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The reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with one equivalent of L (L = pyridine or substituted pyridines) to give $[WI_2(CO)_3(NCMe)L]$ and $[M(\mu\text{-}I)I(CO)_3L]_2$

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Abstract

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with one equivalent of L in CH_2Cl_2 at room temperature to give initially the mononuclear seven-coordinate complexes $[MI_2(CO)_3(NCMe)L]$ which have been isolated for M = W; L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py. These compounds dimerise to give the iodide-bridged dimers $[M(\mu\text{-}I)I(CO)_3L]_2$ by displacement of acetonitrile. When M = Mo; L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py, and when M = Mo and W; L = py, 2Me-py (for M = W only), 4Me-py, 3,5-Me_2-py, 2Cl-py and 2Br-py, only the dimeric complexes have been isolated. The ease of dimerisation of $[MI_2(CO)_3(NCMe)L]$ is discussed in terms of the steric and electronic effects of the substituted pyridines.

Introduction

There is considerable current interest in seven-coordinate complexes of molybdenum(II) and tungsten(II): in particular the complexes $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) which have recently been found to be catalysts for the ring-opening polymerisation of norbornene and norbornadiene [1,2]. The rate-determining step in the mechanism is cleavage of the metal–phosphorus or –arsenic bond. We have been investigating the reactions of the highly versatile compounds $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), which have labile acetonitrile ligands [3].

Results and discussion

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) in CH_2Cl_2 at room temperature react with L to give either the mononuclear complexes $[WI_2(CO)_3(NCMe)L]$ (L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py) and/or the dimeric

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Table 1

Physical and analytical data for the mononuclear complexes $[WI_2(CO)_3(NCMe)L]$ and dimeric compounds $[M(\mu\text{-}I)I(CO)_3L]_2$

