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Selective Oxidation of Cp_2MoS_2 and Cp_2MoS_4 To Give Cp_2MoS_2O and Cp_2MoS_4O, Respectively: A Novel Thermally Induced Oxygen Migration Converting 1-Oxo-Cp_2MoS_4O to 2-Oxo-Cp_2MoS_4O

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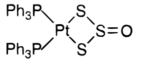
Summary: Oxidation of Cp_2MoS_x, where $x = 2, 4$, with m-chloroperbenzoic acid gave Cp_2MoS_2O and Cp_2MoS_4O, respectively. In Cp_2MoS_4O the oxygen is attached to the 2-sulfur atom of the S_4 ligand; however, an intermediate was isolated and identified as the 1-oxo isomer. It thermally rearranges via first-order kinetics with rate dependence on solvent polarity to give the final 2-oxo product.

Recently, the first homogeneous catalysts of the industrially important Claus reaction[1] ($2H_2S + SO_2 \rightarrow {}^3/_8S_8 + 2H_2O$) were reported.[2] The complex *cis*-$(PPh_3)_2Pt(SH)_2$ catalyzes the reaction via the intermediate **1**, which contains a 2-oxotrisulfido ligand. The oxygen transfer reaction leading to **1** and the mobility of the oxygen atom observed[3] in the transformation of **2** to **3** suggest that complexes containing oxopolysulfido ligands may represent activated forms of sulfur oxides leading to novel chemistry. However, easy access to such systems has not been possible in the past.[4] We report here the facile and selective oxidation of Cp_2MoS_x where $x = 2$, 4 to give the new complexes Cp_2MoS_2O and both isomers of Cp_2MoS_4O. The 1-oxo isomer undergoes a novel oxygen migration reaction to give the 2-oxo isomer.



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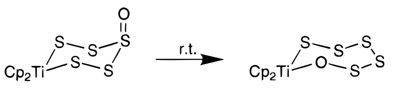
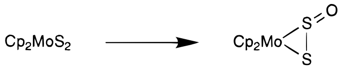
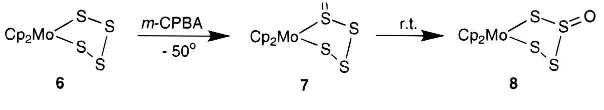


2 **3**



4 **5**



6 **7** **8**

Treatment of Cp_2MoS_2[5a] with *m*-chloroperbenzoic acid (*m*-CPBA) at −50 °C gave **5** in 82% yield.[6] The structure of **5**, shown in Figure 1, contains a S_2O ligand similar to that observed in $Cp_2Nb(S_2O)Cl$.[7] The nonplanarity of the MoS_2O ring results in two peaks for the Cp rings in the NMR spectrum, which is invariant in temperature up to 140 °C in DMSO-d_6.

Treatment of Cp_2MoS_4, **6**,[5b] with acid *m*-CPBA in

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[1] Grancher, P. *Hydrocarbon Process.* **1978**, *57*, 155−160.

[2] Shaver, A.; El-khateeb, M.; Lebuis, A.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2362−2363.

[3] Steudel, R.; Prenzel, A.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 550−552.

[4] Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1987**, *65*, 1190−1194. For a recent review on organometallic sulfenates see: Weigand, W.; Wünsch, R. *Chem. Ber.* **1996**, *129*, 1409−1419.

[5] (a) Köpf, H.; Hazari, S. K. S.; Leitner, M. *Z. Naturforsch.* **1978**, *33B*, 1398−1404. (b) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 375.

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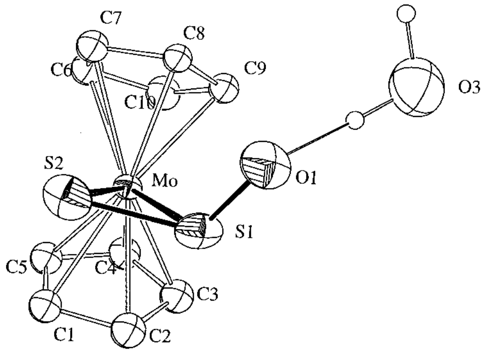

Figure 1. ORTEP drawing (40% probability) of Cp_2MoS_2O (**5**) showing the major orientation (90%) for the S_2O ligand (O1−O3, 2.897(8)). Selected bond distances (Å) and angles (deg): Mo−S1, 2.492(2); Mo−S2, 2.464(2); S1−S2, 2.036(3); S1−O1, 1.511(5); S1−Mo−S_2, 48.50(7); Mo−S1−S2, 65.02(7); Mo−S1−O1, 117.1(2); Mo−S2−S1, 66.48(7); O1−S1−S2, 114.5(2).

methylene chloride at −78 °C gave the final product **8**[8] in 52% yield. The structure of **8**, showing the position of the oxygen atom, is depicted in Figure 2. The geometry of the 2-S_4O ligand, the first of its kind to be structurally characterized, is quite similar to that determined for the S_4^{2-} ligand in **6**. The MoS_4O ring is also nonplanar and similarly results in two peaks for the Cp rings in the NMR spectrum, which are temperature invariant to at least 140 °C in DMSO-d_6.

