Seven-co-ordinate Dibromo Complexes of Molybdenum(II) and Tungsten(II) derived from $[MBr_2(CO)_3(NCMe)_2]$. Crystal Structures of the Isostructural Complexes $[WX_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (X = Br or I)†

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Reaction of the complexes *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) (prepared *in situ*) with an equimolar quantity of Br_2 at −78 °C afforded high yields of the seven-co-ordinate complexes $[MBr_2(CO)_3(NCMe)_2]$. The reaction of these complexes with an equimolar amount of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature gave the new mixed-ligand complexes $[MBr_2(CO)_3(NCMe)L]$. The molecular structure of $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ and its diiodo analogue $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ have been crystallographically determined. Crystals of the former are monoclinic of space group $P2_1/c$, a = 8.302(3), b = 26.199(3), c = 13.020(4) Å, β = 97.53(2)°, Z = 4. Crystals of the latter are also monoclinic of space group $P2_1/c$, a = 8.450(2), b = 25.941(6), c = 13.042(4) Å, β = 96.47(2)°, Z = 4. The two complexes are isostructural and can best be described as distorted capped trigonal prismatic with one triangular face having three carbonyl ligands and the other triangular face having X(2), Sb and N. The X(1) atom caps the rectangular face defined by C(1), X(2), N and C(3). The low-temperature (−60 °C, $CDCl_3$) ^{13}C NMR spectrum of $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ was obtained and correlated with the solid-state structure. Reaction of $[WBr_2(CO)_3(NCMe)_2]$ with 2 equivalents of $AsPh_3$ in CH_2Cl_2 at room temperature gave $[WBr_2(CO)_3(AsPh_3)_2]$.

In the 1960s and 1970s considerable effort was made to prepare seven-co-ordinate dihalogenocarbonyl complexes of molybdenum(II) and tungsten(II).[1–12] The importance of this work has become evident since Bencze *et al.*[13,14] have shown that the complexes $[MX_2(CO)_3L_2]$ (M = Mo or W, X = Cl or Br, L = PPh_3 or $AsPh_3$) are single component catalysts for the ring-opening polymerisation of norbornene and norbornadiene. The structures of seven-co-ordinate complexes of molybdenum(II) and tungsten(II) have been shown[15,16] to have (*i*) capped octahedral, (*ii*) capped trigonal prismatic, (*iii*) pentagonal bipyramidal, or (*iv*) the so-called '4:3' geometry. The most common geometry of this type of complex is capped octahedral.[17]

In 1986[18] we described the reaction of *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) (prepared *in situ*[19,20]) with an equimolar quantity of X_2 (X = Br or I) at 0 °C to afford the seven-co-ordinate dihalogeno complexes $[MX_2(CO)_3(NCMe)_2]$. Although a wide range of chemistry of the diiodo complexes $[MI_2(CO)_3(NCMe)_2]$ with both donor ligands[21–24] and alkynes[25,26] has been described, hitherto the chemistry of the dibromo complexes has not been attempted mainly due to the difficulty in isolating $[MBr_2(CO)_3(NCMe)_2]$ in a pure state by this synthetic route. In order to improve the synthesis of the dibromobis(acetonitrile) complexes $[MBr_2(CO)_3(NCMe)_2]$ we describe in this paper the reactions of *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) (prepared *in situ*[19,20]) with an equimolar amount of Br_2 at −78 °C to give improved yields and purity of $[MBr_2(CO)_3(NCMe)_2]$. The reactions of $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an equimolar quantity of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature to give $[MBr_2(CO)_3(NCMe)L]$ are also described. In addition the molecular structures of the isostructural distorted capped trigonal-prismatic complexes $[WX_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (X = Br or I) are discussed.

Results and Discussion

The air-sensitive complexes *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) were prepared by reacting $[M(CO)_6]$ in refluxing acetonitrile for 24 (M = Mo) or 96 h (M = W) respectively.[19,20] They were then cooled at −78 °C before an equimolar amount of Br_2 was added to give orange-brown solutions. The solutions were allowed to return to room temperature, followed by stirring for 30 min and then removal of the solvent *in vacuo* gave high yields of the seven-co-ordinate complexes $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo **1** or W **2**). Complexes **1** and **2** were characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2) and ^1H NMR spectroscopy (Table 3). They are considerably less stable than their diiodo analogues $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W);[18] in particular the molybdenum complex **1** was unstable both in solution and the solid state and it was difficult to obtain satisfactory analytical data. However, the complex was stable enough to be used as a reagent if used soon after its preparation. Complexes **1** and **2** are both soluble in chlorinated solvents such as CH_2Cl_2, $CHCl_3$ and also in NCMe and acetone, but only sparingly soluble in hydrocarbon solvents and diethyl ether.