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))		
			C	H	N
$[WI_2(CO)_3(NCMe)(3Cl\text{-}py)]$ (**1**)	Brown	77	18.0	1.1	3.8
			(17.8)	(1.0)	(4.1)
$[WI_2(CO)_3(NCMe)(3Br\text{-}py)]$ (**2**)	Brown	94	16.3	1.2	3.4
			(16.7)	(1.0)	(3.9)
$[WI_2(CO)_3(NCMe)(4Cl\text{-}py)]$ (**3**)	Brown	52	17.8	1.0	4.0
			(17.8)	(1.0)	(4.1)
$[WI_2(CO)_3(NCMe)(4Br\text{-}py)]$ (**4**)	Brown	45	15.3	0.9	3.7
			(16.7)	(1.0)	(3.9)
$[Mo(\mu\text{-}I)I(CO)_3(py)]_2$ (**5**)	Brown	86	18.9	1.2	2.5
			(18.7)	(1.0)	(2.7)
$[W(\mu\text{-}I)I(CO)_3(py)]_2$ (**6**)	Brown	92	15.7	1.1	2.4
			(16.0)	(0.8)	(2.3)
$[W(\mu\text{-}I)I(CO)_3(2Me\text{-}py)]_2$ (**7**)	Yellow	51	16.5	1.2	2.0
			(17.6)	(1.2)	(2.3)
$[Mo(\mu\text{-}I)I(CO)_3(4Me\text{-}py)]_2$ (**8**)	Black	59	20.0	1.6	3.0
			(20.5)	(1.3)	(2.7)
$[W(\mu\text{-}I)I(CO)_3(4Me\text{-}py)]_2$ (**9**)	Brown	41	16.5	1.2	2.3
			(17.6)	(1.2)	(2.3)
$[Mo(\mu\text{-}I)I(CO)_3(2Cl\text{-}py)]_2$ (**10**)	Black	72	16.4	1.1	2.6
			(17.6)	(0.7)	(2.6)
$[W(\mu\text{-}I)I(CO)_3(2Cl\text{-}py)]_2$ (**11**)	Green	82	14.1	0.7	2.1
			(15.1)	(0.6)	(2.2)
$[Mo(\mu\text{-}I)I(CO)_3(2Br\text{-}py)]_2$ (**12**)	Black	54	16.3	1.0	2.8
			(16.2)	(0.7)	(2.4)
$[W(\mu\text{-}I)I(CO)_3(2Br\text{-}py)]_2$ (**13**)	Green	71	14.5	1.0	2.2
			(14.1)	(0.6)	(2.1)
$[Mo(\mu\text{-}I)I(CO)_3(3Cl\text{-}py)]_2$ (**14**)	Brown	81	18.0	1.0	2.9
			(17.6)	(0.7)	(2.6)
$[W(\mu\text{-}I)I(CO)_3(3Cl\text{-}py)]_2$ (**15**)	Yellow	77	15.3	0.8	1.8
			(15.1)	(0.6)	(2.2)
$[Mo(\mu\text{-}I)I(CO)_3(3Br\text{-}py)]_2$ (**16**)	Green	75	16.5	1.0	2.4
			(16.2)	(0.7)	(2.4)
$[W(\mu\text{-}I)I(CO)_3(3Br\text{-}py)]_2$ (**17**)	Green	79	14.0	0.8	1.6
			(14.1)	(0.6)	(2.1)
$[Mo(\mu\text{-}I)I(CO)_3(4Cl\text{-}py)]_2$ (**18**)	Black	42	17.2	0.9	2.7
			(17.6)	(0.7)	(2.6)
$[W(\mu\text{-}I)I(CO)_3(4Cl\text{-}py)]_2$ (**19**)	Brown	43	15.2	0.8	2.2
			(15.1)	(0.6)	(2.2)
$[Mo(\mu\text{-}I)I(CO)_3(4Br\text{-}py)]_2$ (**20**)	Black	44	15.8	0.9	2.5
			(16.2)	(0.7)	(2.4)
$[W(\mu\text{-}I)I(CO)_3(4Br\text{-}py)]_2$ (**21**)	Yellow	38	14.7	0.8	1.7
			(14.1)	(0.6)	(2.1)
$[Mo(\mu\text{-}I)I(CO)_3(3,5\text{-}Me_2\text{-}py)]_2$ (**22**)	Brown	67	21.0	1.9	2.3
			(22.2)	(1.7)	(2.6)
$[W(\mu\text{-}I)I(CO)_3(3,5\text{-}Me_2\text{-}py)]_2$ (**23**)	Brown	62	19.6	1.5	2.2
			(19.1)	(1.4)	(2.2)

Table 2

IR data [a] for the complexes $[WI_2(CO)_3(NCMe)L]$ and $[M(\mu\text{-}I)I(CO)_3L]_2$

Complex	ν(CO) (cm^{-1})
1	2035(s), 1934(s) and 1908(m)
2	2040(s), 1930(s) and 1920(s)
3	2010(s), 1945(s) and 1924(s)
4	2030(s), 1940(s) and 1925(s)
5	2075(m), 2025(s) and 1940(s)
6	2070(m), 2010(s) and 1925(s)
7	2075(s), 2005(s) and 1920(s)
8	2070(s), 2010(s) and 1943(s)
9	2070(s), 2020(s) and 1930(s)
10	2065(s), 2025(s) and 1953(s)
11	2070(s), 2025(s), 2000(s) and 1932(s)
12	2075(s), 2020(s) and 1957(s)
13	2070(s), 2025(s) 2005(s) and 1937(s)
14	2080(m), 2025(s) and 1940(s)
15	2075(s), 2010(s) 1945(s) and 1937(s)
16	2075(m), 2030(s) and 1955(s)
17	2075(s), 2015(s) and 1940(s)
18	2075(m), 2040(s) and 1960(s)
19	2075(s), 2030(s) and 1940(s)
20	2075(s), 2040(s) and 1961(s)
21	2075(s), 2010(s) and 1940(s)
22	2075(s), 2025(s) 1953(s) and 1913(m)
23	2070(s), 2010(s) and 1930(s)

