Inorganica Chimica Acta, *162* (1989) 179–181

Seven-coordinate Complexes. Reactions of the Complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with Bidentate Nitrogen Donor Ligands

PAUL K. BAKER* and ANTONY J. QUINLAN

Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW (U.K.)

(Received February 3, 1989; revised May 4, 1989)

Although a large number of seven-coordinate dihalocarbonyl compounds of molybdenum(II) and tungsten(II) of the type $[\mathrm{MX_2(CO)_3L_2}]$ (M = Mo or W; X = Cl, Br or I; L = monodentate donor ligands; $\mathrm{L_2}$ = bidentate donor ligands) are known [1–11] very few tin halide complexes of this type have been reported. In 1968, Lewis and coworkers [12] reported the reaction of the zero-valent molybdenum complex $[\mathrm{Mo(CO)_4(bipy)}]$ (bipy = 2,2′-bipyridine) with one equivalent of $\mathrm{SnCl_4}$ to give the seven-coordinate compound $[\mathrm{MoCl(SnCl_3)(CO)_3(bipy)}]$. Kummer and Graham [13] extended this type of reaction by using $\mathrm{SnX_4}$ (X = Br and I) and $\mathrm{GeX_4}$ (X = Cl, Br or I). More recently, in 1985 Panizo and Cano [14] have reported the synthesis of the seven-coordinate compounds $[\mathrm{MoCl(SnCl_3)(CO)_2\{P(4\text{-}XC_6H_4)_3\}(bipy)}]$ (X = F, Cl or Me). In the same year, Bell and Walton [15] reported the reaction of the zero-valent complex $[\mathrm{Mo(CO)_4(RN{:}CHCH{:}NR)}]$ (R = $\mathrm{Pr^i}$, $\mathrm{Bu^t}$ or Cy) with $\mathrm{SnCl_4}$, to give the seven-coordinate compounds $[\mathrm{MoCl(SnCl_3)(CO)_3(RN{:}CHCH{:}NR)}]$.

We have recently described the synthesis of the reactive seven-coordinate bisacetonitrile complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ [16]. The complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ is prepared *in situ* by reacting the trisacetonitrile compound $[\mathrm{Mo(CO)_3(NCMe)_3}]$ [17] with an equimolar quantity of $\mathrm{SnCl_4}$. In this paper we wish to describe its reactions with bidentate nitrogen donor ligands.

Experimental

The complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ was prepared by the published method [16]. The 1,4-diaza-1,3-butadiene ligands RN:CHCH:NR (R = $\mathrm{Bu^i}$, Cy and *p*-MeOPh) were prepared by the published method [18–20]. All chemicals were purchased from commercial sources except $[\mathrm{Mo(CO)_6}]$, which was kindly donated by Amax Speciality Metals U.K. Ltd.

Elemental analyses (C, H and N) were determined using a Carlo Erba elemental analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer. Magnetic susceptibility measurements were measured on a Johnson-Matthey magnetic susceptibility balance.

$[\mathrm{MoCl(SnCl_3)(CO)_3(bipy)}]$ (1)

To $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ (0.50 g, 0.957 mmol) dissolved in acetone (15 $\mathrm{cm^3}$) with continuous stirring under a stream of dry nitrogen, was added bipy (0.149 g, 0.957 mmol). After stirring the solution for 2 h, removal of the solvent *in vacuo* and washing with 60–80 petroleum ether and diethyl ether gave purple crystals of $[\mathrm{MoCl(SnCl_3)(CO)_3(bipy)}]$ (**1**) (yield = 0.42 g, 74%), which were recrystallised from acetone.

Similar reactions of $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with one equivalent of $\mathrm{N\hat{}N}$ ($\mathrm{N\hat{}N}$ = 1,10-phenanthroline, $\mathrm{Bu^iN{:}CHCH{:}NBu^i}$, CyN:CHCH:NCy and *p*-MeOPhN:CHCH:NPhOMe-*p*) gave the compounds $[\mathrm{MoCl(SnCl_3)(CO)_3(N\hat{}N)}]$ (**2–5**) (See Table 1 for physical and analytical data).

