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Seven-coordinate complexes of molybdenum(II) and tungsten(II) containing imidazole and methyl-substituted imidazoles as attached ligands

Paul K. Baker* and Marit van Kampen
Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW (UK)

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Abstract

The reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an equimolar amount of L {L = imidazole (im), 2Me-imidazole (2Me-im) (for M = W only) or 4Me-imidazole (4Me-im)} gave $[M(\mu\text{-}I)I(CO)_3L]_2$ (**1–5**). Two equivalents of L (L = im, 2Me-im or 4Me-im) react with $[MI_2(CO)_3(NCMe)_2]$ to afford $[MI_2(CO)_3L_2]$ (**6–11**). A series of mixed-ligand complexes of the type $[MI_2(CO)_3LL']$ (M = Mo or W, L = im, L′ = PPh_3, $AsPh_3$ or $SbPh_3$; L = 2Me-im, L′ = PPh_3; for M = W, L = 4Me-im, L′ = PPh_3 or $SbPh_3$) (**12–21**) have also been prepared. The new complexes **1–21** have all been characterised by elemental analysis (C, H and N), IR and ^{1}H NMR spectroscopy. Magnetic susceptibility measurements show all the complexes **1–21** to be diamagnetic.

Introduction

Although a wide range of seven-coordinate complexes of molybdenum(II) and tungsten(II) containing pyridines and substituted pyridines as attached ligands have been reported [1–6], as far as we are aware no examples of such complexes containing imidazoles and substituted imidazoles as coordinated ligands have been reported.

The discovery in 1986 [7] of the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) which contain easily displaced acetonitrile ligands has enabled a wide range of new seven-coordinate diiodo complexes to be prepared [8–11]. In this paper we describe the synthesis of a number of new seven-coordinate complexes of molybdenum(II) and tungsten(II) which contain imidazole and substituted imidazoles as attached ligands.

Experimental

The reactions described in this paper were carried out using standard Schlenk line techniques. The starting materials, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared by the published method [7]. All chemicals used were purchased from commercial sources. The solvent used, namely CH_2Cl_2 was dried over P_2O_5 under dinitrogen and distilled before use.

Elemental analyses (C, H and N) were determined by a Carlo Erba elemental analyser MOD 1106 (using helium as the carrier gas). IR spectra were recorded on a Perkin-Elmer IR spectrophotometer. ^{1}H NMR spectra were obtained from a Bruker AC 250 CP/MAS NMR spectrometer (all spectra were calibrated against tetramethylsilane). Magnetic susceptibilities were measured by using a Johnson-Matthey magnetic susceptibility balance.

$[Mo(\mu\text{-}I)I(CO)_3(im)]_2$ (1)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.97 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added imidazole (im) (0.066 g, 0.97 mmol). After stirring the solution for 30 s, filtration followed by removal of solvent *in vacuo* gave dark brown crystals of $[Mo(\mu\text{-}I)I(CO)_3(im)]_2$ (**1**) which were recrystallised from CH_2Cl_2/Et_2O. (Yield of pure product = 0.21 g, 44%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of L (L = im or 2Me-im, M = W; L = 4Me-im, M = Mo or W) for 30 s in CH_2Cl_2 at room temperature gave $[M(\mu\text{-}I)I(CO)_3L]_2$ (**2–5**).

$[MoI_2(CO)_3(im)_2]$ (6)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.97 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added imidazole (im) (0.13 g, 1.94 mmol). After stirring the solution for 10 min, filtration followed by removal of the solvent *in vacuo*

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*Author to whom correspondence should be addressed.

gave brown crystals of $[MoI_2(CO)_3(im)_2]$ (**6**) which were recrystallised from CH_2Cl_2/Et_2O. (Yield of pure product 0.23 g, 42%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with two equivalents of L (L = im, M = W; L = 2Me-im or 4Me-im, M = Mo or W) for 10 min in CH_2Cl_2 at room temperature gave $[MI_2(CO)_3L_2]$ (**7–11**).

