Reactions of the Seven-co-ordinate Complexes $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ (M = Mo or W; L = PPh_3, $AsPh_3$ or $SbPh_3$) with Dithiocarbamate Ligands

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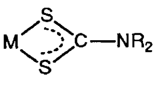
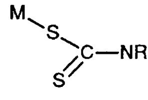
The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with 1 equivalent of $Na[S_2CN(CH_2Ph)_2]$ eventually to give the iodo-bridged dimers $[\{M(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$. The reaction of $[MI_2(CO)_3(NCMe)_2]$ with 1 equivalent of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) gave $[MI_2(CO)_3(NCMe)L]$ which when treated *in situ* with $Na[S_2CNR_2]$ (R = Me, Et or CH_2Ph) afforded $[MI(CO)_3L(S_2CNR_2)]$. The complexes $[MoI(CO)_3L(S_2CNR_2)]$ prepared as described above when treated *in situ* with 1 equivalent of $[S_2CNR_2]^-$ generally give the mixed-ligand oxides $[Mo_2O_3(S_2CNR_2)_2(S_2CNR'_2)_2]$. The complexes $[WI(CO)_3(PPh_3)(S_2CNR_2)]$ (R = Me, Et or CH_2Ph) when treated *in situ* with $Na[S_2CNR'_2]$ afforded $[W(CO)_2(PPh_3)(S_2CNR_2)(S_2CNR'_2)]$ (R = Me, R′ = Et; R = Me, R′ = CH_2Ph; R = Et, R′ = CH_2Ph), whereas reaction with the $AsPh_3$ and $SbPh_3$ complexes in an analogous manner gave $[W(CO)_3(S_2CNR_2)(S_2CNR'_2)]$ in low yield. Reaction of $[MoI_2(CO)_3(NCMe)_2]$ with 2 equivalents of $Na[S_2CNEt_2]\cdot 3H_2O$ gave the previously reported oxide compound $[Mo_2O_3(S_2CNEt_2)_4]$, whereas $[WI_2(CO)_3(NCMe)_2]$ reacts to give $[W(CO)_3(S_2CNEt_2)_2]$. Two equivalents of $Na[S_2CN(CH_2Ph)_2]$ react with $[MoI_2(CO)_3(NCMe)L]$ to give for L = PPh_3 and $AsPh_3$ the oxides $[Mo_2O_3\{S_2CN(CH_2Ph)_2\}_4]$ and the seven-co-ordinate complex $[Mo(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ for L = $SbPh_3$. The complexes $[W(CO)_2L\{S_2CN(CH_2Ph)_2\}_2]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$) were prepared in an analogous manner. Low-temperature ^{13}C NMR spectra are interpreted to suggest the likely stereochemistry of several of these complexes.

Dithiocarbamate ligands have generally been found to co-ordinate to a transition metal as a bidentate ligand **a**,[1,2] however, monodentate co-ordination **b** as in $[W(CO)_3(S_2CNMe_2\text{-}S)(\eta^5\text{-}C_5H_5)]$[3] and $[Mo(S_2CNEt_2\text{-}S)(S_2CNEt_2\text{-}SS')\{HB(dmpz)_3\}]$ (dmpz = 3,5-dimethylpyrazolyl)[4] have also been reported. Molybdenum complexes containing anionic sulphur-donor ligands such as dithiocarbamates have received considerable attention since it is believed that the Mo–S binding site in the nitrogenase enzyme is the active site for reduction of dinitrogen to ammonia.[5,6] Six- and seven-co-ordinate dithiocarbamate complexes of molybdenum(II) and tungsten(II) such as $[M(CO)_n(S_2CNR_2)_2]$ (M = Mo or W, n = 2 or 3, R = Me, Et or Pr^i) have been extensively studied.[7–15] However, few reports of monodithiocarbamate seven-co-ordinate complexes have been published.[16]



a



b

We have been studying the chemistry of the seven-co-ordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)[17] which are synthesised in quantitative yield by an *in situ* reaction of the tris(acetonitrile) complexes $[M(CO)_3(NCMe)_3]$ with an equimolar quantity of I_2. In this paper we describe full details of the reactions of $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$)[18] with dithiocarbamates which afford a wide variety of products. A preliminary report of this work has appeared.[16]

Results and Discussion

The seven-co-ordinate diiodo complexes $[MI_2(CO)_3(NCMe)_2]$ and $[MI_2(CO)_3(NCMe)L]$ (M = Mo or W; L = PPh_3, $AsPh_3$ or $SbPh_3$) react with 1 or 2 equivalents of $Na[S_2CNR_2]$ (R = Me, Et or CH_2Ph) in CH_2Cl_2 at room temperature to give a wide range of different seven-co-ordinate dithiocarbamate complexes, **1**–**32**, or oxides of the type $[Mo_2O_3(S_2CNR_2)_4]$ or $[Mo_2O_3(S_2CNR_2)_2(S_2CNR'_2)_2]$ (see Experimental section). The complexes described in this paper have been fully characterised by elemental analysis (C, H and N) (Table 1), infrared (Table 1) and ^1H NMR spectroscopy (Table 2). The iodo-bridged dimers **1** and **2** are air-sensitive, however they can be stored under nitrogen for several days. The monodithiocarbamate compounds $[MI(CO)_3L(S_2CNR_2)]$ **3**–**20** are all moderately air-stable in the solid state, but are much more air-sensitive in solution. The mixed and bis(dithiocarbamate) complexes **21**–**32** are all very air-sensitive (particularly the molybdenum complexes many of which decomposed to the oxides). The seven-co-ordinate complexes **1**–**32** are soluble in $CHCl_3$ and CH_2Cl_2 and very soluble in MeOH, and as expected only slightly soluble in diethyl ether and hydrocarbon solvents.

