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The Reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W).

Part 3. The Synthesis and Spectral Properties of the Seven-coordinate Complexes $[MI_2(CO)_3(L-L)]$ (M = Mo and W; L–L = py_2, 2,2'-bipyridyl and 1,10-phenanthroline)

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In a previous paper in this series [1] we described a new high-yielding synthesis of the complexes $[MI_2(CO)_3L_2]$ (M = Mo and W; L = PPh_3, $AsPh_3$ and $SbPh_3$). Although the molybdenum dichloro and dibromo complexes containing nitrogen donor ligands $[MoX_2(CO)_3(L-L)]$ (X = Cl and Br; L–L = py_2, 2,2'-bipyridyl and 1,10-phenanthroline) have been reported by Colton and Tomkins [2], and the tungsten bispyridine compounds $[WX_2(CO)_3(py)_2]$ (X = Cl and Br) by Westland and Muriithi [3], to date there has been no report of the diiodo complexes with the exception of the tungsten compounds $[WI_2(CO)_3(L-L)]$ (L–L = py_2 [3] and 2,2'-bipyridyl [4]) which have been prepared by reacting the zerovalent complexes $[W(CO)_4(L-L)]$ with iodine. The small number of diiodide complexes known is almost certainly due to the difficulty of synthesising the iodide bridged dimers $[M(\mu\text{-}I)I(CO)_4]_2$ (M = Mo and W) [5, 6]. We now wish to report a new high-yielding synthesis of the complexes $[MI_2(CO)_3(L-L)]$ (M = Mo and W; L = py_2, 2,2'-bipyridyl and 1,10-phenanthroline), from the reaction of $[MI_2(CO)_3(NCMe)_2]$ with the appropriate nitrogen donor ligand.

Experimental

$[MI_2(CO)_3(NCMe)_2]$ were prepared according to literature methods [7], an pyridine, 2,2'-bipyridyl and 1,10-phenanthroline were purchased from Aldrich Chemical Company. CH_2Cl_2 was dried and distilled before use.

^1H NMR spectra were recorded on a Jeol FX60 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin–Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

$[MoI_2(CO)_3(py)_2]CH_2Cl_2$ (1)

To $MoI_2(CO)_3(NCMe)_2$ (0.27 g, 0.523 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added pyridine (0.083 g, 1.049 mmol), and the mixture was left stirring for 4 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(py)_2]CH_2Cl_2$ (yield = 0.23 g, 65%): ^1H NMR $\delta\{(CD_3)_2SO\}$ 8.83 (d, 2H) 8.27 (m, 2H) 7.89 (d, 1H), 5.73 (s, 2H, CH_2Cl_2).

$WI_2(CO)_3(py)_2$ (2)

To $WI_2(CO)_3(NCMe)_2$ (0.229 g, 0.379 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added pyridine (0.06 g, 0.759 mmol), and the mixture was left stirring for 10 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[WI_2(CO)_3(py)_2]$ (yield = 0.21 g, 82%): ^1H NMR $\delta\{(CD_3)_2SO\}$ 8.79 (d, 2H), 8.28 (m, 2H), 7.73 (d, 1H).

$MoI_2(CO)_3(bipy)$ (3)

To $MoI_2(CO)_3(NCMe)_2$ (0.33 g, 0.640 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added 2,2'-bipyridyl (0.10 g, 0.640 mmol), and the mixture was left stirring for 5 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(bipy)]$ (yield = 0.32 g, 85%): ^1H NMR $\delta\{(CD_3)_2SO\}$ 9.5 (d, 2H), 8.67 (m, 4H), 7.88 (d, 2H).

$WI_2(CO)_3(bipy)$ (4)

To $WI_2(CO)_3(NCMe)_2$ (0.34 g, 0.563 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added 2,2'-bipyridyl (0.088 g, 0.563 mmol), and the mixture was left stirring for 5 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[WI_2(CO)_3(bipy)]$ (yield = 0.29 g, 76%): ^1H NMR $\delta\{(CD_3)_2SO\}$ 9.69 (d, 2H), 8.71 (m, 4H), 7.91 (d, 2H).

$[MoI_2(CO)_3(phen)]CH_2Cl_2$ (5)

To $MoI_2(CO)_3(NCMe)_2$ (0.26 g, 0.504 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added 1,10-phenanthroline (0.091 g, 0.505 mmol), and the mixture was left stirring for 10 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(phen)]CH_2Cl_2$ (yield = 0.24 g, 68%): ^1H NMR $\delta\{(CD_3)_2SO\}$ 10.01 (m, 2H), 9.23 (m, 2H), 8.44 (m, 4H), 5.79 (s, 2H, CH_2Cl_2).