The IR spectra for complexes **1** and **2** in $CHCl_3$ each have three carbonyl bands at 2090, 2035, 1966 cm^{-1} (**1**) and 2094, 2038 and 1949 cm^{-1} (**2**). The diiodo analogues $[MI_2(CO)_3(NCMe)_2]$ have carbonyl bands[18] at 2038, 1968, 1940 cm^{-1} (M = Mo) and 2040, 1980 and 1945 cm^{-1} (M = W).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Physical and analytical data * for the seven-co-ordinate carbonyl complexes of molybdenum(II) and tungsten(II)

Complex	Colour	Yield (%)	Analysis (%) C	H	N
1 $[MoBr_2(CO)_3(NCMe)_2]$	Orange–brown	89	17.4 (19.9)	1.6 (1.4)	6.8 (6.6)
2 $[WBr_2(CO)_3(NCMe)_2]$	Dark brown	86	16.0 (16.5)	1.3 (1.2)	5.4 (5.5)
3 $[MoBr_2(CO)_3(NCMe)(PPh_3)]$	Brown	56	42.7 (42.9)	3.4 (2.8)	2.6 (2.2)
4 $[WBr_2(CO)_3(NCMe)(PPh_3)]$	Orange	47	38.2 (37.8)	2.7 (2.5)	1.2 (1.9)
5 $[MoBr_2(CO)_3(NCMe)(AsPh_3)]$	Mustard	64	40.6 (40.2)	2.9 (2.6)	1.7 (2.0)
6 $[WBr_2(CO)_3(NCMe)(AsPh_3)]$	Orange	58	36.4 (35.7)	2.5 (2.3)	1.1 (1.8)
7 $[MoBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$	Orange	71	35.7 (35.2)	2.6 (2.4)	1.8 (1.7)
8 $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$	Orange	40	31.9 (31.8)	2.2 (2.2)	1.3 (1.5)
9 $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$	Orange–brown	68	28.2 (27.6)	1.8 (2.1)	1.4 (1.4)
10 $[WBr_2(CO)_3(AsPh_3)_2]$	Yellow	49	44.6 (45.0)	2.9 (2.9)	0.0 (0.0)

* Calculated values are in parentheses.

Table 2 Infrared data * for complexes

Complex	$\tilde{\nu}(CO)/cm^{-1}$	$\tilde{\nu}(NC)/cm^{-1}$
1	2090w, 2035s, 1966s	2312m, 2283w
2	2094m, 2038s, 1949s	2310w, 2290w
3	2034s, 1954s, 1904s	2295w
4	2044s, 1971s, 1913s	2289w
5	2032s, 1962s, 1927m, 1873s	2361w, 2334w
6	2045s, 1972s, 1942m, 1915m	2288w
7	2030s, 1937s, 1860s	2360m, 2339w
8	2023s, 1972s, 1946s, 1911s	2358w
9	2027s, 1967s, 1903s	2289w
10	2009s, 1932s, 1893s	—

s = Strong, m = medium, w = weak.
* Spectra recorded in $CHCl_3$ as thin films between NaCl plates.

Table 3 Proton NMR data[a] for the complexes

Complex	δ
1	2.00 (s, NCMe)
2	2.02 (s, NCMe)
3	7.51–7.38 (br m, 15 H, Ph), 1.98 (s, 3 H, NCMe)
4	7.60–7.48 (br m, 15 H, Ph), 1.96 (s, 3 H, NCMe)
5	7.61–7.53 (br m, 15 H, Ph), 1.97 (s, 3 H, NCMe)
6	7.40 (m, 15 H, Ph), 1.96 (s, 3 H, NCMe)
7	7.63–7.35 (br m, 15 H, Ph), 5.28 (s, 2 H, CH_2Cl_2), 1.97 (s, 3 H, NCMe)
8	7.58–7.42 (br m, 15 H, Ph), 5.28 (s, 2 H, CH_2Cl_2), 1.80 (s, 3 H, NCMe)
9	7.56–7.39 (br m, 15 H, Ph), 5.22 (s, 2 H, CH_2Cl_2), 1.92 (s, 3 H, NCMe)
10[b]	7.34 (m, 18 H, Ph), 7.24 (m, 12 H, Ph)

s = singlet, m = multiplet, br m = broad multiplet. [a] Spectra recorded in $CDCl_3$ (+25 °C) referenced to $SiMe_4$. [b] Spectrum recorded in $(CD_3)_2CO$ (+25 °C) referenced to $SiMe_4$.

