spectroscopy and negative ion mass spectrometry confirmed that the more electron-rich phosphine is protonated in $[HL][MI_3(CO)_3(PPh_3)]$ [L = $PPh_2(C_6H_{11})$ or $PPh(C_6H_{11})_2$]. The structure of the complex $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]\cdot Et_2O$ was determined by *X*-ray analysis. The co-ordination geometry about the tungsten is capped octahedral with a carbonyl ligand in the unique capping position. The capped face contains two carbonyl groups and the triphenylantimony ligand, with the three iodide ligands occupying the uncapping face. The low-temperature (−70 °C, CD_2Cl_2) spectrum of the related complex $[NBu^n_4][WI_3(CO)_3(SbPh_3)]$ prepared by treating $[WI_2(CO)_3(NCMe)(SbPh_3)]$ *in situ* with 1 equivalent of $[NBu^n_4]I$ in CH_2Cl_2 showed two carbonyl resonances at δ = 209.68 and 235.50 p.p.m. with an intensity ratio of 2:1. The lower-field resonance can be ascribed to the unique capping carbonyl ligand and the higher-field resonance to the two equivalent carbonyl ligands on the octahedron. The low-temperature ^{13}C n.m.r. spectrum of $[NBu^n_4][MoI_3(CO)_3(PPh_3)]$ shows a single resonance at δ = 222.20 p.p.m. which suggests a different capped octahedral structure with the triphenylphosphine ligand capping the three carbonyl ligands.

Considerable effort was devoted to the synthesis of seven-co-ordinate halogenocarbonyl complexes of molybdenum(II) and tungsten(II) during the 1960s and early 1970s.[1–6] More recently complexes such as $[MX_2(CO)_3L_2]$ (M = Mo or W, X = Cl or Br, L = PPh_3 or $AsPh_3$) have been shown by Bencze and co-workers[7,8] to be catalysts for the ring-opening polymerisation of norbornene and norbornadiene. Although a wide range of complexes of the type $[MX_2(CO)_3L_2]$ (M = Mo or W, X = Cl, Br, or I; L = neutral nitrogen, phosphorus, arsenic, or antimony donor ligands) have been reported,[1–6] the only 'mixed' complexes of the type $[MX_2(CO)_3L(L')]$ to be reported are the tungsten compounds $[WX_2(CO)_3L(L')]$[X = Cl, Br, or I; L, L' = PMe_3, $AsMe_3$, $SbMe_3$, $AsMe_2H$, $P(OMe)_3$, or pyridine (py)] by Umland and Vahrenkamp.[9] These complexes were prepared by reaction of $[WX_2(CO)_4L]$ with L'.

In recent years we have been investigating the chemistry of the highly versatile complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)[10] which are prepared in quantitative yield from reaction of the zerovalent compounds $[M(CO)_3(NCMe)_3]$ *in situ* with 1 equivalent of I_2. In this paper we describe the preparation of the new seven-co-ordinate mixed complexes $[MI_2(CO)_3L(L')]$ [M = Mo or W; L,L' = PPh_3, $PPh_2(C_6H_{11})$, $PPh(C_6H_{11})_2$, $AsPh_3$, or $SbPh_3$] and rearrangement of several of the phosphine complexes to the seven-co-ordinate anions $[HL][MI_3(CO)_3L']$. Preliminary results of this work were described in an earlier communication.[11]

Results and Discussion

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and L (L = PPh_3, $AsPh_3$, or $SbPh_3$) react in CH_2Cl_2 to give $[MI_2(CO)_3(NCMe)L]$ which when treated *in situ* with 1 equivalent of L'[L' = PPh_3, $PPh_2(C_6H_{11})$, $PPh(C_6H_{11})_2$, $AsPh_3$, or $SbPh_3$] give good yields of the new 'mixed' seven-co-ordinate complexes $[MI_2(CO)_3L(L')]$ (**1**)—(**18**). Several of the phosphine complexes $[MI_2(CO)_3(PPh_3)L]$ [M = Mo, L = $PPh_2(C_6H_{11})$ or $PPh(C_6H_{11})_2$; M = W, L = $PPh(C_6H_{11})_2$], and $[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)]$ disproportionate in CH_2Cl_2 to give the new anionic seven-co-ordinate complexes $[HL][MI_3(CO)_3L']$ (**19**)—(**22**). The complexes $[MI_2(CO)_3(NCMe)_2]$ react with 1 equivalent of L (M = Mo, L = PPh_3; M = W, L = $SbPh_3$) in CH_2Cl_2 to give $[MI_2(CO)_3(NCMe)L]$ which react *in situ* with 1 equivalent of $[NBu^n_4]I$ to afford the anionic complexes $[NBu^n_4][MI_3(CO)_3L]$ (**23**) and (**24**). All the complexes (**1**)—(**24**) were fully characterised by elemental analysis (C, H, and N) (Table 1), i.r. (Table 2), and ^1H n.m.r.