$[MoI_2(CO)_3(im)(PPh_3)]$ (12)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.55 g, 1.07 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added, PPh_3 (0.28 g, 1.07 mmol). After stirring the solution for 1 min, imidazole (im) (0.073 g, 1.07 mmol) was added and the mixture was stirred for a further 30 min. Filtration, followed by removal of the solvent *in vacuo* gave green crystals of $[MoI_2(CO)_3(im)(PPh_3)]$ (**12**), which were recrystallised from CH_2Cl_2/Et_2O. (Yield of pure product = 0.70 g, 85%.)

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L′, followed by L {L′ = PPh_3 (for M = W), $AsPh_3$ or $SbPh_3$, L = im, M = Mo or W; L′ = PPh_3, L = 2Me-im, M = Mo or W; L′ = PPh_3 or $SbPh_3$, L = 4Me-im, M = W} in CH_2Cl_2 at room temperature gave the new seven-coordinate compounds $[MI_2(CO)_3LL']$ (**13–21**). Reaction times for $[MI_2(CO)_3(NCMe)_2] + L' \rightarrow [MI_2(CO)_3(NCMe)L']$ and $[MI_2(CO)_3(NCMe)L'] + L \rightarrow [MI_2(CO)_3LL']$ are as follows: **14**: M = Mo, L′ = $AsPh_3$, 3 min; L = im, 10 min. **16**: M = Mo, L′ = $SbPh_3$, 5 min; L = im, 10 min. Similar times were recorded for the preparation of complexes **13**, **15** and **17–21**.

Results and discussion

The starting materials for this research, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), are prepared by reaction of the tris(acetonitrile) complex *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo and W) [12] *in situ* with an equimolar quantity of I_2 [7]. Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) and L {L = im, 2Me-im (for M = W only), 4Me-im} in CH_2Cl_2 at room temperature gave the iodo-bridged dimers $[M(\mu\text{-}I)I(CO)_3L]_2$ (**1–5**). Complexes **1–5** were characterised by elemental analysis (C, H and N) (Table 1), IR and ^1H NMR spectroscopy (Tables 2 and 3). The complexes **1–5** were stable for several hours in the solid state when stored under nitrogen; however they decomposed fairly rapidly when exposed to air in solution. They are soluble in polar chlorinated solvents such as $CHCl_3$ and CH_2Cl_2, but they are mainly insoluble in hydrocarbon solvents. It should be noted that the sterically crowded 2Me-imidazole complexes were considerably less stable compared to the imidazole and 4Me-imidazole complexes, hence after many attempts the molybdenum dimer $[Mo(\mu\text{-}I)I(CO)_3(2Me\text{-}im)]_2$ could not be isolated in a pure state. It is very likely that the initially formed products from the 1:1 reactions are $[MI_2(CO)_3(NCMe)L]$ which lose acetonitrile via a dissociative process to afford the iodo-bridged dimers **1–5** (see Scheme 1). Evidence to support this mechanism comes from the reactions of $[WI_2(CO)_3(NCMe)_2]$

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

$$2[MI_2(CO)_3(NCMe)L] \longrightarrow [M(\mu\text{-}I)I(CO)_3L]_2 + 2NCMe \quad (ii)$$

Scheme 1.

with an equimolar quantity of electron deficient pyridines, L(L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py) which gave the fully characterised mononuclear compounds $[WI_2(CO)_3(NCMe)L]$, which dimerised to give the iodo-bridged complexes $[W(\mu\text{-}I)I(CO)_3L]_2$ [4]. Several attempts were made to try and isolate the mononuclear imidazole complexes $[MI_2(CO)_3(NCMe)(im)]$ by using short reaction times and lower temperature (−10 °C) without success. The greater ease of dimerisation of the imidazole complexes $[MI_2(CO)_3(NCMe)(im)]$ compared to $[WI_2(CO)_3(NCMe)L]$ (L = 3Cl-py, 3Br-py, 4Cl-py and 4Br-py) is likely to be due to the electronegative substituents on the pyridine which would make the metal centre more positive and hence strengthen the M–NCMe bond. Since the X-ray crystal structure of the bromo-bridged dimer $[W(\mu\text{-}Br)Br(CO)_4]_2$ has been reported [13], it is likely that the imidazole complexes $[M(\mu\text{-}I)I(CO)_3L]_2$ (**1–5**) have a similar structure with each metal in a capped-octahedral environment.