The carbonyl bands for **1** and **2** are as expected at higher frequency than those of $[MI_2(CO)_3(NCMe)_2]$. Complexes **1** and **2** also have weak doublets at 2312 and 2283 cm^{-1} (**1**) and 2310 and 2290 cm^{-1} (**2**) corresponding to the co-ordinated acetonitrile ligands. The room-temperature ^1H NMR spectra in $CDCl_3$ for **1** and **2** have single resonances at δ 2.00 and 2.02 respectively due to the methyl groups of the acetonitrile ligands.

Several unsuccessful attempts were made to grow suitable single crystals of complexes **1** and **2** for X-ray crystallography. However, the molecular structure of the tungsten diiodo analogue $[WI_2(CO)_3(NCMe)_2]$ has been previously described[27] and has a capped octahedral geometry with a carbonyl ligand in the unique capping position. Colton and Kevekordes[28] have previously shown how low-temperature ^{13}C NMR spectra in the carbonyl region for seven-co-ordinate halogenocarbonyl complexes of molybdenum(II) and tungsten(II) can often be correlated with their solid-state structures. The low-temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectrum for $[WI_2(CO)_3(NCMe)_2]$ has two resonances at δ 228.48 and 202.36 in a ratio of 1 : 2.[27] It was suggested that the low-field resonance at δ 228.48 was due to a carbonyl ligand in the unique capping position, with the other two carbonyls being in equivalent octahedral positions as shown in Fig. 1. The room-temperature (+25 °C, CD_2Cl_2) ^{13}C NMR spectrum for the dibromo complex $[WBr_2(CO)_3(NCMe)_2]$ **2** has three carbonyl resonances at δ 222.20, 209.11 and 205.03. Although the resonance at δ 222.20 may be due to a carbonyl ligand in the unique capping position, the presence of three bands suggested a structure distorted from that shown in Fig. 1. This distortion from a perfect capped octahedral or trigonal-prismatic geometry is not unusual, and the molecular structures of $[WX_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (X = Br or I) are distorted between capped trigonal-prismatic and capped octahedral geometries (see later).

Equimolar quantities of complexes **1** and **2** and L (L = PPh_3, $AsPh_3$ or $SbPh_3$) react in CH_2Cl_2 at room temperature to afford the new mono(acetonitrile) complexes $[MBr_2(CO)_3(NCMe)L]$ **3**–**8**. They were fully characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (Tables 1–3). The triphenylstibine complexes $[MBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (M = Mo **7** or W **8**) were confirmed as CH_2Cl_2 solvates by repeated elemental analysis, ^1H NMR spectroscopy and for M = W, by X-ray crystallography. The mono(ligand) complexes **3**–**8** are considerably more stable than their bis(acetonitrile) complexes **1** and **2**. However, they are air-sensitive in solution but reasonably air-stable in the solid state. Although complexes **3**–**8** are soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ they are less soluble than **1** and **2**. It is likely that the reactions of **1** and **2** with L proceed by a dissociative displacement of NCMe since the complexes $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) obey the effective atomic number rule.

The solution IR spectra ($CHCl_3$) of **3**–**8** have either three or four carbonyl bands. Complexes **5**, **6** and **8** with four bands may exist as two isomers in solution. They also have weak nitrile bands at ≈2300 cm^{-1}. The ^1H NMR spectra for **3**–**8** all conform with the complexes having one acetonitrile and one other ligand, L, attached to the metal.

Single crystals of $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **8** for X-ray crystallography were grown from a CH_2Cl_2–Et_2O (80 : 20) solution cooled to −17 °C for 24 h. It was of interest to compare the effect of the halide on the structures of seven-co-ordinate complexes, and hence we decided to prepare and grow single crystals of the previously reported complex $[WI_2(CO)_3(NCMe)(SbPh_3)]$.[29] Complex $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **9** was therefore prepared as previously described[29] and fully characterised (see Tables 1–3). It should be noted that complex **9** was not previously formulated

Table 4 Crystal data and details of data collection and refinement for $[WX_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (X = Br **8** or I **9**)