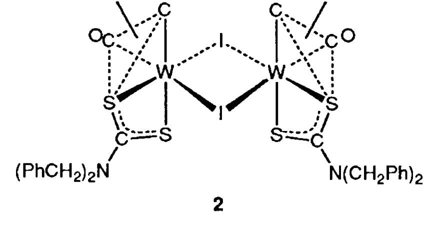
Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $Na[S_2CN(CH_2Ph)_2]$ react in CH_2Cl_2 eventually to afford the iodo-bridged dimers $[\{M(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$ **1** and **2**. It is likely that these reactions proceed with initial formation of the monoacetonitrile complexes $[MI(CO)_3(NCMe)\{S_2CN(CH_2Ph)_2\}]$. However, these intermediates could not be isolated since they rapidly dimerised with loss of acetonitrile to give the dimers **1** and **2**. The dimeric nature of **1** and **2** was confirmed by molecular-weight measurements using Rast's method[19] (see Experimental section). Since the X-ray crystal structure of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ has been determined by Cotton *et al.*[20] and shown to have bromide bridges it is highly likely that complexes **1** and **2** contain iodide bridges, although a possible structure containing metal–metal double bonds and no iodide bridges cannot be ruled out. Each tungsten atom in $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ is in a capped-octahedral environment[20] with carbonyl ligands capping each octahedral face. The structures of seven-co-ordinate complexes of

Table 1 Physical, analytical[a] and infrared spectroscopic data[b] for the seven-co-ordinate dithiocarbamate complexes of molybdenum(II) and tungsten(II)

Complex	Colour	Yield (%)	Analysis (%)			$\nu(CO)/cm^{-1}$	$\nu(CN)/cm^{-1}$
			C	H	N		
1 $[\{Mo(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$	Black	62	37.1 (37.3)	2.5 (2.4)	2.6 (2.4)	2020s, 1981s, 1945s	1495m
2 $[\{W(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$	Brown	54	32.9 (32.4)	2.1 (2.1)	2.0 (2.1)	2005s, 1926s, 1905s	1481m
3 $[MoI(CO)_3(PPh_3)(S_2CNMe_2)]$	Brown	64	42.2 (41.8)	3.2 (3.1)	1.9 (2.0)	2040s, 1960s, 1939s	1533m
4 $[MoI(CO)_3(AsPh_3)(S_2CNMe_2)]$	Brown	66	39.2 (39.3)	3.1 (2.9)	2.0 (1.9)	2040s, 1958s, 1937s	1528m
5 $[MoI(CO)_3(SbPh_3)(S_2CNMe_2)]$	Brown	60	37.4 (37.0)	2.9 (2.7)	1.7 (1.8)	2035s, 1960s, 1930s	1532m
6 $[MoI(CO)_3(PPh_3)(S_2CNEt_2)]$	Brown	55	43.3 (43.5)	4.0 (3.5)	1.8 (2.0)	2020m, 1935s, 1857m	1493m
7 $[MoI(CO)_3(AsPh_3)(S_2CNEt_2)]$	Brown	65	40.8 (41.0)	3.6 (3.3)	2.0 (1.8)	2025s, 1953s, 1934s	1500m
8 $[MoI(CO)_3(SbPh_3)(S_2CNEt_2)]$	Brown	58	38.7 (38.6)	3.4 (3.1)	1.6 (1.7)	2020s, 1959s, 1932m	1505m
9 $[MoI(CO)_3(PPh_3)\{S_2CN(CH_2Ph)_2\}]$	Black	58	51.2 (51.4)	3.6 (3.5)	1.5 (1.7)	2020s, 1940s, 1905s	1490m
10 $[MoI(CO)_3(AsPh_3)\{S_2CN(CH_2Ph)_2\}]$	Black	58	47.5 (47.5)	3.3 (3.3)	1.7 (1.6)	2025s, 1945s, 1865m	1482m
11 $[MoI(CO)_3(SbPh_3)\{S_2CN(CH_2Ph)_2\}]$	Black	67	45.1 (45.1)	3.4 (3.1)	1.4 (1.5)	2025s, 1945s, 1930s	1478m
12 $[WI(CO)_3(PPh_3)(S_2CNMe_2)]$	Brown	70	36.7 (37.1)	2.8 (2.7)	1.7 (1.8)	2025s, 1930s, 1915s	1534m
13 $[WI(CO)_3(AsPh_3)(S_2CNMe_2)]$	Orange	75	34.7 (35.1)	2.6 (2.6)	1.4 (1.7)	2030s, 1935s, 1922s	1533m
14 $[WI(CO)_3(SbPh_3)(S_2CNMe_2)]$	Orange	65	33.0 (33.2)	2.5 (2.4)	1.4 (1.6)	2020s, 1920s, 1909s	1532m
15 $[WI(CO)_3(PPh_3)(S_2CNEt_2)]$	Orange	68	39.2 (38.8)	3.4 (3.1)	1.8 (1.7)	2010s, 1920s, 1832s	1429m
16 $[WI(CO)_3(AsPh_3)(S_2CNEt_2)]$	Orange	68	36.5 (36.8)	3.0 (3.0)	1.5 (1.7)	2010s, 1928s, 1912s	1494m
17 $[WI(CO)_3(SbPh_3)(S_2CNEt_2)]$	Orange	62	34.8 (34.9)	3.0 (2.8)	1.3 (1.6)	2005s, 1955s, 1900s	1501m
18 $[WI(CO)_3(PPh_3)\{S_2CN(CH_2Ph)_2\}]$	Brown	69	46.0 (46.5)	3.4 (3.1)	1.5 (1.5)	2030s, 1925s, 1845s	1482m
19 $[WI(CO)_3(AsPh_3)\{S_2CN(CH_2Ph)_2\}]$	Brown	51	43.7 (44.4)	3.1 (3.0)	1.5 (1.4)	2020s, 1977s, 1924s	1480m
20 $[WI(CO)_3(SbPh_3)\{S_2CN(CH_2Ph)_2\}]$	Brown	51	41.7 (42.4)	2.7 (2.9)	1.5 (1.4)	2020s, 1979s, 1935s	1480m
21 $[Mo(CO)_2(PPh_3)(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$	Brown	82	57.6 (57.5)	4.7 (4.7)	3.3 (3.4)	1925s, 1850s	1481m
22 $[Mo(CO)_2(SbPh_3)(S_2CNMe_2)\text{-}\{S_2CN(CH_2Ph)_2\}]$	Brown	58	51.1 (50.9)	3.8 (3.9)	2.7 (3.1)	1925s, 1845s	1478m
23 $[Mo(CO)_2(SbPh_3)(S_2CNEt_2)\text{-}\{S_2CN(CH_2Ph)_2\}]\cdot 0.5CH_2Cl_2$	Brown	61	49.9 (50.2)	3.9 (4.2)	3.1 (2.9)	1930s, 1845s	1479m
24 $[W(CO)_2(PPh_3)(S_2CNMe_2)(S_2CNEt_2)]$	Red	85	44.0 (43.6)	4.4 (4.1)	3.4 (3.6)	1918s, 1825s	1478m
25 $[W(CO)_2(PPh_3)(S_2CNMe_2)\{S_2CN(CH_2Ph)_2\}]$	Red	63	51.0 (51.0)	4.1 (3.9)	3.0 (3.1)	1925s, 1835s	1481m
26 $[W(CO)_2(PPh_3)(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$	Red	58	51.6 (52.1)	4.7 (4.3)	3.2 (3.6)	1919s, 1825s	1482m
27 $[W(CO)_3(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$	Brown	21	35.3 (34.9)	4.1 (3.5)	4.0 (4.1)	2005s, 1919s, 1822s	1478m
28 $[W(CO)_3(S_2CNEt_2)_2]$	Brown	56	27.0 (27.7)	3.7 (3.6)	5.0 (5.0)	2010s, 1924s, 1905 (sh)	
29 $[Mo(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$	Brown	54	56.8 (57.2)	4.2 (4.1)	2.4 (2.7)	1925s, 1842s	1478m
30 $[W(CO)_2(PPh_3)\{S_2CN(CH_2Ph)_2\}_2]$	Red	83	57.4 (57.4)	4.1 (4.1)	2.4 (2.7)	1922s, 1835s	1478m
31 $[W(CO)_2(AsPh_3)\{S_2CN(CH_2Ph)_2\}_2]$	Brown	61	55.3 (55.1)	4.2 (4.0)	2.2 (2.6)	1918s, 1830s	1478m
32 $[W(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$	Brown	54	52.4 (52.8)	3.7 (3.8)	2.3 (2.5)	1925s, 1840s	1475m

