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Article

Rearrangement of Molybdocene Tetraoxotetrasulfide $Cp_2MoS_4O_4$ to Give $[(Cp_2MoS_2H)_2](HSO_4)_2$: A Novel Proton-Stabilized Molybdocene Disulfide Dimer

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Cp_2MoS_4, **1**, in CH_2Cl_2 undergoes extensive oxidation by *m*-CPBA at –78 °C to give a 1,1,4,4-tetroxide, **2** (59%). Tetraoxide **2** rearranges at room temperature to give an unusual sulfur-atom protonated molybdocene disulfide dimer $[(Cp_2MoS_2H)_2](HSO_4)_2$, **3**. Crystal data for **3** are $P\bar{1}$, $a = 6.751(2)$ Å, $b = 9.865(4)$ Å, $c = 11.549(5)$ Å, $\alpha = 109.95(3)°$, $\beta = 96.11(3)°$, $\gamma = 108.22(3)°$, $V = 666.9(4)$ Å^3, and $Z = 1$. The dimer was also obtained directly when the oxidation was conducted at 0 °C in DMF. Under basic conditions, the dimer is cleaved to give molybdocene disulfide Cp_2MoS_2, while treatment of the latter with acid converts it to the dimer **3**.

Introduction

Previous work on the mechanism of the Claus reaction ($2H_2S + SO_2 \rightarrow {}^{3}/_{8}S_8 + 2H_2O$) suggests that oxidized metallopolysulfide moieties of the type $MS_x(O)_y$ are active sites for rearrangements and nucleophilic substitutions, further oxidation, disproportionation, and oxygen transfer.[1] For example, $CpRu(PPh_3)_2SS(O)R$ disproportionates to the RuSSR and $RuSS(O)_2R$ moieties.[2] The complex *cis*-$(PPh_3)_2PtS_3O$ is the active intermediate in the homogeneous catalysis of the Claus process by *cis*-$(PPh_3)_2Pt(SH)_2$.[3] Other examples of the reactivity of oxidized polysulfur systems include oxidized titanocene pentasulfide[4] and germanium sulfide[5] derivatives. Apparently, certain heteroatoms enhance the reactivity of the adjacent sulfinyl group.

We have studied the oxygen migration in molybdocene tetrasulfide 1-oxide and molybdocene disulfide 1-oxide.[6] Molybdocene tetrasulfide 1-oxide undergoes an oxygen migration to give the 2-oxide even at room temperature, while molybdocene disulfide 1-oxide easily reacts with SO_2 to give corresponding bisdithiosulfates.[7] Here, we report the formation of an unusual dicationic molybdocene disulfide dimer by the rearrangement of a putative molybdocene 1,1,4,4-tetraoxotetrasulfide generated by exhaustive oxidation of the sulfur atoms adjacent to the molybdenum center.

Experimental Section

Molybdenum pentachloride, sodium borohydride, dicyclopentadiene, sodium hexafluorophosphate, boron trifluoride ethyl etherate, elemental sulfur, anhydrous dimethylformamide (DMF), butyllithium in hexanes, and *m*-chloroperbenzoic acid (*m*-CPBA) were purchased from the Aldrich Chemical Co. Methylene chloride (reagent) and hexanes (ACS) were purchased from Fisher. Cp_2MoS_4, **1**,[8] and Cp_2MoS_2, **5**,[8] were prepared according to literature methods. Iodometric titration was used to determine the purity of *m*-CPBA.[9] All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The methylene chloride used in reactions was distilled from P_2O_5. Acetonitrile was distilled over calcium hydride. DMF and deuterated solvents were used as received, while $CDCl_3$ was stored over molecular sieves. Solvents used for recrystallization and chromatography were reagent grade. Acetone used for extraction was purged with nitrogen before use. ^1H NMR (270 MHz) and ^{13}C NMR (67.94 MHz) spectra were recorded on a JEOL CPF270 spectrometer. Chemical shifts were measured relative to solvent peaks (for DMSO, ^1H NMR peak at 2.49 ppm and ^{13}C at 77.0 ppm; for MeCN, ^1H NMR peak at 1.94 ppm and ^{13}C at 1.3 ppm). Infrared spectra were obtained using KBr