	8	**9**
Formula	$C_{23}H_{18}Br_2NO_3SbW\cdot CH_2Cl_2$	$C_{23}H_{18}I_2NO_3SbW\cdot CH_2Cl_2$
M	906.73	1000.71
Crystal system	Monoclinic	Monoclinic
a/Å	8.302(3)	8.450(2)
b/Å	26.199(3)	25.941(6)
c/Å	13.020(4)	13.042(4)
β/°	97.53(2)	96.47(2)
U/Å^3	2807.5(14)	2840.6(13)
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
D_c/g cm^{-3}	2.145	2.340
F(000)	1696	1840
μ(Mo-Kα)/cm^{-1}	81.19	73.85
Crystal size/mm	0.30 × 0.10 × 0.05	0.22 × 0.16 × 0.10
h_{min}, h_{max}	−8, 9	−9, 7
k_{min}, k_{max}	−30, 29	−29, 16
l_{min}, l_{max}	−15, 7	−14, 14
θ Range/°	1.76–24.95	1.76–25.07
Total data measured	8470	8213
Total unique	4240	4120
R_{int}	0.0536	0.0373
Absorption correction factors, min., max.	0.877, 1.204	0.923, 1.231
No. of parameters	328	328
ρ_{min}, ρ_{max}/e Å^{-3}	−0.92, 0.80	−1.01, 1.14
$(\Delta/\sigma)_{max}$	0.005	0.009
R_1^{a}	0.0491 (0.0292)^b	0.0369 (0.0284)^b
wR_2^{a}	0.0992 (0.0702)^b	0.0843 (0.0719)^b

^{a} $R_1 = \Sigma(\Delta F)/\Sigma(F_o)$, $wR_2 = \{\Sigma[w\Delta(F^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)^2$. ^{b} Values in parentheses are calculated for data with $F_o > 2\sigma(F_o^2)$.

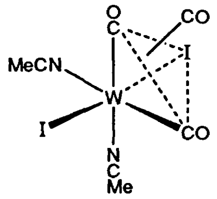

Fig. 1 Solid-state structure of $[WI_2(CO)_3(NCMe)_2]$

as a CH_2Cl_2 solvate,[29] which may have been due to the rapid recrystallisation of the complex from CH_2Cl_2,[29] rather than the slow crystallisation [CH_2Cl_2–Et_2O (80:20) at −17 °C for 24 h] in order to obtain single crystals for X-ray crystallography.

The molecular structure of $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **8** is shown in Fig. 2, together with the atom numbering scheme used. Complex $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **9** also has the same structure and atom numbering. Crystals of both **8** and **9** consist of discrete monomeric molecules of $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ and $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ respectively, held together by van der Vaals forces. Both complexes also contain CH_2Cl_2 molecules of crystallisation in their lattices. The crystal data and bond lengths and angles of the two complexes are given in Tables 4 and 5. From a comparison of the unit-cell parameters and molecular geometry parameters it is clear that complexes **8** and **9** are isostructural, with only minor differences attributable to the relative size differences of the Br and I atoms. They have the same seven-co-ordinate geometry around the metal centre. The co-ordination geometry is best described in terms of a distorted capped trigonal prism (Fig. 2), with identical ligand dispositions.

The capped trigonal prism consists of a triangular face whose corners are occupied by the carbon atoms of the three carbonyl ligands and a second triangular face consisting of Sb, N and Br(2) for **8** or I(2) for **9**. The Br(1) and I(1) atoms occupy the capping position on the rectangular face as defined by C(1), Br(2), N and C(3) for **8** and C(1), I(2), N and C(3) for **9**.

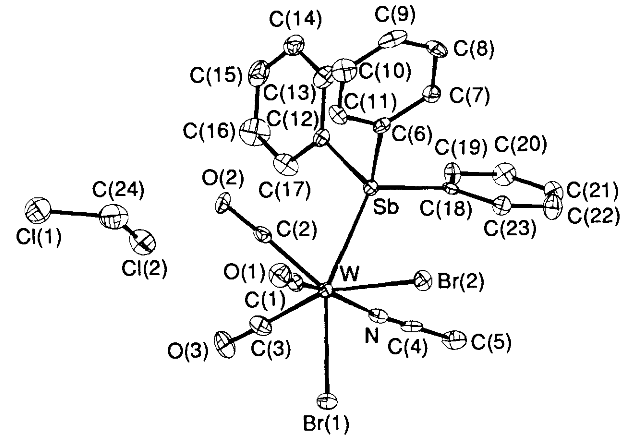

Fig. 2 Crystal structure of $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **8** showing the atom numbering scheme. The analogous iodo complex **9** has the same structure with identical atom numbering

The W–C(CO) bond lengths in **8** [2.011(11)–1.948(8) Å] as expected, are slightly longer than their respective values in **9** [1.981(9)–1.937(9) Å]. As complex **8** contains the more electronegative bromide ligands, the electron density at the metal centre will be reduced and back donation to the carbonyl ligands will decrease, resulting in the lengthening of the W–C(CO) bonds. The W–N and W–Sb bond lengths in **8** [2.190(7), 2.762(1) Å] are comparable with their respective values in **9** [2.160(7), 2.745(1) Å]. The W–Br distances in **8** [2.643(1), 2.646(1) Å] are ≈0.20 Å shorter than the W–I bond lengths in **9** [2.832(1), 2.844(1) Å] as expected on the basis of the difference in the covalent radii of the Br and I. In both complexes, although the two halides occupy different co-ordination sites they are equidistant from the metal centre. The

