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Oxidation of $[Mo(CO)_3(NCMe)_3]$ with $SnCl_4$ to give the seven-coordinate compound $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$. Reactions of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with phosphine donor ligands

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Abstract

The trisacetonitrile complex $[Mo(CO)_3(NCMe)_3]$ reacts in situ with an equimolar quantity of $SnCl_4$ to give a quantitative yield of the new seven-coordinate complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$. This reacts with two equivalents of PPh_3 in acetone at room temperature to give a good yield of the stable complex $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$. Reaction of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with one equivalent of $PPh_2(CH_2)_nPPh_2$ ($n = 1$–3, 6) in acetone at room temperature gives the expected seven-coordinate species $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$.

Introduction

Although a wide range of dihalocarbonyl seven-coordinate compounds of molybdenum(II) and tungsten(II) of the type $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl, Br or I; L = neutral nitrogen, phosphine, arsine, or antimony donor ligands) have been reported [1–12], very few analogous halotin carbonyl complexes have been described. Some examples include $[MoCl(SnCl_3)(CO)_3(bipy)]$ [13], $[MoCl(SnCl_3)(CO)_2(bipy)\{P(C_6H_4X\text{-}p)_3\}]$ (X = F, Cl or CH_3) [14] and $[MCl(SnCl_3)(CO)_3(RN{=}CHCH{=}NR)]$ (M = Mo or W; R = ^{i}Pr, ^{n}Bu or Cy) [15].

In recent years we have been investigating the chemistry of the highly versatile diiodo seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) [16–19], which are prepared in quantitative yield by reaction of $[M(CO)_3(NCMe)_3]$ with an equimolar quantity of I_2 at 0 °C [20]. In this paper we describe the preparation by an analogous route of the new halotin seven-coordinate complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$, and its reactions with phosphine donor ligands.

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Results and discussion

Treatment of $[Mo(CO)_3(NCMe)_3]$ (prepared in situ by refluxing $[Mo(CO)_6]$ in acetonitrile for 24 h [21]) in situ with an equimolar amount of $SnCl_4$ rapidly gives a deep orange solution, which after removal of the solvent in vacuo affords a quantitative yield of the new seven-coordinate complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**). The complex is air-sensitive in the solid state and extremely air-sensitive in solution, but it can be stored under nitrogen in the solid state for several days. Complex **1** is only slightly soluble in chlorinated solvents such as $CHCl_3$ and CH_2Cl_2, but considerably more soluble in acetone. The complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**) was fully characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (see experimental). The complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**) is diamagnetic, as expected since **1** obeys the effective atomic number rule. Many attempts were made to prepare and isolate the analogous tungsten complex $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ by treating $[W(CO)_3(NCMe)_3]$ (prepared in situ) with one equivalent of $SnCl_4$. The expected oxidative reaction does occur, to give a bright orange solution that after removal of the solvent in vacuo gives a bright orange crystalline solid $[WCl(SnCl_3)(CO)_3(NCMe)_2]$, but this complex is considerably less stable than the molybdenum complex **1**, and so far it has not been possible to obtain satisfactory analytical data for it. However, the infrared spectrum of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ shows three carbonyl bands at $\nu(CO)$ 2017, 1978 and 1934 cm^{-1} and nitrile stretching bands at $\nu(CN)$ 2299, 2242(w) cm^{-1}, which are similar to those for **1** and the diiodide compounds previously described [20]. The room temperature ^1H NMR spectrum of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ shows the expected single resonance at $\delta(CDCl_3)$ 2.46 ppm. It is noteworthy that these relative stabilities are in contrast to those for diiodo systems, where the tungsten complex $[WI_2(CO)_3(NCMe)_2]$ is more stable than the molybdenum diiodo compound, and both are more stable than the dibromo complexes [20].