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† Cyclohexyldiphenylphosphonium tricarbonyltri-iodo(triphenylstibine)tungstate(II)–diethyl ether (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Physical and analytical* data for the complexes $[MI_2(CO)_3L(L')]$ and $[HL][MI_3(CO)_3L']$

	Complex	Colour	Yield (%)	Analysis (%) C	Analysis (%) H
(1)	$[MoI_2(CO)_3(PPh_3)(AsPh_3)]$	Yellow	86	47.1 (46.7)	3.2 (3.0)
(2)	$[WI_2(CO)_3(PPh_3)(AsPh_3)]$	Yellow	71	42.9 (43.0)	3.0 (2.8)
(3)	$[MoI_2(CO)_3(PPh_3)(SbPh_3)]$	Brown	78	44.3 (44.7)	3.1 (2.9)
(4)	$[WI_2(CO)_3(PPh_3)(SbPh_3)]$	Green	86	41.0 (41.2)	2.8 (2.7)
(5)	$[MoI_2(CO)_3(AsPh_3)(SbPh_3)]$	Orange	80	42.9 (42.9)	3.0 (2.8)
(6)	$[WI_2(CO)_3(AsPh_3)(SbPh_3)]$	Orange	64	40.0 (39.7)	2.7 (2.6)
(7)	$[MoI_2(CO)_3\{PPh_2(C_6H_{11})\}(PPh_3)]$	Green	59	48.8 (48.6)	3.9 (3.8)
(8)	$[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(PPh_3)]$	Green	75	44.6 (44.5)	3.4 (3.5)
(9)	$[MoI_2(CO)_3\{PPh_2(C_6H_{11})\}(AsPh_3)]$	Brown	75	46.3 (46.5)	3.8 (3.6)
(10)	$[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(AsPh_3)]$	Yellow	61	42.8 (42.7)	3.4 (3.1)
(11)	$[MoI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)]$	Brown	66	44.2 (44.4)	3.5 (3.4)
(12)	$[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)]$	Orange	56	40.9 (41.0)	3.2 (3.2)
(13)	$[MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(PPh_3)]$	Green	76	48.6 (48.3)	4.5 (4.4)
(14)	$[WI_2(CO)_3\{PPh(C_6H_{11})_2\}(PPh_3)]$	Yellow	70	43.6 (44.3)	4.0 (4.0)
(15)	$[MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(AsPh_3)]$	Brown	74	46.7 (46.2)	4.4 (4.2)
(16)	$[WI_2(CO)_3\{PPh(C_6H_{11})_2\}(AsPh_3)]$	Orange	57	42.1 (42.5)	3.7 (3.8)
(17)	$[MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(SbPh_3)]$	Brown	66	43.8 (44.1)	4.1 (4.0)
(18)	$[WI_2(CO)_3\{PPh(C_6H_{11})_2\}(SbPh_3)]$	Orange	72	40.6 (40.8)	3.9 (3.7)
(19)	$[PPh_2(C_6H_{11})H][MoI_3(CO)_3(PPh_3)]$	Yellow	53	42.3 (42.9)	3.4 (3.4)
(20)	$[PPh(C_6H_{11})_2H][MoI_3(CO)_3(PPh_3)]$	Yellow	29	42.6 (42.7)	4.1 (4.0)
(21)	$[PPh(C_6H_{11})_2H][WI_3(CO)_3(PPh_3)]$	Yellow	13	38.9 (39.5)	3.6 (3.7)
(22)	$[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]$	Yellow	40	36.9 (36.9)	3.0 (2.9)

* Calculated values in parentheses.

Table 2. I.r.[a] data for the complexes $[MI_2(CO)_3L(L')]$ and $[HL][MI_3(CO)_3L']$

Complex	$\tilde{\nu}(CO)/cm^{-1}$
(1)	2 025s, 1 965s, 1 940s
(2)	2 015m, 1 942s, 1 912s
(3)	2 025s, 1 964s, 1 938s
(4)	2 010m, 1 942s, 1 910m
(5)	2 025s, 1 963s, 1 919m
(6)	2 003m, 1 938s, 1 900m
(7)	2 025s, 1 955s, 1 934s
(8)	2 010s, 1 930s, 1 915s
(9)	2 030s, 1 960s, 1 905s
(10)	2 015s, 1 940s, 1 916s
(11)	2 030s, 1 963s, 1 906s
(12)	2 020s, 1 942s, 1 907s
(13)	2 025s, 1 954s, 1 903s
(14)	2 020s, 1 944s, 1 897s
(15)	2 025s, 1 960s, 1 900s
(16)	2 020s, 1 945s, 1 890s
(17)	2 030s, 1 960s, 1 896s
(18)	2 025s, 1 943s, 1 889s
(19)[b]	2 015m, 1 933s, 1 915s
(20)[b]	2 020m, 1 947s, 1 921s
(21)[b]	2 020m, 1 935s, 1 912s
(22)[b]	2 015m, 1 936s, 1 853m

[a] Spectra recorded in $CHCl_3$; s = strong and m = medium. [b] Showed a weak band at *ca.* 2 370 cm^{-1} due to ν(P–H).