[a] Calculated values in parentheses. [b] Spectra recorded in $CHCl_3$; s = strong, m = medium, w = weak, br = broad and sh = shoulder.

molybdenum(II) and tungsten(II) have generally been found to be capped octahedral.[21] Colton and Kevekordes[22] have described how ^{13}C NMR spectroscopy can be used to indicate if there is a carbonyl ligand in the unique capping position in capped-octahedral complexes. The low-temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectrum of $[\{W(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$ **2** was measured and showed three carbonyl resonances at δ 199.63, 200.44 and 228.03 ppm. In view of the structure of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$,[20] and Colton and Kevekordes observations[22] it is highly likely that the low-field resonance at δ 228.03 ppm is due to equivalent (one on each tungsten) carbonyls in capped-octahedral positions, and the resonances at δ 199.63 and 200.44 ppm due to equivalent pairs of octahedral carbonyls. A possible structure for this complex is shown below.



2

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) react with 1 equivalent of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature to give $[MI_2(CO)_3(NCMe)L]$,[18] which when treated *in situ* with $Na[S_2CNR_2]$ (R = Me, Et or CH_2Ph) afford good yields of the monodithiocarbamate complexes $[MI(CO)_3L(S_2CNR_2)]$ **3**–**20**. The low-temperature ^{13}C NMR (−70 °C, CD_2Cl_2) spectra of a number of complexes **3**–**20** were measured, however, due to their low solubility, no satisfactory spectra were obtained. Many unsuccessful attempts were made to grow crystals of complexes **3**–**20**. It should also be noted that the S_2CNMe_2 complexes **3**–**5** and **12**–**14** all show two well separated methyl resonances in the ^1H NMR spectra even at 60 °C. Hence the barrier to rotation about the C–N bond in these complexes is likely to be high.

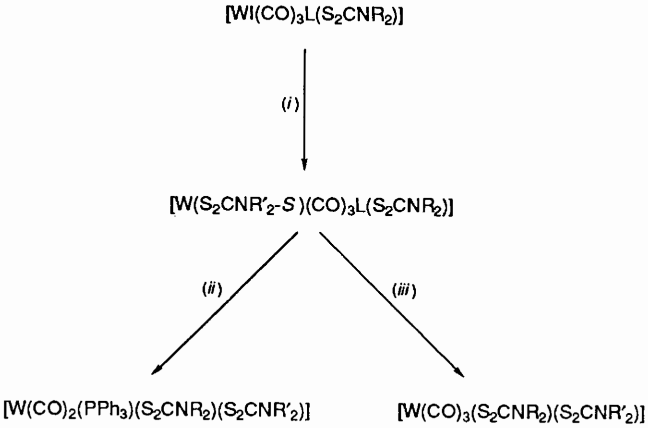
Reaction of the molybdenum complexes $[MoI(CO)_3L(S_2CNR_2)]$ *in situ* with 1 equivalent of $[S_2CNR'_2]^-$ generally afforded the purple oxides $[Mo_2O_3(S_2CNR_2)_2(S_2CNR'_2)_2]$ (see Experimental section). This type of reaction was previously observed by Colton and co-workers.[7,8,23] They treated $[\{Mo(\mu\text{-}Cl)Cl(CO)_4\}_2]$ with $Na[S_2CNEt_2]$ which afforded $[Mo_2O_3(S_2CNEt_2)_4]$. It is likely that these reactions result from the initial formation of the seven-co-ordinate complexes $[Mo(CO)_2L(S_2CNR_2)(S_2CNR'_2)]$, but due to the extreme sensitivity of these complexes they decompose readily to the oxide. However, the seven-co-ordinate molybdenum complexes $[Mo(CO)_2(PPh_3)(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$ **21** and $[Mo(CO)_2(SbPh_3)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}]$ (R = Me or Et), **22** or **23**, were formed from the reaction of $[MoI(CO)_3L(S_2CNR_2)]$ with $[S_2CNR'_2]^-$. These are the first examples of mixed dithiocarbamate seven-co-ordinate complexes of molybdenum(II) and tungsten(II) to be reported. The triphenylphosphinetungsten complexes $[WI(CO)_3(PPh_3)(S_2CNR_2)]$

Table 2 Proton NMR spectroscopic data * (δ) for the seven-co-ordinate dithiocarbamate complexes

