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Synthesis of some new cationic seven-coordinate complexes of molybdenum(II) and tungsten(II)

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Abstract

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with L (L = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature to give the complexes $[MI_2(CO)_3(NCMe)L]$, which react in situ with one equivalent of N⌒N {N⌒N = 2,2′-bipyridyl, 1,10-phenanthroline or 1,2-phenylenediamine (for M = W, L = PPh_3, for M = Mo, L = $SbPh_3$)} or two equivalents of pyridine (py) (for L = PPh_3 and $AsPh_3$) to give good yields of the cationic seven-coordinate complexes $[MI(CO)_3(N^\frown N)L]I$ or $[MI(CO)_3(py)_2L]I$. The ionic nature of these complexes was confirmed by the reaction of $[MoI(CO)_3(bipy)(PPh_3)]I$ (prepared in situ) with $Na[BF_4]$ in CH_2Cl_2/MeOH to give the tetrafluoroborate salt $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$. Reaction of $[MoI_2(CO)_3(py)(PPh_3)]$ with an equimolar amount of py affords the iodide displaced product $[MoI(CO)_3(py)_2(PPh_3)]I$.

Introduction

Cationic seven-coordinate complexes have attracted considerable interest in recent years. For example, Connor and co-workers [1] have described the synthesis of the dicationic compounds $[Mo(CO)_2(NCMe)(N^\frown N)_2][BF_4]_2$ (N⌒N = 2,2′-bipyridyl or 1,10-phenanthroline), which are prepared by oxidation of the zero-valent complexes $[Mo(CO)_2(N^\frown N)_2]$ with $Ag[BF_4]$ in acetonitrile; the complexes $[Mo(CO)_2(NCMe)(N^\frown N)_2][BF_4]_2$ show a wide range of reactions [2–4]. Lippard and co-workers [5–13] and Walton and co-workers [14–16] have synthesised and studied the chemistry of cationic isonitrile seven-coordinate complexes of the types $[MX(CNR)_6]^+$ or $[M(CNR)_7]^{2+}$ (M = Mo or W).

In recent years we have been studying the reactions of the versatile seven-coordinate compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), which are prepared by treating the zero-valent compounds $[M(CO)_3(NCMe)_3]$ with an equimolar quantity of I_2 in acetonitrile at 0 °C [17]. In this paper we describe a simple high yield

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preparation of some new cationic seven-coordinate complexes derived from $[MI_2(CO)_3(NCMe)_2]$.

Results and discussion

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with one equivalent of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) to give the substituted products $[MI_2(CO)_3(NCMe)L]$, which when treated in situ with an equimolar quantity of $(N^\frown N)$ $\{N^\frown N$ = 2,2′-bipyridyl, 1,10-phenanthroline or 1,2-phenylenediamine (for M = W, L = PPh_3, for M = Mo, L = $SbPh_3$)$\}$ or two equivalents of pyridine (py) (for L = PPh_3 and $AsPh_3$ only) afford the new cationic complexes $[MI(CO)_3(N^\frown N)L]I$ (**1–14**) or $[MI(CO)_3(py)_2L]I$ (**15–18**). The complex $[MoI(CO)_3(bipy)(PPh_3)]I$ reacts in situ with an equimolar quantity of $Na[BF_4]$ in CH_2Cl_2/MeOH (1/1 mixture) to give the tetrafluoroborate salt $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$ (**19**). The compounds **1–19** have been characterised by elemental analysis (C, H and N) (Table 1), infrared spectroscopy, and in selected cases by ^1H NMR spectroscopy (see Experimental). The magnetic susceptibilities of the complexes **1–19** show the complexes to be diamagnetic, which would be expected for coordinatively saturated seven-coordinate compounds of molybdenum(II) and tungsten(II). The bispyridine complex $[MoI(CO)_3(py)_2(PPh_3)]I \cdot CH_2Cl_2$ (**15**) was shown to be a dichloromethane solvate from repeated elemental analyses and ^1H NMR spectroscopy (see Experimental). The complexes **1–19** are moderately soluble in CH_2Cl_2 or $CHCl_3$, but they are much more soluble in acetone. They are insoluble in diethyl ether and hydrocarbon solvents, as expected for ionic compounds. The compounds containing bidentate ligands **1–14** are considerably more stable than the bispyridine compounds **15–18** probably owing to the chelate effect [18].