Table 3. Proton n.m.r. (δ)* data for the complexes $[MI_2(CO)_3L(L')]$

Complex	
(7)	7.69, 7.41 (m, 25 H, Ph), 1.62 (m, 11 H, C_6H_{11})
(8)	7.69, 7.52 (m, 25 H, Ph), 1.63 (m, 11 H, C_6H_{11})
(9)	7.63, 7.33 (m, 25 H, Ph), 1.57 (m, 11 H, C_6H_{11})
(10)	7.38 (m, 25 H, Ph), 1.69 (m, 11 H, C_6H_{11})
(11)	7.62, 7.36 (m, 25 H, Ph), 1.71 (m, 11 H, C_6H_{11})
(12)	7.42 (m, 25 H, Ph), 1.63 (m, 11 H, C_6H_{11})
(13)	7.49, 7.24 (m, 20 H, Ph), 1.67 (m, 22 H, C_6H_{11})
(14)	7.40, 7.35 (m, 20 H, Ph), 1.77 (m, 22 H, C_6H_{11})
(15)	7.68, 7.32 (m, 20 H, Ph), 1.68 (m, 22 H, C_6H_{11})
(16)	7.35 (m, 20 H, Ph), 1.50 (m, 22 H, C_6H_{11})
(17)	7.67, 7.35 (m, 20 H, Ph), 1.63 (m, 22 H, C_6H_{11})
(18)	7.65, 7.45 (m, 20 H, Ph), 1.69 (m, 22 H, C_6H_{11})

* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$.

spectroscopy (Table 3). It should be noted that although the *X*-ray crystal structure of $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]$ was determined as a diethyl ether solvate, the complex analysed unsolvated after continual drying *in vacuo*. The neutral compounds **(1)**—**(18)** are stable in the solid state when stored under nitrogen and are soluble in $CHCl_3$ and CH_2Cl_2. The phosphonium salts are air-stable in the solid state and insoluble in $CHCl_3$ and CH_2Cl_2, but soluble in acetone, nitromethane, and dimethyl sulphoxide. However the tetrabutylammonium salts **(23)** and **(24)** (see Experimental section) are soluble in $CHCl_3$ and CH_2Cl_2.

$$[MI_2(CO)_3(NCMe)_2] \longrightarrow [MI_2(CO)_3(NCMe)] + NCMe \quad (1)$$

$$[MI_2(CO)_3(NCMe)] + L \longrightarrow [MI_2(CO)_3(NCMe)L] \quad (2)$$

$$[MI_2(CO)_3(NCMe)L] \longrightarrow [MI_2(CO)_3L] + NCMe \quad (3)$$

$$[MI_2(CO)_3L] + L' \longrightarrow [MI_2(CO)_3L(L')] \quad (4)$$

Scheme.

The reactions of $[MI_2(CO)_3(NCMe)_2]$ with L followed by L′ eventually to give $[MI_2(CO)_3L(L')]$ are likely to proceed *via* successive dissociative mechanisms (Scheme). The complexes $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ obey the effective atomic number rule and are crowded with weakly bonded acetonitrile ligands. Evidence to support this mechanism comes from the fact that the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)L]$ have been isolated and fully characterised.[12] It should also be noted that Tripathi *et al.*[13] have prepared and characterised the six-co-ordinate 16-electron complexes $[MoX_2(CO)_3L]$ (X = Cl, Br, or I; L = PPh_3, $AsPh_3$, or $SbPh_3$) by reaction of $[Mo(CO)_5L]$ with 1 equivalent of X_2 in hexane. The complexes $[MoX_2(CO)_3L]$ are analogous to the proposed intermediates $[MI_2(CO)_3(NCMe)]$ and $[MI_2(CO)_3L]$ shown in the Scheme.

Table 4. Low-temperature ^{13}C n.m.r. data (δ/p.p.m.)* (C≡O) for selected complexes $[WI_2(CO)_3L(SbPh_3)]$ and $[NBu^n{}_4][MI_3(CO)_3(L_3)]$

	Complex	
(4)	$[WI_2(CO)_3(PPh_3)(SbPh_3)]$	208.90 [d, ^2J(P–C) = 19.75 Hz], 254.8
(12)	$[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)]$	209.25, 230.20
(18)	$[WI_2(CO)_3\{PPh(C_6H_{11})_2\}(SbPh_3)]$	209.32, 234.63
(23)	$[NBu^n{}_4][MoI_3(CO)_3(PPh_3)]$	222.2 [d, ^2J(P–C) = 37.04 Hz]
(24)	$[NBu^n{}_4][WI_3(CO)_3(SbPh_3)]$	209.68, 235.50

* Spectra recorded in CD_2Cl_2 (−70 °C) and referenced to $SiMe_4$.