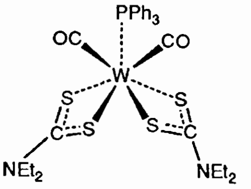
Complex	
1	5.07 (s, 4 H, CH_2), 7.37 (s, 10 H, Ph)
2	4.76 (s, 2 H, CH_2), 4.88 (s, 2 H, CH_2), 7.4 (s, 10 H, Ph)
3	3.31 (s, 3 H, CH_3), 3.57 (s, 3 H, CH_3), 7.38 (s, 15 H, Ph)
4	3.40 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 7.51 (s, 15 H, Ph)
5	2.73 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 7.45 (s, 15 H, Ph)
6	1.18 (m, 6 H, CH_3), 3.89 (m, 4 H, CH_2), 7.53 (m, 15 H, Ph)
7	1.4 (t, J = 7.8, 6 H, CH_3), 3.92 (m, 4 H, CH_2), 7.34 (m, 15 H, Ph)
8	1.26 (t, J = 6.6, 6 H, CH_3), 3.91 (m, 4 H, CH_2), 7.39 (m, 15 H, Ph)
9	4.89 (s, 4 H, CH_2), 7.31, 7.39, 7.47 (m, 25 H, Ph)
10	4.78 (s, 2 H, CH_2), 5.07 (s, 2 H, CH_2), 7.35, 7.61, (m, 25 H, Ph)
11	4.85 (m, 4 H, CH_2), 7.39 (m, 25 H, Ph)
12	2.79 (s, 3 H, CH_3), 3.11 (s, 3 H, CH_3), 7.4 (s, 15 H, Ph)
13	2.61 (s, 3 H, CH_3), 3.25 (s, 3 H, CH_3), 7.48 (s, 15 H, Ph)
14	2.72 (s, 3 H, CH_3), 3.24 (s, 3 H, CH_3), 7.39 (s, 15 H, Ph)
15	1.18 (m, 6 H, CH_3), 3.26 (m, 2 H, CH_2), 3.57 (m, 2 H, CH_2), 7.38 (m, 15 H, Ph)
16	0.96 (t, J = 7.2, 6 H, CH_3), 3.16 (q, J = 7.8, 2 H, CH_2), 3.81 (m, 2 H, CH_2), 7.37 (m, 15 H, Ph)
17	1.41 (t, J = 8.4, 6 H, CH_3), 3.75 (m, 4 H, CH_2), 7.36 (m, 15 H, Ph)
18	4.13 (m, 2 H, CH_2), 4.66, 4.85 (m, 2 H, CH_2), 7.29, 7.39, 7.45 (m, 25 H, Ph)
19	4.75, 4.85, 5.03 (m, 4 H, CH_2), 7.34 (s, 25 H, Ph)
20	4.7, 4.85, 5.08 (m, 4 H, CH_2), 7.39 (s, 25 H, Ph)
21	1.32 (t, J = 6.6, 6 H, $CH_2C\mathit{H}_3$), 3.92 (m, 4 H, $C\mathit{H}_2CH_3$), 4.94 (s, 4 H, $C\mathit{H}_2Ph$), 7.32, 7.52 (m, 25 H, Ph)
22	3.42 (s, 6 H, NCH_3), 4.96 (s, 4 H, $C\mathit{H}_2Ph$), 7.36 (s, 25 H, Ph)
23	1.26 (m, 6 H, $CH_2C\mathit{H}_3$), 3.92 (m, 4 H, $C\mathit{H}_2CH_3$), 4.91 (5, 4 H, $C\mathit{H}_2Ph$), 5.3 (s, 1 H, $C\mathit{H}_2Cl_2$), 7.31, 7.36 (m, 25 H, Ph)
24	1.18 (m, 6 H, $CH_2C\mathit{H}_3$), 3.11 (s, 6 H, $NC\mathit{H}_3$), 3.56 (m, 4 H, $C\mathit{H}_2CH_3$), 7.32 (s, 15 H, Ph)
25	3.3 (s, 6 H, $NC\mathit{H}_3$), 4.84 (s, 4 H, $C\mathit{H}_2Ph$), 7.31, 7.35, 7.52 (m, 25 H, Ph)
26	1.3 (t, J = 8.4, 6 H, $CH_2C\mathit{H}_3$), 3.15, 3.25 (q, J = 6, 4 H, $C\mathit{H}_2CH_3$), 4.9 (s, 4 H, $C\mathit{H}_2Ph$), 7.3, 7.35, 7.51, 7.69 (m, 25 H, Ph)
27	1.42 (t, J = 7.2, 6 H, $CH_2C\mathit{H}_3$), 3.0, 3.14 (q, J = 8.4, 4 H, $C\mathit{H}_2CH_3$), 7.33 (s, 10 H, Ph)
29	4.94 (s, 8 H, CH_2), 7.36 (s, 35 H, Ph)
30	4.84 (s, 8 H, CH_2), 7.31 (s, 35 H, Ph)
31	4.89 (s, 8 H, CH_2), 7.32 (s, 35 H, Ph)
32	4.9 (s, 8 H, CH_2), 7.36 (s, 35 H, Ph)

* Spectra recorded in $CDCl_3$ (25 °C) and referenced to $SiMe_4$; J values in Hz; s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

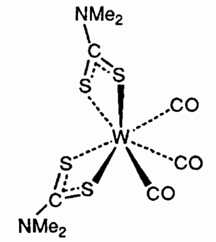
when treated *in situ* with Na[$S_2CNR'_2$] afforded good yields of the bright red complexes [$W(CO)_2(PPh_3)(S_2CNR_2)(S_2CNR'_2)$] **24–26**. These complexes are remarkably stable and do not appear to disproportionate in solution. However, the triphenyl-arsine and stibine complexes [$WI(CO)_3L(S_2CNR_2)$] react *in situ* with 1 equivalent of Na[$S_2CNR'_2$] to give the tricarbonyl complexes [$W(CO)_3(S_2CNR_2)(S_2CNR'_2)$]. These complexes were very unstable and disproportionated in solution, however, [$W(CO)_3(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}$] **27** was isolated and fully characterised. This difference in reaction type between PPh_3 and the more weakly co-ordinated $AsPh_3$ and $SbPh_3$ complexes is illustrated in Scheme 1. An explanation for this behaviour may be that the monodentate dithiocarbamate initially formed from iodide displacement prefers to displace carbon monoxide rather than the strongly bonded triphenylphosphine ligand, whereas the more weakly bonded (and larger) triphenyl-arsine and -stibine ligands are displaced in preference to carbon monoxide in these complexes. The low-temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectra of the seven-co-ordinate mixed dithiocarbamate complex [$W(CO)_2(PPh_3)(S_2CNMe_2)\{S_2CN(CH_2Ph)_2\}$] **25** shows carbonyl resonances at δ 204.62, 207.42, 212.23 and 212.62 ppm. From these data it appears that there is no carbonyl ligand in the capping position (no very low-field resonance) which is confirmed by the X-ray crystal structure[24] of the related bis(diethyldithiocarbamate) complex [$W(CO)_2(PPh_3)(S_2CNEt_2)_2$] shown below, which has a 4:3 tetragonal base–trigonal base geometry.



