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Article

Insertion of SO_2 into the S–S Bond of Cp_2MoS_2 and Cp_2MoS_2O To Give Molybdocene Dithiosulfate and Bis(*O*-alkylthiosulfates)

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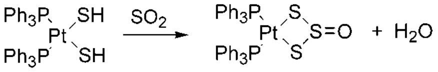
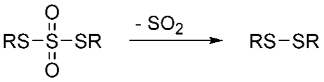
Cp_2MoS_2, **3**, reacts with SO_2 in CH_2Cl_2/EtOH mixtures to give $Cp_2MoS_3O_2$, **4**, wherein the SO_2 has inserted into the S–S bond to give a dithiosulfate ligand. Crystal data for **4**: $P2_1/n$, $a = 7.6782(6)$ Å, $b = 14.580(3)$ Å, $c = 10.2730(10)$ Å, $\beta = 92.04(1)°$, $V = 1149(3)$ Å^3, $Z = 4$. Cp_2MoS_2O, **5**, reacts with SO_2 in CH_2Cl_2 to give low yields of **4** plus other identified products. **5** reacts with SO_2 in MeOH and EtOH to give the corresponding bis(*O*-alkylthiosulfate), **6a** and **6b**, respectively. Crystal data for **6a**: $P\bar{1}$, $a = 8.3226(13)$ Å, $b = 8.4736(11)$ Å, $c = 12.382(2)$ Å, $\alpha = 87.803(11)°$, $\beta = 77.758(11)°$, $\gamma = 86.383(12)°$, $V = 851.4(2)$ Å^3, $Z = 2$.

The importance of SO_2 and H_2S abatement processes generates continuous interest in new catalysts for these reactions.[1] Recently, homogeneous catalysts of the Claus reaction ($2H_2S + SO_2 \rightarrow {}^3/_8S_8 + H_2O$) and a plausible model of the catalytic cycle were reported for the first time.[2] The reaction of $(PPh_3)_2Pt(SH)_2$, **1**, with SO_2 gave $(PPh_3)_2PtS_3O$, **2**, which in turn reacted with H_2S to regenerate complex **1** (eq 1). Both **1** and **2** were active in the catalytic cycle.[2]



1 **2**

(1)



$$RS{-}\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}{-}SR \xrightarrow{-\ SO_2} RS{-}SR \qquad (2)$$

In general, access to molecules such as **2** which possess S═O bonds is limited. Recently we reported an approach via the oxidation of metallocene polysulfides.[3] In the present paper the insertion of SO_2 into the S−S bond in molybdocene disulfides is reported. This is analogous to the insertion of SO_2 into O−O bonds of side-on bonded O_2^{2-} ligands which gives organometallic sulfates.[4] SO_2 also inserts into linear O−O bonds such as in metalloporphyrin peroxo complexes.[5] However, insertion of SO_2 into an S−S bond in either organic or inorganic molecules has not been reported. On the contrary, there is evidence that trisulfide 2,2-dioxides lose SO_2 to give disulfides (eq 2).[6] We describe here the reactions of molybdocene disulfide and disulfide oxide with SO_2 in different solvents to give molybdocene dithiosulfate and molybdocene bis(*O*-alkylthiosulfate).

Results and Discussion

The treatment of Cp_2MoS_2, **3**, with a large excess of SO_2 in ethanol/dichloromethane solvent mixtures[7] gave $Cp_2MoS_3O_2$, **4**, in quantitative yield, wherein an SO_2 molecule inserted into the S−S bond to give an S_3O_2 ligand. Compound **4** was characterized by ^{1}H and ^{13}C NMR as well as by IR spectroscopy. Its structure was confirmed by X-ray crystallography[8] and is shown in Figure 1. The bond lengths in the S_3O_2 ligand of **4** are very similar to those observed in the only known[9] dithiosulfato complex ion, $[Mo_2O_2S_2(S_3O_2)]^{2-}$.

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(7) The reaction proceeded in neat dichloromethane at a considerably slower rate. On the other hand, poor solubility of **3** in neat ethanol also hampered the reaction.