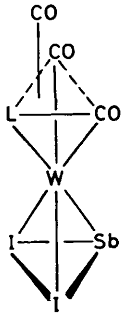

Figure 1. Proposed capped octahedral structure for the complexes $[WI_2(CO)_3L(SbPh_3)][L = PPh_3, PPh_2(C_6H_{11}), \text{or } PPh(C_6H_{11})_2]$

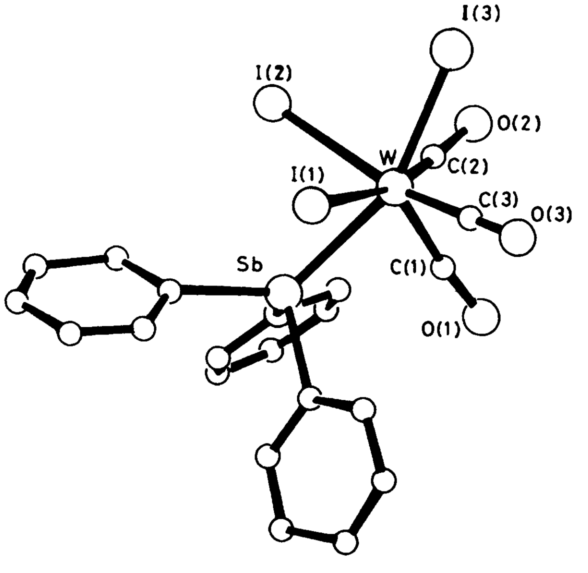

Figure 2. *X*-Ray crystal structure of the anion $[WI_3(CO)_3(SbPh_3)]^-$

Seven-co-ordinate complexes of the type $[MX_2(CO)_3L_2]$ have generally been found to have capped octahedral geometry.[14] Colton and Kevekordes[15] have recently shown how low-temperature ^{13}C n.m.r. spectroscopy can be used to indicate if there is a carbonyl ligand in the unique capping position in capped octahedral complexes. Ganscow and Vernon[16] have suggested that the capping carbonyl is the most strongly bonded carbonyl due to π back donation and δ(C≡O) is shifted to lower field in the ^{13}C n.m.r. spectrum. The low-temperature (−70 °C, CD_2Cl_2) ^{13}C n.m.r. spectra of the triphenylantimony tungsten complexes $[WI_2(CO)_3L(SbPh_3)]$ [L = PPh_3 (**4**), $PPh_2(C_6H_{11})$ (**12**), or $PPh(C_6H_{11})_2$ (**18**)], Table 4, showed two carbonyl resonances. The intensity ratio of the lower-field to the higher-field resonance was 1 : 2. The resonance at lower field for each of the complexes is most likely to be due to a carbonyl ligand in the unique capping position in view of Ganscow's suggestion.[16] The resonance at lower frequency can be ascribed to the two carbonyls in equivalent octahedral positions. A proposed structure for these complexes which is consistent with these data is shown in Figure 1, the smaller phosphorus donor atom being in the more crowded capped face of the octahedron.

The seven-co-ordinate complexes $[MI_2(CO)_3(PPh_3)L]$ [M = Mo, L = $PPh_2(C_6H_{11})$ or $PPh(C_6H_{11})_2$; M = W, L = $PPh(C_6H_{11})_2$] slowly disproportionated in CH_2Cl_2 at room temperature to give the anionic complexes $[HL][MI_3(CO)_3(PPh_3)]$. These salts are analogous to $[PPh_3H][MI_3(CO)_3(PPh_3)]$ reported by Lewis and Whyman[17] in 1967 and Colton and Rix[18] in 1969. Attempts were made to form salts of the other $[MI_2(CO)_3L(L')]$ complexes by refluxing in CH_2Cl_2 or $CHCl_3$ for long periods, but without success. However, on cooling a solution of $[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)]$ in CH_2Cl_2–Et_2O at −40 °C for 2 months small yellow crystals of $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]\cdot Et_2O$ (**22**) were obtained. The structure of (**22**) was determined by *X*-ray crystallography (see next section). ^{31}P-$\{^1H\}$ N.m.r. spectroscopy was used to confirm that PPh_3 is co-ordinated to the molybdenum in $[HL][MoI_3(CO)_3(PPh_3)]$. The spectra of complexes (**19**) and (**20**) showed two resonances each at δ(CD_3NO_2, +25 °C) = +74.6 and +18.8 and +74.6 and +30.2 p.p.m. respectively. The corresponding spectrum of $[PPh_3H][MoI_3(CO)_3(PPh_3)]$ showed resonances at δ = +74.7 and +7.9 p.p.m., and that of $[NBu^n{}_4][MoI_3(CO)_3(PPh_3)]$ showed a single resonance at δ = +74.6 p.p.m. Hence the ^{31}P n.m.r. resonances at δ = +30.2, +18.8, and +7.9 p.p.m. can be ascribed to the phosphonium cations $[PPh(C_6H_{11})_2H]^+$, $[PPh_2(C_6H_{11})H]^+$, and $[PPh_3H]^+$ respectively. Further evidence to support this formulation comes from negative ion fast atom bombardment (f.a.b.) mass spectrometry on the complexes (**19**), (**20**), and $[PPh_3H][MoI_3(CO)_3(PPh_3)]$ which all gave a parent anion with a molecular weight of 823 associated with the anion $[MoI_3(CO)_3(PPh_3)]^-$. Hence, as expected, the more basic phosphines $PPh_2(C_6H_{11})$ and $PPh(C_6H_{11})_2$ are protonated in preference to PPh_3.

