

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

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Abstract

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

Introduction

Although a wide range of dihalocarbonyl seven-coordinate compounds of molybdenum(II) and tungsten(II) of the type $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$, 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{bipy})]$ [13], $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_2(\text{bipy})\{\text{P}(\text{C}_6\text{H}_4\text{X}-p)_3\}]$ ($\text{X} = \text{F}$, Cl or CH_3) [14] and $[\text{MCl}(\text{SnCl}_3)(\text{CO})_3(\text{RN}=\text{CHCH}=\text{NR})]$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{}^i\text{Pr}$, $\text{}^n\text{Bu}$ or Cy) [15].

In recent years we have been investigating the chemistry of the highly versatile diiodo seven-coordinate complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) [16–19], which are prepared in quantitative yield by reaction of $[\text{M}(\text{CO})_3(\text{NCMe})_3]$ 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$, and its reactions with phosphine donor ligands.

Results and discussion

Treatment of $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ (prepared in situ by refluxing $[\text{Mo}(\text{CO})_6]$ 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (**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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (**1**) was fully characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (see experimental). The complex $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (**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 $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ by treating $[\text{W}(\text{CO})_3(\text{NCMe})_3]$ (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 $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$, 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 $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ shows three carbonyl bands at $\nu(\text{CO})$ 2017, 1978 and 1934 cm^{-1} and nitrile stretching bands at $\nu(\text{CN})$ 2299, $2242(\text{w})\text{ cm}^{-1}$, which are similar to those for **1** and the diiodide compounds previously described [20]. The room temperature ^1H NMR spectrum of $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ shows the expected single resonance at $\delta(\text{CDCl}_3)$ 2.46 ppm. It is noteworthy that these relative stabilities are in contrast to those for diiodo systems, where the tungsten complex $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ 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 , $(\text{CD}_3)_2\text{CO}$) of $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (**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 $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$, 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 $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ [23]. However the resonances at $\delta \approx 227\text{ ppm}$ 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (**1**) reacts with two equivalents of PPh_3 in acetone at room temperature to give the stable seven-coordinate compound $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ (**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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2\}]$

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))	
			C	H
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ (2)	Yellow	98	48.6 (48.5)	2.9 (3.1)
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)\text{PPh}_2\}]$ (3)	Buff	99	41.4 (40.8)	3.2 (2.9)
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$ (4)	Orange -brown	97	40.8 (41.5)	3.1 (2.9)
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2\}]$ (5)	Orange	96	42.4 (42.3)	3.6 (3.1)
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_6\text{PPh}_2\}]$ (6)	Mustard -yellow	98	44.0 (44.3)	4.2 (3.6)

bisacetonitrile compound 1. Attempts to prepare the 16 electron dicarbonyl compound $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_2]$ by refluxing $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ 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 $[\text{MoX}_2(\text{CO})_3(\text{PPh}_3)_2]$ lose carbon monoxide to give $[\text{MoX}_2(\text{CO})_2(\text{PPh}_3)_2]$ when refluxed in CHCl_3 .

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

Table 2

IR^a and ¹H NMR^b data for the complexes $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2\}]$

Complex	$\nu(\text{CO})$ (cm^{-1})	¹ H 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, $\text{PCH}_2\text{CH}_2\text{CH}_2$)

^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 $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2), which give different products depending on M and X [10]. This lack of reactivity of $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$ with one equivalent of $\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2$ 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 $[\text{MX}_2(\text{CO})_3\text{L}_2]$ and $[\text{MX}_2(\text{CO})_3(\text{L}-\text{L})]$ 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 $[\text{M}(\text{CO})_3(\text{NCMe})_3]$ (M = Mo or W) were prepared by the published method [21]. $[\text{Mo}(\text{CO})_6]$ 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1) was recorded on a Bruker WH-400 NMR spectrometer. The magnetic susceptibilities were determined with a Johnson–Matthey magnetic susceptibility balance.

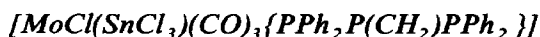
$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1)

A suspension of $[\text{Mo}(\text{CO})_6]$ (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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1), which was recrystallised from acetonitrile (yield 7.5 g, 94%). Analysis Found: C, 15.8; H, 1.1; N, 5.5. $\text{C}_7\text{H}_6\text{N}_2\text{O}_3\text{Cl}_4\text{SnMo}$ calc.: C, 16.1; H, 1.2; N, 5.4%. IR: $\nu(\text{C}\equiv\text{O})$ 2026(s), 1939(s) and 1912(s), $\nu(\text{N}\equiv\text{C})$ 2288(w) and 2258(w) cm^{-1} . ^1H NMR (CDCl_3 , 25°C): δ 2.49 (s, Me) ppm.

The tungsten complex $[\text{WCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ 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.

$[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$ (2)

PPh_3 (0.52 g, 2 mmol) was added to a solution of $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{PPh}_3)_2]$. Yield 0.94 g, 98% (see Table 1 for physical and analytical data).



$\text{PPh}_2(\text{CH}_2)\text{PPh}_2$ (0.40 g, 1 mmol) was added to a solution of $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (0.52 g, 1 mmol) in acetone (15 cm³) 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 $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3\{\text{PPh}_2(\text{CH}_2)\text{PPh}_2\}]$ (5) Yield 0.82 g, 99%.

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

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