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disks or solutions in CH_2Cl_2 using a Nicolet Avatar 360 FT-IR spectrometer. Electron impact (EI) mass spectra were obtained by a Kratos MS25 RSA spectrometer with a 70-eV ionizing energy source and used in direct-inlet mode. Melting points were determined in open capillaries on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario, Canada)

Molybdocene Tetraoxotetrasulfide, $Cp_2MoS_4O_4$, 2. Molybdocene tetrasulfide, **1** (100 mg, 0.282 mmol), in methylene chloride (100 mL) was treated with *m*-CPBA (71%, 273 mg, 1.13 mmol) at −78 °C, and the resulting yellow solution was warmed to 0 °C. The solvent was removed under vacuum in an air bath. The green residue was washed with cold (0 °C) diethyl ether (10 mL) and methylene chloride (4 × 10 mL). The solid was dried with a stream of nitrogen at 0 °C and stored at −78 °C (69 mg, 59%). ^{1}H NMR (DMSO-d_6): δ 5.92 (s). ^{13}C NMR (DMSO-d_6): δ 102.50. IR (KBr): $\nu_{(SO)}$ 1056, 1223 cm^{-1}. Anal. Calcd for $C_{10}H_{10}MoO_4S_4$: C, 28.71; H, 2.41; S, 30.66. Found: C, 28.58; H, 2.02; S, 31.13.

[$(Cp_2MoS_2H)_2$](HSO_4)$_2$, 3. Molybdocene tetrasulfide, **1** (500 mg, 1.41 mmol), in DMF was treated at 0 °C with *m*-CPBA (71%, 1.369 mg, 5.65 mmol). The solvent was evaporated under vacuum at 50 °C. The residual solid was washed with dimethylformamide (15 mL) and methylene chloride (3 × 15 mL) to give **3** (290 mg, 53%/mol of **1**). ^{1}H NMR (DMSO-d_6): δ 4.77 (s, 10H), 6.00 (s, 2H, broad), 6.87 (s, 10). ^{13}C NMR (DMSO-d_6): δ 97.13, 102.08. IR (KBr): ν 845, 1001, 1161, 1182, 1225, 1238, 3092, 3414, 3476 cm^{-1}. Decomposition at 235 °C without melting.

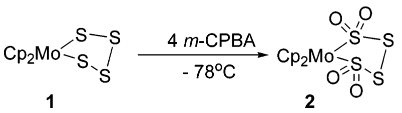
[$(Cp_2MoS_2H)_2$](PF_6)$_2$. A solution of **3** (387 mg, 0.5 mmol) in 120 mL of water was treated with sodium hexafluorophosphate (185 mg, 1.1 mmol) in 10 mL of water. The precipitated hexafluorophosphate salt of the disulfide dimer was washed with water and dried (401 mg, 92%). ^{1}H NMR (DMSO-d_6): δ 4.77 (s, 10 H), 6.00 (s, 1.4 H, broad), 6.87 (s, 10 H). ^{13}C NMR (DMSO-d_6): δ 101.92, 107.5. ^{31}P NMR (DMSO-d_6): δ −143.6 (septet, $J = 709.7$ Hz). IR (KBr): ν 845, 1001, 1161, 1182, 1225, 1238, 3092, 3414, 3476 cm^{-1}.

[$(Cp_2MoS_2H)_2$]I_2. A solution of **3** (387 mg, 0.5 mmol) in water (120 mL) was treated with an aqueous solution of sodium iodide (330 mg, 1.1 mmol, in 10 mL). The precipitated iodide salt was washed with water and dried. Anal. Calcd for $C_{20}H_{22}Mo_2S_4I_2$: C, 28.01; H, 2.49; S, 15.25. Found: C, 28.72; H, 2.65; S, 15.34.