The structure of $[WI_3(CO)_3(SbPh_3)]^-$ is shown in Figure 2 together with the atomic numbering scheme. The tungsten atom is seven-co-ordinate, with an approximately capped octahedral environment. The three iodine atoms form the uncapped face [W–I(1) 2.878(3), W–I(2) 2.839(2), and W–I(3) 2.831(3) Å]. A carbonyl group occupies the unique capping position [W–C(1) 1.864(24) Å] and two carbonyl groups [W–C(2) 1.870(30) and W–C(3) 1.913(28) Å] occupy the capped face together with the $SbPh_3$ group [W–Sb 2.720(3) Å].

The bond lengths from tungsten are as expected; we note that W–I(1) is longer than the other W–I bonds but we identify no reason for this. The iodine atom I(3) is unique because it is *trans* to Sb. Thus the I(3)–W–I angles are 88.7(1) and 86.6(1)° compared to 92.5(1)° for I(1)–W–I(2). The angle I(3)–W–C(1) is considerably greater at 130.3(10)° than the other I–W–C(1)

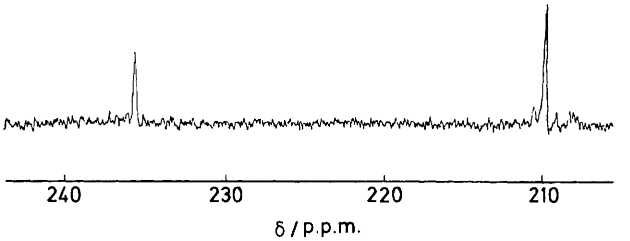

Figure 3. Carbon-13 n.m.r. spectrum (CD_2Cl_2, −70 °C) of $[NBu^n{}_4][WI_3(CO)_3(SbPh_3)]$

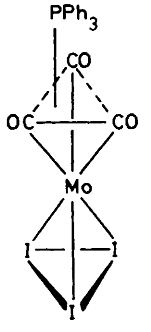

Figure 4. Proposed capped octahedral structure of the complex $[NBu^n{}_4][MoI_3(CO)_3(PPh_3)]$

angles at 122.2(9) and 124.9(8)°. These distortions are only minor and the distortion from ideal geometry is small considering the variation in donor atom size. Using our program[14] for fitting to ideal geometries, we find a root mean square (r.m.s.) deviation of 0.058 Å.

This arrangement of atoms in the co-ordination sphere is somewhat surprising. One might expect, on steric grounds, that the antimony atom is kept as far as possible from the iodine atoms, thus it would be in the capping position with the three carbonyl atoms in the capped face and the three iodine atoms in the uncapped face. We are proposing this structure type for the $[MoI_3(CO)_3(PPh_3)]^-$ anion on the basis of the low-temperature ^{13}C n.m.r. spectrum (see below). Although the phosphonium salt $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]$ is insoluble in $CHCl_3$ and CH_2Cl_2, the tetrabutylammonium salt $[NBu^n{}_4][WI_3(CO)_3(SbPh_3)]$ (**24**) is soluble in these solvents. Hence the low-temperature (−70 °C, CD_2Cl_2) ^{13}C n.m.r. spectrum of $[NBu^n{}_4][WI_3(CO)_3(SbPh_3)]$ showed carbonyl resonances at δ = 209.68 and 235.50 p.p.m. with an intensity ratio of 2:1 (Figure 3). The resonance at δ = 235.50 p.p.m. must be due to the carbonyl ligand in the unique capping position. This is a nice example where low-temperature ^{13}C n.m.r. spectroscopy is in accord with the solid-state crystal structure of a seven-co-ordinate complex. The low-temperature ^{13}C n.m.r. spectrum of $[NBu_4{}^n][MoI_3(CO)_3(PPh_3)]$ (**23**) showed a single resonance at δ = 222.2 p.p.m.; the most likely geometry for this complex would be with the triphenylphosphine ligand occupying the capping position (Figure 4). This difference between the structures of (**23**) and (**24**) is likely to be due to the smaller phosphorus atom preferring to occupy the crowded capping position in (**23**) compared to the larger antimony atom in (**24**).

