

**Supplementary Material Available:** Tables of atomic positions and their estimated standard deviations and calculated hydrogen atom positions for 1-3 (Tables 1, 5, and 8), general temperature factor expressions for 1-3 (Tables 2, 6, 9), and least-squares planes

and dihedral angles for 1 and 3 (Tables 3 and 10) (25 pages); observed and calculated structure factors for 1-3 (Tables 4, 7, and 11) (63 pages). Ordering information is given on any current masthead page.

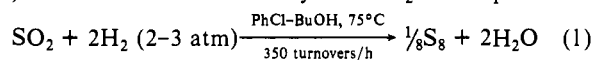
## Cleavage of SO<sub>2</sub> on (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)<sub>2</sub> To Form S<sub>8</sub> and a Thiosulfate Complex, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>). Possible Role in Homogeneous Hydrogenation of SO<sub>2</sub> Catalyzed by Mo-S Complexes

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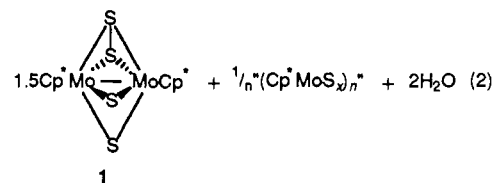
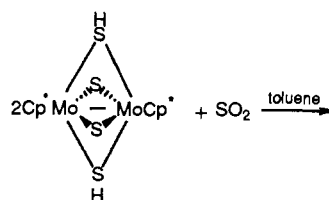
Contribution from the Inorganic and Structural Group (INC-4), Los Alamos National Laboratory, MS C346, Los Alamos, New Mexico 87545. Received March 8, 1989

**Abstract:** Reaction of SO<sub>2</sub> with solutions of Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S) (**1**) initially yields 1·SO<sub>2</sub>, which is shown by crystallography to contain an SO<sub>2</sub> weakly bound to a μ-S (S-S = 2.60 Å). SO<sub>2</sub> further reacts with 1·SO<sub>2</sub> to quantitatively give Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>) (**2**), which now contains an SO<sub>3</sub> bound to the μ-S (S-S = 2.17 Å). Effectively, a μ-S<sub>2</sub>O<sub>3</sub> (thiosulfate) ligand is formed by an oxygen-transfer process, and the source of the oxygen as established by <sup>18</sup>O labeling is SO<sub>2</sub>. S<sub>8</sub> is also produced, showing that SO<sub>2</sub> has undergone net disproportionation to SO<sub>3</sub> and S<sub>8</sub>. The reaction rate is highly dependent on solvent polarity and base promoters such as Et<sub>3</sub>N. Sterically hindered amines do not accelerate the reaction, suggesting that they function as Lewis rather than Brønsted bases. The X-ray structure of **2** is identical with that of a complex formed in low yield (along with dimeric oxosulfido complexes) by air oxidation of **1**. **2** is readily hydrogenated at 25-75 °C to regenerate **1**, indicating that the mechanism of the previously studied hydrogenation of SO<sub>2</sub> to S<sub>8</sub> and H<sub>2</sub>O catalyzed by Mo-S complexes may involve **2** as an intermediate. Weak bases, e.g., Et<sub>3</sub>N, strip off the SO<sub>3</sub> functionality in **2** to give primarily mixtures of isomers of **1** and products of base-SO<sub>3</sub> interaction. Crystallographic data for Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S·SO<sub>2</sub>): space group P2<sub>1</sub>/c; a = 13.738 (2) Å, b = 10.581 (3) Å, c = 17.331 (4) Å, β = 92.41 (2)°; V = 2516.9 Å<sup>3</sup> at 296 K; D<sub>calc</sub> = 1.73 g/cm<sup>-3</sup> for Z = 4; R = 6.2% for 2017 independent reflections with I ≥ 2σ(I) and 2θ ≤ 45°. Crystallographic data for Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>): space group P2<sub>1</sub>/c; a = 13.730 (5) Å, b = 10.635 (3) Å, c = 16.862 (2) Å, β = 93.17 (5)°; V = 2458.5 Å<sup>3</sup> at 296 K; D<sub>calc</sub> = 1.81 g/cm<sup>-3</sup> for Z = 4; R = 4.0% for 2612 reflections with I ≥ 2σ(I) and 2θ ≤ 45°.

The activation of S=O bonds in SO<sub>2</sub> by transition-metal complexes, particularly toward reduction by hydrides and hydrogen,<sup>1-6</sup> has been a major recent focus of our research. We have shown<sup>1</sup> that the complexes investigated by Rakowski DuBois and co-workers,<sup>7</sup> [(Me<sub>n</sub>Cp)Mo(μ-S)(μ-SH)]<sub>2</sub>, where n = 0, 1, or 5 (Cp\*), catalyze homogeneous hydrogenation of SO<sub>2</sub> to S<sub>8</sub> and H<sub>2</sub>O (eq 1) and react stoichiometrically with SO<sub>2</sub> as in eq 2:



The disulfide-bridged product, Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)<sub>2</sub> (**1**), had previously been prepared and structurally characterized by Wachter's group,<sup>8</sup> and polymeric, insoluble (Cp\*MoS<sub>x</sub>)<sub>n</sub> (x = ~3)<sup>9</sup> is the synthetic precursor to [Cp\*MoS(SH)]<sub>2</sub>.<sup>7</sup> Both Mo



products of eq 2 react with H<sub>2</sub> under mild conditions similar to those in the catalytic reaction (eq 1) to regenerate the SH complex.<sup>1,7,8b</sup> Thus, eq 2 was believed to be a logical first step in the mechanism for catalytic reduction of SO<sub>2</sub>.<sup>1</sup> In order to gain more information on the role of **1** in the catalysis, we have studied the reactivity of **1** (and to a partial extent its MeCp analogue) with SO<sub>2</sub> and other oxygen-containing small molecules (SO<sub>3</sub>, O<sub>2</sub>) and report the results here.<sup>10</sup>

The formation of an SO<sub>2</sub> adduct of **1**, Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S·SO<sub>2</sub>), 1·SO<sub>2</sub>, with the SO<sub>2</sub> bound to a μ-S ligand, was not

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- (10) A portion of this work has been previously presented: Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA; American Chemical Society: Washington, DC, 1987; Paper INOR 256. Both we and Wachter's group (ref 11) independently synthesized and structurally characterized **2**.

surprising in view of our previous characterization of  $[\text{Cp}^*\text{W}(\text{CO})_2(\mu\text{-S}\text{SO}_2)]_2$ .<sup>4</sup> However, further reaction with  $\text{SO}_2$  to quantitatively give  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})(\mu\text{-SSO}_3)$  (**2**) and elemental sulfur was unanticipated. Complex **2**, which has also been observed as a minor product of air oxidation of **1** by both Wachter's<sup>11</sup> and our group,<sup>10</sup> formally contains a bridging thio-sulfate ( $\mu\text{-SSO}_3$ ) ligand formed by oxygen transfer from  $\text{SO}_2$ . We have also observed oxygen transfer to give the  $\text{SO}_3$  moiety in the reaction of  $\text{SO}_2$  with  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{H}$  to yield  $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{SO}_3\text{H})$  and  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2(\mu\text{-SSO}_3)$ .<sup>6</sup> These facile  $\text{S}^{\text{IV}} \rightarrow \text{S}^{\text{VI}}$  conversions and the oxygen-donating ability of  $\text{SO}_2$  signal an important new area of  $\text{SO}_2$  reactivity that merits further attention. Furthermore the  $\text{S}_2\text{O}_3$  ligand in **2** displays novel reactivity, e.g., **2** can be hydrogenated back to **1** with elimination of  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . This suggests that **2** may be an intermediate in the catalytic  $\text{SO}_2$  hydrogenation (eq 1) and that thiosulfate species, which have now been found to be produced from  $\text{SO}_2$  in several systems, may play an important role in  $\text{SO}_2$  reduction. The  $\text{SO}_3$  moiety in **2** can also be cleaved off with weak organic bases to regenerate **1**, potentially setting the stage for a catalytic cycle wherein  $\text{SO}_2$  is disproportionated to sulfur and  $\text{SO}_3$ -containing derivatives under mild conditions.

## Experimental Section

**Materials and Instrumentation.** Reactions were carried out under inert atmosphere using Schlenk techniques except for  $\text{O}_2$  oxidations. Reagent-grade solvents,  $\text{SO}_2$ ,  $\text{SO}_3$  (Alfa Inorganics), and  $\text{Mo}(\text{CO})_6$  (Strem Chemical) were usually used as received, but for some reactions, solvents were dried by distillation from appropriate drying agents. Liquid  $\text{SO}_2$  used as solvent was purified by passage through a  $-95^\circ\text{C}$  trap, and both it and  $\text{SO}_3$  were manipulated on a vacuum line. The preparations of  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  were modifications of literature methods,<sup>7a,12</sup> and the synthesis of the MeCp analogue followed the published procedure.<sup>7a</sup>  $\text{S}^{18}\text{O}_2$  (95%) was prepared by reaction of  $\text{S}_8$  and  $\text{N}^{18}\text{O}$ ;  $^{18}\text{O}_2$  was also prepared from  $\text{N}^{18}\text{O}$ .<sup>13</sup>

Infrared and  $^1\text{H}$  NMR spectra were recorded on Perkin-Elmer 521 and Varian EM-390 (90-MHz) instruments, respectively. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Preparation of  $(\text{Cp}^*\text{MoS}_x)_n$  and  $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$ .** The procedure described here is a modification of that reported<sup>9b</sup> and is carried out in one flask. A mixture of  $\text{Mo}(\text{CO})_6$  (9.0 g, 34 mmol) and 100 mL of propionitrile was refluxed for 24 h in a 500-mL flask to form  $\text{Mo}(\text{C}-\text{O})_3(\text{C}_2\text{H}_5\text{CN})_3$ <sup>14</sup> (Caution: large amounts of CO are evolved). Solvent was completely removed in vacuo, 400 mL of THF and 5.3 mL of  $\text{Cp}^*\text{H}$  was added to the residue, and the mixture was refluxed for 30 min. This reaction nearly quantitatively formed  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ ,<sup>3</sup> which is thermally unstable in solution at the reflux temperature and partially converts to  $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2$ , imparting a red color to the solution. After the solution was cooled to  $\sim 25^\circ\text{C}$ , 5.03 g of  $\text{S}_8$  was carefully added portionwise (rapid CO loss and foaming may occur) and the mixture was refluxed for 18 h. The cooled solution was filtered, and the nearly black insoluble precipitate of  $(\text{Cp}^*\text{MoS}_x)_n$  was washed with several generous portions of THF. The solid was dried in vacuo (yield, 7.7 g).