Reaction of [$(Cp_2MoS_2H)_2$](PF_6)$_2$ with Butyllithium. A suspension of dimer **3** (10 mg, 0.0145 mmol) in hexanes (5 mL) was treated with excess butyllithium in hexanes (18.5 μL, 2.5M, 0.058 mmol). Immediately, the color of the suspension became brown. The mixture was stirred for 10 min, and the solvent was removed under vacuum; then, the residue was dissolved in acetonitrile-d_3. The main product was molybdocene disulfide in about an 85% yield, together with molybdocene tetrasulfide, ca. 5%, and some other minor unidentified products.

Results and Discussion

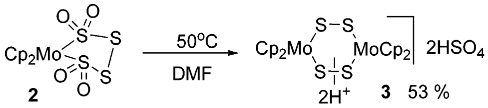
Molybdocene tetrasulfide, **1**, reacts with excess *m*-CPBA at −50 °C in CH_2Cl_2 to give a tetraoxotetrasulfide species which was stable enough to be characterized and assigned structure **2** (eq a).



(a)

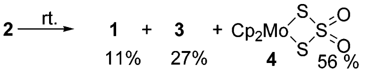
Compound **2** is an olive green solid which decomposes readily at room-temperature both in solution (DMSO, DMF) and in the solid state. The primary decomposition product in the DMSO solution was **1**. The ^{1}H and ^{13}C NMR spectra of **2** in DMSO-d_6 show only singlets at 5.9 and 102.5 ppm, respectively. These values are deshielded in comparison to those observed in unoxidized compound **1** (5.33 and 97.39 ppm, respectively). Strong infrared peaks at 1056 and 1223 cm^{-1} are similar to values reported for similar cobalt,[10] platinum,[11] and iridium[12] sulfinyl derivatives (1040−1070 and 1200−1220 cm^{-1}). The tentative assignment of **2** as the 1,1,4,4 isomer is based on analogy with the products obtained from stoichiometric oxidation of **1**.[6]

Attempts to isolate **2** when the oxidation was conducted in DMF via evaporation under vacuum gave a green precipitate. This was identified as the novel compound **3**; apparently formed via both rearrangement and hydrolysis of **2** (eq b).



(b)

The yield of **3** was maximized (53%) when a solution of **2** in DMF was concentrated under vacuum at ca. 50 °C. Compound is **3** diamagnetic and air stable, and it decomposes without melting at 235 °C. It is sparingly soluble in water with counterions such as chloride, fluoride, or hydrogen sulfate. In the solid state at room temperature, **2** slowly converts, via the loss of SO_2, to a mixture of compounds identified by NMR (DMSO-d_6) to be mostly the molybdocene dithiosulfate **4**,[7] dimer **3**, and **1** (eq c).



(c)

In summary, (a) **1** reacts with SO_2 in dry CH_2Cl_2 to give **2**, (b) **1** reacts with SO_2 in DMF (not dried) to give **3** because of adventitious water, and (c) solid **2** converts to a different mixture of products (dominated by **4**) than when the reaction is conducted in DMF (i.e., in the presence of adventitious water).

The corresponding iodide, bromide, hexafluorophosphate, and tetrafluoroborate salts were easily precipitated from aqueous solutions of **3** by addition of the corresponding alkali metal salts. The hexafluorophosphate derivative is soluble in methylene chloride, acetone, and similar solvents. There are two Cp peaks in both the ^{1}H and ^{13}C NMR spectra. The signals in the ^{1}H NMR are well separated at 4.8 and 6.8 ppm. In addition, a low intensity singlet is observed at 6.01 ppm. It disappears when a drop of D_2O is added to the NMR tube. Regardless of the counteranions present, the ^{1}H NMR spectrum of **3** is consistent with the structure of **3**: two singlets for the axial and equatorial Cp rings and one singlet

