New synthesis and low temperature ^{13}C n.m.r. spectra of some anionic seven-coordinate complexes of molybdenum(II) and tungsten(II) of the type $[NBu_4^n][MI_2X(CO)_3L]$

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Summary

The bisacetonitrile complexes $[MI_2(CO)_3(NCMe)_2]$ react with an equimolar amount of L in CH_2Cl_2 at room temperature to give $[MI_2(CO)_3(NCMe)L]$ which when mixed *in situ* with an equimolar amount of $[NBu_4^n]X$ affords the anionic seven-coordinate compounds $[NBu_4^n][MI_2X(CO)_3L]$ [M = Mo or W, X = I, L = PPh$_3$ (for M = W only), AsPh$_3$ or SbPh$_3$ (for M = Mo only); M = Mo and W, X = Br$_3$ or Br$_2$I, L = PPh$_3$, AsPh$_3$ or SbPh$_3$]. These reactions are likely to occur *via* the stepwise dissociative displacement of two acetonitrile ligands. Low-temperature ($-70°$ C, CD_2Cl_2) ^{13}C n.m.r. spectra (C≡O resonances) are reported for several of the complexes in order to infer the likely stereochemistry of these compounds.

Introduction

The first anionic seven-coordinate complexes to be reported were the *N*-methylpyridinium salts [*N*-Mepy][MX$_3$(CO)$_4$] (M = Mo or W; X = Br or I) by King in 1964[1]. These complexes were prepared by oxidation of the six-coordinate anions [*N*-Mepy][MX(CO)$_5$] with X$_2$. Similarly Ganorkar and Stiddard[2] published the preparation of the tetrabutylammonium salts [NBu$_4^n$][MX$_3$(CO)$_4$] (M = Mo or W; X = Br or I) by an analogous method in 1965. The trichloro- and tribromo-tetracarbonyl complexes [NEt$_4$][MX$_3$(CO)$_4$] (M = Mo or W; X = Cl or Br) were also prepared[3] by reaction of the halide-bridged dimers [M(μ-X)X(CO)$_4$]$_2$ with [NEt$_4$]X and the carbonyl substitution reactions of the molybdenum complexes [NEt$_4$] [MoX$_3$(CO)$_4$] (X = Cl or Br) with L (L = PPh$_3$, AsPh$_3$ or SbPh$_3$) to give [NEt$_4$] [MoX$_3$(CO)$_3$L] have also been reported[4]. The first phosphine-substituted complexes of this type to be published were the phosphonium salts. [PPh$_3$H]-[MX$_3$(CO)$_3$(PPh$_3$)](M = Mo or W; X = Br or I) by Lewis and Whyman in 1967[5]. These were prepared by reaction of either [M(CO)$_3$(PPh$_3$)$_3$] or [M(CO)$_4$-(PPh$_3$)$_2$] with X$_2$. The molybdenum complex [PPh$_3$H]-[MoI$_3$(CO)$_3$(PPh$_3$)] was also prepared[6] by reaction of the iodide-bridged dimer [Mo(μ-I)I(CO)$_4$]$_2$ with PPh$_3$. Tsang, Meek and Wojcicki[7] also reported the preparation of the complexes [NBu$_4^n$][MI$_3$(CO)$_3$(PPh$_3$)] from the reaction of [NBu$_4^n$][MI$_3$(CO)$_4$] and PPh$_3$. In this paper we wish to describe a simple preparation of a wide variety of anionic seven-coordinate complexes of the type [NBu$_4^n$][MI$_2$X(CO)$_3$L]{M = Mo or W, X =I, L = PPh$_3$ (for M =W only), AsPh$_3$ or SbPh$_3$ (for M =Mo only); M = Mo and W, X = Br$_3$ or Br$_2$I, L = PPh$_3$, AsPh$_3$ or SbPh$_3$}.

Results and discussion

The starting materials for this research are the seven-coordinate bis(acetonitrile) complexes [MI$_2$(CO)$_3$-(NCMe)$_2$] (M = Mo or W)[8] which are prepared in quantitative yield by reaction of the zero-valent tris-acetonitrile complexes [M(CO)$_3$(NCMe)$_3$] *in situ* with one equivalent of I$_2$. Equimolar quantities of [MI$_2$(CO)$_3$(NCMe)$_2$] and L react in CH$_2$Cl$_2$ at room temperature to give the acetonitrile substituted products

Table 1. Physical and analytical data for the complexes, [NBu$_4^n$][MI$_2$X(CO)$_3$L].