Table 5 Bond lengths (Å) and angles (°) for $[WX_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ (X = Br **8** or I **9**)

	8	**9**		**8**	**9**
W–C(1)	2.001(9)	1.969(11)	C(8)–C(9)	1.368(13)	1.361(13)
W–C(2)	1.948(8)	1.937(9)	C(9)–C(10)	1.350(15)	1.364(13)
W–C(3)	2.011(11)	1.981(9)	C(10)–C(11)	1.398(13)	1.374(12)
W–N	2.190(7)	2.160(7)	C(12)–C(13)	1.395(13)	1.366(12)
W–Sb	2.762(1)	2.745(1)	C(12)–C(17)	1.383(12)	1.389(12)
W–X(1)	2.643(1)	2.832(1)	C(13)–C(14)	1.384(13)	1.374(12)
W–X(2)	2.646(1)	2.844(1)	C(14)–C(15)	1.362(15)	1.352(14)
Sb–C(6)	2.112(8)	2.097(8)	C(15)–C(16)	1.348(15)	1.350(15)
Sb–C(12)	2.135(8)	2.126(8)	C(16)–C(17)	1.397(14)	1.368(12)
Sb–C(18)	2.140(8)	2.116(8)	C(18)–C(19)	1.370(11)	1.356(11)
O(1)–C(1)	1.156(10)	1.150(10)	C(18)–C(23)	1.404(12)	1.393(11)
O(2)–C(2)	1.163(11)	1.154(10)	C(19)–C(20)	1.382(12)	1.385(11)
O(3)–C(3)	1.145(12)	1.140(10)	C(20)–C(21)	1.379(14)	1.342(12)
N–C(4)	1.165(11)	1.122(10)	C(21)–C(22)	1.391(13)	1.372(12)
C(4)–C(5)	1.461(12)	1.457(12)	C(22)–C(23)	1.382(12)	1.379(11)
C(6)–C(7)	1.383(13)	1.395(11)	Cl(1)–C(24)	1.759(12)	1.746(10)
C(6)–C(11)	1.387(12)	1.380(11)	Cl(2)–C(24)	1.751(12)	1.732(11)
C(7)–C(8)	1.427(12)	1.376(12)			
C(2)–W–C(1)	73.6(3)	73.8(3)	O(2)–C(2)–W	175.5(7)	176.9(7)
C(2)–W–C(3)	71.8(4)	72.2(4)	O(3)–C(3)–W	177.9(8)	177.2(8)
C(1)–W–C(3)	105.9(4)	106.8(3)	N–C(4)–C(5)	179.1(11)	178.5(8)
C(1)–W–N	162.8(3)	162.2(3)	C(11)–C(6)–C(7)	120.5(8)	118.0(8)
C(2)–W–N	123.4(3)	123.9(3)	C(11)–C(6)–Sb	120.0(6)	120.4(6)
C(3)–W–N	83.7(3)	82.9(3)	C(7)–C(6)–Sb	119.4(6)	121.6(6)
C(1)–W–Sb	109.6(3)	110.2(2)	C(8)–C(7)–C(6)	118.5(8)	120.7(8)
C(2)–W–Sb	71.8(2)	72.2(2)	C(9)–C(8)–C(7)	119.6(9)	119.8(9)
C(3)–W–Sb	117.9(3)	117.5(2)	C(8)–C(9)–C(10)	121.5(9)	120.6(9)
N–W–Sb	76.7(2)	76.7(2)	C(9)–C(10)–C(11)	120.3(9)	120.0(9)
C(1)–W–X(1)	80.1(3)	79.7(2)	C(10)–C(11)–C(6)	119.5(9)	120.8(8)
C(2)–W–X(1)	131.4(2)	130.0(2)	C(13)–C(12)–C(17)	119.1(9)	119.1(8)
C(3)–W–X(1)	77.4(3)	76.2(3)	C(13)–C(12)–Sb	120.7(7)	121.0(6)
N–W–X(1)	88.4(2)	88.5(2)	C(17)–C(12)–Sb	120.2(7)	119.7(6)
Sb–W–X(1)	156.66(3)	157.76(2)	C(14)–C(13)–C(12)	120.2(10)	120.3(9)
C(1)–W–X(2)	80.3(3)	79.3(2)	C(15)–C(14)–C(13)	119.3(10)	120.3(10)
C(2)–W–X(2)	127.1(3)	127.7(3)	C(14)–C(15)–C(16)	121.9(11)	119.9(9)
C(3)–W–X(2)	161.0(3)	159.8(3)	C(17)–C(16)–C(15)	119.9(11)	121.3(10)
N–W–X(2)	86.3(2)	86.7(2)	C(16)–C(17)–C(12)	119.6(10)	119.1(10)
Sb–W–X(2)	75.08(3)	76.45(2)	C(19)–C(18)–C(23)	119.7(8)	119.7(8)
X(1)–W–X(2)	86.23(3)	86.34(2)	C(19)–C(18)–Sb	119.6(6)	119.2(6)
C(6)–Sb–C(12)	99.3(3)	99.6(3)	C(23)–C(18)–Sb	120.7(6)	121.1(6)
C(6)–Sb–C(18)	104.2(3)	104.2(3)	C(18)–C(19)–C(20)	121.0(9)	120.7(8)
C(18)–Sb–C(12)	99.5(3)	98.5(3)	C(21)–C(20)–C(19)	119.6(8)	119.9(9)
C(6)–Sb–W	115.1(2)	115.6(2)	C(20)–C(21)–C(22)	120.2(9)	120.5(8)
C(12)–Sb–W	117.3(2)	115.6(2)	C(21)–C(22)–C(23)	120.0(9)	120.5(8)
C(18)–Sb–W	118.5(2)	120.0(2)	C(18)–C(23)–C(22)	119.4(8)	118.8(8)
C(4)–N–W	171.5(7)	172.7(7)	Cl(2)–C(24)–Cl(1)	112.4(4)	112.2(6)
O(1)–C(1)–W	175.4(8)	175.9(7)			