10.1021/ic011001a CCC: $22.00

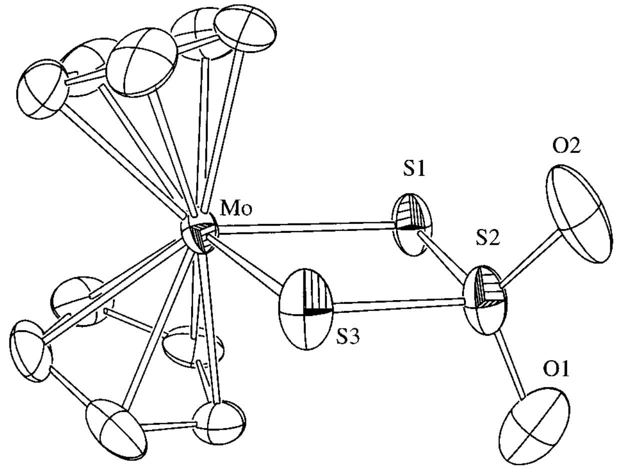
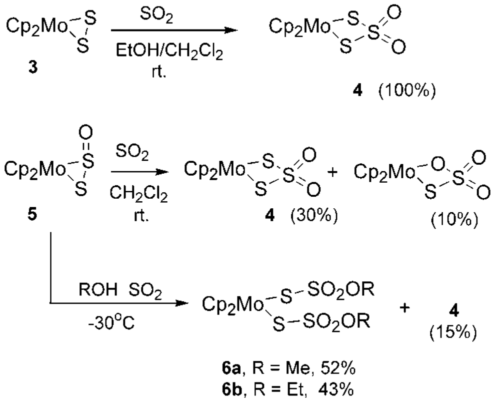


Figure 1. ORTEP drawing of **4**. Selected bond distances (Å) and angles (deg): Mo−S1, 2.452(2); Mo−S3, 2.434(2); S1−S2, 2.061(2); S2−S3, 2.060(3); S2−O1, 1.439(6); S2−O2, 1.441(6); S1−Mo−S3, 77.63(6); S1−S2−S3, 95.27(10); O1−S2−O2, 114.0(4); Mo−S3−S2−S1, 3.25(11).

Scheme 1



Treatment of Cp_2MoS_2O, **5**,[3] with a large excess of SO_2 gave mixtures of different compounds in varying proportions depending on the temperature, solvent and reaction time as shown in Scheme 1. In aprotic solvents such as DMF or CH_2Cl_2, a complex mixture formed with **4** being the major component accompanied by molybdocene *O*,*S*-thiosulfate $Cp_2MoS_2O_3$.[10] The identities of the other products are still under investigation. When the reaction was conducted in methanol or ethanol, formation of the corresponding bis(*O*-alkylthiosulfates), **6**, along with **4** could be established. The structure of **6a** was determined[11] and is shown in Figure 2. The structural parameters of the thiosulfate ligand in **6** are similar to those in the gold thiosulfate derivative, $Na_3Au(S_2O_3)_2$,[12] where the S−S and S−O distances were determined as 2.060(5) and 1.46(1) Å, respectively. Apparently, esterification of the thiosulfate ligand does not significantly influence the geometry of the molecule. The **6**/**4** product ratio appears to be controlled by temperature of saturation with SO_2. It increases from 0.7 at room temperature to 2.7 at −78 °C. Complexes **4** and **6** are remarkably stable; they can be purified without decomposition by column chromatography. Compound **6** slowly decomposed on prolonged storage (several months) at room temperature.

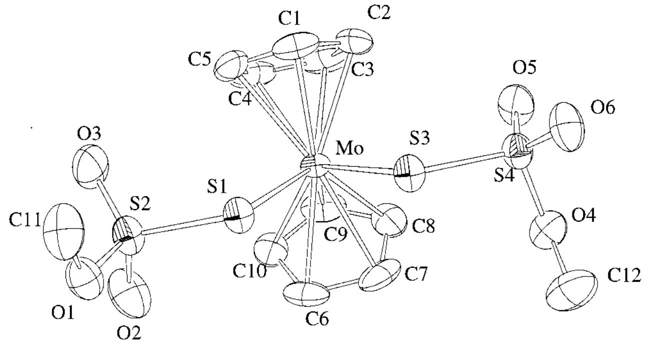


Figure 2. ORTEP drawing of **6a**. Selected bond distances (Å) and angles (deg): Mo−S1, 2.4868(9); Mo−S3, 2.4795(5); S1−S2, 2.0489(12), S3−S4, 2.0372(12); S2−O1, 1.565(3); S2−O2, 1.432(3); S2−O3, 1.410(3); S4−O4, 1.582(3); S4−O5, 1.426(2); S4−O6, 1.426(3); S3−Mo−S1, 74.36; S2−S1−Mo, 108.88(4); S4−S3−Mo, 111.69(4).