	Complex	Colour	Yield (%)	Found (Calcd.) (%) C	H	N
(1)	[NBu$_4^n$][WI$_3$(CO)$_3$(PPh$_3$)]	Yellow	75	38.3(38.5)	4.4(4.5)	0.9(1.2)
(2)	[NBu$_4^n$][MoI$_3$(CO)$_3$(AsPh$_3$)]	Orange	66	40.4(40.1)	4.6(4.6)	1.4(1.3)
(3)	[NBu$_4^n$][WI$_3$(CO)$_3$(AsPh$_3$)]	Yellow	77	36.8(37.1)	4.3(4.3)	0.9(1.2)
(4)	[NBu$_4^n$][MoI$_3$(CO)$_3$(SbPh$_3$)]	Orange	61	37.9(38.4)	4.4(4.5)	1.1(1.2)
(5)	[NBu$_4^n$][MoI$_2$(Br$_3$)(CO)$_3$(PPh$_3$)]C$_6$H$_{14}$	Brown	56	40.3(40.9)	5.0(5.2)	1.2(1.1)
(6)	[NBu$_4^n$][WI$_2$(Br$_3$)(CO)$_3$(PPh$_3$)]C$_4$H$_{10}$O	Yellow	33	37.1(36.7)	4.4(4.6)	1.0(1.1)
(7)	[NBu$_4^n$][MoI$_2$(Br$_3$)(CO)$_3$(AsPh$_3$)]C$_4$H$_{10}$O	Brown	36	38.0(38.0)	4.8(4.7)	1.2(1.1)
(8)	[NBu$_4^n$][WI$_2$(Br$_3$)(CO)$_3$(AsPh$_3$)]	Green	46	34.3(33.9)	4.4(3.9)	1.1(1.1)
(9)	[NBu$_4^n$][MoI$_2$(Br$_3$)(CO)$_3$(SbPh$_3$)]	Yellow	75	34.9(35.0)	4.1(4.1)	1.0(1.1)
(10)	[NBu$_4^n$][WI$_2$(Br$_3$)(CO)$_3$(SbPh$_3$)]	Green	73	33.0(32.8)	4.0(3.8)	0.9(1.0)
(11)	[NBu$_4^n$][MoI$_2$(Br$_2$I)(CO)$_3$(PPh$_3$)]	Brown	76	37.0(36.3)	4.6(4.2)	1.2(1.1)
(12)	[NBu$_4^n$][WI$_2$(Br$_2$I)(CO)$_3$(PPh$_3$)]	Brown	28	34.8(33.8)	4.0(3.9)	0.9(1.1)
(13)	[NBu$_4^n$][MoI$_2$(Br$_2$I)(CO)$_3$(AsPh$_3$)]	Brown	72	34.7(35.0)	4.5(4.1)	1.2(1.1)
(14)	[NBu$_4^n$][WI$_2$(Br$_2$I)(CO)$_3$(AsPh$_3$)]	Brown	51	33.8(32.8)	3.9(3.8)	1.0(1.0)
(15)	[NBu$_4^n$][MoI$_2$(Br$_2$I)(CO)$_3$(SbPh$_3$)]	Brown	44	33.9(33.8)	4.0(3.9)	1.1(1.1)
(16)	[NBu$_4^n$][WI$_2$(Br$_2$I)(CO)$_3$(SbPh$_3$)]	Yellow	63	31.1(31.7)	4.2(3.7)	1.0(1.0)

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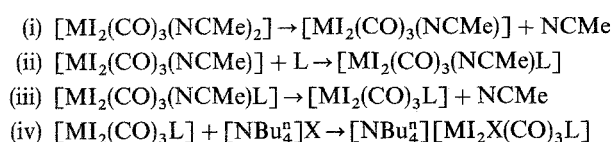**Table 2.** I.r. data^a for the complexes [NBu$_4^n$][MI$_2$X(CO)$_3$L].