Reduction of solvent volume from the filtrate of the reaction gave a side product,<sup>9b</sup>  $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$  (0.57 g of black microcrystals were obtained from a 3.5 $\times$  smaller scale reaction upon solvent reduction to 10 mL). This complex can also be used as a precursor to  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$ .<sup>7</sup> The reaction sequence here produced proportionately more  $(\text{Cp}^*\text{MoS}_x)_n$  than  $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$  in comparison to the previously reported<sup>9b</sup> reaction of  $\text{S}_8$  with  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$  purified by sublimation, possibly because of the in situ procedure and the 6-h longer reflux period for the final step.

**Preparation of  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$ . From  $\text{H}_2$  Reduction.** Into a heavy-walled glass 250-mL Fischer-Porter pressure vessel were placed 2.1 g of  $(\text{Cp}^*\text{MoS}_x)_n$ , 30 mL of chlorobenzene, 15 mL of ethanol, and 1 mL of  $\text{Et}_3\text{N}$ . The mixture was degassed by two freeze-pump-thaw cycles and 1 atm  $\text{H}_2$  was added to the vessel while nearly totally immersed in liquid nitrogen, giving  $\sim 3$  atm  $\text{H}_2$  pressure on warming to  $25^\circ\text{C}$ . The lower portion of the vessel containing the liquid phase was then immersed in an oil bath at  $100^\circ\text{C}$ , and the mixture was stirred magnetically. The

solution became red and reaction appeared to be complete within an hour. The mixture was stirred for an additional period (overnight in one case) to ensure complete reaction, then cooled to  $25^\circ\text{C}$ , and filtered to remove a fine black solid. Solvent volume was reduced to 10 mL, 15 mL of *n*-BuOH was added, and the resultant precipitate of  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  was collected, washed first with ethanol and then hexane, and dried in vacuo for a short period (some decomposition may occur upon prolonged pumping). The yield of dark red-brown microcrystals from an 18-h reaction was 1.38 g (73% based on formulating  $x = 3$  in  $(\text{Cp}^*\text{MoS}_x)_n$ ).

**From  $\text{LiEt}_3\text{BH}$  Reduction.**  $(\text{Cp}^*\text{MoS}_x)_n$  (4.14 g) was stirred with 45 mL of 1 M  $\text{LiEt}_3\text{BH}$  in THF (Aldrich) for 2 h, as reported for the Cp analogue.<sup>12</sup> Reaction was incomplete however, and an additional 35 mL of the hydride was added. After overnight reaction, unreacted starting material was still present and 15 mL more hydride was added (95 mL total, about twice the amount used for the Cp analogue). Further stirring for 2 h finally gave complete reaction, and the mixture was quenched by dropwise addition of  $\text{H}_2\text{O}$ . Addition of 50 mL of  $\text{H}_2\text{O}$  and reduction of solvent volume to  $\sim 80$  mL in vacuo gave 2.84 g (76%) of  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$ , isolated as above (except initial wash with  $\text{H}_2\text{O}$ ).

$\text{NaEt}_3\text{BH}$  was also used as a reducing agent in other reactions, but once again large excesses of the hydride (up to 10 equiv/equiv of  $(\text{Cp}^*\text{MoS}_x)_n$ ) and 18-h reaction period were necessary.  $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$  was also found to be reducible to  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  by  $\text{NaEt}_3\text{BH}$  under similar conditions.

**Preparation of  $\text{Cp}^*_2\text{Mo}_2(\text{S}_2)(\text{S})_2$  (**1**) from  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  and  $\text{SO}_2$ .**  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  (2.57 g) in 150 mL of toluene was saturated with  $\text{SO}_2$  and stirred for  $\sim 40$  min (or until NMR of aliquots no longer showed the presence of starting complex). The red reaction mixture was then immediately pumped in vacuo to remove all unreacted and complexed  $\text{SO}_2$  (and some solvent). When the solution color became the deep blue characteristic of **1**, the reaction mixture was filtered to remove 0.32 g of polymeric violet-brown  $(\text{Cp}^*\text{MoS}_x)_n$  coproduct. Removal of most of the solvent and addition of hexane yielded 2.0 g of dark blue **1** containing  $\sim 5\text{--}10\%$  **2**. The latter is difficult to remove by recrystallization but can be reduced to **1** by adding  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  ( $\sim 0.12$  g or an amount equivalent to the quantity of **2** present) to the crude solution of **1** and stirring for 2 h. Recrystallization from  $\text{CHCl}_3$ -hexane yielded **1** pure enough for most purposes (note:  $\text{CH}_2\text{Cl}_2$  should not be used as a solvent for **1** because of alkylation of sulfide ligands). Alternatively, chromatography<sup>8a</sup> on silica yields pure **1** (excess red SH complex elutes first using 4:1 toluene-ether). **1** is air sensitive and slightly thermally unstable and should be stored in a refrigerator under inert atmosphere.

**Preparation of  $(\text{MeCp})_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$  from  $[(\text{MeCp})\text{MoS}(\text{SH})]_2$  and  $\text{SO}_2$ .** The synthesis was similar to that for **1** except that, because of much lower solubility, some of the MeCp complex may coprecipitate with insoluble  $[(\text{MeCp})\text{MoS}_x]_n$ . In this case, the desired complex can readily be separated from the latter by solvent extraction. The properties of the complex are similar to those described in the literature.<sup>7b</sup> Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{S}_4\text{Mo}_2$ : C, 30.13; H, 2.95; S, 26.82. Found: C, 29.70; H, 2.85; S, 26.95.

**Preparation of  $\text{Cp}^*_2\text{Mo}_2(\text{S}_2)(\text{S})(\text{S}\text{-SO}_2)$  (**1-SO}\_2**).** Treatment of a saturated solution of **1** in toluene with excess  $\text{SO}_2$  yielded a deep red crystalline precipitate of **1-SO}\_2**, which was collected on a frit and dried in a stream of  $\text{SO}_2$ . Further crops can be obtained by addition of  $\text{SO}_2$ -saturated hexane or partial solvent removal followed by readdition of  $\text{SO}_2$ . **1-SO}\_2** readily loses  $\text{SO}_2$  and must be stored in an  $\text{SO}_2$ -enriched atmosphere. The MeCp analogue was difficult to isolate as a solid, but a reversible color change from blue to red in solution on addition of  $\text{SO}_2$  indicated adduct formation.

**Isomerization and Alkylation of **1**.** After several days in toluene or  $\text{CHCl}_3$  solution at  $25^\circ\text{C}$  under  $\text{N}_2$ , **1** began to isomerize to  $[\text{Cp}^*\text{MoS}]_2(\mu\text{-S}_2)$  (**1'**) ( $\delta_{\text{CDCl}_3}$  1.97), and after 14 days,  $\sim 20\%$  conversion occurred. In  $\text{CH}_2\text{Cl}_2$ , alkylation of a bridging sulfide of **1** occurred in addition to isomerization, and these reactions were much more rapid than the above. NMR showed that **1** was absent within 5 days, and after 14 days, nine Cp\* resonances were observed in the range  $\delta_{\text{CDCl}_3}$  1.93-2.37, including a major signal at  $\delta$  2.01 due to another isomer of **1**,  $[\text{Cp}^*\text{MoS}(\mu\text{-S})]_2$  (**1''**). Major signals near  $\delta$  2.25 were apparently due to alkylated species, e.g.,  $[\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})(\mu\text{-SCH}_2\text{Cl})]\text{Cl}$ . In comparison, alkylation of **1** in  $\text{CH}_2\text{Cl}_2$  with  $\text{MeSO}_3\text{F}$  or  $\text{EtI}$  rapidly gave monoalkylated products with  $\delta$  2.28 and 2.24, respectively.

**Reactions of **1** with  $^{18}\text{O}_2$  and  $\text{H}_2^{18}\text{O}$ .** Reaction of  $^{18}\text{O}_2$  (0.3 mmol) with **1** (40 mg, 0.068 mmol) in 15 mL of  $\text{CHCl}_3$  (undried) in a 50-mL flask overnight gave a mixture of **2** ( $\sim 25\%$ ) and oxo-sulfido complexes, similar to the reaction carried out by Wachter and co-workers<sup>8a</sup> at  $50^\circ\text{C}$  in toluene. IR showed that **2** was partially  $^{18}\text{O}$ -labeled and that the oxo species were fully labeled. An identical reaction but with  $\text{SO}_2$  (1 mmol) present gave negligible reaction overnight, but if  $\text{Et}_3\text{N}$  (20  $\mu\text{L}$ ) was present the reaction gave  $\sim 3:1$  ratio of unlabeled **2** to labeled oxo complexes ( $\sim 2:1$   $^{18}\text{O}/^{16}\text{O}$ ).