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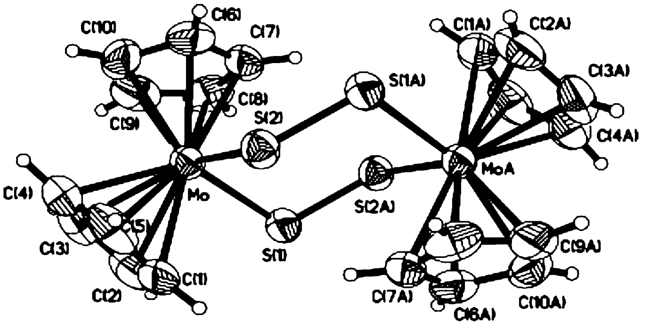


Figure 1. Structure of the core of dimer **3**. Selected bond lengths (Å): Mo−S1, 2.417(2); Mo−S2, 2.411(2); S−S, 2.015(2). Selected angles (deg): S1−Mo−S2, 94.59(6); Mo−S1−S2A, 112.29(7); Mo−S2−S1A, 116.00(7).

at 6.01 ppm for the 2 protons attached to the sulfur atoms.[13] The latter are coupled to the Cp protons (NOESY) and exchange with D_2O. Similarly, the ^{13}C NMR spectrum is characterized by two singlets originating from Cp rings in the axial and equatorial positions. The IR spectrum of **3** does not show any peak in the S−H region.

The crystallization of **3** from H_2O/acetic acid provided dark-green crystals which were characterized by single-crystal X-ray structure analysis (Figure 1).[14] The dimer features a six-membered ring core with S−S bonds that are somewhat shorter than those observed in the analogous titanocene disulfide dimer $(Cp_2TiS_2)_2$ (2.014 vs 2.061 Å[15] in the titanocene derivative). The Mo−S bond lengths in **3** (ca. 2.41 Å) are slightly shorter than those observed in Cp_2MoS_4[16] or $Cp_2MoS_3O_2$[7] (2.44−2.46 Å) but resemble those of other cyclic molybdenum tetrasulfide derivatives (2.38−2.43 Å).[17] The S1−Mo−S2 angle (94.41°) is significantly larger than those typically observed for d^2 complexes (82−88°).[18]

The value of the S−Mo−S angle of **3** (94.59°) is a very interesting feature of the molecule. It is more typical of d^0 compounds such its titanocene disulfide counterpart $(Cp_2TiS_2)_2$ (92.47°)[12] or titanocene pentasulfide (94.59°)[19] than of a d^2 derivative. The established Alcock−Green model links the S−M−S angle to the HOMO orbital.[20,21] The protons probably stabilize the HOMO of **3** which is antibonding thus making the MoS_4Mo core stable.[22] Unfortunately, it was not possible to determine the position of the two protons in the crystal structure. The molecule of **3** is symmetrical with all Mo−S and S−S bonds being identical. No obvious distortion that might be expected from localized S−H bonds was observed. Most likely, the protons exchange rapidly between the sulfur atoms. The **3** dication is accompanied by two bisulfate anions and two molecules of water. While there appears to be hydrogen bonding between the water molecule and the bisulfate anion, the bisulfate anions are too far from the core of the molecule for any appreciable interactions.

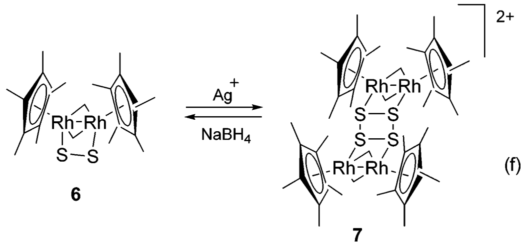
Compound **3** is immediately deprotonated by bases (B) such as tetrabutylammonium hydroxide, butyllithium, or even aqueous sodium carbonate (eq d).

$$[(Cp_2MoS_2H)_2](HSO_4)_2 \xrightarrow{B} 2Cp_2MoS_2 \tag{d}$$

Extraction of the resulting solution with CH_2Cl_2 gave mainly molybdocene disulfide, **5**. This reaction is reversible. Treatment of molybdocene disulfide (**5**) with acids (A) such as sulfuric acid or trifluoroborane etherate rapidly gave **3** as a green precipitate which was identified by NMR (eq e).

$$2Cp_2MoS_2 \xrightarrow{A} [(Cp_2MoS_2H)_2](A)_2 \tag{e}$$

Dimerization of a metal disulfide by oxidation has precedent. Oxidation of rhodium disulfide **6** with the silver cation Ag^+ (eq f)[23] gives **7** which can be very easily converted back to **6** upon reduction with $NaBH_4$.