Complex	ν(CO)/cm^{-1}
(1)	2005(s), 1930(s) and 1912(s)
(2)	2015(s), 1951(s) and 1890(s)
(3)	2010(s), 1940(s) and 1882(s)
(4)	2020(s), 1959(s), 1890(m) and 1857(m)
(5)	2075(s), 2020(s) and 1948(s)
(6)	2080(s), 2010(s), 1933(s) and 1880(m)
(7)	2030(s), 1961(s) and 1899(m)
(8)	2025(s), 1941(s) and 1894(m)
(9)	2075(s), 2025(s) and 1953(s)
(10)	2075(s), 2015(s) and 1938(m)
(11)	2075(s), 2025(s) and 1948(m)
(12)	2075(m), 2005(s) and 1937(s)
(13)	2025(s), 1955(s) and 1895(s)
(14)	2070(w), 2010(s), 1940(s) and 1900(m)
(15)	2070(s), 2020(s), 1950(s) and 1887(w)
(16)	2070(s), 2005(s), 1937(s) and 1875(m)

^{a}Spectra recorded in CHCl$_3$.

[MI$_2$(CO)$_3$(NCMe)L] which when treated *in situ* with [NBu$_4^n$]X affords good yields of the anionic compounds [NBu$_4^n$][MI$_2$X(CO)$_3$L] {M = Mo or W, X = I, L = PPh$_3$ (for M = W only), AsPh$_3$ or SbPh$_3$ (for M = Mo only); M = Mo and W, X = Br$_3$ or Br$_2$I, L = PPh$_3$, AsPh$_3$, or SbPh$_3$} (1–16). The complexes (1–16) were fully characterised by microanalysis (C, H and N) (Table 1) and infrared spectroscopy (Table 2). Repeated elemental analyses and ^{1}H n.m.r. spectroscopy confirmed the solvent of crystallisation associated with (5–7) (see Experimental). The triiodide complexes (1–4) are stable in the solid state when stored under nitrogen. However, the mixed halogen compounds [NBu$_4^n$] [MI$_2$X(CO)$_3$L] (5–16) decompose upon exposure to air in the solid state, although they can be stored for short periods at 0° C under nitrogen. All the complexes are air-sensitive in solution. The compounds (1–16) are soluble in CHCl$_3$ and CH$_2$Cl$_2$ but insoluble in hydrocarbon solvents. The triiodide complexes are insoluble in MeOH whereas the "mixed" halide complexes (5–16) are soluble in MeOH.

The reactions of [MI$_2$(CO)$_3$(NCMe)$_2$] with L followed by an *in situ* reaction with [NBu$_4^n$]X are likely to proceed *via* successive dissociative mechanisms as shown in Scheme 1. Evidence to support this scheme comes from the fact that the monoacetonitrile complexes [MI$_2$(CO)$_3$(NCMe)L] have been isolated and fully characterised[9]. Also the six-coordinate complexes [MoX$_2$(CO)$_3$L](X = Cl, Br or I; L = PPh$_3$, AsPh$_3$ or SbPh$_3$) have been prepared[10] by reaction of the pentacarbonyl complexes [Mo(CO)$_5$L] with X$_2$ in hexane. These results support the formulation of the proposed intermediates [MI$_2$(CO)$_3$(NCMe)] and [MI$_2$(CO)$_3$L] shown in Scheme 1.

The x-ray crystal structures of both neutral and anionic seven-coordinate complexes of molybdenum(II) and tungsten(II) have generally been found to have capped octahedral geometry[11–19]. The low temperature ^{13}C n.m.r. spectra δ(C≡O) of (1, 6, 8, 9, 11, 13, 15) have

(i) [MI$_2$(CO)$_3$(NCMe)$_2$] → [MI$_2$(CO)$_3$(NCMe)] + NCMe

(ii) [MI$_2$(CO)$_3$(NCMe)] + L → [MI$_2$(CO)$_3$(NCMe)L]

(iii) [MI$_2$(CO)$_3$(NCMe)L] → [MI$_2$(CO)$_3$L] + NCMe

(iv) [MI$_2$(CO)$_3$L] + [NBu$_4^n$]X → [NBu$_4^n$][MI$_2$X(CO)$_3$L]

Scheme 1

been measured in order to gain insight into the geometry of some of the complexes described in this paper. The low temperature ($-70°$ C, CD$_2$Cl$_2$) ^{13}C n.m.r. spectrum of the complex [NBu$_4^n$][WI$_3$(CO)$_3$(PPh$_3$)] (1) showed three carbonyl resonances of equal intensity at $\delta = 212.54$, 215.67 (d, $^2J_{C-P} = 28.87$ Hz) and 240.51 (d, $^2J_{C-P} = 34.46$ Hz)ppm. In view of the work of Colton and Kevekordes[20] on other seven-coordinate complexes of molybdenum(II) and tungsten(II), the low-field resonance at $\delta = 240.51$ ppm can be ascribed to a carbonyl ligand in the unique capping position. Ganscow and Vernon[21] have suggested that the carbonyl ligand in the unique capping position is most strongly bound due to π-back donation and as such δ(CO) is shifted to higher frequency in the ^{13}C n.m.r. spectrum. Since the two octahedral carbonyls for (1) are in different environments as indicated by the ^{13}C n.m.r. spectrum a possible structure for this complex is shown in Figure 1.