Colton and Kevekordes [22] have shown how ^{13}C NMR spectroscopy can be used to show whether there is a carbonyl ligand in the unique capping position in capped octahedral complexes. The low temperature spectra (−70 °C, $(CD_3)_2CO$) of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**) show a number of carbonyl resonances at δ 227.84, 226.29, 222.55, 212.75, 211.99, 211.95, 211.01, 210.10, 206.76, 206.36, 203.65 and 201.97 ppm in the carbonyl region, and hence there must be several different isomers in solution. This is in contrast to the result for $[WI_2(CO)_3(NCMe)_2]$, which showed carbonyl resonances at δ (−70 °C, CD_2Cl_2) 202.36 and 228.48 ppm with an intensity ratio of 2/1, in keeping with the crystal structure of $[WI_2(CO)_3(NCMe)_2]$ [23]. However the resonances at $\delta \simeq 227$ ppm for **1** are in the region expected for a carbonyl ligand in the unique capping position in a capped octahedral structure. Several unsuccessful attempts were made to grow a suitable single crystal of **1** for X-ray crystallography.

The complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**) reacts with two equivalents of PPh_3 in acetone at room temperature to give the stable seven-coordinate compound $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ (**2**) via substitution of the labile acetonitrile ligands. Compound **2** was fully characterised by elemental analysis (C, H and N) (Table 1) and IR and ^1H spectroscopy (Table 2), and shown to be diamagnetic by magnetic susceptibility measurements. This compound is considerably more stable than the

Table 1

Physical and analytical data for the complexes $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ and $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))	
			C	H
$[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ (2)	Yellow	98	48.6 (48.5)	2.9 (3.1)
$[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)PPh_2\}]$ (3)	Buff	99	41.4 (40.8)	3.2 (2.9)
$[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_2PPh_2\}]$ (4)	Orange-brown	97	40.8 (41.5)	3.1 (2.9)
$[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_3PPh_2\}]$ (5)	Orange	96	42.4 (42.3)	3.6 (3.1)
$[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_6PPh_2\}]$ (6)	Mustard-yellow	98	44.0 (44.3)	4.2 (3.6)

bisacetonitrile compound **1**. Attempts to prepare the 16 electron dicarbonyl compound $[MoCl(SnCl_3)(CO)_2(PPh_3)_2]$ by refluxing $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ in $CHCl_3$ for 24 h were unsuccessful; this was surprising, since Colton and coworkers [24] have found that the analogous dichloro and dibromo compounds $[MoX_2(CO)_3(PPh_3)_2]$ lose carbon monoxide to give $[MoX_2(CO)_2(PPh_3)_2]$ when refluxed in $CHCl_3$.

The bidentate phosphorus donor ligands $PPh_2(CH_2)_nPPh_2$ ($n = 1$–3 and 6) reacted with one equivalent of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ in acetone at room temperature to give the expected seven-coordinate compounds $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$ (**3–6**), which were fully characterised (Tables 1 and 2). Complexes **3–6** were found to be diamagnetic. Reaction of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with two equivalents of $PPh_2(CH_2)_2PPh_2$ in acetone at room temperature for 24 h gave $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_2PPh_2\}]$ and unchanged $PPh_2(CH_2)_2PPh_2$. This is in contrast to the reactions of the halide bridged dimers $[M(\mu\text{-}X)X(CO)_4]_2$

Table 2

IR[a] and ^1H NMR[b] data for the complexes $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ and $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$

Complex	$\nu(CO)$ (cm^{-1})	^1H NMR (δ) ppm
2	1961(s), 1943(s) and 1881(s)	7.1(m, Ph)
3	1980(s), 1953(s) and 1891(s)	7.5(m, 20H, Ph), 2.9(m, 2H, PCH_2)
4	2038(s), 1977(s) and 1946(s)	7.5(m, 20H, Ph), 3.07(m, 4H, PCH_2)
5	1949(s), 1885(s) and 1868(s)	7.4(m, 20H, Ph), 3.04(m, 4H, PCH_2) 1.62(m, 2H, CH_2)
6	1984(s), 1957(s) and 1881(s)	7.4(m, 20H, Ph), 2.67(m, 4H, PCH_2) 1.69(m, 4H, PCH_2CH_2), 0.91(m, 4H, $PCH_2CH_2CH_2$

[a] Spectra recorded as thin films in $CHCl_3$ between NaCl plates; s, strong. [b] Spectra recorded in $CDCl_3$ (25 °C) and referenced to Me_4Si.