Scheme 1 (*i*) Na[$S_2CNR'_2$]; (*ii*) L = PPh_3, −CO; (*iii*) L = $AsPh_3$ or $SbPh_3$, −$AsPh_3$ or $SbPh_3$



The bis(acetonitrile)molybdenum complex [$MoI_2(CO)_3(NCMe)_2$] reacts in CH_2Cl_2 with 2 equivalents of Na[S_2CNEt_2]·$3H_2O$ eventually to afford the oxide [$Mo_2O_3(S_2CNEt_2)_4$] (see Experimental section) previously reported by Colton and Rose.[23] They prepared this type of complex by oxidation in acetone of [$Mo(CO)_2L(S_2CNR_2)_2$]. It could be that the water of crystallisation in Na[S_2CNEt_2]·$3H_2O$ is providing the oxygen for the formation of the oxo-complex [$Mo_2O_3(S_2CNEt_2)_4$]. It is interesting that they found[23] the oxidation of [$Mo(CO)_2L(S_2CNR_2)_2$] in CCl_4–benzene gave oxides of empirical formulae [$MoO_2(S_2CNR_2)_2$]. As expected, reaction of the tungsten complex [$WI_2(CO)_3(NCMe)_2$] with 2 equivalents of Na[S_2CNEt_2]·$3H_2O$ afforded the tricarbonyl seven-co-ordinate compound [$W(CO)_3(S_2CNEt_2)_2$] **28**. Tricarbonyl tungsten bis(dithiocarbamates) of this type have been previously reported, and the X-ray crystal structure of [$W(CO)_3(S_2CNMe_2)_2$] has been determined and is shown below.[25]



Reaction of the molybdenum complexes [$MoI_2(CO)_3(NCMe)L$] (L = PPh_3, $AsPh_3$ and $SbPh_3$) with 2 equivalents of Na[$S_2CN(CH_2Ph)_2$] afforded the seven-co-ordinate complexes [$Mo(CO)_2L\{S_2CN(CH_2Ph)_2\}_2$] which were identified by infrared spectroscopy, *e.g.* ν(CO)/cm^{-1} ($CHCl_3$) 1920 and 1840 (L = PPh_3), 1922 and 1835 (L = $AsPh_3$) and 1925 and 1840 (L = $SbPh_3$). These complexes were extremely air-sensitive and it was difficult to obtain satisfactory analytical data. However, the compound $[Mo(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ **29** was isolated and fully characterised. The considerably more air-stable tungsten complexes $[W(CO)_2L\{S_2CN(CH_2Ph)_2\}_2]$ **30**–**32** were prepared by treating $[WI_2(CO)_3(NCMe)L]$ *in situ* with 2 equivalents of $Na[S_2CN(CH_2Ph)_2]$. The low-temperature (−70 °C, CD_2Cl_2) ^{13}C NMR spectra of **30** and **32** showed carbonyl resonances at δ 207.35 and 212.68 and 208.06, 208.33 and 209.59 ppm respectively. These resonances are typical for carbonyl ligands in normal octahedral environments and the structure is likely to be similar to that shown for $[W(CO)_2(PPh_3)(S_2CNEt_2)_2]$,[24] *i.e.* a 4:3 tetragonal base–trigonal base geometry.

Experimental

All reactions described were carried out under an atmosphere of dry nitrogen unless otherwise stated using standard Schlenk-line techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared by the published procedure.[17] All chemicals used were purchased from commercial sources. Proton and ^{13}C NMR spectra were recorded on either a JEOL FX60 or a Bruker WH 400 spectrometer and calibrated against tetramethylsilane, infrared spectra on a Perkin-Elmer 197 spectrophotometer. Elemental analysis (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas) by Mr. E. Lewis of the Department of Chemistry, University of Wales, Bangor. Molecular weights were determined by Rast's method[19] using camphor (bornan-2-one) as the solvent. Magnetic susceptibilities were determined using a Johnson-Matthey magnetic susceptibility balance.

$[\{Mo(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$ **1**.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $Na[S_2CN(CH_2Ph)_2]$ (0.286 g, 0.968 mmol) and MeOH (10 cm^3). The mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the black crystalline solid $[\{Mo(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$ (yield = 0.35 g, 62%) which was recrystallised from CH_2Cl_2; M_r 1094 (calc. 1158).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with an equimolar quantity of $Na[S_2CN(CH_2Ph)_2]$ afforded $[\{W(\mu\text{-}I)(CO)_3[S_2CN(CH_2Ph)_2]\}_2]$ **2**. See Table 1 for colour and yield; M_r 1027 (calc. 1334).