$[\mathrm{Mo(SnCl_3)(CO)_2(Bu^iN{:}CHCH{:}NBu^i)_2]Cl}$ (8)

To $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ (0.5 g, 0.957 mmol) dissolved in acetone (15 $\mathrm{cm^3}$) with continuous stirring under a stream of dry nitrogen, was added $\mathrm{Bu^iN{:}CHCH{:}NBu^i}$ (0.32 g, 1.914 mmol). After stirring the solution for 2 h, removal of the solvent *in vacuo* and washing with 60–80 petroleum ether and diethyl ether gave light brown crystals of $[\mathrm{Mo(SnCl_3)(CO)_2(Bu^iN{:}CHCH{:}NBu^i)_2]Cl}$ (**8**) (yield = 0.52 g, 72%) which were recrystallised from acetone.

Similar reactions of $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with two equivalents of $\mathrm{N\hat{}N}$ ($\mathrm{N\hat{}N}$ = 2,2′-bipyridine, 1,10-phenanthroline, CyN:CHCH:NCy and *p*-MeOPhN:CHCH:NPhOMe-*p*) afford the cationic complexes $[\mathrm{Mo(SnCl_3)(CO)_2(N\hat{}N)_2]Cl}$ (**6, 7, 9, 10**) (See Table 1 for physical and analytical data).

Results and Discussion

Reaction of the seven-coordinate bisacetonitrile complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with an equimolar quantity of the bidentate nitrogen donor ligands $\mathrm{N\hat{}N}$ ($\mathrm{N\hat{}N}$ = 2,2′-bipyridine, 1,10-phenanthroline, $\mathrm{Bu^iN{:}CHCH{:}NBu^i}$, CyN:CHCH:NCy and *p*-MeOPhN:CHCH:NPhOMe-*p*) in acetone at room temperature affords the substituted products $[\mathrm{MoCl(SnCl_3)(CO)_3(N\hat{}N)}]$ (**1–5**) in high yield. In contrast, reaction of the bisacetonitrile complex $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with two equivalents of $\mathrm{N\hat{}N}$ ($\mathrm{N\hat{}N}$ = 2,2′-bipyridine, 1,10-phenanthroline, $\mathrm{Bu^iN{:}CHCH{:}}$-

---

*Author to whom correspondence should be addressed.

0020-1693/89/\$3.50

TABLE 1. Physical and analytical data for the complexes $[\mathrm{MoCl(SnCl_3)(CO)_3(N^\frown N)}]$ and $[\mathrm{Mo(SnCl_3)(CO)_2(N^\frown N)_2}]\mathrm{Cl}$

Complex	Colour	Yield (%)	Analysis (%)[a]		
			C	H	N
$[\mathrm{MoCl(SnCl_3)(CO)_3(bipy)}]$ (**1**)	purple	74	26.1 (25.9)	1.3 (2.0)	4.7 (4.6)
$[\mathrm{MoCl(SnCl_3)(CO)_3(phen)}]$ (**2**)	red	75	29.1 (29.1)	1.7 (1.3)	4.7 (4.5)
$[\mathrm{MoCl(SnCl_3)(CO)_3(Bu^iN{:}CHCH{:}NBu^i)}]$ (**3**)	light brown	83	25.5 (25.6)	3.0 (3.3)	5.1 (4.7)
$[\mathrm{MoCl(SnCl_3)(CO)_3(CyN{:}CHCH{:}NCy)}]$ (**4**)	red	62	31.1 (30.8)	4.6 (3.6)	3.9 (4.2)
$[\mathrm{MoCl(SnCl_3)(CO)_3(}p\text{-}\mathrm{MeOPhN{:}CHCH{:}NPhOMe\text{-}}p)]$ (**5**)	brown	50	32.0 (32.2)	3.1 (2.3)	4.1 (4.0)
$[\mathrm{Mo(SnCl_3)(CO)_2(bipy)_2}]\mathrm{Cl}$ (**6**)	red	73	36.8 (36.5)	2.3 (2.2)	7.1 (7.7)
$[\mathrm{Mo(SnCl_3)(CO)_2(phen)_2}]\mathrm{Cl}$ (**7**)	dark brown	67	40.4 (40.4)	2.2 (2.1)	6.8 (7.1)
$[\mathrm{Mo(SnCl_3)(CO)_2(Bu^iN{:}CHCH{:}NBu^i)_2}]\mathrm{Cl}$ (**8**)	light brown	72	35.8 (35.3)	4.9 (5.3)	7.5 (7.5)
$[\mathrm{Mo(SnCl_3)(CO)_2(CyN{:}CHCH{:}NCy)_2}]\mathrm{Cl}$ (**9**)	dark red	85	40.6 (42.2)	6.2 (5.6)	5.9 (6.6)
$[\mathrm{Mo(SnCl_3)(CO)_2(}p\text{-}\mathrm{MeOPhN{:}CHCH{:}NPhOMe\text{-}}p)_2]\mathrm{Cl}$ (**10**)	dark red	58	42.0 (43.0)	3.4 (3.4)	6.3 (5.9)