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Table I. Spectroscopic Data for New Complexes and Related Sulfides

complex	$\nu_{\text{SO}}$ , cm <sup>-1</sup> <sup>a</sup>	$\delta$ , ppm <sup>b</sup>
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (μ-S) <sub>2</sub> (1)		2.14
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (S) <sub>2</sub> 1'		1.97
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (S) <sub>2</sub> 1''		2.02
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (μ-S)(μ-S-SO <sub>2</sub> ) (1-SO <sub>2</sub> )	1229, 1080, 533	2.13
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> CH <sub>2</sub> (μ-S) <sub>2</sub>		2.25 <sup>c</sup>
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> CH <sub>2</sub> (μ-S)(μ-S-SO <sub>2</sub> )	1243, 1088, 535	2.21 <sup>d</sup>
[Cp*W(CO) <sub>2</sub> (μ-S-SO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>	1198, 1053	2.20
[CpW(CO) <sub>3</sub> ](μ-S-SO <sub>2</sub> )	1213, 1074	5.04 <sup>e</sup>
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (μ-S)(μ-SSO <sub>3</sub> ) 2	1242, 1205, 1010, 604, 523	2.31
Cp* <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (μ-S)(μ-SS <sup>18</sup> O <sub>3</sub> )	1204, 1172, 960, 594, 515	2.31
MeCp <sub>2</sub> Mo <sub>2</sub> (μ-S) <sub>2</sub> (μ-S)(μ-SSO <sub>3</sub> )	1228, 1210, 1010, 600, 525	2.43

<sup>a</sup> Nujol mulls. <sup>b</sup> Resonance for Cp\*; CDCl<sub>3</sub> solvent, 90 MHz (CW), TMS reference. <sup>c</sup>  $\delta(\text{CH}_2)$  2.40. <sup>d</sup>  $\delta(\text{CH}_2)$  obscured. <sup>e</sup> Resonance for Cp, C<sub>6</sub>D<sub>6</sub> solvent.

A solution of **1** (30 mg, 0.05 mmol) in 5 mL of dried toluene containing H<sub>2</sub><sup>18</sup>O (50  $\mu$ L, 2.5 mmol) was stirred 18 h in the presence of atmospheric O<sub>2</sub> (~0.8 mmol) in a closed 100-mL flask. After solvent removal, NMR and IR of the residue showed nearly fully <sup>18</sup>O-labeled **2** and primarily unlabeled oxo complexes ( $\nu_{\text{Mo=O}}$  at 905–909 cm<sup>-1</sup>) (**2** does not undergo oxygen exchange with H<sub>2</sub><sup>18</sup>O under the reaction conditions here). A similar reaction in CH<sub>2</sub>Cl<sub>2</sub> gave primarily unlabeled **2**, essentially unlabeled oxo complexes, and some unreacted **1**. Similar 2-day reactions in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub> using unlabeled H<sub>2</sub>O or no added H<sub>2</sub>O gave mainly isomerization and alkylation products plus ~10% **2**.

**Preparation of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S<sub>2</sub>O<sub>3</sub>) (2) from [Cp\*MoS(SH)]<sub>2</sub>.** A solution of [Cp\*MoS(SH)]<sub>2</sub> (0.253 g) and 0.1 mL of Et<sub>3</sub>N (promoter) in 20 mL of CHCl<sub>3</sub> was treated with excess SO<sub>2</sub>. After 2 h the solvent was reduced to small volume in vacuo and ethanol (~10 mL) was added. Further pumping yielded 0.205 g (72%) of **2**, which was filtered off, washed with ethanol, and dried in vacuo. Anal. Calcd for C<sub>20</sub>H<sub>30</sub>S<sub>3</sub>O<sub>3</sub>Mo<sub>2</sub>: C, 35.82; H, 4.51; S, 23.91; Mo, 28.61. Found: C, 35.80; H, 4.71; S, 23.59; Mo, 28.19. **2** was stable in air and on heating to 100 °C in vacuo or under N<sub>2</sub>, whereupon slow decomposition with negligible gas evolution began.

Complete solvent removal from the above filtrate gave a red-brown oily residue, which apparently contained Et<sub>3</sub>NH<sup>+</sup> salts ( $\nu_{\text{NH}}$  = 2500 cm<sup>-1</sup>;  $\delta$  3.1 (q, CH<sub>2</sub>), 1.3 (t, CH<sub>3</sub>)).

**Preparation of 2 from 1: Preparation of MeCp Analogue of 2.** In CH<sub>2</sub>Cl<sub>2</sub>, **1** (0.50 g) in 8 mL of CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mL of Et<sub>3</sub>N was reacted with SO<sub>2</sub> as above. A small amount of black precipitate was filtered, and complete solvent removal in vacuo gave 0.615 g of a mixture of **2** and Et<sub>3</sub>N<sup>+</sup> salts. Extraction of this residue with H<sub>2</sub>O yielded an oily solid (~60 mg) with  $\nu_{\text{SO}}$  bands and NMR Et resonances consistent with the presence of Et<sub>3</sub>NH<sup>+</sup> salts of oxysulfur anions. The remaining solid **2** was fairly pure and the yield nearly quantitative. **2** can be easily purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane.

The MeCp analogue of **2** was prepared by allowing a saturated solution of (MeCp)<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)<sub>2</sub> in toluene-CHCl<sub>3</sub> to stand for ~64 h in a closed flask in the presence of excess SO<sub>2</sub> (not rigorously anaerobic). Crystals of the desired complex formed and exhibited physical and spectral properties similar to **2** (Table I).

**In Liquid SO<sub>2</sub>. Identification of S<sub>8</sub> as a Product.** Into a 250-mL heavy-wall glass Fischer & Porter pressure vessel was placed 0.50 g of **1**. SO<sub>2</sub> was condensed into the flask on a vacuum line, and the solution (~10 mL of liquid SO<sub>2</sub>) was allowed to stand overnight at 25 °C. Removal of SO<sub>2</sub>, extraction of the residue with CS<sub>2</sub> (5 mL), filtration, and removal of CS<sub>2</sub> yielded a rose-colored residue. Washing the latter with ~1 mL of CHCl<sub>3</sub> left a small amount (~5 mg) of a light-colored solid that was sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> and toluene but very soluble in CS<sub>2</sub>. When the solid was heated in vacuo, a yellow sublimate formed, and when ignited with a torch on a glass slide, it burned leaving no residue. These properties were clearly characteristic of S<sub>8</sub>. The total yield of **2** (mainly recovered from the original extraction residue) was 0.57 g (92%).

**Preparation of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S<sub>2</sub><sup>18</sup>O<sub>3</sub>) from 1 and S<sup>18</sup>O<sub>2</sub> (But Not SO<sub>2</sub> + <sup>18</sup>O<sub>2</sub> or H<sub>2</sub><sup>18</sup>O).** A solution of **1** (40 mg, 0.068 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (3 mL) containing Et<sub>3</sub>N (50 mL, 0.36 mmol) in a 15-mL flask was treated with 2 equiv of S<sup>18</sup>O<sub>2</sub> (95%) on a vacuum line. After 3 h, addition of ethanol and partial solvent removal precipitated nearly fully <sup>18</sup>O-labeled **2**, characterized by IR (Table I). Analogous closed-flask reactions using normal SO<sub>2</sub> (>2 equiv) in the presence of either <sup>18</sup>O<sub>2</sub> (90 Torr, 0.1 mmol) or H<sub>2</sub><sup>18</sup>O (50  $\mu$ L, 2.5 mmol) gave little or no incorporation of <sup>18</sup>O into **2**.

**NMR Studies of Rates of Reaction of 1 with SO<sub>2</sub> to Give 2 in Various Solvents.** Qualitative rates of conversion of **1** to **2** (summarized in Table II) were studied by saturating solutions of **1** (~10 mg) in various solvent systems with SO<sub>2</sub> in 5-mm NMR tubes or small volume flasks and

Table II. Summary of Reactions of SO<sub>2</sub> with 1<sup>a</sup>

solvent	promoter, mmol	SO <sub>2</sub> , mmol	reactn time	% compln <sup>b</sup>	
liquid SO <sub>2</sub>		11.0	30 min	50	
			45 min	66	
			120 min	100	
Et <sub>3</sub> N	1.00	11.0	5 min	100	
		0.72	11.0	5 min <sup>c</sup>	75
		0.04	11.0	8 min <sup>c</sup>	15
	(t-Bu) <sub>2</sub> Mepy	1.00	11.0	8 min <sup>c</sup>	33
		0.65	11.0	8 min <sup>c</sup>	0
			0.7	7 days	<5
CDCl <sub>3</sub>	Et <sub>3</sub> N	0.14	0.7 <sup>d</sup>	4 h	50
				24 h	85
			45 h	100	
	py	0.14	0.7	10 min	50
				20 min	75
				60 min	93
	(t-Bu) <sub>2</sub> Mepy	0.14	0.7	120 min	95 <sup>e</sup>
				1 h	<5
				5 h	65
			8 h	87	
		3 h	100		
CDCl <sub>3</sub> -CD <sub>3</sub> OD (10:1)		satd	60 min	100	
		satd	10 min	100	
CH <sub>3</sub> NO <sub>2</sub>	py	0.25	satd	6 h	100
			satd	4 days	<5
CD <sub>3</sub> CN	Et <sub>3</sub> N	0.10	0.4	22	
			satd	4 days	22
benzene	py	0.07	0.7	50	
			satd	4 h	100
PhCl	py	0.07	0.7	50 <sup>f</sup>	
			satd	4 h	100
PhCl-CD <sub>3</sub> OD (1:1)		0.7	5 min	50 <sup>f</sup>	
			10 min	100	
	Et <sub>3</sub> N	0.07	0.7	2.5 min	50
				8 min	100
	py	0.07	0.7	2.5 min	75
				6 min	100
	(t-Bu) <sub>2</sub> Mepy	0.07	0.7	4 min	70
				11 min	100

<sup>a</sup> Reactions were carried out either in sealed NMR tubes or in small volume vessels, using 2–5 mg (0.003–0.008 mmol) of **1** in ~0.5 mL of solvent; satd, saturated with SO<sub>2</sub>. <sup>b</sup> As judged by relative intensities of Cp\* NMR resonances of **1** and **2**. <sup>c</sup> At 0 °C. <sup>d</sup> Reaction used 15 mg of **1** and measured amount of SO<sub>2</sub> (other CDCl<sub>3</sub> reactions utilized SO<sub>2</sub>-saturated solutions, which correspond to approximately 0.7 mmol SO<sub>2</sub> in 0.5 mL of CDCl<sub>3</sub>). <sup>e</sup> Reaction appeared to reach an equilibrium. <sup>f</sup> Reaction was relatively slow initially (10% complete after 2.25 min), but rate increased rather than decreased as for most of the other reactions.

following the reaction by proton NMR. Integration of the Cp\* resonances gave product to starting material ratios. In most cases the tubes were sealed to keep out air or contain liquid SO<sub>2</sub>. For the reaction of **1** (purified by chromatography) in liquid SO<sub>2</sub>, formation of **2** was ~50% complete in 0.5 h, ~70% complete in 0.75 h, and complete in 2 h. A small amount of insoluble deep violet solid was found on opening the sealed tube, evaporating SO<sub>2</sub>, and extracting **2** from the residue with CHCl<sub>3</sub>.