$[WI(CO)_3(SbPh_3)(S_2CNMe_2)]$ **14**.—To $[WI_2(CO)_3(NCMe)_2]$ (0.222 g, 0.368 mmol) dissolved in CH_2Cl_2–MeOH (1:1, 20 cm^3) with continuous stirring under a stream of nitrogen was added $SbPh_3$ (0.130 g, 0.368 mmol). After stirring for 5 min, $Na[S_2CNMe_2]\cdot 2H_2O$ (0.066 g, 0.368 mmol) was added and the mixture stirred for 25 min. Removal of solvent *in vacuo* afforded a brown powder which was dissolved in CH_2Cl_2 and filtered. Removal of solvent *in vacuo* gave orange crystals of $[WI(CO)_3(SbPh_3)(S_2CNMe_2)]$ **14**; yield of pure product = 0.206 g, 65%.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L (L = PPh_3, $AsPh_3$ or $SbPh_3$) and $Na[S_2CNMe_2]\cdot 2H_2O$ gave the complexes $[MI(CO)_3L(S_2CNMe_2)]$ **3**–**5**, **12** and **13**. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L]$ and $Na[S_2CNMe_2]\cdot 2H_2O \longrightarrow [MI(CO)_3L(S_2CNMe_2)] + 2NCMe + NaI$ at 25 °C are: **3** (M = Mo), L = PPh_3, 1 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 30 min; **4** (M = Mo), L = $AsPh_3$, 3 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 27 min; **5** (M = Mo), L = $SbPh_3$, 5 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 25 min. Similar times were recorded for the tungsten complexes **12**–**14**. See Table 1 for colours and yields.

$[MoI(CO)_3(PPh_3)(S_2CNEt_2)]$ **6**.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.21 g, 0.407 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.107 g, 0.408 mmol). After stirring for 1 min, $Na[S_2CNEt_2]\cdot 3H_2O$ (0.092 g, 0.408 mmol) was added and the mixture was stirred for 2 h. After filtration, removal of solvent *in vacuo* gave brown crystals of $[MoI(CO)_3(PPh_3)(S_2CNEt_2)]$ **6** (yield = 0.16 g, 55%), which were recrystallised from CH_2Cl_2.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L (L = PPh_3, $AsPh_3$ or $SbPh_3$) and $Na[S_2CNEt_2]\cdot 3H_2O$ gave the complexes $[MI(CO)_3L(S_2CNEt_2)]$. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L]$ and $Na[S_2CNEt_2]\cdot 3H_2O \longrightarrow [MI(CO)_3L(S_2CNEt_2)] + 2NCMe$ at 25 °C are: **6** (M = Mo), L = PPh_3, 1 min; $Na[S_2CNEt_2]\cdot 3H_2O$, 120 min; **7** (M = Mo), L = $AsPh_3$, 3 min; $Na[S_2CNEt_2]\cdot 3H_2O$, 66 min; **8** (M = Mo), L = $SbPh_3$, 5 min; $Na[S_2CNEt_2]\cdot 3H_2O$, 180 min. Similar times were recorded for the tungsten complexes **15**–**17**. See Table 1 for colours and yields.

$[MoI(CO)_3(PPh_3)\{S_2CN(CH_2Ph)_2\}]$ **9**.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.969 mmol). After stirring for 1 min, $Na[S_2CN(CH_2Ph)_2]$ (0.268 g, 0.968 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the black crystalline solid $[MoI(CO)_3(PPh_3)\{S_2CN(CH_2Ph)_2\}]$ **9** (yield 0.47 g, 58%), which was recrystallised from CH_2Cl_2.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with L (L = PPh_3, $AsPh_3$ or $SbPh_3$) and $Na[S_2CN(CH_2Ph)_2]$ gave the complexes $[MI(CO)_3L\{S_2CN(CH_2Ph)_2\}]$. Reaction times for $[MI_2(CO)_3(NCMe)_2] + L \longrightarrow [MI_2(CO)_3(NCMe)L]$ and $Na[S_2CN(CH_2Ph)_2] \longrightarrow [MI(CO)_3L\{S_2CN(CH_2Ph)_2\}] + 2NCMe$ at 25 °C are: **9** (M = Mo), L = PPh_3, 1 min; $Na[S_2CN(CH_2Ph)_2]$, 18 h; **10** (M = Mo), L = $AsPh_3$, 3 min: $Na[S_2CN(CH_2Ph)_2]$, 18 h; **11** (M = Mo), L = $SbPh_3$, 5 min; $Na[S_2CN(CH_2Ph)_2]$, 18 h. Similar times were recorded for the tungsten complexes **18**–**20**. See Table 1 for colours and yields.

Reactions of $[MoI(CO)_3L(S_2CNR_2)]$ *with* $Na[S_2CNR'_2]$.—$[MoI(CO)_3(PPh_3)(S_2CNMe_2)]$ *with* $Na[S_2CNEt_2]$. To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.969 mmol). After stirring for 1 min, $Na[S_2CNMe_2]\cdot 2H_2O$ (0.174 g, 0.969 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 2 h, after which $Na[S_2CNEt_2]\cdot 3H_2O$ (0.218 g, 0.969 mmol) and MeOH (10 cm^3) were added and the mixture stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give an orange product which rapidly formed a purple product, which was washed in diethyl ether to give $[Mo_2O_3(S_2CNMe_2)_2(S_2CNEt_2)_2]$ (yield 0.27 g, 72%) and recrystallised from CH_2Cl_2 (Found: C, 25.0; H, 4.3; N, 7.0. $C_{16}H_{32}Mo_2N_4O_3S_8$ requires C, 24.7; H, 4.2; N, 7.2%). ^1H NMR ($CDCl_3$, 25 °C): δ 1.2, 1.32, 1.43 (t, *J* 6, 12 H, CH_2CH_3), 3.42 (s, 12 H, NCH_3), 3.62, 3.76, 3.88 and 4.0 (q, *J* 7.2 Hz, 8 H, CH_2CH_3).

Similar reactions of $[MoI_2(CO)_3(NCMe)_2]$ with L (L = $AsPh_3$ or $SbPh_3$), followed by $Na[S_2CNMe_2]\cdot 2H_2O$ and $Na[S_2CNEt_2]\cdot 3H_2O$ gave the purple complex $[Mo_2O_3(S_2CNMe_2)_2(S_2CNEt_2)_2]$.

Reaction times for $[MoI(CO)_3NCMe)_2] + L \longrightarrow [MoI_2(CO)_3(NCMe)L] + Na[S_2CNMe_2]\cdot 2H_2O$ and $Na[S_2CNEt_2]\cdot 3H_2O \longrightarrow [Mo_2O_3(S_2CNMe_2)_2(S_2CNEt_2)_2] + 2NCMe$ at 25 °C are: M = Mo, L = $AsPh_3$, 3 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 2 h; $Na[S_2CNEt_2]\cdot 3H_2O$, 18 h; yield = 66% (Found: C, 24.8; H, 4.2; N, 6.8. $C_{16}H_{32}Mo_2N_4O_3S_8$ requires C, 24.7; H, 4.2; N, 7.2%); M = Mo, L = $SbPh_3$, 5 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 2 h; $Na[S_2CNEt_2]\cdot 3H_2O$, 18 h; yield = 45% (Found: C, 24.6; H, 4.2; N, 6.8. $C_{16}H_{32}Mo_2N_4O_3S_8$ requires C, 24.7; H, 4.2; N, 7.2%).