Two equivalents of L (L = im, 2Me-im or 4Me-im) react with $[MI_2(CO)_3(NCMe)_2]$ in CH_2Cl_2 at room temperature to yield the acetonitrile replaced products $[MI_2(CO)_3L_2]$ (**6–11**) in good yield. Complexes **6–11** have been characterised by elemental analysis (C, H and N) (Table 1), IR and ^1H NMR spectroscopy (Tables 2 and 3). The bis-ligand complexes **6–11** are more stable compared to the iodo-bridged dimers **1–5**. Also the bis(2Me-imidazole) complexes **8** and **9** are less stable compared to their imidazole and 4Me-imidazole analogues.

Reaction of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of L′ (L′ = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 for 1, 3 and 5 min, respectively, affords the mononuclear compounds $[MI_2(CO)_3(NCMe)L']$ (previously prepared and characterised [8]), which when reacted *in situ* with an equimolar amount of L {L = im, M = Mo or W; L′ = PPh_3, L = 2Me-im, M = Mo or W; L′ = PPh_3 or $SbPh_3$, L = 4Me-im, M = W} gives generally high yields of the mixed-ligand complexes $[MI_2(CO)_3LL']$ (**12–21**).

TABLE 1. Physical and analytical data[a] for the seven-coordinate molybdenum(II) and tungsten(II) imidazole and substituted imidazole complexes

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
$[Mo(\mu\text{-}I)I(CO)_3(im)]_2$ (**1**)	dark brown	44	13.6 (14.4)	1.3 (0.8)	5.4 (5.6)
$[W(\mu\text{-}I)I(CO)_3(im)]_2$ (**2**)	brown	42	12.3 (12.2)	1.2 (0.7)	5.0 (4.8)
$[W(\mu\text{-}I)I(CO)_3(2Me\text{-}im)]_2$ (**3**)	red	52	13.4 (13.9)	1.4 (1.0)	5.1 (4.6)
$[Mo(\mu\text{-}I)I(CO)_3(4Me\text{-}im)]_2$ (**4**)	dark brown	58	16.6 (16.3)	1.8 (1.2)	5.5 (5.4)
$[W(\mu\text{-}I)I(CO)_3(4Me\text{-}im)]_2$ (**5**)	brown	64	14.5 (13.9)	1.4 (1.0)	5.0 (4.6)
$[MoI_2(CO)_3(im)_2]$ (**6**)	brown	42	19.0 (19.0)	1.7 (1.4)	10.2 (9.8)
$[WI_2(CO)_3(im)_2]$ (**7**)	brown	50	16.2 (16.4)	1.5 (1.2)	9.0 (8.5)
$[MoI_2(CO)_3(2Me\text{-}im)_2]$ (**8**)	brown	76	21.7 (22.1)	2.3 (2.0)	9.4 (9.3)
$[WI_2(CO)_3(2Me\text{-}im)_2]$ (**9**)	red	56	19.6 (19.3)	2.1 (1.8)	7.8 (8.2)
$[MoI_2(CO)_3(4Me\text{-}im)_2]$ (**10**)	brown	62	21.7 (22.1)	2.5 (2.0)	9.6 (9.4)
$[WI_2(CO)_3(4Me\text{-}im)_2]$ (**11**)	orange–brown	53	19.1 (19.0)	2.5 (2.0)	8.4 (8.2)
$[MoI_2(CO)_3(im)(PPh_3)]$ (**12**)	green	85	37.8 (37.7)	3.0 (2.5)	3.3 (3.7)
$[WI_2(CO)_3(im)(PPh_3)]$ (**13**)	yellow	55	34.1 (33.8)	2.5 (2.3)	3.1 (3.3)
$[MoI_2(CO)_3(im)(AsPh_3)]$ (**14**)	orange–brown	61	34.6 (35.6)	2.4 (2.4)	3.3 (3.4)
$[WI_2(CO)_3(im)(AsPh_3)]$ (**15**)	orange	48	31.8 (32.2)	2.3 (2.1)	3.2 (3.1)
$[MoI_2(CO)_3(im)(SbPh_3)]$ (**16**)	light brown	43	34.1 (33.7)	2.6 (2.2)	3.2 (3.3)
$[WI_2(CO)_3(im)(SbPh_3)]$ (**17**)	orange	61	30.2 (30.6)	2.0 (2.0)	3.0 (3.0)
$[MoI_2(CO)_3(2Me\text{-}im)(PPh_3)]$ (**18**)	orange–brown	48	38.0 (38.6)	3.0 (2.7)	3.5 (3.6)
$[WI_2(CO)_3(2Me\text{-}im)(PPh_3)]$ (**19**)	orange	63	34.2 (34.6)	2.7 (2.4)	2.8 (3.2)
$[WI_2(CO)_3(4Me\text{-}im)(PPh_3)]$ (**20**)	orange	51	35.0 (34.7)	2.5 (2.4)	2.9 (3.2)
$[WI_2(CO)_3(4Me\text{-}im)(SbPh_3)]$ (**21**)	orange	63	31.1 (31.4)	2.3 (2.2)	2.7 (3.0)