**Reaction of 2 with [Cp\*MoS(SH)]<sub>2</sub> to Give 1.** **2** (18 mg, 0.027 mmol) and [Cp\*MoS(SH)]<sub>2</sub> (16 mg, 0.027 mmol) were placed into an NMR tube, CDCl<sub>3</sub> was added, and the solution was degassed. <sup>1</sup>H NMR

Table III. Summary of Reactions of **2** with H<sub>2</sub> and Weak Bases

solvent/reactant <sup>a</sup>	condns <sup>b</sup>	time, h	product ratios, ~%				
			unreact <b>2</b>	<b>1</b>	<b>1'</b>	oxo <sup>c</sup>	other
CDCl <sub>3</sub> + H <sub>2</sub> (1 atm)	A, 25 °C	18	30	65			5 <sup>d</sup>
CDCl <sub>3</sub> + H <sub>2</sub> (1 atm)	B, 25 °C	96	70				30 <sup>d</sup>
CDCl <sub>3</sub> + Et <sub>3</sub> N + H <sub>2</sub> (1 atm)	B, 25 °C	4					100 <sup>d</sup>
BuOH-PhCl (1:1) + Et <sub>3</sub> N + H <sub>2</sub> (3 atm)	A, 75 °C	0.15					100 <sup>d</sup>
CHCl <sub>3</sub> -H <sub>2</sub> O (20:1)	A, reflux	48	100				
PhCl	A, 75 °C	18	100				
<b>BuOH-PhCl</b> (1:1)	A, 75 °C	2	10		45	25	20 <sup>e</sup>
<b>BuOH</b>	A, 75 °C	1	30		60	10	
<b>MeOH</b>	A, 75 °C	1.5	15		30	25	10 <sup>e</sup>
MeOH + Et <sub>3</sub> N	A, 75 °C	1	44	10	44	12	
<b>BuOH-PhCl</b> (1:1) + Et <sub>3</sub> N	A, 75 °C	0.67	28	44	28		
MeOH-CHCl <sub>3</sub> (1:1) + Et <sub>3</sub> N	A, 75 °C	5	10	40	50		
CDCl <sub>3</sub> + Et <sub>3</sub> N	B, 25 °C	96	50	40	10		
CDCl <sub>3</sub> -Et <sub>3</sub> N (1:4)	A, 25 °C	18	2	90	5	3	
<b>MeOH-CHCl<sub>3</sub></b> (4:1) + H <sub>2</sub> O	A, 75 °C	17		25	50	25	
<b>DMSO-<i>d</i><sub>6</sub>-CDCl<sub>3</sub></b> (3:1) + H <sub>2</sub> O	B, 75 °C	1.5			100		
<b>DMSO-<i>d</i><sub>6</sub>-CDCl<sub>3</sub></b> (1:1) + H <sub>2</sub> O	B, 25 °C	120	50		30	20	
<b>DMSO-CHCl<sub>3</sub>-H<sub>2</sub>O</b> (8:6:1)	A, 75 °C	0.75		5	95		
<b>acetone-CHCl<sub>3</sub>-H<sub>2</sub>O</b> (8:6:1)	A, 75 °C	18		15	70	15	

<sup>a</sup> Known or probable reactant with **2** is given in bold face. Amounts of **2** reacted ranged from 5 to 50 mg in 0.7–10 mL of solvent. The volume of Et<sub>3</sub>N and H<sub>2</sub>O adds typically were 2–5% of the solvent volume. <sup>b</sup> A, flask reaction; B, NMR tube reaction. <sup>c</sup> Primarily Cp\*<sub>2</sub>Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub> with lesser amounts of Cp\*<sub>2</sub>Mo<sub>2</sub>OS<sub>3</sub>. <sup>d</sup> [Cp\*Mo(S)(SH)]<sub>2</sub>. <sup>e</sup> **1'**.

showed approximately equal intensity peaks due to Cp\* of each complex. Et<sub>3</sub>N promoter (10 μL, 0.071 mmol) was then added and reaction was soon evident: a peak due to **1** grew in as the other two signals diminished. About 50% conversion occurred in 14 min and formation of **1** was complete in 40 min. No other significant Cp\* signals were observed, although an unidentified peak possibly due to OH or NH functionality appeared at low field and shifted to δ 2.5 during the reaction (final intensity ratio of this peak to Cp\* was 1:15). The quartet signal of Et<sub>3</sub>N shifted downfield by ~0.1 ppm, indicative of protonation to Et<sub>3</sub>NH<sup>+</sup>.

A larger scale reaction (0.843 g of **2**, 0.736 g of SH complex in 20 mL CH<sub>2</sub>Cl<sub>2</sub>, plus 0.5 mL of Et<sub>3</sub>N) stirred for 1.5 h yielded 1.29 g of **1** on partial solvent removal and heptane addition. The product was contaminated by ~7% unreacted **2** and ~3% alkylated **1**. Formation of the latter can be avoided if CHCl<sub>3</sub> is used as solvent.

**Reductions of **2** with H<sub>2</sub> to Give **1** and Ultimately [Cp\*MoS(SH)]<sub>2</sub>.** A solution of **2** (60 mg) in 1:1 PhCl-BuOH (20 mL) and Et<sub>3</sub>N (50 μL) was pressurized with H<sub>2</sub> (3 atm, large excess) and heated to 75 °C in a 250-mL glass Fischer & Porter pressure vessel. Within minutes the color became blue, characteristic of **1**, and then red, indicative of [Cp\*MoS(SH)]<sub>2</sub>. NMR of the residue from solvent removal showed pure SH complex.

A solution of **2** (~5 mg) in CDCl<sub>3</sub> in an NMR tube under 1 atm H<sub>2</sub> at 35 °C gave very slow reaction (only 30% conversion after 4 days). However, when Et<sub>3</sub>N (20 μL) was present, conversion to the SH complex was complete within 4 h at 25 °C. Initially **1** was produced, which then further reacted with H<sub>2</sub> at a slower rate. After 1 h mostly **1** was present as product; after 2 h, NMR showed nearly equal amounts of **1** and SH complex.

**Identification of SO<sub>2</sub> and H<sub>2</sub>O as Products of Above Reaction.** A 0.556-g (0.83 mmol) aliquot of **2** in 13 mL of dry PhCl was placed into a reaction vessel with a total volume of 40 mL. Bu<sub>3</sub>N (20 μL, 0.084 mmol) was added, and the solution was degassed on a vacuum line. H<sub>2</sub> (585 Torr, 0.85 mmol) was then placed into the vessel, and the mixture was stirred magnetically at 22 °C. After 1.5 h the solution began to attain a red color characteristic of the presence of **1**-SO<sub>2</sub>, and after 17 h the red solution color indicated substantial amounts of **1**-SO<sub>2</sub>. The vessel was cooled to -196 °C and found to contain no unreacted H<sub>2</sub> on opening to a vacuum gauge. The vessel was warmed to 25 °C and all volatiles were pumped into a U-trap at -196 °C. Separation via passage through a trap at -95 °C gave 0.34 mmol of a gas identified to be SO<sub>2</sub> and a residual solvent mixture containing immiscible H<sub>2</sub>O reaction product, estimated to be 10–15 μL (0.55–0.83 mmol). A sample of the solid Mo-S reaction products was found by NMR to contain a ~2:1 ratio of **1** to unreacted **2**. The reaction did not consume all of the **2** because part of the H<sub>2</sub> (at least 0.2 mmol) went into a side reaction with **1** to form [Cp\*MoS(SH)]<sub>2</sub>, which then reacted with SO<sub>2</sub> via eq 2 to give back most of the **1** plus (Cp\*MoS<sub>2</sub>)<sub>n</sub>. The latter polymer (0.065 g, ~0.1 mmol based on n = 2) was found to be a reaction product by dissolving the solid product mixture in CHCl<sub>3</sub> and collecting the insoluble polymer on a frit. Back-calculation of product amounts based on the amount of polymer formed showed that a minimum of 0.2 mmol of **2** should have been unreacted and that 0.53 mmol of SO<sub>2</sub> and 0.68 mmol of H<sub>2</sub>O should

have been produced. These are consistent with the experimental results (some SO<sub>2</sub> may have been lost in the separation process).

**Reaction of **2** with Weak Bases.** Dilute solutions of **2** in various solvent mixtures containing weak bases were reacted either in closed flasks or in NMR tubes under a variety of conditions. Product analyses were conducted using NMR methods and are summarized in Table III along with reaction conditions.