The low-temperature ($-70°$ C, CD$_2$Cl$_2$) ^{13}C n.m.r. spectrum of the "mixed" halide complex [NBu$_4^n$]-[MoI$_2$(Br$_3$) (CO)$_3$(SbPh$_3$)] (9) shows two resonances at $\delta = 206.92$ and 238.67 ppm with an intensity ratio of 2:1. For complex (9) the low field resonance at $\delta = 238.67$ ppm is due to a carbonyl ligand in the unique capping position and the resonance at $\delta = 206.92$ ppm can be ascribed to two equivalent octahedral carbonyls. Generally the halide ligands make up the opposite face to the capped face and hence the structure proposed for (9) is shown in Figure 2.

However, the low-temperature ($-70°$ C, CD$_2$Cl$_2$) ^{13}C n.m.r. spectra of the related complexes (6), (8) and (11–13, 15) all show a single resonance at $\delta = 199.83$, 204.32, 207.06, 206.94 and 207.21 ppm, respectively. Hence, it is likely that these complexes are fluxional even at $-70°$ C, since these carbonyl ligands in octahedral environments cannot all be equivalent in these complexes. Fluxionality has been previously observed for seven-coordinate halocarbonyl complexes[22–24]. It should also be noted that complexes (4), (6) and (14–16) show 4 carbonyl bands in their infrared spectra (Table 2) and it is highly likely that different isomers of these complexes exist in solution.

Experimental

All reactions described in this paper were carried out under an atmosphere of dry N$_2$. The complexes [MI$_2$(CO)$_3$(NCMe)$_2$] (M = Mo or W) were synthesised by the literature method[8]. All chemicals used were purchased from commercial sources except [NBu$_4^n$]X(X = Br$_3$ or Br$_2$I) which were prepared by the published method[25]. CH$_2$Cl$_2$ was distilled before use.
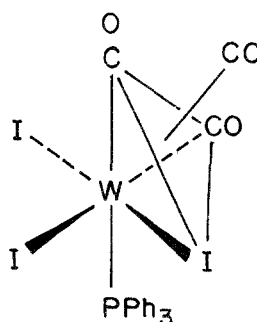
Figure 1. Proposed structure for the complex [NBu$_4^n$][WI$_3$(CO)$_3$(PPh$_3$)] (1).
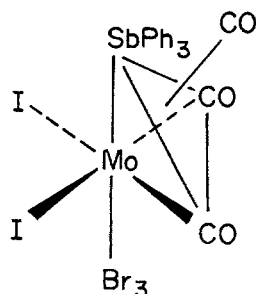
Figure 2. Proposed structure for the complex [NBu$_4^n$][MoI$_2$(Br$_3$)(CO)$_3$(SbPh$_3$)] (9).

Elemental analyses for C, H and N were recorded on a Carlo Erba Elemental Analyser Mod 1106 (using helium as the carrier gas). Infrared spectra were recorded as CHCl$_3$ films between NaCl plates on a Perkin-Elmer 197 i.r. spectrophotometer. The ^{1}H n.m.r. spectra of complexes (5–7) were recorded on a Jeol FX60 MHz n.m.r. spectrometer. Low temperature ^{13}C n.m.r. spectra were recorded on a Bruker WH-400 MHz n.m.r. spectrometer at the University of Warwick (all spectra were calibrated against tetramethylsilane).

[NBu$_4^n$] [MoI$_3$(CO)$_3$(SbPh$_3$)] (4)

To [MoI$_2$(CO)$_3$(NCMe)$_2$](0.219 g, 0.425 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of N$_2$ was added SbPh$_3$ (0.150 g, 0.425 mmol). After stirring for 5 min, [NBu$_4^n$]I (0.157 g, 0.425 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 an orange precipitate of [NBu$_4^n$][MoI$_3$(CO)$_3$(SbPh$_3$)]. This was filtered and dried under vacuum (yield = 0.30 g, 61%).