The reactions of $[MI_2(CO)_3(NCMe)_2]$ with L followed by either $N^\frown N$ or 2py's are likely to proceed via successive dissociative substitutions of the two acetonitrile ligands and iodide displacement, to give eventually the cationic compounds $[MI(CO)_3(N^\frown N)L]I$ or $[MI(CO)_3(py)_2L]I$, since the compounds $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ [19] are coordinatively saturated and highly crowded. It is noteworthy that the reaction of $[MoI_2(CO)_3(py)(PPh_3)]$ [20] with an equimolar quantity of py in CH_2Cl_2 also gives the iodide displaced product $[MoI(CO)_3(py)_2(PPh_3)]I$ (see Experimental). Iodide is the most easily displaced ligand in the series $[MX_2(CO)_3L_2]$ (X = Cl, Br or I), and so this facile displacement of I^- from $[MI_2(CO)_3(py)L]$ would be expected.

The infrared spectra of **1–19** all show three carbonyl bands in the 2000 cm^{-1} region, with similar patterns to those for other seven-coordinate complexes of molybdenum(II) and tungsten(II) of the type $[MX_2(CO)_3L_2]$ [21–31]. The infrared spectrum (KBr disc) of the complex $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$ (**19**) also showed the expected broad bands at $\nu(BF) \simeq 1016$ cm^{-1} and a strong sharp band at 529 cm^{-1} due to the tetrafluoroborate anion [32]. It is likely that the structures of $[MI(CO)_3(N^\frown N)L]I$ or $[MI(CO)_3(py)_2L]I$ are capped octahedral, since other seven-coordinate carbonyl complexes with similar infrared spectral properties exhibit this geometry [33]. Furthermore the crystal structure of the dicationic complex $[Mo(CNEt)_3(bipy)_2][BF_4]_2$ has been determined [34], and shows it to have capped octahedral geometry. Several unsuccessful attempts were made to grow single crystals of some of the cationic seven-coordinate complexes **1–19** described in this paper.

Table 1

Physical and analytical data for the complexes $[MI(CO)_3(N^\frown N)L]I$, $[MI(CO)_3(py)_2L]I$ and $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$

Complex	Colour	Yield (%)	Analysis (Found)(calcd.)(%))		
			C	H	N
$[MoI(CO)_3(bipy)(PPh_3)]I$ **(1)**	Orange	45	43.6	2.8	3.0
			(43.7)	(2.9)	(3.3)
$[WI(CO)_3(bipy)(PPh_3)]I$ **(2)**	Brown	87	39.2	2.8	3.0
			(39.6)	(2.7)	(3.0)
$[MoI(CO)_3(bipy)(AsPh_3)]I$ **(3)**	Dark-brown	86	41.9	2.7	3.2
			(41.5)	(2.8)	(3.1)
$[WI(CO)_3(bipy)(AsPh_3)]I$ **(4)**	Orange	86	37.4	2.4	2.8
			(37.8)	(2.5)	(2.9)
$[MoI(CO)_3(bipy)(SbPh_3)]I$ **(5)**	Dark-brown	42	40.0	2.6	2.8
			(39.5)	(2.7)	(3.0)
$[WI(CO)_3(bipy)(SbPh_3)]I$ **(6)**	Orange	75	35.8	2.3	2.7
			(36.1)	(2.4)	(2.7)
$[MoI(CO)_3(phen)(PPh_3)I]$ **(7)**	Dark-brown	85	45.3	3.2	3.0
			(45.2)	(3.3)	(3.2)
$[WI(CO)_3(phen)(PPh_3)]I$ **(8)**	Brown	85	40.7	2.9	2.8
			(41.1)	(2.8)	(2.9)
$[MoI(CO)_3(phen)(AsPh_3)]I$ **(9)**	Dark-brown	76	42.9	3.0	3.0
			(43.1)	(2.9)	(3.0)
$[WI(CO)_3(phen)(AsPh_3)]I$ **(10)**	Orange	89	39.8	2.4	2.3
			(39.3)	(2.7)	(2.8)
$[MoI(CO)_3(phen)(SbPh_3)]I$ **(11)**	Dark-brown	58	40.6	2.6	2.9
			(41.0)	(2.8)	(2.9)
$[WI(CO)_3(phen)(SbPh_3)]I$ **(12)**	Orange	90	37.4	2.2	2.5
			(37.6)	(2.6)	(2.7)
$[WI(CO)_3(diam)(PPh_3)]I$ **(13)**	Brown	81	36.3	2.8	2.8
			(36.3)	(2.6)	(3.1)
$[MoI(CO)_3(diam)(SbPh_3)]I$ **(14)**	Brown	69	35.5	3.0	3.3
			(36.2)	(2.6)	(3.1)
$[MoI(CO)_3(py)_2(PPh_3)]I \cdot CH_2Cl_2$ **(15)**	Brown	53	41.3	3.0	2.9
			(40.9)	(2.9)	(3.0)
$[WI(CO)_3(py)_2(PPh_3)]I$ **(16)**	Light-brown	87	39.4	2.8	3.4
			(39.5)	(2.7)	(3.0)
$[MoI(CO)_3(py)_2(AsPh_3)]I$ **(17)**	Brown	92	41.8	3.1	3.0
			(41.4)	(2.8)	(3.1)
$[WI(CO)_3(py)_2(AsPh_3)]I$ **(18)**	Brown	47	37.2	2.1	2.3
			(37.8)	(2.5)	(2.8)
$[MoI(CO)_3(bipy)(PPh_3)][BF_4]$ **(19)**	Orange	56	46.3	2.9	3.0
			(45.9)	(3.3)	(3.5)