**Reaction of **1** with SO<sub>3</sub>. Formation of **2**.** Solutions of **1** (30 mg) in 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> were reacted on a vacuum line with various ratios of SO<sub>3</sub> (measured in the gas phase by PVT methods). The SO<sub>3</sub> was condensed onto frozen solutions of **1**, and warming to room temperature produced an immediate blue to red color change. For a 1:1 ratio, NMR of the residue from solvent removal showed that **2** was the primary product (a signal at δ 2.06 was also present). For a 2:1 ratio of SO<sub>3</sub> to **1**, the results were similar except that a small amount of red solid was produced. The latter also slowly crystallized in the NMR samples from both reactions. For a 4:1 ratio, most of the product was the unknown red compound plus a pale powder. The latter was the main product when excess liquid SO<sub>3</sub> was syringed into solutions of **1** and was soluble in water but not organics. The red species was soluble in polar organics (δ 2.65 in CD<sub>3</sub>NO<sub>2</sub>) but decomposed rapidly in aqueous solution or if air was present.

**Preparation of Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>CH<sub>2</sub>)(μ-S)<sub>2</sub>. Reactions with SO<sub>2</sub> and SO<sub>3</sub>.** The synthesis was analogous to that of the Cp analogue.<sup>15</sup> To a solution of [Cp\*MoS(SH)]<sub>2</sub> (0.888 g, 1.5 mmol) in 15 mL of dry THF was added CH<sub>2</sub>Br<sub>2</sub> (0.14 mL, 2.0 mmol) followed by a MeOH solution (10 mL) of NaOMe (~3.5 mmol, prepared from 0.082 g of Na). The solution was stirred overnight (reaction appeared to be slower than that reported for the Cp analogue), solvent was removed in vacuo, and the residue was extracted with 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. Reduction of filtered extract volume to ~8 mL, addition of 10–15 mL of MeOH, and further solvent reduction to ~15 mL gave deep blue microcrystals. The product (0.83 g) was collected and washed with MeOH, but <sup>1</sup>H NMR revealed the presence of ~10% impurities (two Cp\* peaks near δ 2.1). These were removed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-MeOH to give 0.55 g (60%) of pure Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>CH<sub>2</sub>)(S)<sub>2</sub>. Anal. Calcd for C<sub>21</sub>H<sub>32</sub>S<sub>4</sub>Mo<sub>2</sub>: C, 41.72; H, 5.34; S, 21.21. Found: C, 41.17; H, 5.41; S, 21.57.

The deep blue Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>CH<sub>2</sub>)(S)<sub>2</sub> formed a red, reversible SO<sub>2</sub> adduct analogous to **1**-SO<sub>2</sub>. However, no further reaction to a thiosulfate occurred. Reaction with 1.5 equiv of SO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> gave initially a reddish solution, which later deposited a light-green water-soluble precipitate as the primary product. IR analysis of this species and the filtrate showed no bands characteristic of μ-S<sub>2</sub>O<sub>3</sub>.

**Structural Determination of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S-SO<sub>2</sub>)(**1**-SO<sub>2</sub>) and Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(SSO<sub>3</sub>)(**2**).** Crystals of **1**-SO<sub>2</sub> suitable for X-ray diffraction were grown by slowly cooling a saturated solution of the complex in SO<sub>2</sub>-saturated toluene-acetone. Crystals of **2** (synthesized from SO<sub>2</sub>) were grown in CHCl<sub>3</sub> by slow cooling.

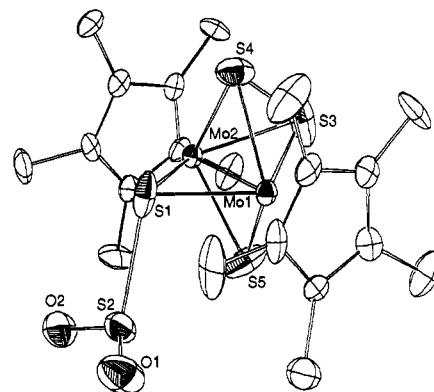
**Table IV.** X-ray Data for Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S·SO<sub>2</sub>) and Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S<sub>2</sub>O<sub>3</sub>)

chem formula	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub> S <sub>5</sub> Mo	C <sub>20</sub> H <sub>30</sub> O <sub>3</sub> S <sub>5</sub> Mo
cryst system	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a, Å	13.738 (2)	13.730 (5)
b, Å	10.581 (3)	10.635 (3)
c, Å	17.331 (4)	16.862 (2)
β, deg	92.41 (2)	93.17 (5)
V, Å <sup>3</sup>	2516.9	2458.5
Z	4	4
D <sub>meas</sub> , g/cm <sup>3</sup>	1.73	1.81
λ (Mo Kα <sub>1</sub> )	0.70930	0.70930
temp, °C	23	23
cryst color	deep red	red
dimens, mm	0.30 × 0.20 × 0.10	0.28 × 0.17 × 0.13
abs coeff, cm <sup>-1</sup>	13.9	14.2
abs corr type	φ × spherical	φ × spherical
sphere rad, mm	0.2	0.2
transmn, min, max	0.58, 0.67	0.58, 0.71
av peak width, ω, deg	1.0	0.8
scan range (2θ max), deg	45	45
scan type	θ-2θ	θ-2θ
scan rate	variable	variable
index range	±h, ±k, ±l	±h, ±k, ±l
no. measd reflns	3476	6722
no. of unique reflns	3285	3218
R <sub>F</sub> equiv reflns, %	3.2	2.1
I ≥ 2σ(I)	2017	2612
no. of refined params	263	272
R <sub>F</sub> obs reflns, %	6.2	4.0
R <sub>wF</sub> obs reflns, %	6.5	6.2

Room-temperature data were collected by variable speed θ-2θ scans on an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo Kα radiation. The structures were solved by standard Patterson and difference Fourier methods and refined to the observed data (I ≥ 2σ(I)) with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.<sup>16</sup> Refinements included anisotropic thermal parameters for all atoms and a correction for secondary extinction.<sup>17</sup> Final Fourier difference maps failed to show peaks that could be interpreted as hydrogen atoms. The Los Alamos Crystal Structure Codes<sup>18</sup> were used for all calculations. Data were corrected for absorption by using the relative intensity of a low-angle reflection measured as a function of Ψ (mapped to φ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development. The function minimized was  $R_F = \sum w^2 [F_o - F_c]^2$  and weights were calculated as  $w^2 = 4F^2 / \sigma^2(I)$  where  $\sigma(I) = \sigma_c(I) + (0.030I)^2$ ;  $\sigma_c(I)$  is the error based on counting statistics. Lattice and data collection parameters are given in Table IV; tables of fractional coordinates for the atoms, anisotropic thermal parameters, and a listing of observed and calculated structure factor amplitudes are given as supplementary material.

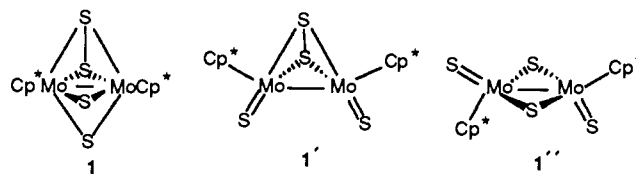
## Results

**Synthesis and Properties of Mo-S Complexes.** The chemistry described in this paper was initiated by studies of SO<sub>2</sub> reaction with [(CpMe<sub>n</sub>)MoS(SH)]<sub>2</sub> used to catalyze SO<sub>2</sub> hydrogenation (eq 1). Two procedures for synthesis of this SH complex<sup>7a</sup> or its Cp analogue<sup>7a,12</sup> have been reported, both of which we have used and found to have some minor disadvantages. Reaction of the immediate precursor, (Cp\*MoS<sub>x</sub>)<sub>n</sub>, with H<sub>2</sub> (~3 atm, 75–100 °C) in CHCl<sub>3</sub> required 3–4 days,<sup>7a</sup> and reduction of (Cp\*MoS<sub>x</sub>)<sub>n</sub> with LiHBEt<sub>3</sub> or NaHBEt<sub>3</sub> analogous to that reported<sup>12</sup> for the Cp analogue gave variable results. Incomplete reactions often occurred primarily because of difficulties in determining the proper excess amount of hydride reagent to be used. As much as 23 mmol

**Figure 1.** Molecular geometry and atom-labeling scheme for Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S·SO<sub>2</sub>) (1·SO<sub>2</sub>; 35% ellipsoids).

of hydride per gram of (Cp\*MoS<sub>x</sub>)<sub>n</sub> (~1.5 mmol based on x = 3,<sup>1</sup> n = 2) was required in some cases, possibly because of variable composition of the (Cp\*MoS<sub>x</sub>)<sub>n</sub> or the presence of impurities (H<sub>2</sub>O, S<sub>8</sub>). In comparison to the conditions reported for the Cp case, longer reaction periods (18 h) were also necessary. This was particularly true for NaHBEt<sub>3</sub> addition to [Cp\*MoS(μ-S)]<sub>2</sub>, a coproduct of the (Cp\*MoS<sub>x</sub>)<sub>n</sub> synthesis, which was also found to be reducible to the SH complex. Overall we found that H<sub>2</sub> reduction of (Cp\*MoS<sub>x</sub>)<sub>n</sub> is the more reliable procedure and can be improved time-wise by using 2:1 chlorobenzene-ethanol containing Et<sub>3</sub>N (~1 mL) as solvent, which is similar to the solvent mixture used in eq 1. Good yields of [Cp\*MoS(SH)]<sub>2</sub> were obtained in hours rather than days. The function of the amine is unclear here, but as we originally found for eq 1, many of the reactions of the Mo-S complexes (see below) are promoted by amines and other weak organic bases.