Similar *in situ* reactions of [MI$_2$(CO)$_3$(NCMe)L] with [NBu$_4^n$]I gave the complexes, [NBu$_4^n$] [MI$_3$(CO)$_3$L]. Reaction times for [MI$_2$(CO)$_3$(NCMe)$_2$] + L → [MI$_2$-(CO)$_3$(NCMe)L] and [NBu$_4^n$]I → [NBu$_4^n$][MI$_3$-(CO)$_3$L] + 2NCMe at 25° C are:

(1) M = W, L = PPh$_3$, 1 min; [NBu$_4^n$]I, 22 min;

(2) M = Mo, L = AsPh$_3$, 3 min; [NBu$_4^n$]I, 60 min;

(3) M = W; L = AsPh$_3$, 3 min; [NBu$_4^n$]I, 19 min;

[NBu$_4^n$][WI$_2$(Br$_3$)(CO)$_3$(SbPh$_3$)] (10)

To [WI$_2$(CO)$_3$(NCMe)$_2$] (0.210 g, 0.348 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of N$_2$ was added SbPh$_3$ (0.123 g, 0.348 mmol). After stirring for 5 min [NBu$_4^n$]Br$_3$ (0.168 g, 0.348 mmol) was added and the mixture stirred for a further 40 min. After filtration, removal of solvent *in vacuo* gave green crystals of [NBu$_4^n$] [WI$_2$(Br$_3$)(CO)$_3$(SbPh$_3$)] (yield = 0.346 g, 73%), which were recrystallised from CH$_2$Cl$_2$.

Similar *in situ* reactions of [MI$_2$(CO)$_3$(NCMe)L] with [NBu$_4^n$]X(X = Br$_3$ and Br$_2$I) gave the complexes [NBu$_4^n$] [MI$_2$X(CO)$_3$L]. Reaction times for [MI$_2$(CO)$_3$(NCMe)$_2$] + L → [MI$_2$(CO)$_3$(NCMe)L] and [NBu$_4^n$]X → [NBu$_4^n$][MI$_2$X(CO)$_3$L] + 2NCMe at 25° C are:

(5)* M = Mo; L = PPh$_3$, 1 min; [NBu$_4^n$]Br$_3$, 44 min;

(6)† M = W; L = PPh$_3$, 1 min; [NBu$_4^n$]Br$_3$, 44 min;

(7)† M = Mo; L = AsPh$_3$, 3 min; [NBu$_4^n$]Br$_3$, 42 min;

(8) M = W; L = AsPh$_3$, 3 min; [NBu$_4^n$]Br$_3$, 57 min;

(9) M = Mo; L = SbPh$_3$, 5 min; [NBu$_4^n$]Br$_3$, 40 min;

(11) M = Mo; L = PPh$_3$, 1 min; [NBu$_4^n$]Br$_2$I, 44 min;

(12) M = W; L = PPh$_3$, 1 min, [NBu$_4^n$]Br$_2$I, 49 min;

(13) M = Mo; L = AsPh$_3$, 3 min; [NBu$_4^n$]Br$_2$I, 47 min;

(14) M = W; L = AsPh$_3$, 3 min; [NBu$_4^n$]Br$_2$I, 42 min;

(15) M = Mo; L = SbPh$_3$, 5 min; [NBu$_4^n$]Br$_2$I, 50 min;

(16) M = W; L = SbPh$_3$, 5 min; [NBu$_4^n$]Br$_2$I, 40 min.

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* Complex precipitated out of CH$_2$Cl$_2$ solution upon addition of hexane. The room temperature ^{1}H n.m.r. spectrum of (5) in CDCl$_3$ showed resonances at δ = 1.27 (brm, 50 H, Bu^n and C$_6$H$_{14}$) and 7.56 (m, 15 H, Ph).

† Complexes precipitated out of CH$_2$Cl$_2$ solution upon addition of Et$_2$O. The room temperature ^{1}H n.m.r. spectrum of (6) in CDCl$_3$ showed resonances at δ = 1.81 (brm, 40 H, Bu^n + OCH$_2$CH$_3$), 4.08 (q, 4 H, OCH$_2$) and 8.04 (m, 15 H, Ph). At room temperature the ^{1}H n.m.r. spectrum of (7) in CDCl$_3$ showed resonances at δ = 1.32 (brm, 42 H, Bu^n + OCH$_2$CH$_3$), 3.47 (q, 4 H, OCH$_2$) and 7.45 (m, 15 H, Ph).