The complexes $[MI(CO)_3(N^\frown N)L]I$ were refluxed in CH_2Cl_2 or $CHCl_3$ to attempt to get reattack of the iodide to obtain neutral complexes of the type $[MI_2(CO)_2(N^\frown N)L]$. These reactions were unsuccessful however, and only decomposition products were isolated.

Experimental

All reactions were carried out under nitrogen by Schlenk line techniques. The compounds $[MI_2(CO)_3(NCMe)_2]$($M = Mo$ or W) were prepared by the published method [17], and all chemicals were purchased from commercial sources except for $[Mo(CO)_6]$, which was kindly donated by Amax Speciality Metals limited. Elemental analyses were carried out by Mr. E. Lewis (UCNW) on a Carlo Erba elemental analyser MOD 1106. IR spectra were recorded as $CHCl_3$ thin films between NaCl plates on a Perkin–Elmer 1430 ratio recording infrared spectrophotometer. ^1H NMR spectra were recorded on either a Jeol FX 60 MHz or a Bruker AC250 CPMAS NMR spectrometer, chemical shifts are relative to internal tetramethylsilane. Magnetic susceptibility measurements were recorded on a Johnson–Matthey Magnetic Susceptibility balance.

Preparation of $[MoI(CO)_3(bipy)(PPh_3)]I$ (1)

$[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.969 mmol) was dissolved in degassed CH_2Cl_2 (15 cm^3) with stirring under a stream of nitrogen and PPh_3 (0.254 g, 0.969 mmol) was added with continued stirring. After 1 min bipy (0.151 g, 0.969 mmol) was added, and the mixture was stirred for a further 5 min. Dropwise addition of diethyl ether caused complete precipitation of the orange cationic complex $[MoI(CO)_3(bipy)(PPh_3)]I$ (**1**), which was recrystallised from CH_2Cl_2/Et_2O (yield of pure product 0.37 g, 45%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L ($L = PPh_3$, $AsPh_3$ or $SbPh_3$) to give $[MI_2(CO)_3(NCMe)L]$ followed by an in situ reaction with one equivalent of $N^\frown N$ $\{N^\frown N = 2,2'$-bipyridyl, 1,10-phenanthroline or 1,2-phenylenediamine (for M = W, $L = PPh_3$, for M = Mo, $L = SbPh_3$)$\}$ gave $[MI(CO)_3(N^\frown N)L]I$ (**2–14**) (see Table 1 for colours and yields). Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \rightarrow [MI_2(CO)_3(NCMe)L]$ and $N^\frown N \rightarrow [MI(CO)_3(N^\frown N)L]I$: (**1**) PPh_3, 1 min, bipy, 5 min; (**3**) $AsPh_3$, 3 min, bipy 5 min; (**5**) $SbPh_3$, 5 min, bipy, 5 min. Similar times were recorded for the analogous complexes **2**, **4** and **6–14**.

IR $\{\nu(C{\equiv}O)\ cm^{-1}\}$ spectral data: (**1**) 2010, 1975 and 1925; (**2**) 2005, 1960 and 1940; (**3**) 2015, 1960 and 1915; (**4**) 2005, 1945 and 1900; (**5**) 2005, 1975 and 1923; (**6**) 2005, 1950 and 1900; (**7**) 2005, 1960 and 1940; (**8**) 2005, 1940 and 1920; (**9**) 2005, 1955 and 1930; (**10**) 2005, 1940 and 1885; (**11**) 2010, 1960 and 1940; (**12**) 2005, 1945 and 1915; (**13**) 2010, 1955 and 1930; (**14**) 2020, 1965 and 1940.