Because of thermal instability, Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)<sub>2</sub> (**1**) must be synthesized under mild conditions such as those employed in Wachter's<sup>8a</sup> original preparation ([Cp\*Mo(CO)]<sub>2</sub> and S<sub>8</sub> in toluene at 45 °C for 22 h, 30% yield after chromatography). We find that good yields of **1** (or its MeCp analogue) can be obtained by reaction of excess SO<sub>2</sub> with [Cp\*MoS(SH)]<sub>2</sub> according to eq 2 without need for chromatography. Complex **1** is novel in that it has two isomers that are thermally and photochemically<sup>17</sup> interconvertible at 25 °C: **1** is the least stable thermally while



[Cp\*MoS(μ-S)]<sub>2</sub> (**1''**) is the most stable (see below), and photolysis<sup>17</sup> of any isomer leads to the other two isomers. The formal oxidation state of the metal in these metal-metal bonded dimers increases from Mo<sup>IV</sup> to Mo<sup>V</sup> on isomerization to **1''**. Chemical oxidation with I<sub>2</sub> and cyclic voltammetry shows that **1** can be oxidized to an apparent dicationic species in reversible or quasi-reversible fashion.<sup>20</sup> The color of **1** in solution is a very distinctive intense sky-blue (**1'** and **1''** are brown), and reactions of **1** are readily followed by color changes.

**Reactions of Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)<sub>2</sub> (**1**) with SO<sub>2</sub> and SO<sub>3</sub>.** SO<sub>2</sub> Adduct Formation and Cleavage of SO<sub>2</sub> to S<sub>8</sub> and Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>) (**2**). In the presence of SO<sub>2</sub>, **1** reversibly forms an adduct, **1**·SO<sub>2</sub>, from which the SO<sub>2</sub> readily dissociates at 25 °C. Crystalline **1**·SO<sub>2</sub> can be isolated under an SO<sub>2</sub>-enriched atmosphere, and X-ray crystallography (see below and Figure 1) shows that one SO<sub>2</sub> is bound to a bridging sulfide and that a very long S-S bond consistent with the high lability is present. IR ν<sub>SO</sub>

(16) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Table 2.2A. (b) Cromer, D. T. *Ibid.* Table 2.3.1.

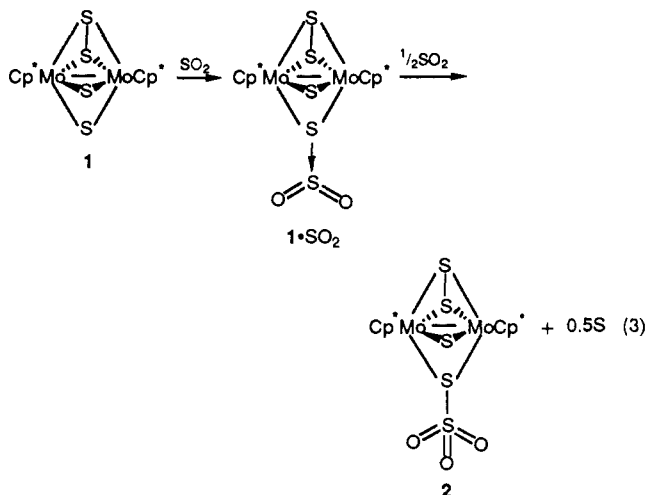
(17) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664.

(18) Larson, A. C. *Am. Crystallogr. Soc. Proc.*, Program Abstr. Bull., Ser. 2, **1977**, 67.

(19) Bruce, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 3433.

(20) (a) Brunner, H.; Meier, W.; Wachter, J.; Weber, P.; Ziegler, M. L.; Enemark, J. H.; Young, C. G. *J. Organomet. Chem.* **1986**, *309*, 313. (b) Smith, W.; Kubas, G. J.; Kubat-Martin, K. A., unpublished results. (c) Wachter, J., private communication.

bands (Table I) are also consistent with ligand-bound  $\text{SO}_2$ .<sup>21</sup> The spectacular color change from bright blue to bright red on adduct formation is noteworthy considering that the  $\text{SO}_2$  is weakly bound to a ligand rather than the metal.  $1 \cdot \text{SO}_2$  was found to undergo a further, irreversible reaction with  $\text{SO}_2$  in various organic solvents and liquid  $\text{SO}_2$  (eq 3). The product is  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})(\mu\text{-SSO}_3)$  (**2**), which possesses an  $\text{SO}_3$  rather than an  $\text{SO}_2$  bound to sulfide. Effectively a  $\mu\text{-S}_2\text{O}_3$  ligand (S-bound thiosulfate) is created by an oxygen-transfer process, and the source of the oxygen as established by  $^{18}\text{O}$  labeling is clearly  $\text{SO}_2$  (see below) and not adventitious  $\text{O}_2$  or  $\text{H}_2\text{O}$ . No other Mo-containing product is formed and elemental sulfur is also produced, indicating that  $\text{SO}_2$  has effectively been disproportionated to  $\text{S}_8$  and coordinated  $\text{SO}_3$ . Complex **2** can also be prepared from  $[\text{Cp}^*\text{MoS}(\text{SH})_2]$  by coupling eq 2 and 3. The less soluble MeCp analogues exhibit chemistry similar to the  $\text{Cp}^*$  species.



Formation of **2** according to eq 3 occurs spontaneously under ambient conditions and, as for all reactions discussed in this paper, can easily be monitored by  $^1\text{H}$  NMR.<sup>22</sup> No intermediates are observed, and the reaction rate shows dependence upon  $\text{SO}_2$  concentration and a high dependence on solvent polarity and the presence of organic base promoters such as  $\text{Et}_3\text{N}$ , pyridine, or even alcohols. Qualitative rates determined by NMR studies are summarized in Table II, and reaction completion times range from 5 min (in 10:1 liquid  $\text{SO}_2\text{-Et}_3\text{N}$ ) to months (no reaction in benzene after months in a sealed NMR tube even in the presence of amine). In chlorinated hydrocarbon solvents, the presence of amines ( $\sim 1\%$  of solvent volume) or alcohols (10–50%) accelerated the reaction rates by several orders of magnitude. Reaction rates were fastest when both an alcohol and an amine were present. Sterically hindered amines such as 2,6-di-*tert*-butyl-4-methylpyridine (*t*-Bu)<sub>2</sub>Mepy were much less effective than unhindered amines, and the rate of reaction showed dependence on amine: $\text{SO}_2$  ratio. The amine was always present in large excess ( $>10:1$ ) in relation to **1** but usually  $<1:5$  with respect to  $\text{SO}_2$ . In liquid  $\text{SO}_2$  containing  $\text{Et}_3\text{N}$  (amine: $\text{SO}_2 = 0.07$ ), conversion of **1** to **2** was complete in 8 min but only 15% conversion occurred in this time for amine: $\text{SO}_2 = 0.0036$ . In amine-promoted reactions the rates often became slower as the reaction progressed, possibly due to some “back-reaction” of **2** with amine to give **1** (see eq 7 below). In some cases, an apparent equilibrium was reached at  $\sim 95\%$  conversion (Table II). Solid state conversion of  $1 \cdot \text{SO}_2$  to **2** occurs very slowly ( $t_{1/2} \sim$  month) at  $25^\circ\text{C}$  in a closed vessel under 1 atm  $\text{SO}_2$ .

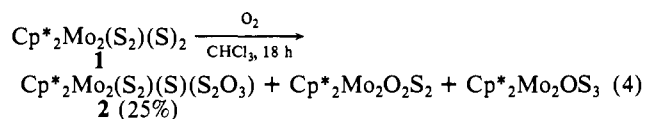
$\text{Cp}^*_2\text{Mo}_2(\text{S}_2)(\text{S})(\text{SSO}_3)$  is air stable, does not release sulfur oxides on heating, and also forms on treatment of **1** with  $\text{SO}_3$  in

$\text{CH}_2\text{Cl}_2$  below  $25^\circ\text{C}$ . The reaction is less clean than eq 3 however, and use of  $\text{SO}_3:1$  ratios  $> 2$  give mostly unidentified products. Transfer of  $\text{SO}_3$  to **1** from  $\text{Me}_3\text{NSO}_3$  does not occur, although Pfauntsch<sup>11c</sup> obtained 49% yields of **2** by treating **1** with pyridine- $\text{SO}_3$  in  $\text{CH}_3\text{CN}$ . Thus, it appears that the strength of the donor-acceptor S- $\text{SO}_3$  bond in **2** falls in between that of the two amine- $\text{SO}_3$  complexes (see Discussion).

A complex closely related to **1**,  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S}_2\text{CH}_2)(\mu\text{-S})_2$ , which also is deep blue in color, formed a red, reversibly bound  $\text{SO}_2$  adduct but did not react further with  $\text{SO}_2$ . Reaction of this complex, which contains a methanedithiolate ligand instead of  $\text{S}_2$ , with  $\text{SO}_3$  also failed to give a thiosulfate. The  $\text{SO}_2$  adduct gives  $\nu_{\text{SO}}$  bands (Table I) similar to  $1 \cdot \text{SO}_2$  and presumably contains  $\mu\text{-S-SO}_2$  binding.

**Reactions of 1 with  $\text{O}_2$ ,  $\text{SO}_2\text{-O}_2$ ,  $\text{SO}_2\text{-H}_2\text{O}$ , and  $\text{O}_2\text{-H}_2\text{O}$  Mixtures.**  **$^{18}\text{O}$  Labeling Experiments.** In order to verify that  $\text{SO}_2$  rather than adventitious  $\text{O}_2$  or  $\text{H}_2\text{O}$  is the source of the third oxygen in **2** produced in eq 3,  $^{18}\text{O}$  labeling studies were carried out. Reaction of 2 equiv of  $\text{S}^{18}\text{O}_2$  (95%) with **1** in  $\text{CH}_2\text{Cl}_2$  containing  $\text{Et}_3\text{N}$  promoter gave primarily fully labeled  $\text{Cp}^*_2\text{Mo}_2(\text{S}_2)(\text{S})(\text{S}_2^{18}\text{O}_3)$  (Table I gives IR isotopic shift data), indicating that the oxygen originates exclusively from  $\text{SO}_2$ . When normal  $\text{SO}_2$  was reacted with **1** in the presence of either  $^{18}\text{O}_2$  or  $\text{H}_2^{18}\text{O}$ ,  $^{18}\text{O}$  was not incorporated into **2**, further corroborating that the  $\text{SSO}_3$  ligand is formed by oxygen transfer from  $\text{SO}_2$  in preference to  $\text{O}_2$ .