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TABLE I. Analytical (C, H and N)[a] and IR Data[b] for $[MI_2(CO)_3(L-L)]$

Complex		Analysis (%)[a]			ν(CO)[b] (cm^{-1})
$[MoI_2(CO)_3(py)_2]CH_2Cl_2$	(1)	C	24.92	(24.84)	2015(s), 1934(s) and 1900(m)
		H	2.06	(1.79)	
		N	4.17	(4.14)	
$[WI_2(CO)_3(py)_2]$	(2)	C	22.82	(22.97)	2005(s). 1920(s) and 1905(s)
		H	1.46	(1.48)	
		N	3.89	(4.12)	
$[MoI_2(CO)_3(bipy)]$	(3)	C	26.53	(26.47)	2035(s), 1960(s) and 1912(s)
		H	1.46	(1.37)	
		N	4.62	(4.75)	
$[WI_2(CO)_3(bipy)]$	(4)	C	23.50	(23.03)	2025(s), 1945(s) and 1895(s)
		H	1.49	(1.19)	
		N	4.11	(4.13)	
$[MoI_2(CO)_3(phen)]CH_2Cl_2$	(5)	C	27.06	(27.50)	2040(s), 1963(s) and 1934(s)
		H	1.60	(1.44)	
		N	4.00	(4.01)	
$[WI_2(CO)_3(phen)]CH_2Cl_2$	(6)	C	24.35	(24.42)	2020(s), 1940(s) and 1915(s)
		H	1.35	(1.28)	
		N	3.53	(3.56)	

[a]Calculated values in parenthesis. [b]Spectra recorded in $CHCl_3$ unless stated, m, medium, s, strong.

$[WI_2(CO)_3(phen)]CH_2Cl_2$ (6)

To $WI_2(CO)_3(NCMe)_2$ (0.268 g, 0.444 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon was added 1,10-phenanthroline (0.08 g, 0.444 mmol), and the mixture was left stirring for 11 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[WI_2(CO)_3(phen)]CH_2Cl_2$ (yield = 0.27 g, 77%): ^{1}H NMR $\delta\{(CD_3)_2SO\}$ 10.12 (d, 2H), 9.21 (d, 2H), 8.32 (m, 4H), 5.75 (s, 2H, CH_2Cl_2).

Results and Discussion

Elemental analysis (C, H and N) and infrared spectroscopy (Table I) and ^{1}H NMR spectroscopy (see 'Experimental') support the formulation of the complexes $[MI_2(CO)_3(L-L)]$ (M = Mo and W; L–L = py$_2$, 2,2'-bipyridyl, and 1,10-phenanthroline). Two acetonitrile ligands are readily replaced from $[MI_2(CO)_3(NCMe)_2]$ by nitrogen donor ligands. The complexes are both air and light sensitive and are stored under argon in the dark.

Since the complexes $[MI_2(CO)_3(NCMe)_2]$ can be synthesised in high yield {>90% based on $M(CO)_6$} by the reaction sequence shown in eqn. (1) [7] and the reaction of these compounds with nitrogen donors also gives very good yields (see 'Experimental'), this has proved to be an excellent method of synthesising these complexes.

$$[M(CO)_6] \xrightarrow[\Delta]{NCMe} [M(CO)_3(NCMe)_3] \xrightarrow{I_2} [MI_2(CO)_3(NCMe)_2] \qquad (1)$$

It is interesting to note that Stiddard [4] reported that reaction of I_2 with $[Mo(CO)_4(bipy)]$ in $CHCl_3$ gave the iodide bridged dimer $[Mo(\mu\text{-}I)I(CO)_3(bipy)]_2$ with the 2,2'-bipyridyl ligand bonded as a monodentate ligand to the molybdenum. The infrared spectrum of this complex ($CHCl_3$) showed bands [4] at ν(CO) cm^{-1} = 2040, 2018, 1976, 1935, and 1888, which is different from our product $[MoI_2(CO)_3(bipy)]$ from reaction of $[MoI_2(CO)_3(NCMe)_2]$ and 2,2'-bipyridyl in CH_2Cl_2 showing carbonyl stretching bands ($CHCl_3$) at ν(CO) cm^{-1} = 2035(s), 1960(s) and 1912(s) typical of mononuclear seven-coordinate complexes of molybdenum(II) and tungsten(II).

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