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LETTER

Reactions of the Novel $[Cp_2MoCl_2]^{2+}$ Cation with Organothiolates to Give Molybdenocene (VI) Dithiolates and the Oxidation of $Cp_2Mo(SR)_2$ to Give $[Cp_2Mo(SR)_2]^{2+}$

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We are at present interested in the synthesis and characterization of metallocene species of the early transition elements containing the central metal atom in its highest oxidation state [1]. The molybdenocene(VI) dichloride dication $[Cp_2MoCl_2]^{2+}$ ($Cp = \eta^5\text{-}C_5H_5$) was prepared in liquid SO_2 by the reaction of Cp_2MoCl_2 with three equivalents of AsF_5 according to eqn. (1) [2]

$$Cp_2MoCl_2 + 3AsF_5 \xrightarrow{SO_2} \underset{\mathbf{I}}{[Cp_2MoCl_2]^{2+}[AsF_6]_2^-} + AsF_3 \quad (1)$$

The structures of **I** and its tungsten analogue were elucidated by single-crystal X-ray diffraction [2]. **I** is the first 16-electron metallocene dichloride species of a group VI element and it is isoelectronic with the niobium monocation $[Cp_2NbCl_2]^+$ in $[Cp_2NbCl_2]^+[SbF_6]^-$ [1] and the neutral zirconocene dichloride.

While the group IV metallocene dichlorides Cp_2MCl_2 (M = Ti, Zr, Hf) react quantitatively in organic solvents with alkali metal thiolates to give the corresponding dithiolates (eqn. 2)) [3–6], Cp_2MoCl_2 behaves differently. It does not react in benzene or methylene dichloride or in liquid sulfur dioxide with NaSR. However, a number of $Cp_2Mo(SR)_2$ complexes have been prepared from Cp_2MoCl_2 and RSH in a mixture of ethanol/water in the presence of a stoichiometric amount of NaOH (eqn. (3)) [7, 8].

$$Cp_2MCl_2 + 2NaSR \xrightarrow{\text{org. solvent}} Cp_2M(SR)_2 + 2NaCl$$
$$(M = Ti,\ Zr,\ Hf;\ R = \text{alcyl, aryl}) \quad (2)$$

$$Cp_2MoCl_2 + 2NaOH + 2RSH \xrightarrow{C_2H_5OH/H_2O} Cp_2Mo(SR)_2 + 2NaCl + 2H_2O \quad (3)$$

In the present paper we report the synthesis and characterization of the first molybdenocene(VI) dithiolate complexes, which can be prepared either by reaction of the $[Cp_2MoCl_2]^{2+}$ cation with a stoichiometric amount of organothiolates in liquid SO_2 or the direct oxidation of the neutral $Cp_2Mo(SR)_2$ species with three equivalents of AsF_5.

Experimental

$[Cp_2MoCl_2]^{2+}[SbF_6]_2^-$ (**II**) [2] and $Cp_2Mo(SC_6H_4\text{–}p\text{-}CH_3)_2$ (**III**) [7] were prepared as described in the cited literature. $NaSCH_3$ (Merck, dried *in vacuo* over P_4O_{10}) and AsF_5 (Union Carbide, purified by distillation) are commercially available, $LiSC_6H_4\text{–}p\text{-}CH_3$ was prepared from $HSC_6H_4\text{–}p\text{-}CH_3$ (Merck) and butyl lithium in hexane solution. All reactions took place at room temperature in an SO_2 atmosphere ($P = 3.5$ bar); the handling of the solid material (sample preparation) was carried out in an Ar atmosphere in a dry box. The vessels were flame dried and rinsed with BF_3; the solvent (SO_2, Messer–Griesheim) was distilled twice, degassed and dried over CaH_2.

$[Cp_2Mo(SC_6H_4\text{–}p\text{-}CH_3)_2]^{2+}[SbF_6]_2^-$ (IV)

Compound **II** (0.100 g; 0.13 mmol) was dissolved in 10 ml SO_2 at -78 °C and was reacted with 0.034 g (0.26 mmol) $LiSC_6H_4\text{–}p\text{-}CH_3$. The reaction mixture was warmed to room temperature, filtered and evaporated to dryness, giving a black residue. Recrystallization of the solid from SO_2 gave analytically pure **IV**; yield 0.088 g (0.093 mmol; 72%).