**1** does slowly react with atmospheric oxygen in the absence of  $\text{SO}_2$  to form **2** in low yield (25%) along with a mixture of oxo-sulfido dimers in their various isomeric forms:



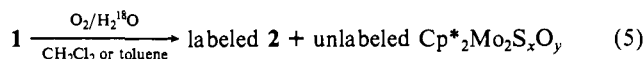
Proton NMR showed that eq 4 was complete in 18 h at  $25^\circ\text{C}$  in  $\text{CHCl}_3$ . Brunner et al.<sup>11</sup> independently found that air oxidation of **1** under somewhat different conditions ( $50^\circ\text{C}$ , toluene, 18 h) yielded a similar product mixture. Mass spectral analysis of the volatile components of our reaction mixtures showed that insignificant quantities (approximately background level) of  $\text{SO}_2$  were present after either partial or complete reaction. Thus it would appear that insufficient amounts of  $\text{SO}_2$  (potentially generable via sulfide ligand oxidation, see Discussion) were present to convert **1** to **2** according to eq 3. When excess  $\text{SO}_2$  was included as a reactant in eq 4 ( $\text{SO}_2:\text{O}_2 = 4$ ), very little reaction beyond formation of  $1 \cdot \text{SO}_2$  occurred in 18 h. Thus, coordination of  $\text{SO}_2$  to the sulfide in **1** apparently blocks reactivity with  $\text{O}_2$  (see Discussion). It is also important to note that very little conversion of  $1 \cdot \text{SO}_2$  to **2** via eq 3 occurs in this system in 18 h because this reaction is very slow in  $\text{CHCl}_3$  without promoter (see Table II). Reaction of **1** with  $^{18}\text{O}_2$  in  $\text{CHCl}_3$  (16 h) according to eq 4 gave, as expected, the  $^{18}\text{O}$  isotopomers of both **2** and the oxo dimers (as shown by  $\sim 40 \text{ cm}^{-1}$  isotopic shifts in  $\nu_{\text{Mo-O}}$ <sup>11b</sup> near  $900 \text{ cm}^{-1}$ ). When  $\text{SO}_2$  was present in the latter reaction ( $\text{SO}_2:^{18}\text{O}_2 = 4$ ) along with  $\text{Et}_3\text{N}$  promoter, it proceeded to completion in 18 h and the product distribution was now unlabeled **2** (75%) and partially  $^{18}\text{O}$ -labeled oxo dimers (25%). Only a small amount of presumably the  $\text{SS}^{16}\text{O}^{18}\text{O}$  isotopomer was present, as indicated by a weak  $\nu_{\text{SO}}$  band at  $992 \text{ cm}^{-1}$ . The absence of significant  $^{18}\text{O}$ -labeled **2** showed that formation of **2** occurred via amine-promoted disproportionation of  $\text{SO}_2$  (eq 3) rather than the  $^{18}\text{O}_2$  oxidation pathway (eq 4), presumably because the rate of eq 3 is much faster than eq 4 under these conditions. This further confirms that oxygen from  $\text{O}_2$  does not become incorporated into the thiosulfate ligand and provides a check that isotopic exchange of  $^{18}\text{O}_2$  and  $\text{SO}_2$  is not occurring prior to any reaction with **1**. The formation of oxo species containing  $^{18}\text{O}$  indicates that some reaction of  $^{18}\text{O}_2$  with Mo sulfide complex occurred. Because the oxo ligands were only partially labeled ( $\sim 2:1$   $^{18}\text{O}/^{16}\text{O}$ ),  $^{16}\text{O}$  originating from  $\text{SO}_2$  ultimately became involved in their formation at some point. The mechanism for this is not clear but could involve side reaction of **2** with amine to give an  $\text{SO}_3$ -containing species (see eq 7) that

(21) (a) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182. (b) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47.

(22) (a) A single sharp, intense  $\text{Cp}^*$  resonance is observed for most of the complexes discussed here, allowing use of a 90-MHz continuous-wave instrument even for dilute solutions; all NMR data are given for  $\text{CDCl}_3$  solutions. (b) We find that the  $\text{Cp}^*$  resonances occur  $\sim 0.04$  ppm lower than those previously reported (recorded on a Varian T-360, ref 8).

could act as a source of oxo ligand.

In the presence of H<sub>2</sub><sup>18</sup>O, solutions of **1** (H<sub>2</sub><sup>18</sup>O:1 = ~30–50) reacted with atmospheric oxygen (H<sub>2</sub><sup>18</sup>O:O<sub>2</sub> = ~3) in a closed flask for 16 h to give **2** predominantly labeled with <sup>18</sup>O and oxo complexes that were predominantly unlabeled.

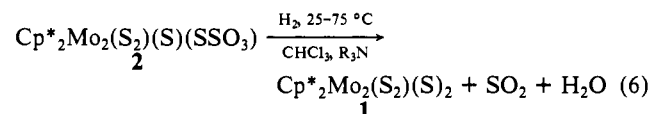


Water alone showed no significant reaction with **1** in this time frame, and the nonincorporation of <sup>18</sup>O into the oxo clusters showed that they formed from O<sub>2</sub> and not H<sub>2</sub>O. The unexpected incorporation of <sup>18</sup>O into **2** points to an intermediate that rapidly exchanges its oxygen with oxygen in H<sub>2</sub>O. One possibility is SO<sub>2</sub>, which was verified by IR to undergo rapid exchange (minutes or less) with H<sub>2</sub><sup>18</sup>O in organic solvents. However the lack of a detectable steady-state concentration of SO<sub>2</sub> in O<sub>2</sub> oxidation of **1** indicates either noninvolvement of SO<sub>2</sub> or very fast reaction of an SO<sub>2</sub> intermediate, much faster than found in eq 3 for example.

**Isomerization, Alkylation, and Protonation of 1.** Solutions of **1** are unstable, even when carefully deoxygenated and kept in darkness (**1** isomerizes photochemically<sup>19</sup>). At 25 °C **1** slowly thermally isomerizes to **1'** and, eventually, to the most stable isomer, **1''**, in solution and solid (**1** was reported to isomerize to **1'** at 45 °C (3 days) in toluene<sup>8a</sup>). In CHCl<sub>3</sub> or toluene, solutions of **1** are stable for days before NMR evidence for **1'** formation appears, but in CH<sub>2</sub>Cl<sub>2</sub> the latter along with several new species start to appear in hours and **1** completely disappears in days. This higher instability is possibly due to alkylation of a μ-S ligand by CH<sub>2</sub>Cl<sub>2</sub> to give [Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SCH<sub>2</sub>Cl)]Cl, as evidenced by appearance of a Cp\* NMR signal near δ 2.24. This shift is similar to that of alkylation products formed in situ on addition of MeSO<sub>3</sub>F or EtI to **1** (δ 2.24–2.28) and to that of [Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(SMe)]PF<sub>6</sub> (δ 2.33<sup>22b</sup>) isolated by Wachter and co-workers.<sup>8b</sup> Similar alkylation of μ-S by CH<sub>2</sub>Cl<sub>2</sub> and also CHCl<sub>3</sub> was previously reported for Pt<sub>2</sub>(μ-S)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>.<sup>23</sup> A solution of **1** in CH<sub>2</sub>Cl<sub>2</sub> after 5 days showed three Cp\* resonances near δ 2.24, and later, six more peaks appeared at δ 1.92–2.37, including those due to the major species, **1'** and **1''**. The alkylated complex also formed as an impurity (~5%) in the preparation of **1** when CH<sub>2</sub>Cl<sub>2</sub> was used as solvent. Thus caution must be exercised in the use of halocarbon solvents for sulfide complexes; several reactions of **1** were performed in CH<sub>2</sub>Cl<sub>2</sub> before this problem was discovered, although the level of alkylation here (<5%) did not significantly effect the outcome. It is unclear why CHCl<sub>3</sub>, which usually is more reactive toward nucleophiles than CH<sub>2</sub>Cl<sub>2</sub>, does not detectably alkylate **1** on a similar time scale.

In view of the above, it was not surprising to find that **1** is readily protonated in solution by strong acids such as CF<sub>3</sub>SO<sub>3</sub>H and HPF<sub>6</sub>. The color of the protonated complex in CHCl<sub>3</sub> is a dull red similar to that for **2**. Amines effected deprotonation back to the bright blue color of **1**. Acetic acid did not react with **1** and aqueous 12 N HCl appeared to only partially protonate **1**. Neither protonated nor alkylated **1** reacted with SO<sub>2</sub>.

**Reduction of 2 and Reactions of 2 with Weak Bases.** **2** can be rapidly reduced back to **1** by reaction with hydrogen (1 atm) under very mild conditions (eq 6, Table III). Water and SO<sub>2</sub> are



coproducts, and the SO<sub>2</sub> may partially associate with **1** in relatively concentrated solutions in a closed system (dilution favors SO<sub>2</sub> dissociation). Whether H<sub>2</sub> reduction directly gives **1** or **1**·SO<sub>2</sub> cannot be readily ascertained, in the same manner that it is not known whether **1** or **1**·SO<sub>2</sub> directly reacts with SO<sub>2</sub> to give **2** (eq 3). Equation 6 is accelerated by Et<sub>3</sub>N: at 25 °C, reduction with

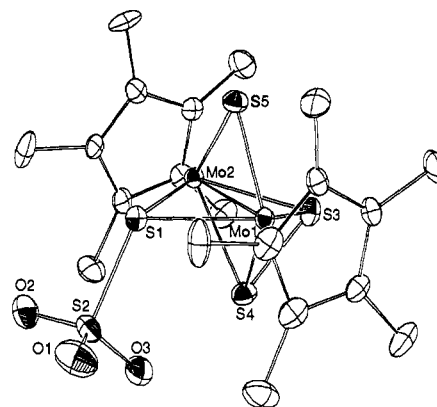
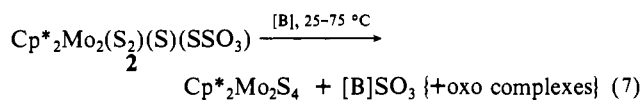


Figure 2. Molecular geometry and atom-labeling scheme for Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>) (**2**; 35% ellipsoids).