[a] Calculated values in parentheses.

$\mathrm{NBu^i}$, CyN:CHCH:NCy or p-MeOPhN:CHCH:NPhOMe-p) gave the cationic complexes $[\mathrm{Mo(SnCl_3)(CO)_2(N^\frown N)_2}]\mathrm{Cl}$ (**6**–**10**). The seven-coordinate molybdenum complexes **1**–**10** have been characterised by elemental analysis (C, H and N) (Table 1) and infrared spectroscopy (Table 2). Magnetic susceptibility measurements on the seven-coordinate compounds show that the complexes are diamagnetic.

TABLE 2. Infrared data[a] for the complexes $[\mathrm{MoCl(SnCl_3)(CO)_3(N^\frown N)}]$ and $[\mathrm{Mo(SnCl_3)(CO)_2(N^\frown N)_2}]\mathrm{Cl}$

Complex	$\nu(\mathrm{C{\equiv}O})$ ($\mathrm{cm^{-1}}$)	$\nu(\mathrm{C{=}N})$ ($\mathrm{cm^{-1}}$)
1	2030(s), 1935(s) and 1900(m)	
2	2010(s), 1980(s) and 1920(m)	
3	2080(m), 2050(m) and 1978(s)	1599(s)
4	2005(m), 1965(s) and 1900(s)	1495(m)
5	2060(s), 1984(s) and 1910(m)	1525(m)
6	1879(s) and 1820(s)	
7	1900(s) and 1840(s)	
8	1910(s) and 1865(s)	1460(m)
9	1900(m) and 1840(s)	1410(s)
10	1930(m) and 1880(s)	1442(s)

[a] Spectra were recorded as thin films in $\mathrm{CHCl_3}$ between NaCl plates; m, medium; s, strong.

The neutral complexes $[\mathrm{MoCl(SnCl_3)(CO)_3(bipy)}]$ (**1**) [12] and $[\mathrm{MoCl(SnCl_3)(CO)_3(CyN{:}CHCH{:}NCy)}]$ (**4**) [15] have been previously described, whereas **2**, **3** and **5**–**10** are new compounds. The neutral (**1**–**5**) and cationic (**6**–**10**) complexes are moderately stable when stored under nitrogen in the dark; however they decompose when exposed to air in solution. The compounds **1**–**10** are moderately soluble in acetone and only sparingly soluble in chlorinated sovlents such as $\mathrm{CHCl_3}$ and $\mathrm{CH_2Cl_2}$. They are insoluble in hydrocarbon solvents and diethyl ether. The reactions of $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ with $\mathrm{N^\frown N}$ are considerably slower than the reactions of seven-coordinate diiodo compounds $[\mathrm{MI_2(CO)_3(NCMe)_2}]$ (M = Mo or W) with bidentate nitrogen donor ligands $\mathrm{N^\frown N}$ ($\mathrm{N^\frown N}$ = 2,2′-bipyridine and 1,10-phenanthroline) to give $[\mathrm{MI_2(CO)_3(N^\frown N)}]$ [21].