Experimental

The synthesis and purification of the complexes described were carried out under an atmosphere of dry nitrogen using a vacuum Schlenk line. The compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared by the literature method.[10] All chemicals used were purchased from commercial sources except $PPh_2(C_6H_{11})$ and $PPh(C_6H_{11})_2$ which were prepared by Open University S304 Summer School students at Nottingham University. Dichloromethane was dried and distilled before use. Infrared spectra were recorded on a Perkin-Elmer 197 spectrophotometer, ^1H n.m.r. spectra on a JEOL FX 60 spectrometer, and low-temperature ^{13}C n.m.r. spectra on a Bruker WH-400 spectrometer at the University of Warwick. All spectra were calibrated against tetramethylsilane. The ^{31}P n.m.r. spectra were recorded on a Bruker WP 200 spectrometer referenced to 85% H_3PO_4, at the University of Edinburgh. Negative ion f.a.b. mass spectrometry was performed on a Kratos M5 50TC mass spectrometer at the University of Edinburgh. Elemental analyses (C, H, and N) were carried out on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas) by Mr. E. Lewis of the Department of Chemistry, University College of North Wales, Bangor.

$[MoI_2(CO)_3(PPh_3)(AsPh_3)]$ (**1**).—To $[MoI_2(CO)_3(NCMe)_2]$ (0.46 g, 0.892 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of nitrogen was added PPh_3 (0.234 g, 0.892 mmol). After stirring for 1 min, $AsPh_3$ (0.273 g, 0.892 mmol) was added and the mixture stirred for a further 3 min. After filtration, removal of solvent *in vacuo* gave dark yellow crystals of $[MoI_2(CO)_3(PPh_3)(AsPh_3)]$ (yield = 0.77 g, 86%), which were recrystallised from CH_2Cl_2.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with PPh_3, $AsPh_3$, or $SbPh_3$ gave the complexes $[MI_2(CO)_3L(L')]$. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L] + NCMe$ and $[MI_2(CO)_3(NCMe)L] + L' \longrightarrow [MI_2(CO)_3L(L')] + NCMe$ at 25 °C are: (**2**) M = W; L = PPh_3, 1 min; L′ = $AsPh_3$, 3 min; (**3**) M = Mo; L = PPh_3, 1 min; L′ = $SbPh_3$, 5 min; (**4**) M = W; L = PPh_3, 1 min; L′ = $SbPh_3$, 5 min; (**5**) M = Mo; L = $AsPh_3$, 3 min; L′ = $SbPh_3$, 5 min; and (**6**) M = W; L = $AsPh_3$, 3 min; L′ = $SbPh_3$, 5 min.

$[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(AsPh_3)]$ (**10**).—To $[WI_2(CO)_3(NCMe)_2]$ (0.207 g, 0.343 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of nitrogen was added $AsPh_3$ (0.105 g, 0.343 mmol). After stirring for 3 min, $PPh_2(C_6H_{11})$ (0.092 g, 0.343 mmol) was added and the mixture stirred for a further 25 min. After filtration, removal of solvent *in vacuo* gave yellow crystals of $[WI_2(CO)_3\{PPh_2(C_6H_{11})\}(AsPh_3)]$ (yield = 0.23 g, 61%), which were recrystallised from CH_2Cl_2.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L = PPh_3, $AsPh_3$, or $SbPh_3$ and L′ = $PPh_2(C_6H_{11})$ gave the complexes $[MI_2(CO)_3L(L')]$. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L] + NCMe$ and $[MI_2(CO)_3(NCMe)L] + L' \longrightarrow [MI_2(CO)_3L(L')] + NCMe$ at 25 °C are: [L′ = $PPh_2(C_6H_{11})$] (**7**) M = Mo; L = PPh_3, 1 min; L′, 34 min; (**8**) M = W; L = PPh_3, 1 min; L′, 29 min; (**9**) M = Mo; L = $AsPh_3$, 3 min; L′, 25 min; (**11**) M = Mo; L = $SbPh_3$, 5 min; L′, 25 min; and (**12**) M = W; L = $SbPh_3$, 5 min; L′, 25 min.

$[MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(SbPh_3)]$ (**17**).—To $[MoI_2(CO)_3(NCMe)_2]$ (0.184 g, 0.357 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of nitrogen was added $SbPh_3$ (0.126 g, 0.357 mmol). After stirring for 5 min, $PPh(C_6H_{11})_2$ (0.098 g, 0.357 mmol) was added and the mixture stirred for a further 25 min. After filtration, removal of solvent *in vacuo* gave brown crystals of $[MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(SbPh_3)]$ (yield = 0.248 g, 66%), which were recrystallised from CH_2Cl_2.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L = PPh_3, $AsPh_3$, or $SbPh_3$ and L′ = $PPh(C_6H_{11})_2$ gave the complexes $[MI_2(CO)_3L(L')]$. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L] + NCMe$ and $[MI_2(CO)_3(NCMe)L] + L' \longrightarrow [MI_2(CO)_3L(L')] + NCMe$ at 25 °C are:

Table 5. Fractional atomic co-ordinates (× 10^4) for complex (**22**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 431(1)	1 905(1)	113(1)	C(35)	141(27)	−2 523(47)	3 239(48)
I(1)	1 098(1)	2 229(2)	−584(2)	C(36)	763(20)	−1 463(26)	2 118(31)
I(2)	3 454(1)	3 010(2)	−2 738(2)	P	2 373(5)	6 019(6)	5 767(8)
I(3)	2 684(2)	4 398(2)	−340(3)	C(41)	2 281(14)	5 445(23)	4 718(26)
C(1)	2 425(16)	398(23)	1 588(24)	C(42)	2 395(24)	6 168(36)	3 355(37)
O(1)	2 441(12)	−552(20)	2 611(22)	C(43)	2 245(20)	5 588(34)	2 658(32)
C(2)	3 414(15)	1 999(17)	173(17)	C(44)	2 053(24)	4 359(33)	3 253(39)
O(2)	4 054(15)	2 316(22)	298(29)	C(45)	1 935(16)	3 656(24)	4 477(30)
C(3)	1 640(16)	1 718(28)	1 737(24)	C(46)	2 013(20)	4 071(32)	5 401(38)
O(3)	1 198(15)	1 551(24)	2 760(25)	C(61)	3 168(16)	7 423(22)	4 761(28)
Sb	2 183(1)	45(2)	−484(2)	C(62)	3 911(22)	7 069(35)	4 110(39)
C(11)	3 108(16)	−844(19)	−676(23)	C(63)	4 591(19)	8 309(33)	3 189(40)
C(12)	3 647(25)	−632(28)	−102(28)	C(64)	4 653(24)	8 809(37)	4 087(50)
C(13)	4 187(18)	−1 284(33)	−233(35)	C(65)	4 008(27)	9 070(40)	4 761(45)
C(14)	4 285(21)	−2 086(32)	−698(35)	C(66)	3 294(18)	7 899(26)	5 678(37)
C(15)	3 744(24)	−2 263(26)	−1 153(34)	C(71)	1 514(16)	6 363(20)	6 497(22)
C(16)	3 146(23)	−1 653(27)	−1 149(34)	C(72)	1 051(19)	6 929(27)	5 777(33)
C(21)	1 929(21)	228(23)	−2 177(31)	C(73)	363(17)	7 099(35)	6 389(40)
C(22)	2 487(23)	572(29)	−3 460(46)	C(74)	210(18)	6 904(28)	7 738(36)
C(23)	2 245(27)	508(28)	−4 516(30)	C(75)	585(25)	6 393(28)	8 455(37)
C(24)	1 588(29)	168(33)	−4 323(46)	C(76)	1 331(18)	6 185(27)	7 866(34)
C(25)	977(26)	−109(28)	−3 047(38)	C(91)	4 514(29)	2 829(42)	3 300(47)
C(26)	1 154(16)	−117(20)	−2 025(28)	C(92)	3 979(43)	3 064(66)	2 716(76)
C(31)	1 246(13)	−1 509(22)	1 080(27)	O(93)	4 296(38)	4 453(60)	1 360(66)
C(32)	1 131(18)	−2 523(39)	982(42)	C(94)	4 277(37)	5 143(56)	2 384(65)
C(33)	560(30)	−3 648(25)	2 034(57)	C(95)	4 813(25)	4 672(38)	3 123(44)
C(34)	29(22)	−3 641(45)	3 292(40)				

Table 6. Dimensions (distances in Å, angles in °) in the co-ordination sphere of complex (**22**)

W–I(1)	2.878(3)	W–C(2)	1.870(30)
W–I(2)	2.839(2)	W–C(3)	1.913(28)
W–I(3)	2.831(3)	W–Sb	2.720(3)
W–C(1)	1.864(24)		
I(1)–W–I(2)	92.55(7)	I(2)–W–C(3)	159.2(9)
I(1)–W–I(3)	88.68(9)	I(3)–W–C(3)	76.9(9)
I(2)–W–I(3)	86.61(7)	C(1)–W–C(3)	75.8(12)
I(1)–W–C(1)	122.2(9)	C(2)–W–C(3)	114.0(12)
I(2)–W–C(1)	124.9(8)	I(1)–W–Sb	77.33(8)
I(3)–W–C(1)	130.3(10)	I(2)–W–Sb	76.09(7)
I(1)–W–C(2)	167.5(4)	I(3)–W–Sb	157.06(9)
I(2)–W–C(2)	76.4(5)	C(1)–W–Sb	72.6(10)
I(3)–W–C(2)	84.9(6)	C(2)–W–Sb	105.1(7)
C(1)–W–C(2)	69.7(10)	C(3)–W–Sb	115.8(10)
I(1)–W–C(3)	74.7(10)		

[L′ = $PPh(C_6H_{11})_2$] (**13**) M = Mo; L = PPh_3, 1 min; L′, 29 min; (**14**) M = W; L = PPh_3, 1 min; L′, 29 min; (**15**) M = Mo; L = $AsPh_3$, 3 min; L′, 27 min; (**16**) M = W; L = $AsPh_3$, 3 min; L′, 27 min; (**18**) M = W; L = $SbPh_3$, 5 min; L′, 25 min.