The insertion of SO_2 into the O−O bond of a metal peroxo complex is believed to begin with cleavage of the metal−oxygen bond followed by insertion of SO_2 between metal and oxygen atoms. Rearrangement gives the sulfate ligand. Such a mechanism was supported by ^{18}O isotopic labeling experiments[13] as well as by theoretical calculations[14] and is presented in eq 3.

As for disulfide **3**, however, this mechanism probably does not apply as it would result in the formation of a Mo−O bond as in **7**. A Mo−O bond is ca. 23−30 kcal/mol stronger than a Mo−S bond.[15] Thus, subsequent cleavage of a Mo−O bond in favor of the Mo−S bond to give **4** appears to be unlikely. An alternative mechanism involves initial formation of a labile SO_2 adduct as observed with $Cp^*{}_2Mo_2S_4$ (**8**) (Cp*

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(8) Compound **4** $Cp_2MoS_3O_2$. An orange diamond-shaped crystal of **4** (0.40 × 0.15 × 0.06 mm) was used for data collection. The crystal is monoclinic, $P2_1/n$, $a = 7.6782(6)$ Å, $b = 14.580(3)$ Å, $c = 10.2730(10)$ Å, $\beta = 92.04(1)°$, $V = 1149(3)$ Å^3, $Z = 4$, $Z'' = 1$, $d_{calcd} = 2.048$, $2\Theta = 120°$; radiation used: Cu Kα, 1.54178 Å. Data were collected in the $\bar{\omega}/2\Theta$ scan mode at 22 °C; 1845 reflections measured, 1705 independent ($R_{int} = 0.012$) used in refinement on $|F^2|$. Data corrected absorption (ψ scans) ($\mu = 14.278$ mm^{-1}, transmission range = 0.41−1.00); 146 parameters refined, all non-H atoms anisotropic, H atoms constrained. Final R1 = 0.0394 ($I > 2\sigma(I)$), 0.0489 (all); ϖR2 = 0.0911 ($I > 2\sigma(I)$), 0.0952 (all data). Residual electron density: −0.700 to +0.475 e Å^{-3}.

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(11) Compound **6a** $Cp_2Mo(SSO_3Me)_2$. A red thick plate-shaped crystal of **6a** (0.47 × 0.36 × 0.20 mm) was used for data collection. The crystal is triclinic, $P\bar{1}$, $a = 8.3226(13)$ Å, $b = 8.4736(11)$ Å, $c = 12.382(2)$ Å, $\alpha = 87.803(11)°$, $\beta = 77.758(11)°$, $\gamma = 86.383(12)°$, $V = 851.4(2)$ Å^3, $Z = 2$, $Z' = 1$, $d_{calcd} = 1.874$, $2\Theta_{max} = 50°$; radiation used: MoKα, 0.71069 Å. Data were collected in the $\bar{\omega}/2\Theta$ scan mode at 22 °C; 6405 reflections measured, 2991 unique ($R_{int} = 0.053$) used in refinement on $|F^2|$. Data corrected absorption (ψ scans) ($\mu = 1.285$ mm^{-1}, transmission range = 0.80−1.00). The structure was solved by a direct method using Shelxs-96, 211 parameters refined for 2991 reflections, all non-H atoms anisotropic, H atoms constrained to the parent site. Final agreement factors R1 = 0.0309 ($I > 2\sigma(I)$), 0.0393 (all); $\bar{\omega}$R2 = 0.0666 ($I > 2\sigma(I)$) 0.0694 (all data). Residual electron density: −0.824 to +0.647 e Å^{-3}.

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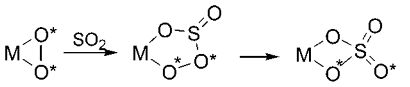
$= C_5Me_5$).[16] In the case of **3**, the SO_2 group could insert into the strained S−S bond with the formation of the dithiosulfate ligand in **4** (eq 4).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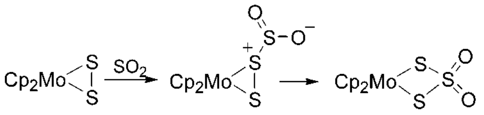
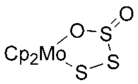

3 **4**
(4)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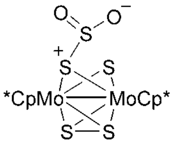
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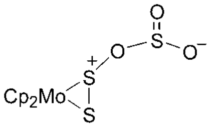
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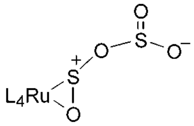
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In the case of **5**, the key factor may be a strongly localized negative charge on the oxygen atom. As a consequence of this, attack by SO_2 may form adduct **9** analogous to the known compound **10**.[17]

If **9** lost SO_3, to give **3**, this would lead to give **4** as observed. However, no evidence for **9** was detected. The reaction of **5** with SO_2 in alcohol to give **6** must involve other steps, but their details are unknown. Even in the presence of alcohol, some dithiosulfate **4** and other products form.