^1H NMR ($CDCl_3$, +20 °C): (**1**) 9.62 (m, 2H), 9.17 (m, 2H), 8.71 (m, 2H), 8.17 (m, 2H), 7.48–7.80 (m, 15H, Ph). (**2**) 9.68 (d, 2H), 9.2 (d, 2H), 8.38 (m, 2H), 8.14 (m, 2H), 7.4–7.7 (m, 15H, Ph) (**3**) 9.34 (m, 2H), 8.33 (m, 2H), 8.12 (m, 2H), 7.62 (m, 2H) 7.25–7.45 (m, 15H, Ph). (**7**) 9.9 (m, 2H), 9.68 (m, 2H), 8.6 (m, 2H), 8.12 (m, 2H), 7.4–7.73 (m, 15H, Ph). (**8**) 9.48 (m, 2H), 9.69 (m, 2H), 8.78 (m, 2H), 8.14 (m, 2H), 7.42–7.72 (m, 15H, Ph). (**12**) 8.27 (m, 4H), 8.17 (m, 4H), 7.3–7.64 (m, 15H, Ph).

Preparation of $[MoI(CO)_3(py)_2(PPh_3)]I \cdot CH_2Cl_2$ (15)

$[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.969 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with stirring under a stream of dry nitrogen and PPh_3 (0.254 g, 0.969 mmol) was added with continued stirring. After 1 min, py (0.16 cm^3, 1.94 mmol) was added, and the mixture stirred for a further 5 min. Dropwise addition of diethyl ether caused complete precipitation of the brown crystalline cationic complex $[MoI(CO)_3(py)_2(PPh_3)]I \cdot CH_2Cl_2$ (**15**), which was recrystallised from CH_2Cl_2/Et_2O (yield of pure product = 0.48 g, 53%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L ($L = PPh_3$ or $AsPh_3$) to give $[MI_2(CO)_3(NCMe)L]$, followed by an in situ reaction with two equivalents of pyridine gave $[MI(CO)_3(py)_2L]I$ **(16–18)** (see Table 1 for colours and yields). Reaction times for $[MI_2(CO)_3\text{-}(NCMe)_2] + L \rightarrow [MI_2(CO)_3\text{-}(NCMe)L]$ and $2py \rightarrow [MI(CO)_3(py)_2L]I$: **(15)** PPh_3, 1 min; 2 py, 5 min; **(16)** $AsPh_3$, 3 min; 2py, 5 min. Similar times were recorded for the tungsten complexes **17** and **18**. IR $\{\nu(C{\equiv}O)\ cm^{-1}\}$ spectral data: **(15)** 2010, 1945 and 1925; **(16)** 2010, 1940 and 1900; **(17)** 2000, 1960 and 1920; **(18)** 2005, 1930 and 1910. ^1H NMR ($CDCl_3$, +20 °C) **(15)** showed resonances at δ 8.96 (d, 4H), 8.61 (m, 4H), 8.05 (m, 2H), 7.0–7.7 (m, 15H, Ph) and 5.72 (s, 2H, CH_2Cl_2).

Preparation of $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$ (19)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.969 mmol) in a 1/1 mixture of CH_2Cl_2/CH_3OH (20 cm^3) PPh_3 (0.254 g, 0.969 mmol) was added with stirring under nitrogen. After 1 min bipy (0.151 g, 0.969 mmol) was added and the mixture stirred for 30 min. $Na[BF_4]$ (0.1066 g, 0.969 mmol) was added in situ and stirring was continued for a further 30 min. The solvent was removed in vacuo and the complex redissolved in CH_2Cl_2 (20 cm^3) followed by filtration through Celite under nitrogen. Removal of the solvent in vacuo gave the orange cationic complex $[MoI(CO)_3(bipy)(PPh_3)][BF_4]$ **(19)**, which was recrystallised from CH_2Cl_2/Et_2O (yield of pure product = 0.44 g, 56%) IR $\{\nu(C{\equiv}O)\ cm^{-1}\}$ spectral data: **(19)** 2010, 1975 and 1925. ^1H NMR ($CDCl_3$, +20 °C): **(19)** 9.6 (m, 2H), 9.14 (m, 2H), 8.73 (m, 2H), 8.17 (m, 2H), 7.40–7.71 (m, 15H, Ph).