Anal. Calc. for $C_{24}H_{24}F_{12}MoS_2Sb_2$: C, 30.5; H, 2.6. Found: C, 31.2; H, 2.6%. Molecular weight 944.0. IR spectrum (CsI) ν (cm^{-1}): 3130m, 1490w, 1440s, 1430m, 1125w, 1075vw, 1030w, 1010w, 865s, 832vw, 810w, 662vs, 488vw, 410w, 288vs. Mass spectrum (*EI*, 70 eV, 180 °C); m/z (I_{rel}): 246 (63) $(CH_3C_6H_4S)_2^+$, 182 (22) $(CH_3C_6H_4)_2^+$, 123 (100) $CH_3C_6H_4S^+$, 91 (71) $C_6H_4CH_3^+$, 77 (50) $C_6H_5^+$.

$[Cp_2Mo(SCH_3)_2]^{2+}[SbF_6]_2^-$ (V)

The reaction was carried out similarly to that described for the synthesis of **IV**. Compound **II** (0.300 g; 0.39 mmol) was reacted with 0.055 g (0.78 mmol) $NaSCH_3$ to give **V** after recrystallization

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TABLE 1. ^1H NMR data of compounds II to V, Cp_2MoCl_2 and $Cp_2Mo(SCH_3)_2$

Complex	Solvent	δ_{Cp} (ppm)^a	δ_{CH_3} (ppm)^a
II	DMSO-d_6	5.90	
III	$CDCl_3$	5.17	2.13
IV	SO_2	5.75	2.35
V	SO_2	5.78	2.68
Cp_2MoCl_2	SO_2	5.67	
$Cp_2Mo(SCH_3)_2$	SO_2	5.61^b	1.88^b

^{a}Relative to: δ(DMSO-d_5) = 2.49 ppm, $\delta(CHCl_3)$ = 7.27 ppm, δ(TMS, ext in SO_2) = 0.00 ppm. ^{b}From ref. 11.

as a green–black solid; yield 0.14 g (0.177 mmol, 45%).

Anal. Calc. for $C_{12}H_{16}F_{12}MoS_2Sb_2$: C, 18.2; H, 2.0. Found: C, 18.7; H, 2.1%. Molecular weight 791.8. IR spectrum (CsI) ν (cm^{-1}): 3120m, 2970vw, 2920w, 1440m, 1428m, 1268m, 1155s, 1027w, 998w, 962w, 908m, 858sh, 845s, 657vs, 500w,br, 399w, 288vs. ^1H NMR spectrum: see Table 1.

$[Cp_2Mo(SC_6H_4\text{-}p\text{-}CH_3)_2]^{2+}[AsF_6]_2^-$ (VI)

Onto a frozen solution of 0.326 g (0.69 mmol) III in 10 ml SO_2, 0.354 g (2.07 mmol) AsF_5 was condensed. The reaction mixture was warmed to room temperature, stirred for 30 min and evaporated to dryness, yielding a green–black product which was recrystallized from SO_2 to give analytically pure VI; yield 0.48 g (0.56 mmol; 82%).

Anal. Calc. for $C_{24}H_{24}As_2F_{12}MoS_2$: C, 33.9; H, 2.8. Found: C, 33.6; H, 2.7%. Molecular weight 852.4. IR spectrum (CsI) ν (cm^{-1}): 3130m, 2960w, 1590w, 1490m, 1462m, 1442m, 1415m, 1210w, 1188w, 1120w, 1015w, 998w, 850s,br, 815s, 699vvs, 675sh, 505m, 397vvs. ^1H NMR spectrum: see Table 1.

Results and Discussion

The new molybdenocene(VI) dithiolate dications $[Cp_2Mo(SCH_3)_2]^{2+}$ and $[Cp_2Mo(SC_6H_4\text{-}p\text{-}CH_3)_2]^{2+}$ have been prepared as their hexafluoropnicogenate salts. These species are, as far as we are aware, the first examples of molybdenocene dithiolate complexes with the central metal atom in its highest oxidation state. The identity of all compounds was established by elemental analysis, ^1H NMR and IR data; the decomposition behaviour of IV was elucidated by means of mass spectroscopy.

The molybdenocene dithiolate cations are prepared most conveniently by the direct oxidation of the neutral Mo(IV) species with AsF_5 (eqn. (4))

$$\underset{\textbf{III}}{Cp_2Mo(SC_6H_4\text{-}p\text{-}CH_3)_2} + 3AsF_5 \xrightarrow{SO_2} \underset{\textbf{VI}}{[Cp_2Mo(SC_6H_4\text{-}p\text{-}CH_3)_2]^{2+}[AsF_6]_2^-} + AsF_3 \qquad (4)$$

It is interesting that the molybdenocene dichloride dication II reacts directly with the alkali metal thiolate (eqn. (5)) while the neutral 18-electron species Cp_2MoCl_2 does not (see above).