Two equivalents of $\mathrm{N^\frown N}$ ($\mathrm{N^\frown N}$ = 2,2′-bipyridine, 1,10-phenanthroline, $\mathrm{Bu^iN{:}CHCH{:}NBu^i}$, CyN:CHCH:NCy and p-MeOPhN:CHCH:NPhOMe-p) react with $[\mathrm{MoCl(SnCl_3)(CO)_3(NCMe)_2}]$ to give the cationic dicarbonyl compounds $[\mathrm{Mo(SnCl_3)(CO)_2N^\frown N)_2}]\mathrm{Cl}$. These cationic dicarbonyl compounds (**6**–**10**) are probably prepared via reaction of $[\mathrm{MoCl(SnCl_3)(CO)_3(N^\frown N)}]$ with $\mathrm{N^\frown N}$, which displaces a carbon monoxide ligand and an ionisable chloride ion. These cationic dicarbonyl compounds are analogous to previously reported complexes of the types $[MX(CO)_2(L^\frown L)_2]X$ (M = Mo, X = Cl or Br; $L^\frown L$ = 2,2′-bipyridine; M = Mo, X = Cl, $L^\frown L$ = 1,10-phenanthroline [22]) and *cis*-$[MI(CO)_2(dmpe)_2]I$ (dmpe = $Me_2P(CH_2)PMe_2$; M = Mo [23, 24] or W [23]). The infrared spectra of the cationic seven-coordinate compounds $[Mo(SnCl_3)(CO)_2(N^\frown N)_2]Cl$ (**6**–**10**) all show two carbonyl bands between 1820 and 1930 cm^{-1}.

The vast majority of seven-coordinate complexes of molybdenum(II) and tungsten(II) have capped octahedral geometry [25], and since the infrared carbonyl pattern of **1**–**5** is similar to other $[MX_2(CO)_3(L^\frown L)]$ complexes which have been shown to have capped octahedral geometry [26–30], it is likely these tin halocarbonyl seven-coordinate complexes will exhibit capped octahedral geometry.

Acknowledgements

We wish to thank Amax Speciality Metals U.K. Ltd for their generous gift of $[Mo(CO)_6]$.

References

1 F. A. Cotton and B. F. G. Johnson, *Inorg. Chem., 3* (1964) 1609.
2 B. F. G. Johnson, *J. Chem. Soc., A* (1967) 475.
3 R. Colton, G. P. Scollary and I. B. Tomkins, *Aust. J. Chem., 21* (1968) 15.
4 W. S. Tsang, D. W. Meek and A. Wojcicki, *Inorg. Chem., 7* (1968) 1263.
5 R. Colton and C. J. Rix, *Aust. J. Chem., 22* (1969) 305.
6 J. A. Bowden and R. Colton, *Aust. J. Chem., 22* (1969) 905.
7 J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, (1970) 595.
8 R. Colton, *Coord. Chem. Rev., 6* (1971) 269.
9 A. D. Westland and N. Muriithi, *Inorg. Chem., 12* (1973) 2356.
10 P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta, 116* (1986) L1.
11 P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta, 130* (1987) 61.
12 K. Edgar, B. F. G. Johnson, J. Lewis and S. B. Wild, *J. Chem. Soc. A*, (1968) 2851.
13 R. Kummer and W. A. G. Graham, *Inorg. Chem., 7* (1968) 310.
14 M. Panizo and M. Cano, *J. Organomet. Chem., 287* (1985) 221.
15 A. Bell and R. A. Walton, *J. Organomet. Chem., 290* (1985) 341.
16 P. K. Baker and A. Bury, *J. Organomet. Chem., 359* (1989) 189.
17 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem., 1* (1962) 433.
18 L. A. Cort and N. R. Francis, *J. Chem. Soc.*, (1964) 2799.
19 J. M. Kleigman and R. K. Barnes, *Tetrahedron Lett., 22* (1970) 1859.
20 A. T. T. Hsieh and B. O. West, *J. Organomet. Chem., 112* (1976) 285.
21 P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta, 116* (1986) L3.
22 R. Colton and C. J. Rix, *Aust. J. Chem., 21* (1968) 1155.
23 J. A. Connor, G. K. McEwen and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, (1974) 589.
24 J. A. Connor, G. K. McEwen and C. J. Rix, *J. Less-Common Met., 36* (1974) 207.
25 M. G. B. Drew, *Prog. Inorg. Chem., 23* (1977) 67, and refs. cited therein.
26 M. G. B. Drew and C. J. Rix, *J. Organomet. Chem., 102* (1975) 467.
27 M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, (1972) 1329.
28 A. Mercer and J. Trotter, *Can. J. Chem., 52* (1974) 3331.
29 J. C. Dewan, K. Henrick, D. L. Keppert, K. R. Trigwell, A. H. White and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, (1975) 546.
30 M. G. B. Drew and A. P. Wolters, *Acta Crystallogr., Sect. B, 33* (1977) 205.