Reaction of $[MoI_2(CO)_3(py)(PPh_3)]$ with py

$[MoI_2(CO)_3(py)(PPh_3)]$ (0.5 g, 0.645 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen and py (0.051 g, 0.646 mmol) was added with continued stirring. After 5 min dropwise addition of diethyl ether caused complete precipitation of the brown crystalline cationic complex $[MoI(CO)_3\text{-}(py)_2(PPh_3)]I \cdot CH_2Cl_2$, which was recrystallised from CH_2Cl_2/Et_2O (yield of pure product = 0.365 g, 60%). Elemental analysis: Found: C, 41.0, H, 2.7; N, 2.6. $C_{32}H_{27}N_2Cl_2I_2O_3PMo$ calcd.: C, 40.9; H, 2.9; N, 3.0%. ^1H NMR spectrum ($CDCl_3$, +25 °C) showed resonances at δ 8.92 (d, 4H), 8.60 (m, 4H), 8.04 (m, 2H), 6.95–7.8 (m, 15H, Ph) and 5.73 (s, 2H, CH_2Cl_2).

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References

1 J.A. Connor, E.J. James, C. Overton and N. El. Muir, J. Chem. Soc., Dalton Trans., 225 (1984).
2 J.A. Connor and E.J. James, J. Organomet. Chem., 297 (1985) 301.
3 J.A. Connor, E.J. James, C. Overton, J.M.A. Walshe and R.A. Head, J. Chem. Soc., Dalton Trans., 511 (1986).
4 J.A. Connor and E.J. James, J. Organomet. Chem., 316 (1986) 79.
5 D.F. Lewis and S.J. Lippard, Inorg. Chem., 11 (1972) 621.
6 M. Novotny and S.J. Lippard, J. Chem. Soc., Chem. Commun., (1973) 202.
7 D.L. Lewis and S.J. Lippard, J. Am. Chem. Soc., 97 (1975) 2697.
8 C.T. Lam, M. Novotny, D.L. Lewis and S.J. Lippard, Inorg. Chem., 17 (1978) 2127.
9 C.W.R. Cornfield, L.M. Baltusis and S.J. Lippard, Inorg. Chem., 20 (1981) 922.

10 J.C. Dewan, C.M. Giandomenico and S.J. Lippard, Inorg. Chem., 20 (1981) 4049.

11 J.C. Dewan and S.J. Lippard, Inorg. Chem., 21 (1982) 1682.

12 C.M. Giandomenico, C.T. Lam and S.J. Lippard, J. Am. Chem. Soc., 104 (1982) 1263.

13 C. Carvana, C.M. Giandomenico and S.J. Lippard, Inorg. Chem., 21 (1982) 1860.

14 T.E. Wood, J.C. Deaton, J. Corning, R.E. Wild and R.A. Walton, Inorg. Chem., 19 (1980) 2614.

15 W.S. Mialki, R.E. Wild and R.A. Walton, Inorg. Chem., 20 (1981) 1380.

16 D.D. Klendworth, W.W. Weltes and R.A. Walton, Organometallics, 1 (1982) 336.

17 P.K. Baker, S.G. Fraser and E.M. Keys, J. Organomet. Chem., 309 (1986) 319.

18 See for example F.A. Cotton and G. Wilkinson (Eds.), Advanced Inorganic Chemistry, A Comprehensive Test, 4th edit., p. 71, John Wiley and Sons Ltd., 1980.

19 P.K. Baker and S.G. Fraser, Transition-Met. Chem., 12 (1987) 560.

20 P.K. Baker, S.G. Fraser and M.J. Snowden, Inorg. Chim. Acta, 148 (1988) 247.

21 M.H.B. Stiddard, J. Chem. Soc. A, (1962) 4712.

22 F.A. Cotton and B.F.G. Johnson, Inorg. Chem., 3 (1964) 1609.

23 J. Lewis and R. Whyman, J. Chem. Soc. A, (1967) 77.

24 R. Colton and C.J. Rix, Aust. J. Chem., 22 (1969) 305.

25 W.S. Tsang, D.W. Meek and A. Wojcicki, Inorg. Chem., 7 (1968) 1263.

26 J.R. Moss and B.L. Shaw, J. Chem. Soc. A, 595 (1970).

27 R. Colton, Coord. Chem. Rev., 6 (1971) 269 and ref. cited therein.

28 L. Bencze, J. Organomet. Chem., 37 (1972) C37.

29 A.D. Westland and N. Muriithi, Inorg. Chem., 12 (1973) 2356.

30 S.C. Tripathi, S.C. Srivastava and A.K. Shrimal, Inorg. Chim. Acta, 18 (1976) 231.

31 P.K. Baker and S.G. Fraser, Inorg. Chim. Acta, 116 (1986) L1.

32 K. Nakamoto, Infrared spectra of Inorganic and Coordination Compounds, John Wiley and Sons inc., New York, London, 1961.

33 M.G.B. Drew, Prog. Inorg. Chem., 23 (1977) 67.

34 M.B. Hursthouse, M.A. Thornton-Pett, J.A. Connor and C. Overton, Acta Cryst. C, 41 (1985) 184.