$$\textbf{II} + 2NaSCH_3 \xrightarrow{SO_2} \underset{\textbf{V}}{[CP_2Mo(SCH_3)_2]^{2+}[SbF_6]_2^-} + 2NaCl \qquad (5)$$

This shows that the d^0 configuration of the 16-electron $[Cp_2MoCl_2]^{2+}$ dication behaves similarly to the isoelectronic Cp_2ZrCl_2 and the different reaction behaviour of Cp_2MoCl_2 (d^2) and $[Cp_2MoCl_2]^{2+}$ (d^0) can be explained easily by the different electron distribution in the two Mo species. In $[Cp_2MoCl_2]^{2+}$ (and in Cp_2ZrCl_2) the LUMO (a_1) has an essentially non-bonding character [9] and the base ($R\text{–}S^-$) may coordinate to the 16-electron fragment, giving a penta-coordinated 18-electron species as the intermediate (eqn. (6)). This step is followed by the elimination of chloride (eqn. (6)), yielding again a 16-electron complex which can be attacked by another thiolate anion.

$$[Cp_2MoCl_2]^{2+} + {}^-S\text{–}R \longrightarrow \{[Cp_2MoCl_2(SR)]^+\} \longrightarrow [Cp_2MoCl(SR)]^{2+} + Cl^- \qquad (6)$$

This substitution mechanism is not possible for the neutral d^2 Cp_2MoCl_2, as in the 18-electron complex the a_1 orbital represents the HOMO and the LUMO has strong antibonding character [9].

The electronic situation also explains the different reactivities of $Cp_2Ti(SR)_2$ (and Cp_2TiS_5) and $Cp_2Mo(SR)_2$ toward AsF_5 and SbF_5, respectively. The Ti species contains the titanium atom already in its highest oxidation state and AsF_5 (or SbF_5) oxidizes the sulfur (which can be regarded as a sulfide), yielding a disulfide (or elemental sulfur for Cp_2TiS_5) and the F-coordinated titanocene bis(hexafluoropnicogenate) complex (eqn. (7)) [10]

$$Cp_2TiS_5 + 3AsF_5 \xrightarrow{SO_2} Cp_2Ti(AsF_6)_2 + \tfrac{5}{8}\,S_8 + AsF_3 \qquad (7)$$

The ^1H NMR spectra of IV to VI clearly show a low-field shift compared with the neutral counterparts (Table 1). This is in good agreement with the cationic character of the thiolate species and fits nicely in the observed high-frequency (low-field) shift from Cp_2MoCl_2 to $[Cp_2MoCl_2]^{2+}$.

The IR spectra of **IV** to **VI** in all cases show as the most intense unsplit absorptions those corresponding to the ν_3 (ν(EF)) and ν_4 (δ(EF)) modes of the octahedral $[\mathrm{EF_6}]^-$ anions (E = As, Sb) (see Experimental). This is well in agreement with the postulated ionic structure of **IV** to **VI** with free, uncoordinated $[\mathrm{EF_6}]^-$ units as counterions. The absence of the Mo–Cl stretching mode ($\mathrm{Cp_2MoCl_2}$: 293vs, 262s $\mathrm{cm^{-1}}$; $[\mathrm{Cp_2MoCl_2}]^+$: 334s, 311vs $\mathrm{cm^{-1}}$ [11]) in **IV** and **V** agrees with the substitution of both chlorides by the thiolate ligands.

The decomposition behaviour of **VI** was investigated by means of mass spectroscopy. The cationic complex decomposes on heating in a redox reaction and eliminates the corresponding disulfide and presumably **VII** (eqn. (8)), which, however, is unstable itself and decomposes by elimination of $\mathrm{SbF_5}$ (from the coordinated $\mathrm{SbF_6}$ unit) followed by fluorination of the organometal fragment (cf. ref. 12)

$$\mathbf{VI} \longrightarrow \underset{\mathbf{VII}}{[\mathrm{Cp_2Mo(SbF_6)(SC_6H_4}\text{-}p\text{-}\mathrm{CH_3)}]^+[\mathrm{SbF_6}]^-} + \tfrac{1}{2}(\mathrm{CH_3C_6H_4S})_2 \qquad (8)$$

It is likely that the new molybdenocene(VI) dithiolate complexes **IV**–**VI** are not thermodynamically stable in terms of a reductive elimination of disulfide (eqn. (8)) but are kinetically stabilized, as the first step in the decomposition pathway involves a high activation barrier (formation of the $\mathrm{R{-}S^{\bullet}}$ radical) because a direct intermolecular reaction between these cations (direct formation of R–S–S–R) is very unlikely.

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