$[Mo(CO)_2(PPh_3)(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$ **21**.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.969 mmol). After stirring for 1 min, $Na[S_2CNEt_2]\cdot 3H_2O$ (0.218 g, 0.969 mmol) and MeOH were added. The mixture was stirred for 2 h after which $Na[S_2CN(CH_2Ph)_2]$ (0.268 g, 0.969 mmol) and MeOH (10 cm^3) were added and the mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the brown crystalline product $[Mo(CO)_2(PPh_3)(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$ **21**, yield = 0.67 g (82%), which was recrystallised from CH_2Cl_2.

Similar reactions of $[MoI_2(CO)_3(NCMe)_2]$ with $SbPh_3$ followed by $Na[S_2CNMe_2]\cdot 2H_2O$ or $Na[S_2CNEt_2]\cdot 3H_2O$ and $Na[S_2CN(CH_2Ph)_2]$ gave the complexes $[Mo(CO)_2(SbPh_3)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}]$ (R = Me or Et). Reaction times for $[MoI_2(CO)_3(NCMe)_2] + SbPh_3 \longrightarrow [MI_2(CO)_3(NCMe)(SbPh_3)] + Na[S_2CNMe_2]\cdot 2H_2O$ or $Na[S_2CNEt_2]\cdot 3H_2O$ followed by $Na[S_2CN(CH_2Ph)_2] \longrightarrow [Mo(CO)_2(SbPh_3)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}] + 2NCMe$ at 25 °C are: **22** (M = Mo), $SbPh_3$, 5 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 2 h; $Na[S_2CN(CH_2Ph)_2]$, 18 h; **23** (M = Mo), $SbPh_3$, 5 min; $Na[S_2CNEt_2]\cdot 3H_2O$, 2 h; $Na[S_2CN(CH_2Ph)_2]$, 18 h. See Table 1 for colours and yields.

Reactions of $[WI(CO)_3L(S_2CNR_2)]$ *with* $Na[S_2CNR'_2]$.—$[W(CO)_2(PPh_3)(S_2CNMe_2)(S_2CNEt_2)]$ **24**. To $[WI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.2172 g, 0.828 mmol). After stirring for 1 min, $Na[S_2CNMe_2]\cdot 2H_2O$ (0.148 g, 0.826 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 2 h, after which $Na[S_2CNEt_2]\cdot 3H_2O$ (0.187 g, 0.829 mmol) and MeOH (10 cm^3) were added, and the mixture stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give a bright red product $[W(CO)_2(PPh_3)(S_2CNMe_2)(S_2CNEt_2)]$ **24** (yield = 0.54 g, 85%), which was recrystallised from CH_2Cl_2.

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with PPh_3 and $Na[S_2CNR_2]$ (R = Me or Et) followed by $Na[S_2CN(CH_2Ph)_2]$ gave the complexes $[W(CO)_2(PPh_3)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}]$. Reaction times for $[WI(CO)_2(NCMe)_2] + PPh_3 \longrightarrow [WI_2(CO)_3(NCMe)(PPh_3)]$ and $Na[S_2CNR_2]\cdot xH_2O$ (R = Me or Et, x = 2 or 3) followed by $Na[S_2CN(CH_2Ph)_2] \longrightarrow [W(CO)_2(PPh_3)(S_2CNR_2)\{S_2CN(CH_2Ph)_2\}] + 2NCMe$ at 25 °C are: **25** (M = W), PPh_3, 1 min; $Na[S_2CNMe_2]\cdot 2H_2O$, 2 h; $Na[S_2CN(CH_2Ph)_2]$, 18 h; **26** (M = W), PPh_3, 1 min; $Na[S_2CNEt_2]\cdot 3H_2O$, 2 h; $Na[S_2CN(CH_2Ph)_2]$, 18 h.

$[W(CO)_3(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$ **27**. To $[WI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $AsPh_3$ (0.2535 g, 0.828 mmol). After stirring for 3 min, $Na[S_2CNEt_2]\cdot 3H_2O$ (0.187 g, 0.829 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 2 h, after which $Na[S_2CN(CH_2Ph)_2]$ (0.245 g, 0.827 mmol) and MeOH (10 cm^3) were added and the mixture stirred for 18 h. The solvents were removed *in vacuo*, and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to afford a golden-brown product which after washing with diethyl ether and recrystallisation from CH_2Cl_2 gave the brown complex $[W(CO)_3(S_2CNEt_2)\{S_2CN(CH_2Ph)_2\}]$ **27** (yield of pure product = 0.12 g, 21%).

Reactions of $[MI_2(CO)_3(NCMe)_2]$ *with* 2 *equivalents of* $Na[S_2CNEt_2]\cdot 3H_2O$.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.25 g, 0.485 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $Na[S_2CNEt_2]\cdot 3H_2O$ (0.218 g, 0.968 mmol). After stirring for 160 min, and filtration, removal of the solvent *in vacuo* gave purple crystals of $[Mo_2O_3(S_2CNEt_2)_4]$, yield of pure product = 0.14 g (69%) (Found: C, 28.5; H, 4.8; N, 6.6. $C_{20}H_{40}Mo_2N_4O_3S_8$ requires C, 28.8; H, 4.8; N, 6.7%).

To $[WI_2(CO)_3(NCMe)_2]$ (0.23 g, 0.381 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring was added $Na[S_2CNEt_2]\cdot 3H_2O$ (0.172 g, 0.763 mmol). After stirring for 90 min and filtration, removal of solvent *in vacuo* gave brown crystals of $[W(CO)_3(S_2CNEt_2)_2]$ **28**, yield of pure product = 0.12 g (56%).