(M = Mo or W; X = Cl, Br or I) with four equivalents of $PPh_2(CH_2)_nPPh_2$ ($n = 1$ or 2), which give different products depending on M and X [10]. This lack of reactivity of $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_2PPh_2\}]$ with one equivalent of $PPh_2(CH_2)_2PPh_2$ may be due to the bulk of the $SnCl_3$ group attached to the molybdenum.

The crystal structures of many seven-coordinate complexes of the types $[MX_2(CO)_3L_2]$ and $[MX_2(CO)_3(L{-}L)]$ reveal capped octahedral geometry [25–34]. It is likely that complexes **2–6**, containing mono- and bi-dentate phosphine donor ligands, have a similar geometry, since their infrared spectral properties are similar to the previously reported dihalo complexes.

Experimental

All reactions were carried out under nitrogen by standard Schlenk line techniques. The complexes $[M(CO)_3(NCMe)_3]$ (M = Mo or W) were prepared by the published method [21]. $[Mo(CO)_6]$ was kindly donated by Amax speciality metals UK Ltd. All other chemicals were purchased from commercial sources. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (with helium as a carrier gas). Infrared spectra were recorded on a Mattson Cygnus 100 FT IR spectrometer. ^1H NMR spectra were recorded on a JEOL FX 60 MHz NMR spectrometer (shifts are relative to internal tetramethylsilane). The ^{13}C NMR spectrum (−70 °C) of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**) was recorded on a Bruker WH-400 NMR spectrometer. The magnetic susceptibilities were determined with a Johnson–Matthey magnetic susceptibility balance.

$[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (1)

A suspension of $[Mo(CO)_6]$ (4.0 g, 15.2 mmol) in degassed acetonitrile (120 cm^3) was refluxed under nitrogen for 24 h to give a deep yellow solution. Addition of $SnCl_4$ (3.95 g, 15.2 mmol) (from a nitrogen filled syringe) resulted in the immediate formation of an orange solution. Removal of the solvent in vacuo gave the orange crystalline complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (**1**), which was recrystallised from acetonitrile (yield 7.5 g, 94%). Analysis Found: C, 15.8; H, 1.1; N, 5.5 $C_7H_6N_2O_3Cl_4SnMo$ calc.: C, 16.1; H, 1.2; N, 5.4%. IR: $\nu(C{\equiv}O)$ 2026(s), 1939(s) and 1912(s), $\nu(N{\equiv}C)$ 2288(w) and 2258(w) cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ 2.49 (s, Me) ppm.

The tungsten complex $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ was prepared analogously but was found to be considerably more air-sensitive and thermally unstable than the molybdenum complex, and satisfactory analytical data were not obtained.

$[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ (2)

PPh_3 (0.52 g, 2 mmol) was added to a solution of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (0.52 g, 1 mmol) in acetone (15 cm^3) with continuous stirring under a stream of dry nitrogen. The solution immediately became bright yellow. After 30 min stirring, removal of the solvent in vacuo gave the analytically pure yellow crystalline complex $[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$. Yield 0.94 g, 98% (see Table 1 for physical and analytical data).

$[MoCl(SnCl_3)(CO)_3\{PPh_2P(CH_2)PPh_2\}]$

$PPh_2(CH_2)PPh_2$ (0.40 g, 1 mmol) was added to a solution of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (0.52 g, 1 mmol) in acetone (15 cm^3) with continuous stirring under a stream of dry nitrogen. The solution immediately became bright orange. After 30 min stirring, removal of the solvent in vacuo gave the analytically pure orange crystalline compound $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)PPh_2\}]$ (5) Yield 0.82 g, 99%.

Analogous reactions of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with one equivalent of $PPh_2(CH_2)_nPPh_2$ ($n = 2$, 3 and 6) gave the new compounds $[MoCl(SnCl_3)(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$ (4–6). (See Table 1 for physical and analytical data).

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