[a]Calculated values in parentheses.

TABLE 2. IR data[a] for the seven-coordinate molybdenum(II) and tungsten(II) imidazole and substituted imidazole complexes

Complex	$\nu(CO)$ (cm^{-1})
1	2078(s), 2022(s), 1958(m)
2	2074(s), 2007(brs), 1940(brs)
3	2074(s), 2007(brs), 1942(s)
4	2078(s), 2022(s), 1953(brs)
5	2076(s), 2009(s), 1943(brm)
6	2018(s), 1925(sh), 1918(s)
7	2018(s), 1935(s), 1916(sh)
8	2074(m), 2011(s), 1933(s), 1905(sh)
9	2074(m), 2005(s), 1922(s), 1895(sh)
10	2076(s), 2019(s), 1939(brs)
11	2071(m), 2011(s), 1925(brs), 1908(sh)
12	2027(s), 1958(s), 1947(sh), 1912(s)
13	2024(s), 1940(sh), 1937(s), 1905(s), 1901(s)
14	2029(s), 1966(s), 1914(s)
15	2021(s), 1944(s), 1902(s)
16	2029(s), 1966(s), 1910(sh), 1901(s)
17	2022(s), 1947(s), 1898(s)
18	2026(m), 1954(s), 1890(sh)
19	2019(s), 1940(s), 1919(s)
20	2009(s), 1933(s), 1894(s)
21	2023(s), 1949(s), 1899(m)

[a]Spectra obtained in $CHCl_3$ as thin films between NaCl plates; s, strong; m, medium; brs, broad strong; sh, shoulder.

These mixed-ligand complexes **12–21** were fully characterised by elemental analysis (C, H and N) (Table 1), IR and ^1H NMR spectroscopy (Tables 2 and 3). Complexes **12–21** are considerably more stable than **1–11**, and also much more soluble in chlorinated solvents. Magnetic susceptibility measurements have shown that all the complexes described in this paper (**1–21**) are diamagnetic which was expected since they all obey the effective atomic number rule. The solid state structures of a large number of seven-coordinate complexes of the types $[MX_2(CO)_3L_2]$ ($M = Mo$ or W; $X = Cl$, Br, I) have been determined crystallographically [14–20], and the majority have capped octahedral geometry, and hence the structures of the monomers **6–21** are likely to have capped octahedral geometry. The IR spectral properties of **6–21** are also similar to the reported IR spectral data for several of the crystallographically determined complexes which tends to support a capped octahedral structure for **6–21**. However, complexes **8**, **9**, **11**, **12**, **13** and **16** have four or five carbonyl stretching bands in their IR spectra, which suggests the existence of several isomers of these complexes in solution.