(f)

It seems reasonable to postulate that the loss of SO_2 from **2** is a first step toward forming **3** (Scheme 1). An analogous intermediate was previously postulated as the initial step of

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(13) One of the most deshielded protons for a protonated thiolate (ca. 5−6 ppm) was observed in a cationic molybdenum carbonyl compound $[CpFe(CO)_2(HSPh)]BF_4$. Treichel, P. M.; Rosenhein, L. D. *Inorg. Chem.* **1981**, *20*, 942−944.

(14) Compound **3** $[(Cp_2MoS_2H)_2](HSO_4)_2 \cdot 2H_2O$. A dark green prism shaped crystal of **3** (0.36 × 0.18 × 0.11 mm) was used for data collection. The crystal is triclinic, $P\bar{1}$, $a = 6.751(2)$ Å, $b = 9.865(4)$ Å, $c = 11.549(5)$ Å, $\alpha = 109.95(3)°$, $\beta = 96.11(3)°$, $\gamma = 108.22(3)°$, $V = 666.9(4)$ Å^3, $Z = 1$, $Z' = 1/2$, $d_{calcd} = 2.023$ g/cm^3, and Cu Kα radiation, 1.54056 Å. Data were collected in $\varpi/2\Theta$ scan mode at 293(2) K: 21647 measured reflections, 2529 independent ($R_{int} = 0.063$) used in refinement of $|F^2|$. Data corrected absorption (ψ scans, $\mu = 12.689$ mm^{-1}, transmission range = 0.09−0.34), 182 parameters refined, all non-H atoms anisotropic, H atoms constrained. Final R1 = 0.0463 ($I > 2\sigma I$), 0.0504 (all) wR2 = 0.1152 ($I > 2\sigma I$), 0.1152 (all data). GOF = 1.027; residual electron density = −1.009 to 0.685 e Å^{-3}.

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(22) Such a model also explains the characteristic absorption in the UV spectrum displayed by the dimer at 844 nm ($\epsilon = 7760$ M^{-1} cm^{-1}) as a $\pi_3 \rightarrow \pi_4$ transition

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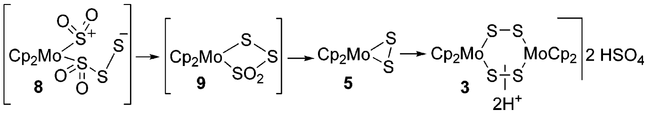
Scheme 1



oxygen migration which converts molybdocene tetrasulfide 1-oxide to the 2-oxide isomer.[6] The loss of another molecule of SO_2, possibly[24] from a trisulfide 1,1-dioxide intermediate such as **9** (not observed), would give molybdocene disulfide, **5**. SO_2 is known to disproportionate[25] in the presence of metal complexes to give elemental sulfur and sulfur trioxide ($3SO_2 \rightarrow 2SO_3 + {}^1/_8S_8$). The presence of adventitious H_2O in the DMF could convert SO_3 to H_2SO_4 and account for the formation of **3**. This step was verified independently via treatment of **5** with either H_2SO_4 or SO_3 which gave **3**. Likely, protonation of disulfide **5** occurs first; however, no species such as $(Cp_2MoS_2H)^+$, analogous to the reported[26] protonated iridium disulfide cation $(dppe_2IrS_2H)^+$, was observed.

The work reported here again demonstrates the lability of organometallic 1-oxopolysulfides. Such compounds are interesting possible models for Claus-type chemistry; in this case, a reverse step generates SO_2.

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Supporting Information Available: X-ray crystallographic file of dimer **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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