[a] Spectra recorded in $CHCl_3$; s, strong; m, medium.

compounds $[M(\mu\text{-}I)I(CO)_3L]$ (L = py, 2Me-py (for M = W only), 4Me-py, 3,5-Me$_2$-py, 2Cl-py, 2Br-py, 3Cl-py, 3Br-py, 4Cl-py or 4Br-py) by displacement of acetonitrile ligands. The complexes have been characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2) and for the monomeric complexes ^{1}H NMR spectroscopy (Table 3). Molecular weights and magnetic susceptibilities of several complexes have been determined in order to confirm the dimeric nature of the complexes $[M(\mu\text{-}I)I(CO)_3L]_2$ (Table 4).

Table 3

^{1}H NMR spectral data for $[WI_2(CO)_3(NCMe)L]$ [a]

Complex	δ(^{1}H) (ppm)
1	2.53 (s,3H), 7.45 (d, J 1.35 Hz, 1H), 7.89 (d, J 2.56 Hz, 1H), 9.05 (brs, 2H).
2	2.52 (s,3H), 7.39 (d, J 1.35 Hz, 1H), 8.00 (d, J 1.80 Hz, 1H), 9.12 (brs, 2H).
3	2.21 (s,3H), 7.40 (d, J 1.65 Hz, 1H) 8.00 (d, J 1.65 Hz, 1H), 9.03 (d, J 1.80 Hz, 2H)
4	2.52 (s,3H), 7.59 (d, J 1.5 Hz, 1H), 8.20 (d, J 1.5 Hz, 1H), 8.85 (d, J 1.2 Hz, 2H)

[a] Spectra recorded in $CDCl_3$ (+25 °C) reference to $SiMe_4$.

Table 4

Magnetic susceptibility and molecular weights of selected $[WI_2(CO)_3(NCMe)L]$ and $[M(\mu\text{-}I)I(CO)_3L]_2$

Complex	Magnetic susceptibility ($\times 10^{-6}$ c.g.s.)	Molecular weights [a]
2	−0.202	692(721)
3	−0.391	609(676)
8	−0.104	996(1054)
9	−0.212	1184(1230)
10	−0.093	847(1095)
11	−0.281	1047(1270)
17	−0.305	1283(1359)
20	−0.149	1108(1184)
22	−0.307	811(1082)
23	−0.276	1065(1258)

[a] Calculated values in parentheses.

The complexes are all air-sensitive and thermally unstable (particularly the dimers) and are best stored under nitrogen at 0 °C. They are all soluble in $CHCl_3$ and CH_2Cl_2, and only sparingly soluble in hydrocarbon solvents.

The structure of the seven-coordinate monomers $[WI_2(CO)_3(NCMe)L]$ (L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py) are likely to be capped octahedral in view of the similarity of the infrared spectra of these complexes to those of seven-coordinate complexes, which have been shown by X-ray crystallography to have capped octahedral geometry [4–11]. The structure of $[WI_2(CO)_3(NCMe)_2]$ has been determined [12] and has a capped octahedral geometry with *trans*-iodide ligands and a carbonyl group in the capping position (Fig. 1), and hence the proposed structures of $[WI_2(CO)_3(NCMe)L]$ are given in Fig. 1. Because of the ease of dimerisation of $[WI_2(CO)_3(NCMe)L]$ it has not been possible to grow crystals for X-ray crystallography which would confirm the solid state geometry of these complexes. The structure of the dimers $[M(\mu\text{-}I)I(CO)_3L]_2$ is likely to be two capped octahedra with bridging iodides, since Cotton and co-workers have recently [13] determined the structure of the dimer $[W(\mu\text{-}Br)Br(CO)_4]_2$, first prepared by Colton and co-workers in 1967 [14,15] which shows the two tungsten atoms to be in capped octahedral environments with a carbonyl ligand capping a $[WBr_3(CO)_3]$ octahedron.