The NMR spectrum of crude product of the above reaction recorded immediately after workup showed Cp peaks due to an intermediate, **7**, in addition to those of **8**. The peaks due to **7** rapidly decreased in intensity concomitant with the growth of the Cp peaks of **8**. Column chromatography gave **7** and permitted its spectral characterization, but its facile conversion[9] to **8** prevented analysis via X-ray crystallography. The physical and chemical properties of **7** are similar to those of **8**: two Cp peaks were observed in the ^{1}H NMR spectrum consistent with the presence of a sulfinyl oxygen; the infrared spectrum[10] of **7** showed a strong band at 1016 cm^{-1}, approximately 45 cm^{-1} lower than ν(SO) in **8** but very similar to that observed for **5** and for $Cp_2Nb(S_2O)Cl$.[7] The SO stretching vibration in **3,** which contains a sulfenic oxygen (S−O), was observed[3] at 868 cm^{-1}, significantly below 1000 cm^{-1}. Therefore the structure of **7** was assigned with the oxygen atom on the 1-sulfur atom.

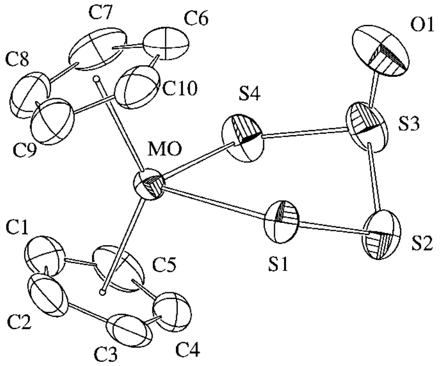

Figure 2. ORTEP drawing (40% probability) of Cp_2MoS_4O (**8**). Selected bond distances (Å) and angles (deg): Mo−S1, 2.446(1); Mo−S4, 2.440(1); S1−S2, 2.060(2); S2−S3, 2.073(2); S3−S4, 2.106(2); S3−O1, 1.479(5); S1−Mo−S_4, 87.25(4); S4−S3−O1, 109.0(2); S1−S2−S3, 101.85(7); S2−S3−S4, 99.01(7).

The rearrangement of **7** to **8** in a variety of solvents was followed by NMR spectroscopy and found to give first-order kinetics with the rate depending on the polarity of the solvent (Figure 3). Rearrangements of linear oxopolysulfides have been frequently rationalized as ionic[11a,b] or radical processes.[11c−e] In cyclic oxopolysulfides, however, photochemical,[11f] radical,[11g] and oxygen-catalyzed[11h] transformations have been observed. The latter do not apply to the rearrangement of **7** since neither BHT, oxygen, nor light influence the reaction rate. We postulate that **7** undergoes ring

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[6] A solution of *m*-CPBA (84 mg, 0.486 mmol) in CH_2Cl_2 (15 mL) was added slowly with stirring to **4** (140 mg, 0.482 mmol) in CH_2Cl_2 (100 mL) at −50 °C. The reaction mixture was allowed to warm slowly to room temperature, washed with $NaHCO_3$ solution, dried, and passed through a chromatographic column (silica gel/chloroform). Elution with $CHCl_3$/acetone (4:1 and 1:1 consecutively) gave a fraction from which **5** (121 mg, 82%) was isolated. Mp 175−180 °C decomp without melt. ^{1}H NMR: δ = 4.96 (s, 5H, Cp), 5.15 (s, 5H, Cp). ^{13}C NMR: δ = 91.6 (s, Cp), 94.6 (s, Cp). IR (CH_2Cl_2): ν(S=O) = 1003 cm^{-1}. Anal. Calcd for $C_{10}H_{10}MoS_2O$: C 39.22, H 3.29, S 20.94. Found: C 39.50, H 3.21, S 21.06. Slow evaporation of a chloroform solution in air gave the crystallographic sample as red prisms containing 0.5 molecule of water of crystallization per molecule of **5**. Crystal data for **5**$\cdot{}^1/_2H_2O$: $C2/c$, a = 28.126(4) Å, b = 5.9198(7) Å, c = 14.290(2) Å, β = 114.722(8)°, V = 2161.3(5) Å^3, Z = 8, D_c = 1.938 g/cm^3, $F(000)$ = 1256, λ (Mo Kα) = 0.710 69 Å, μ (Mo Kα) = 1.527 mm^{-1}. Data collection: AFC6S diffractometer, graphite monochromator, 2θ max = 50°, reflections measured = 4112, independent = 2093, $R_{(int)}$= 0.024, R_1 = 0.035, wR_2 = 0.040 for 1640 reflections with $I > 2\sigma I$. A complete structural report is included in the Supporting Information. The S_2O ligand is disordered over two orientations; the major orientation (90%) is represented in Figure 1.