Reactions of $[MI_2(CO)_3(NCMe)L]$ *with* 2 *equivalents of* $Na[S_2CN(CH_2Ph)_2]$.—To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.254 g, 0.968 mmol). After stirring for 1 min, $Na[S_2CN(CH_2Ph)_2]$ 0.572 g, 1.936 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the purple product $[Mo_2O_3\{S_2CN(CH_2Ph)_2\}_4]$ (yield 0.26 g, 47%) which was washed with ether to remove any unco-ordinated PPh_3 and recrystallised from CH_2Cl_2 (Found: C, 54.2; H, 4.2; N, 4.4. $C_{60}H_{56}Mo_2N_4O_3S_8$ requires C, 54.2; H, 4.3; N, 4.2%).

A similar reaction of $[MoI_2(CO)_3(NCMe)_2]$ with $AsPh_3$, followed by 2 equivalents of $Na[S_2CN(CH_2Ph)_2]$ gave the identical purple complex $[Mo_2O_3\{S_2CN(CH_2Ph)_2\}_4]$. Reaction times for $[MoI_2(CO)_3(NCMe)_2] + AsPh_3 \longrightarrow [MoI_2(CO)_3(NCMe)(AsPh_3)] + 2Na[S_2CN(CH_2Ph)_2] \longrightarrow [Mo_2O_3\{S_2CN(CH_2Ph)_2\}_4]$: $AsPh_3$, 3 min; $2Na[S_2CN(CH_2Ph)_2]$, 18 h (Found: C, 54.4; H, 4.3; N, 4.7. $C_{60}H_{56}Mo_2N_4O_3S_8$ requires C, 54.2; H, 4.3; N, 4.2%), yield = 42%. ^1H NMR ($CDCl_3$, 25 °C): δ 4.94 (s, 16 H, CH_2Ph) and 7.33 (s, 40 H, Ph).

$[Mo(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ **29**. To $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.969 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added $SbPh_3$ (0.342 g, 0.969 mmol). After stirring for 5 min, $Na[S_2CN(CH_2Ph)_2]$ (0.572 g, 1.936 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the brown crystalline product $[Mo(CO)_2(SbPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ **29** (yield = 0.55 g, 54%), which was recrystallised from CH_2Cl_2.

$[W(CO)_2(PPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ **30**. To $[WI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.2172 g, 0.828 mmol). After stirring for 1 min, $Na[S_2CN(CH_2Ph)_2]$ (0.493 g, 1.654 mmol) and MeOH (10 cm^3) were added. The mixture was stirred for 18 h. The solvents were removed *in vacuo* and the resulting product resolvated in CH_2Cl_2 and filtered to remove NaI. The solvent was removed *in vacuo* to give the red crystalline product $[W(CO)_2(PPh_3)\{S_2CN(CH_2Ph)_2\}_2]$ **30** (yield = 0.72 g, 83%), which was recrystallised from CH_2Cl_2.

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with L (L = $AsPh_3$ or $SbPh_3$) and 2 equivalents of $Na[S_2CN(CH_2Ph)_2]$ gave the complexes $[W(CO)_2L\{S_2CN(CH_2Ph)_2\}_2]$. Reaction times for $[WI_2(CO)_3(NCMe)_2] + L \longrightarrow [WI_2(CO)_3(NCMe)L]$ and $2Na[S_2CN(CH_2Ph)_2] \longrightarrow [W(CO)_2L\{S_2CN(CH_2Ph)_2\}_2] + 2NCMe$ at 25 °C are: **31**, L = $AsPh_3$, 3 min; $2Na[S_2CN(CH_2Ph)_2]$, 18 h; **32**, L = $SbPh_3$, 5 min; $2Na[S_2CN(CH_2Ph)_2]$, 18 h. See Table 1 for colours and yields.

References

1 D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **23**, 233.
2 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.
3 H. B. Abrahamson, M. L. Freeman, M. B. Hussain and D. Van der Helm, *Inorg. Chem.*, 1984, **23**, 2286.
4 C. J. Young, S. A. Roberts and J. H. Enemark, *Inorg. Chem.*, 1986, **25**, 3667.

5 J. W. McDonald, J. L. Corbin and W. E. Newton, *J. Am. Chem. Soc.*, 1975, **97**, 1970.

6 E. A. Maata, R. A. D. Wentworth, W. E. Newton, J. W. McDonald and G. D. Watt, *J. Am. Chem. Soc.*, 1978, **100**, 1320.

7 R. Colton, G. R. Scollary and I. B. Tomkins, *Aust. J. Chem.*, 1968, **21**, 15.

8 R. Colton and G. R. Scollary, *Aust. J. Chem.*, 1968, **21**, 1427.

9 G. J.-J. Chen, R. O. Yelton and I. B. Tomkins, *Inorg. Chim. Acta*, 1977, **22**, 249.

10 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 6568.

11 J. L. Tempeton and B. C. Ward, *Organometallics*, 1982, **1**, 1007.

12 J. A. Broomhead and C. G. Young, *Aust. J. Chem.*, 1982, **35**, 277.

13 B. Zhuang, L. Huang, L. He, Y. Yang and J. Lu, *Inorg. Chim. Acta*, 1988, **145**, 225.

14 E. Carmona, K. Doppert, J. M. Marin, M. L. Poreda, L. Sanchez and R. Sanchez-Delgado, *Inorg. Chem.*, 1984, **23**, 530.

15 J. L. Templeton, *Adv. Chem. Ser.*, 1979, **173**, 263.

16 P. K. Baker and S. G. Fraser, *Transition Met. Chem. (Weinheim, Ger.)*, 1986, **11**, 273.

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

18 P. K. Baker and S. G. Fraser, *Transition Met. Chem. (Weinheim, Ger.)*, 1987, **12**, 560.

19 F. G. Mann and B. C. Saunders, *Practical Organic Chemistry*, Longmans Green and Co., London, 1954, pp. 342–344.

20 F. A. Cotton, L. R. Falvello and J. H. Meadows, *Inorg. Chem.*, 1985, **24**, 514.

21 M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67.

22 R. Colton and J. Kevekordes, *Aust. J. Chem.*, 1982, **35**, 895.

23 R. Colton and G. G. Rose, *Aust. J. Chem.*, 1970, **23**, 1111.

24 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1981, **103**, 3743.

25 J. L. Templeton and B. C. Ward, *Inorg. Chem.*, 1980, **19**, 1753.

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