[$PPh(C_6H_{11})_2H$][$MoI_3(CO)_3(PPh_3)$] (**20**).—The complex [$MoI_2(CO)_3\{PPh(C_6H_{11})_2\}(PPh_3)$] (0.230 g, 0.237 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of nitrogen. The mixture was left stirring for 9 h after which time [$PPh(C_6H_{11})_2H$][$MoI_3(CO)_3(PPh_3)$] precipitated. The yellow precipitate was filtered off and dried under vacuum (yield = 0.075 g, 29%).

Similarly, dissolving [$MI_2(CO)_3L(L')$] in CH_2Cl_2 where L and L′ = PPh_3, $PPh_2(C_6H_{11})$, $PPh(C_6H_{11})_2$, or $SbPh_3$ gave the complexes [HL][$MI_3(CO)_3L'$]. Reaction times for [$MI_2(CO)_3L(L')$] $\longrightarrow$ [HL][$MI_3(CO)_3L'$] at 25 °C are: (**19**) M = Mo, L = $PPh_2(C_6H_{11})$, L′ = PPh_3, 72 h; (**21**) M = W, L = $PPh(C_6H_{11})_2$, L′ = PPh_3, 7 h; (**22**) M = W, L = $PPh_2(C_6H_{11})$, L′ = $SbPh_3$; suitable single crystals for *X*-ray crystallography were obtained from a CH_2Cl_2–Et_2O solution of [$WI_2(CO)_3\{PPh_2(C_6H_{11})\}(SbPh_3)$] over a period of 2 months at −40 °C.

[NBu^n_4][$MoI_3(CO)_3(PPh_3)$] (**23**).—To [$MoI_2(CO)_3(NCMe)_2$] (0.193 g, 0.374 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of nitrogen was added PPh_3 (0.098 g, 0.374 mmol). After stirring for 1 min, [NBu^n_4]I (0.138 g, 0.374 mmol) was added and the mixture stirred for a further 90 min. After filtration, the volume was reduced to 5 cm^3 *in vacuo* and addition of MeOH (20 cm^3) gave a yellow precipitate of [NBu^n_4][$MoI_3(CO)_3(PPh_3)$]. This was filtered off and dried under vacuum (yield = 0.29 g, 73%) (Found: C, 41.8, H, 5.0, N, 1.4. $C_{37}H_{51}I_3MoNO_3P$ requires C, 41.7; H, 4.8; N, 1.3%). I.r. ($CHCl_3$, NaCl plates): ν(CO) 2 020s, 1 948s, and 1 900s cm^{-1}.

A similar reaction of [$WI_2(CO)_3(NCMe)_2$] with 1 equivalent of $SbPh_3$ in CH_2Cl_2 followed by reaction of 1 equivalent of [NBu^n_4]I yielded an orange precipitate of [NBu^n_4][$WI_3(CO)_3(SbPh_3)$] (**24**) upon adding MeOH (yield = 0.31 g, 68%) (Found: C, 35.8, H, 4.3, N, 1.0. $C_{37}H_{51}I_3NO_3SbW$ requires C, 35.7, H, 4.1, N, 1.1%). I.r. ($CHCl_3$, NaCl plates): ν(CO) 2 015s, 1 948s, and 1 853s cm^{-1}.

Crystallography.—Crystals were prepared as described above.

Crystal data. [$PPh_2(C_6H_{11})H$][$WI_3(CO)_3(SbPh_3)$]·OC_4H_{10}, $C_{43}H_{47}I_3O_4PSbW$, M = 1343.6, triclinic, space group $P\bar{1}$, a = 18.85(15), b = 12.30(11), c = 11.67(12) Å, α = 62.9(1), β = 71.9(1), γ = 95.1(1)°, U = 2 203.12 Å^3, Z = 2, D_c = 2.02 g cm^{-3}, $F(000)$ = 1 270, λ = 0.7107Å, μ = 55.8 cm^{-1}.

A crystal of approximate size 0.4 × 0.2 × 0.2 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width ω scans. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + sinμ/tanθ). 5 673 Independent reflections were measured of which 3 317 with $I > 2\sigma(I)$ were used in the subsequent refinement. An empirical absorption correction was applied.[19] The structure was determined by the heavy-atom method. All non-hydrogen atoms apart from those in the solvent molecule were refined anisotropically. Hydrogen atoms were included in calculated positions although the methyl hydrogen atoms were refined as rigid groups.

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.075 ($R' = 0.077$). Calculations were carried out using SHELX 76[20] and some of our own programs on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 5 and molecular dimensions in the co-ordination sphere in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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