C≡O, N≡C and C≡C distances are as expected and comparable with the corresponding values in the two complexes.

The difference in the halide atom does not appear to influence the steric requirements of the complex as a whole. A comparison of the analogous bond angles show a maximum deviation of 2° and confirm the isostructural nature of the complexes. The C–W–Br and C–W–I bond angles for both the capping [131.4(2), 80.1(3), 77.4(3)° in **8**, 130.0(2), 79.7(2), 76.2(3)° in **9**] and noncapping halides [161.0(3), 127.1(3), 80.3(3)° in **8**, 159.8(3), 127.7(3), 79.3(2)° in **9**] in both complexes are analogous. The W–N–C angles of 171.5(7)° in **8** and 172.7(7)° in **9** show a large deviation from linearity. The M–C≡O moieties are also slightly non-linear [175.4(8)–177.9(8)° in **8** and 175.9(7)–177.2(8)° in **9**]. The molecular structures of **8** and **9** confirmed the presence of a CH_2Cl_2 solvate in the crystal lattice which verified the stoichiometry proposed by elemental analysis and ^1H NMR spectroscopy.

The low-temperature (−60 °C, $CDCl_3$) ^{13}C NMR spectrum of $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **9** shows three resonances at δ 218.99, 210.93 and 207.53. The appearance of three different carbonyl resonances conforms with the solid-state structure of a distorted capped trigonal prism. It is interesting that the room-temperature (+25 °C, $CDCl_3$) ^{13}C NMR spectrum for **9** shows a single carbonyl resonance at δ 218.40 which suggests that the complex is undergoing a rapid fluxional process (faster than the NMR time-scale).

Reaction of the tungsten complex $[WBr_2(CO)_3(NCMe)_2]$ **2** with 2 equivalents of $AsPh_3$ in CH_2Cl_2 at room temperature gave the bis(triphenylarsine) complex $[WBr_2(CO)_3(AsPh_3)_2]$ **10** in high yield. This complex has been previously prepared[9] by reacting the bromo-bridged dimer $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ with $AsPh_3$. Complex **10** was also characterised by elemental analysis, IR and ^1H NMR spectroscopy (Tables 1–3).