The reaction of the compounds $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L is most likely to proceed via a dissociative mechanism (eq. 1–4), since the seven-coordinate complexes are crowded and also have weakly bound acetonitrile ligands.

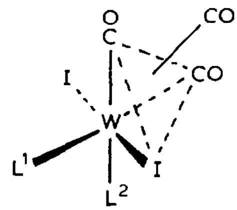

Fig. 1. Structure of $[WI_2(CO)_3(NCMe)_2]$ [12] and proposed structure of $[WI_2(CO)_3(NCMe)L]$ (where L^1 or L^2 = MeCN and L^2 or L^1 = L = 3Cl-py, 3Br-py, 4Cl-py or 4Br-py).

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

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

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

$$2[MI_2(CO)_3L] \rightarrow [M(\mu\text{-}I)I(CO)_3L]_2 \quad (4)$$

"16-electron" complexes of the type $[MX_2(CO)_3L]$ here postulated as intermediates are isolable [16] when M = Mo, X = Cl, Br or I and L = PPh_3, $AsPh_3$ or $SbPh_3$.

Reaction of the complex $[WI_2(CO)_3(NCMe)_2]$ with pyridines at 25 °C containing electronegative substituents affords the mononuclear complexes $[WI_2(CO)_3(NCMe)L]$ (L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py) which are the only complexes to be isolated as monoacetonitrile monomers at room temperature. This was expected since the M–NCMe bond will be strengthened by decrease in the electron density on the metal because acetonitrile is mainly a σ-donor ligand. More bulky ligands will also increase the ease of dimerisation since larger ligands L, will force out the acetonitrile ligand in order to release steric strain (particularly with molybdenum). Hence the most stable complex towards dimerisation was predicted, and found to be $[WI_2(CO)_3(NCMe)(4Cl\text{-}py)]$. Qualitative studies show that the ease of dimerisation increases in the order 4Cl-py < 3Cl-py < 2Cl-py i.e. in the order of bulk of the ligand, and also 4Cl-py < 4Br-py and 3Cl-py < 3Br-py, which is expected from both the steric and electronic effects. It is well known that seven-coordinate molybdenum complexes dimerise more readily than their tungsten counterparts [17]. This trend is seen with reaction of $[MI_2(CO)_3(NCMe)_2]$ with substituted pyridines, since only the iodide bridged dimers have been isolated with molybdenum even with 4Cl-pyridine. As expected, reaction of both the $[MI_2(CO)_3(NCMe)_2]$ complexes with pyridine and "electron-rich" pyridines 2Me-py (for M = W only), 4Me-py and $3,5\text{-}Me_2\text{-}py$ very rapidly affords the dinuclear compounds $[M(\mu\text{-}I)I(CO)_3L]_2$. The dimeric nature of the complexes $[M(\mu\text{-}I)I(CO)_3L]_3$ was confirmed by molecular weight and magnetic susceptibility measurements (Table 4). The six-coordinate complexes would probably have a distorted octahedral geometry. Previously reported X-ray crystal structures of d^4 molybdenum(II) coordinatively unsaturated compounds $[MoBr_2(CO)_2(PPh_3)_2]$, [18], $[Mo(OBu^t)_2(CO)_2(py)_2]$ [19], $[Mo(OPr^i)_2(bipy)_2]$ [20] and $[Mo(SBu^t)_2(CNBu^t)_4]$ [21] have this geometry and $[MI_2(CO)_3L]$ would be expected to be paramagnetic if it were a d^4 octahedral complex contrary to what was found. However, Colton and co-workers found that the seven-coordinate complexes $[MX_2(CO)_3L_2]$ (M = Mo and W; X = Cl, Br and I; L = PPh_3, $P(C_6H_4Me\text{-}m)_3$ and $P(C_6H_4Me\text{-}p)_3$) [14,15,22–24] lose carbon monoxide either readily or in refluxing solvent, to give the blue dicarbonyl compounds, $[MX_2(CO)_2L_2]$. These complexes show two carbonyl stretching bands in the infrared spectrum and are diamagnetic. The complexes are monomers as shown by X-ray crystallography [18], and the diamagnetism was explained by a distortion of the octahedral geometry resulting in a splitting of the degenerate t_{2g} orbitals, and hence allowing the four d electrons to pair up in the lowest two orbitals. Molecular weight measurements rule out the formulation of $[MI_2(CO)_3L]$ as monomeric "16-electon" compounds, and they are highly likely to be the seven-coordinate iodide-bridged complexes $[M(\mu\text{-}I)I(CO)_3L]_2$.