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TABLE 3. ^{1}H NMR data[a, b] for the seven-coordinate molybdenum(II) and tungsten(II) imidazole and substituted imidazole complexes

Complex	^{1}H NMR data (δ (ppm))
1	9.4 (s, 2H, N–C*H*=N), 7.8 (brs, 4H, N–C*H*=C*H*–N)
2	9.0 (s, 2H, N=C*H*–N), 7.5 (brs, 4H, N–C*H*=C*H*–N)
3	7.8 (s, 4H, N–C*H*=C*H*–N), 3.1, 2.9 (2s, 6H, *Me*)
4	8.4 (s, 2H, N–C*H*=N), 7.1 (brs, 2H, NC*H*=CMe), 2.5 (brs, 6H, *Me*)
5	12.0 (brs, 2H, NH), 8.8 (s, 2H, N–C*H*=N), 7.1 (s, 2H, NC*H*=CMe), 2.6 (brs, 6H, *Me*)
6	9.4 (s, 2H, N–C*H*=N), 8.3 (s, 2H, N–C*H*=CH–N), 7.4 (s, 2H, N–C*H*=CH–N)
7	9.4 (s, 2H, N–C*H*=N), 8.5 (s, 2H, N–C*H*=CH–N), 7.6 (s, 2H, N–CH=C*H*–N)
8	7.7 (brs, 4H, N–C*H*=C*H*–N), 2.9 (brs, 6H, *Me*)
9	8.7 (brs, 4H, N–C*H*=C*H*–N), 3.1, 2.9, (2s, 6H, *Me*)
10	9.1 (s, 2H, N–C*H*=N), 7.6 (s, 2H, N–C*H*=CMe), 3.1 (brs, 6H, *Me*)
11	8.8 (s, 2H, N–C*H*=N), 7.2 (s, 2H, N–C*H*=CMe), 2.5 (brs, 6H, *Me*)
12	8.7 (s, 1H, N–C*H*=N), 7.2–7.7 (m, 17H, N–C*H*=C*H*–N and *Ph*)
13	8.7 (s, 1H, N–C*H*=N), 8.1 (brs, 2H, N–C*H*=C*H*–N), 7.3–7.8 (m, 15H, *Ph*)
14	8.6 (s, 1H, N–C*H*=N), 8.1 (brs, 2H, N–C*H*=C*H*–N), 7.3–7.5 (m, 15H, *Ph*)
15	8.8 (s, 1H, N–C*H*=N), 8.4 (brs, 2H, N–C*H*=C*H*–N), 7.3–7.5 (m, 15H, *Ph*)
16	8.5 (s, 1H, N–C*H*=N), 8.3 (brs, 2H, N–C*H*=C*H*–N), 7.1–7.7 (m, 15H, *Ph*)
17	8.7 (s, 1H, N–C*H*=N), 8.3 (brs, 2H, N–C*H*=C*H*–N), 7.2–7.5 (m, 15H, *Ph*)
18	8.5 (brs, 2H, N–C*H*=C*H*–N), 7.4–7.8 (m, 15H, *Ph*), 2.8 (s, 3H, *Me*)
19	8.3 (brs, 2H, N–C*H*=C*H*–N), 7.3–7.8 (m, 15H, *Ph*), 2.7 (s, 3H, *Me*)
20	8.5 (s, 1H, N–C*H*=N), 8.0 (s, 1H, N–C*H*=CMe), 7.2–7.6 (m, 15H, *Ph*), 2.8 (s, 3H, *Me*)
21	9.9 (s, 1H, N*H*), 8.5 (s, 1H, N–C*H*=N), 7.2–7.7 (m, 15H, *Ph*), 7.0 (s, 1H, N–C*H*=CMe), 2.4 (s, 3H, *Me*)

[a] Spectra obtained in CDCl$_3$ (+25 °C) and referenced to Me$_4$Si; s, singlet; brs, broad singlet; m, multiplet. [b] NH resonance was not observed for most of the complexes.

^{1}H NMR and magnetic susceptibilities for several of the complexes.

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