Experimental

The preparation and purification of the complexes were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. All chemicals used were purchased from commercial sources. Dichloromethane was dried and distilled before use. Elemental analyses (C, H and N) were recorded on a Carlo Erba MOD 1106 elemental analyser

Table 6 Atomic coordinates ($\times 10^4$) for $[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **8**

Atom	*x*	*y*	*z*
W	2 201.1(4)	5 480.0(1)	6 765.9(3)
Sb	3 732.1(6)	6 323.9(2)	7 717.8(4)
Br(1)	1 179.3(11)	4 524.4(3)	6 604.1(8)
Br(2)	1 576.3(11)	5 436.5(3)	8 705.0(7)
Cl(1)	2 103(3)	6 578(1)	1 722(8)
Cl(2)	4 665(4)	6 149(1)	3 221(2)
O(1)	−1 579(8)	5 678(3)	6 472(6)
O(2)	1 519(8)	6 384(2)	5 224(5)
O(3)	3 213(8)	5 147(3)	4 611(5)
N	4 622(8)	5 192(3)	7 357(6)
C(1)	−201(11)	5 596(3)	6 539(7)
C(2)	1 831(10)	6 057(3)	5 819(7)
C(3)	2 814(11)	5 266(4)	5 385(8)
C(4)	5 861(11)	5 054(3)	7 792(8)
C(5)	7 403(11)	4 880(4)	8 353(9)
C(6)	2 175(9)	6 855(3)	8 310(7)
C(7)	2 611(11)	7 059(3)	9 286(7)
C(8)	1 598(11)	7 442(3)	9 644(8)
C(9)	216(12)	7 591(4)	9 027(9)
C(10)	−216(11)	7 384(4)	8 082(9)
C(11)	755(11)	7 008(3)	7 708(7)
C(12)	4 948(9)	6 825(3)	6 779(7)
C(13)	5 070(11)	7 345(4)	6 999(8)
C(14)	5 930(11)	7 662(4)	6 416(8)
C(15)	6 588(12)	7 464(4)	5 598(9)
C(16)	6 484(12)	6 963(4)	5 362(9)
C(17)	5 657(10)	6 633(4)	5 955(8)
C(18)	5 641(9)	6 206(3)	8 967(7)
C(19)	7 205(9)	6 331(3)	8 842(7)
C(20)	8 467(10)	6 256(4)	9 631(8)
C(21)	8 157(11)	6 036(4)	10 547(8)
C(22)	6 576(11)	5 908(4)	10 690(8)
C(23)	5 313(10)	5 990(3)	9 905(7)
C(24)	2 708(14)	6 411(5)	3 023(9)

Table 7 Atomic coordinates ($\times 10^4$) for $[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **9**

Atom	*x*	*y*	*z*
W	2 243.1(4)	5 477.3(1)	6 741.0(2)
Sb	3 705.3(6)	6 326.1(2)	7 680.0(4)
I(1)	1 205.1(7)	4 441.1(2)	6 519.2(4)
I(2)	1 497.4(6)	5 406.1(2)	8 809.2(4)
Cl(1)	2 068(3)	6 566(1)	1 630(2)
Cl(2)	4 581(3)	6 200(1)	3 137(2)
O(1)	−1 430(8)	5 652(3)	6 471(5)
O(2)	1 585(7)	6 388(2)	5 226(4)
O(3)	3 306(7)	5 163(3)	4 613(5)
N	4 581(8)	5 194(3)	7 313(5)
C(1)	−80(12)	5 579(3)	6 534(6)
C(2)	1 871(10)	6 055(3)	5 803(7)
C(3)	2 897(10)	5 266(3)	5 391(7)
C(4)	5 747(11)	5 053(3)	7 711(6)
C(5)	7 265(11)	4 882(4)	8 243(7)
C(6)	2 183(9)	6 868(3)	8 250(6)
C(7)	2 529(10)	7 089(3)	9 225(7)
C(8)	1 527(11)	7 449(4)	9 578(7)
C(9)	206(11)	7 604(4)	8 960(8)
C(10)	−178(11)	7 385(4)	8 014(7)
C(11)	806(10)	7 020(3)	7 658(7)
C(12)	4 911(9)	6 812(3)	6 710(6)
C(13)	5 060(10)	7 329(3)	6 899(7)
C(14)	5 906(11)	7 634(4)	6 294(8)
C(15)	6 609(11)	7 425(4)	5 510(8)
C(16)	6 502(12)	6 913(5)	5 332(7)
C(17)	5 657(11)	6 599(4)	5 914(7)
C(18)	5 566(10)	6 232(3)	8 894(6)
C(19)	7 069(10)	6 370(3)	8 738(6)
C(20)	8 317(10)	6 310(3)	9 514(6)
C(21)	8 047(10)	6 105(3)	10 422(7)
C(22)	6 536(10)	5 965(3)	10 599(6)
C(23)	5 274(10)	6 027(3)	9 841(6)
C(24)	2 686(12)	6 462(5)	2 937(8)

(using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer. Proton NMR spectra were recorded on a Bruker AC 250 MHz CP MAS NMR spectrometer at the University of Wales, Bangor and ^{13}C NMR spectra on a Bruker WH 400 MHz NMR spectrometer at the University of Warwick. The ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane.