[7] Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130−3136.

[8] A solution of *m*-CPBA in CH_2Cl_2 (10 mL, 0.31 mmol) was added slowly with stirring to **6** in CH_2Cl_2 at −78 °C (100 mL, 0.28 mmol). The reaction mixture was allowed to warm slowly to room temperature, stirred for 6 h, and then passed through a chromatographic column (silica gel/chloroform). Elution with $CHCl_3$/acetone (9:1 and 4:1 consecutively) gave a fraction from which **8** (54 mg, 52%) was recovered. Recrystallization from DMF/water gave the analytical sample **8**. Selected data for **8**: mp 185−190 °C (decomp without melt); ^{1}H NMR (DMSO-d_6) δ = 5.42 (s, 5H, Cp), 5.69 (s, 5H, Cp); ^{13}C NMR (DMSO-d_6) δ = 97.6 (s, Cp), 97.7 (s, Cp); IR(CH_2Cl_2) ν(SO) = 1061 cm^{-1}; MS (EI, 350 °C, 70 eV) m/z (%) 355 [M$^+$ − O] (11), 292 [M$^+$ − S_2O] (44), 259 [M$^+$ − S_3O] (35), 228 [M$^+$ − S_4O] (100). Anal. Calcd for $C_{10}H_{10}MoOS_4$: C 32.43, H 2.72, S 34.63. Found: C 32.50, H 2.51, S 35.25. Recrystallization from DMF/MeCN gave X-ray quality crystals. Crystal data for **8**: $P2_1/c$, a = 6.610(1) Å b = 13.368(3) Å, c = 14.122(4) Å, β = 100.49(2)°, V = 1227.0(5) Å^3, Z = 4, D_c = 2.005 g/cm^3, $F(000)$ = 736, λ (Mo Kα) = 0.710 73 Å, μ (Mo Kα) = 1.722 mm^{-1}. Data collection: AFC6S diffractometer, 2θ_{max} = 52°, reflections measured = 9251, independent = 2413, $R_{(int)}$ = 0.058, R_1 = 0.034, wR_2 = 0.072 for 2125 reflections with $I > 2\sigma I$. A complete structural report is included in the Supporting Information. The structure was refined using SHELXL-93. Hydrogen atom positions were calculated at idealized geometries using default C−H distances.

[9] A solution of *m*-CPBA in CH_2Cl_2 (10 mL, 0.31 mmol) was added slowly with stirring to a solution of **6** in CH_2Cl_2 at −78 °C (100 mL, 0.28 mmol); grinding in a mortar helped dissolve **6**. The coolant was removed, and the reaction was allowed to warm to −20 °C and then passed through an insulated chromatogrpahic column at −20 °C (silica gel/chloroform). Elution with $CHCl_3$/acetone (4:1) and then with pure acetone gave the product-containing fraction. This was concentrated under vacuum and treated with an equal volume of pentane to give the product, which was collected (decantation), washed with acetone and diethyl ether, and dried under a stream of nitrogen (41 mg, 40%). Selected spectral data for **7**: ^{1}H NMR (DMSO-d_6) δ = 5.29 (s, 5H, Cp), 5.39 (s, 5H, Cp); ^{13}C NMR (DMF-d_7) δ = 98.7 (s, Cp), 100.1 (s, Cp); IR(CH_2Cl_2) ν(S=O) = 1016 cm^{-1}. The rearrangement of **7** to **8** occurs also in the solid state; however, the compound can be stored for several days at −15 °C (after 2 months of storage at this temperature, approximately 35% of **7** had rearranged to **8**).