The reactivity of molybdocene disulfide **3** and disulfide oxide **5** with SO_2 illustrates a new synthetic approach to organometallic polysulfide oxides. Such SO_2-fixing reactions are interesting with respect to the area of Claus-like chemistry.

Experimental Section

All reactions were performed under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a JEOL CPF270 spectrometer. Chemical shifts were measured relative to solvent peaks. Infrared spectra were obtained using KBr disks. Melting points were determined in air and are uncorrected. Electron impact (EI) mass spectra were obtained by a Kratos MS25 RSA spectrometer. Microanalyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario, Canada). Methylene chloride was distilled from P_2O_5. Compounds Cp_2MoS_2 (**3**)[18] and Cp_2MoS_2O (**5**)[3] were prepared according to literature methods.

Preparation of 4. A solution of **3** (100 mg, 0.345 mmol) in methylene chloride (20 mL) was mixed with 20 mL of EtOH and then saturated with SO_2 for 15 min at room temperature. After stirring for an additional 1 h, the solvent was removed under reduced pressure to give pure **4**, 100%. It decomposed without melting above 220 °C. ^1H NMR (DMSO-d_6): $\delta = 5.65$ (s, 10H, Cp). ^{13}C NMR (DMSO-d_6): $\delta = 98.7$ (s, Cp). MS (EI, 300 °C, 70 eV): m/z (%) 355 [M^+] (16), 292 [$M^+ - SO_2$] (19), 259 [$M^+ - S_2O_2$] (12), 228 [$M^+ - S_3O_2$] (57). IR(KBr): $\nu = 586, 834, 1072$ (S═O sym), 1090 (S═O sym); 1229 (S═O asym) cm^{-1}. Anal. Calcd for $C_{10}H_{10}MoO_2S_3$: C, 33.90; H, 2.84; S, 27.15. Found: C, 34.06; H, 2.88; S, 26.89.

Preparation of 6. A solution of **5** (50 mg, 0.163 mmol) in ROH (20 mL) was saturated with a strong stream of SO_2 for 5 min at −78 °C and then kept at −30 °C (freezer) for 48 h. The solution was allowed to warm to room temperature, and solvent was removed under reduced pressure. The residue was extracted with small amounts of CH_2Cl_2 (3×5 mL). The combined extracts were chromatographed on a silica gel column. Elution with 5% acetone in chloroform gave the products **6a** and **6b**.

Data for 6a: decomposed without melting above 120 °C; ^1H NMR (DMSO-d_6) $\delta = 5.81$ (s, 10H, Cp); 3.78 (s, 6H, Me),^{13}C NMR (DMSO-d_6) $\delta = 56.5$ (s, Me), 99.9 (s, Cp); IR (KBr) $\nu =$ 598, 978, (S═O), 1133 (S═O sym); 1298, 1322 (S═O asym) cm^{-1}. Anal. Calcd for $C_{12}H_{16}MoO_6S_4$: C, 30.00; H, 3.36; S, 26.70. Found: C, 30.21; H, 3.51; S, 26.60.

Data for 6b: decomposed without melting above 120 °C; ^1H NMR (DMSO-d_6) $\delta = 5.81$ (s, 10H, Cp), 4.15 (q, 4H, CH_2), 1.28 (t, 6H, Me); ^{13}C NMR (DMSO-d_6) $\delta = 14.5$ (s, Me), 66.6 (s, CH_2), 99.7 (s, Cp); IR (KBr) $\nu = 600, 907$, (S═O), 1134 (S═O sym); 1296 (S═O asym) cm^{-1}; MS (EI, 300 °C, 70 eV) m/z (%) 355 [$M^+ - SSO_2OEt, - OEt$] (4), 307 [$M^+ - SSO_2OEt, - OEt, - O$] (6), 292 [$M^+ - SSO_2OEt, - OEt, - 2\ O$] (19), 263 [$M^+ - SSO_2OEt, - OEt, - SO_2$] (12), 228 [$M^+ - 2\ SSO_2OEt$] (57). Anal. Calcd for $C_{14}H_{20}MoO_6S_4$: C, 33.07; H, 3.96; S, 25.22. Found: C, 33.28; H, 4.09; S, 25.20.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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