Preparations.—$[MoBr_2(CO)_3(NCMe)_2]$ **1**. A suspension of $[Mo(CO)_6]$ (5.36 g, 20.30 mmol) was refluxed in acetonitrile (150 cm^3) for 24 h. The resultant bright yellow solution was cooled to −78 °C in an acetone–liquid nitrogen bath. An equimolar quantity of Br_2 (1.05 cm^3, 3.24 g, 20.30 mmol) was added to the bright yellow solution, resulting in the formation of a light orange-brown solution. The solution was allowed to return to room temperature and stirred for 30 min. Removal of the solvent *in vacuo* gave the orange-brown complex **1** (yield 7.62 g, 89%), which was recrystallised from acetonitrile.

$[WBr_2(CO)_3(NCMe)_2]$ **2**. A suspension of $[W(CO)_6]$ (5.50 g, 15.63 mmol) was refluxed in acetonitrile (150 cm^3) for 96 h. The resultant bright yellow solution was cooled to −78 °C in an acetone–liquid nitrogen bath. An equimolar quantity of Br_2 (0.81 cm^3, 2.50 g, 15.63 mmol) was added to the bright yellow solution, resulting in the formation of a brown-red solution. The solution was allowed to return to room temperature and stirred for 30 min. Removal of the solvent *in vacuo* gave the analytically pure dark brown complex **2** (yield 6.85 g, 86%).

$[WBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **8**. To $[WBr_2(CO)_3(NCMe)_2]$ **2** (0.3 g, 0.5886 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring was added $SbPh_3$ (0.21 g, 0.5886 mmol). The solution was stirred at room temperature for 5 min before being filtered. The solvent was removed *in vacuo* and the resultant orange product was recrystallised from CH_2Cl_2–Et_2O (80:20) at −17 °C for 24 h to afford orange single crystals of complex **8** suitable for X-ray crystallography (yield 0.21 g, 40%).

Similar reactions of $[MBr_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 1 equivalent of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) followed by recrystallisation from CH_2Cl_2–Et_2O at −17 °C gave the analogous complexes: $[MoBr_2(CO)_3(NCMe)(PPh_3)]$ **3** (stirring for 1 min), $[WBr_2(CO)_3(NCMe)(PPh_3)]$ **4** (stirring for 1 min), $[MoBr_2(CO)_3(NCMe)(AsPh_3)]$ **5** (stirring for 3 min), $[WBr_2(CO)_3(NCMe)(AsPh_3)]$ **6** (stirring for 3 min) and $[MoBr_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **7** (stirring for 5 min).

$[WI_2(CO)_3(NCMe)(SbPh_3)]\cdot CH_2Cl_2$ **9**. To $[WI_2(CO)_3(NCMe)_2]$ (0.3 g, 0.4970 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring was added $SbPh_3$ (0.18 g, 0.4970 mmol). The solution was stirred and the resultant orange-brown product was recrystallised from CH_2Cl_2–Et_2O (80:20) at −17 °C for 24 h to afford orange single crystals of complex **9** suitable for X-ray crystallography (yield 0.34 g, 68%).

$[WBr_2(CO)_3(AsPh_3)_2]$ **10**. To $[WBr_2(CO)_3(NCMe)_2]$ (0.3 g, 0.5886 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring was added $AsPh_3$ (0.36 g, 1.1772 mmol). The solution was stirred for 10 min before being filtered. The solvent was removed *in vacuo* and the resultant brown product was recrystallised from CH_2Cl_2–Et_2O at −17 °C to give the analytically pure yellow complex **10** (yield 0.30 g, 49%).

X-Ray Crystallography.—All crystallographic measurements were made at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator with Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[30] The data were corrected for Lorentz and polarisation factors, and also for absorption effects (DIFABS).[31] The structures were solved by direct methods (SHELX-S)[32] and refined by full-matrix least squares on F^2 (SHELXL 93)[33] using all unique data above background. All non-hydrogen atoms were anisotropic; the hydrogen atoms were included in idealised positions with individual U_{iso} values freely refined. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$ which gave satisfactory agreement analyses. Final R_1 (on F), wR_2 (on F_o^2) values were 0.0491, 0.0992 for **8** (328 parameters and 4240 data) and 0.0369, 0.0843 for **9** (328 parameters and 4220 data). The crystal data and full details of data collection and structure refinement, and important bond lengths and angles are given in Tables 4 and 5 respectively. The final atomic coordinates are given in Tables 6 and 7. All calculations were done on a 486DX2/66 personal computer. Fig. 2 was drawn by the program SNOOPI.[34] Sources of scattering factor data are given in ref. 33.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.[34]

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