[10] The infrared spectra of **4** and **6** and their oxides **5**, **7**, and **8** in the ν(S=O) stretching region are complicated by the presence of bonds due to C−H bending vibrations observed due to the breakdown of C_{5v} symmetry (see: Butler, I. S.; Harvey, P. D.; McCall, J. M.; Shaver, A. *J. Raman Spectrosc.* **1986**, *17*, 221). The greater intensity for the ν(S=O) bands was useful in making the assignments.

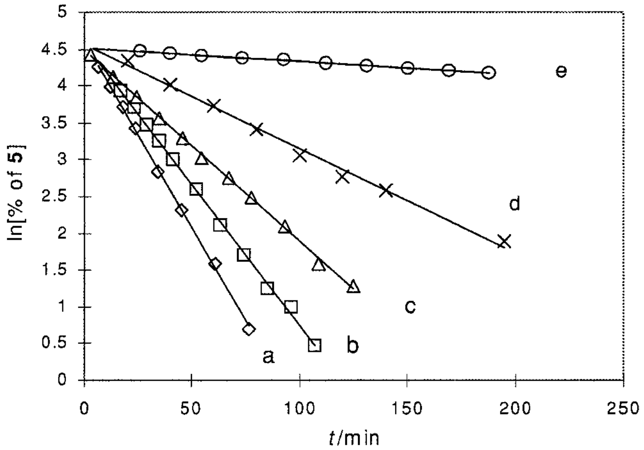
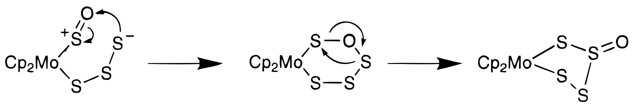


Figure 3. Kinetic study of the rearrangement of **7** to **8**: (a) DMSO-d_6, (b) DMF-d_7, (c) C_5D_5N, (d) $(CD_3)_2CO$, and (e) $CDCl_3$.

cleavage to form an ionic intermediate via an intramolecular reaction, consistent with the kinetic studies. One of the several possibilities is shown below, but further studies are required to determine the exact mechanism.



This work demonstrates that selective access to organometallic oxopolysulfides is possible via simple oxidation.[12] Further, an unprecedented oxygen migration leads to the formation of another oxopolysulfide, thus confirming the notion that such species are chemically novel.

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Supporting Information Available: Tables describing the X-ray analysis (data collection and analysis), crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and least-squares planes for **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) a) Kice, J. L.; Large, G. B. *J. Am. Chem. Soc.* **1968**, *90*, 4969–4076. (b) Derbesy, G.; Harpp, D. N. *J. Org. Chem.* **1995**, *60*, 4468–4474. (c) Miller, E. G.; Rayner, D. R.; Thomas, H. T.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4861–4868. (d) Koch, P.; Ciuffarin, E.; Fava, A. *J. Am. Chem. Soc.* **1970**, *92*, 5971–5977. (e) Chau, M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711–7716. (f) Yomoji, N.; Takahashi, S.; Shin-ichi, C.; Ogawa, S.; Sato, R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1995–2000. (g) Ishii, A.; Nakamura, S.; Yamada, T.; Nakayama, *J. Tetrahedron* **1997**, *53*, 12203–12214. (h) Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499–7506.

(12) Oxidation of Cp_2WS_4 gave $Cp_2W(2\text{-}OS_4)$, the analogue[13a] of **8**. The intermediate analogous to **7** was detected[13b] by ^1H NMR; however, attempted isolation resulted in a mixture of both isomers.

(13) (a) Selected data $Cp_2W(2\text{-}S_4O)$: mp 170–175 °C (decomp without melt); ^1H NMR (DMSO-d_6) $\delta = 5.40$ (s, 5H, Cp), 5.66 (s, 5H, Cp); ^{13}C NMR (DMSO-d_6) $\delta = 95.1$ (s, Cp), 95.5 (s, Cp); IR(KBr) $\nu(S{=}O) = 1043\ cm^{-1}$; MS (EI, 250 °C, 70 eV) m/z (%) 378 $[M^+ - S_2O]$ (100), 345 $[M^+ - S_4O]$ (93), 313 $[M^+ - S_4O]$ (44). Anal. Calcd for $C_{10}H_{10}WOS_4$: C 26.21, H 2.20, S 27.99. Found: C 26.20, H 1.71, S 28.17. (b) Spectral data for $Cp_2W(1\text{-}S_4O)$: ^1H NMR (DMF-d_7) $\delta = 5.36$ (s, 5H, Cp), 5.39 (s, 5H, Cp).