We are investigating the catalytic activity of the complexes $[WI_2(CO)_3(NCMe)L]$ in view of Bencze's recent work [1,2].

Experimental

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared by literature methods [3]. Dichloromethane was distilled before use. ^1H NMR spectra were recorded on a Jeol, FX60 NMR spectrometer (all spectra were measured against tetramethylsilane). Infrared spectra were recorded on a Perkin–Elmer 197 infrared spectrophotometer. Molecular weight determinations were by Rast's method [25] with camphor as the solvent.

Reactions of $[WI_2(CO)_3(NCMe)_2]$ *with L to give* $[WI_2(CO)_3(NCMe)L]$

In a typical reaction, 3Br-py (0.056 g, 0.354 mmol) was added to $[WI_2(CO)_3(NCMe)_2]$ (0.214 g, 0.354 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen. After 30 s stirring the mixture was filtered and the solvent removed in vacuo to give brown crystals of $[WI_2(CO)_3(NCMe)(3Br\text{-}py)]$ (yield 0.24 g, 94%). The product was rapidly recrystallised from CH_2Cl_2.

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with L = 3Cl-py, 4Cl-py and 4Br-py gave the new compounds $[WI_2(CO)_3(NCMe)L]$.

Reactions of $[WI_2(CO)_3(NCMe)L]$ *to give* $[W(\mu\text{-}I)I(CO)_3L]_2$

In a typical reaction $[WI_2(CO)_3(NCMe)(3Br\text{-}py)]$ (0.187 g, 0.2595 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen for 2 minutes, then the solution was filtered and the solvent removed in vacuo to give green crystals of $[W(\mu\text{-}I)I(CO)_3(3Br\text{-}py)]_2$ (yield 0.14 g, 79%). The product was recrystallised from CH_2Cl_2.

Similar procedures with $[WI_2(CO)_3(NCMe)L]$ gave the dimeric complexes $[W(\mu\text{-}I)I(CO)_3L]_2$. Reaction times for $2[WI_2(CO)_3(NCMe)L] \rightarrow [W(\mu\text{-}I)I(CO)_3L]_2 + 2NCMe$ at 25 °C are: (1) L = 3Cl-py, 4 min; (2) L = 3Br-py, 2 min; (3) L = 4Cl-py, 8 min; and (4) L = 4Br-py, 4 min.

Reactions of $[MI_2(CO)_3(NCMe)_2]$ *with L to give* $[M(\mu\text{-}I)I(CO)_3L]_2$

In a typical reaction $[MoI_2(CO)_3(NCMe)_2]$ (0.421 g, 0.816 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen and 4Me-py (0.076 g, 0.816 mmol) was then added. After 30 s stirring filtration followed by removal of the solvent in vacuo gave black crystals of $[Mo(\mu\text{-}I)I(CO)_3(4Me\text{-}py)]_2$ (yield 0.255 g, 59%). The product was recrystallised from CH_2Cl_2.

Similar reactions of $[MoI_2(CO)_3(NCMe)_2]$ with L = 2Cl-py, 2Br-py, 3Cl-py, 3Br-py, 4Cl-py, 4Br-py, py, 3,5-Me_2-py and $[WI_2(CO)_3(NCMe)_2]$ with L = py, 2Cl-py, 2Br-py, 2Me-py, 4Me-py and 3,5-Me_2-py gave the new iodide bridged complexes $[M(\mu\text{-}I)I(CO)_3L]_2$.

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