H<sub>2</sub> is complete within 4 h if amine (~3% of solvent volume) is present but otherwise is incomplete after days. [Cp\*MoS(SH)]<sub>2</sub> is the final product if excess H<sub>2</sub> is present, but NMR shows that **1** is formed initially and is converted to the SH complex during the course of the reduction. The SH complex itself was found to reduce **2** to **1** within 40 min at 25 °C in the presence of Et<sub>3</sub>N. This is an excellent synthetic method for recycling **2** back to **1** because the [Cp\*MoS(SH)]<sub>2</sub> is also converted to **1**, which is thereby the sole organometallic product of the reaction.

Significantly, organic bases such as Et<sub>3</sub>N have been found to react with **2** without reducing agent being present. The SO<sub>3</sub> functionality is stripped off to give primarily mixtures of isomers of **1** and products of base–SO<sub>3</sub> interaction (eq 7, where B = R<sub>3</sub>N,



ROH, DMSO). As shown in Table III, solutions of **2** containing Et<sub>3</sub>N converted in hours at 75 °C to a mixture of **1** and **1'** (ratios depend on reaction time because **1** thermally isomerizes to **1'**). At 25 °C, the reaction was much slower (*t*<sub>1/2</sub> ~ 4 days) and **1** was the predominant organometallic product. The reaction rate also depended on Et<sub>3</sub>N concentration and **2** converted to **1** in 4:1 CHCl<sub>3</sub>–Et<sub>3</sub>N at 25 °C in 16 h. It is conceivable that eq 7 is partially involved in the base promotion of eq 6, but eq 7 occurs at a much slower rate than eq 6.

Alcohols, DMSO, and acetone stripped off SO<sub>3</sub> to give mainly **1'**, but varying amounts of oxo species were also formed. Presumably the SO<sub>3</sub> reacts with alcohols to give an alkylsulfuric acid, ROSO<sub>3</sub>H,<sup>24</sup> which then may be a source of oxo ligand. When both Et<sub>3</sub>N and ROH were present in the reaction, no oxo species formed, indicating that R<sub>3</sub>N reacts preferentially. In an attempt to determine whether H<sub>2</sub>O would react with **2** to possibly give H<sub>2</sub>SO<sub>4</sub>, a CHCl<sub>3</sub> solution of **2** containing excess H<sub>2</sub>O was refluxed for 2 days. However, no reaction occurred. A mixture of DMSO, CHCl<sub>3</sub>, and water did give a reaction in which **1'** was found to be formed nearly quantitatively in 1.5 h at 75 °C. BaCl<sub>2</sub> addition to the reaction product mixture gave a positive test for sulfate ion, but the amount was quite substoichiometric. Thus, primarily oxidation of DMSO by the SO<sub>3</sub> was presumed to have occurred. Substitution of acetone for DMSO gave a much slower reaction in which **1'** was the principal product along with small amounts of oxo species.

**X-ray Crystal Structures of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S·SO<sub>2</sub>) (1·SO<sub>2</sub>) and Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(SSO<sub>3</sub>) (2).** The geometries of the molecules and the atomic numbering scheme are depicted in Figures 1 and 2; selected distances and bond angles are compared in Table V. The crystals of **1**·SO<sub>2</sub> and **2** (synthesized via eq 3) contain discrete molecular units separated by normal van der Waals distances.

(23) (a) Gukathasan, R. R.; Morris, R. H.; Walker, A. *Can. J. Chem.* **1983**, *61*, 2490. (b) Briant, C. E.; Gardner, C. J.; Andy Hor, T. S.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1984**, 2645.

(24) Breslow, D. S.; Hough, R. R.; Fairclough, J. T. *J. Am. Chem. Soc.* **1954**, *76*, 5361.

**Table V.** Comparison of Distances and Angles for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}]_2(\mu\text{-S}_2)(\mu\text{-S})(\mu\text{-S-X})$  (X = SO<sub>2</sub>, SO<sub>3</sub>)

	SO <sub>2</sub>	SO <sub>3</sub>
	Distances, Å	
Mo1-Mo2	2.611 (2)	2.628 (1)
Mo1-S1	2.381 (5)	2.440 (3)
Mo1-S3	2.408 (5)	2.417 (3)
Mo1-S4	2.440 (5)	2.420 (3)
Mo1-S5	2.329 (5)	2.302 (3)
Mo2-S1	2.387 (5)	2.442 (3)
Mo2-S3	2.408 (5)	2.421 (3)
Mo2-S4	2.440 (5)	2.419 (3)
Mo2-S5	2.333 (5)	2.303 (2)
S1-S2	2.601 (8)	2.166 (4)
S3-S4	2.08 (1)	2.064 (4)
S2-O1	1.38 (1)	1.444 (8)
S2-O2	1.42 (1)	1.445 (8)
S2-O3		1.430 (7)
	Angles, deg	
Mo2-Mo1-S1	56.9 (1)	57.48 (6)
Mo2-Mo1-S3	57.2 (1)	57.18 (6)
Mo2-Mo1-S4	57.6 (1)	57.10 (6)
Mo2-Mo1-S5	56.0 (1)	55.21 (6)
S1-Mo1-S3	110.4 (2)	112.24 (9)
S1-Mo1-S4	76.9 (2)	80.20 (8)
S1-Mo1-S5	80.8 (2)	75.15 (9)
S3-Mo1-S4	50.7 (2)	50.51 (9)
S3-Mo1-S5	80.5 (2)	82.40 (9)
S4-Mo1-S5	111.7 (2)	111.04 (9)
Mo1-Mo2-S1	56.7 (1)	57.41 (6)
Mo1-Mo2-S3	57.2 (1)	57.04 (6)
Mo1-Mo2-S4	57.7 (1)	57.13 (6)
Mo1-Mo2-S5	55.9 (1)	55.20 (7)
S1-Mo2-S3	110.2 (2)	112.03 (9)
S1-Mo2-S4	76.8 (2)	80.18 (8)
S1-Mo2-S5	80.6 (2)	75.11 (9)
S3-Mo2-S4	50.7 (2)	50.48 (9)
S3-Mo2-S5	80.5 (2)	82.31 (9)
S4-Mo2-S5	111.5 (2)	111.06 (9)
Mo1-S1-Mo2	66.4 (1)	65.12 (6)
Mo1-S1-S2	101.1 (2)	113.3 (1)
Mo2-S1-S2	100.9 (2)	112.9 (1)
Mo1-S3-Mo2	65.7 (1)	65.78 (7)
Mo1-S3-S4	65.5 (2)	64.8 (1)
Mo2-S3-S4	65.4 (2)	64.7 (1)
Mo1-S4-Mo2	64.7 (1)	65.76 (6)
Mo1-S4-S3	63.9 (2)	64.7 (1)
Mo2-S4-S3	63.8 (2)	64.8 (1)
Mo1-S5-Mo2	68.1 (1)	69.58 (7)
Mo1-S5-S1	50.3 (1)	54.59 (7)
Mo2-S5-S1	50.4 (2)	54.64 (7)
S1-S2-O1	110.6 (7)	103.1 (4)
S1-S2-O2	108.7 (6)	101.9 (4)
S1-S2-O3		107.3 (3)
O1-S2-O2	115.6 (8)	114.8 (5)
O1-S2-O3		113.2 (5)
O2-S2-O3		114.8 (5)

Each molecule in **1**·SO<sub>2</sub> and **2** consists of two Cp\*Mo groups, which are bridged by a S<sub>2</sub> group, a S atom, and a SSO<sub>x</sub> group (x = 2 for **1**·SO<sub>2</sub> and 3 for **2**). The metal-sulfur cores of each molecule are structurally analogous, with each system possessing roughly C<sub>2v</sub> site symmetry. In both complexes, the ring carbon atoms of the Cp\* groups are roughly equidistant from the metal centers, and the methyl carbons of these Cp\* rings are approximately eclipsed. The Mo-S distances range from 2.329 to 2.440 Å for **1**·SO<sub>2</sub> and 2.302 to 2.442 Å for **2**.

We have observed formation of the μ-S-SO<sub>2</sub> ligand in several other reaction systems, the most recent involving addition of SO<sub>2</sub> to Cp\*W(CO)<sub>3</sub>H to form [Cp\*W(CO)<sub>2</sub>(μ-S-SO<sub>2</sub>)<sub>2</sub>]<sup>4</sup>. The longer S-S distance observed for Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S-SO<sub>2</sub>) (2.601 vs 2.408 Å) is consistent with the high lability of the SO<sub>2</sub> group.

Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(SSO<sub>3</sub>) (**2**) has been independently synthesized by air oxidation of **1** and structurally characterized by Wachter and co-workers.<sup>11a,b</sup> Our structure of **2** prepared via SO<sub>2</sub> reaction with **1** is identical.

A significant difference between **1**·SO<sub>2</sub> and **2** is the 0.435-Å longer S-S bond associated with the μ-SSO<sub>2</sub> ligand. As noted by Brunner et al., the metal-metal and metal-sulfur distances are very dependent on the nature of the sulfur bridges.<sup>8a</sup> The longer Mo-Mo distance and Mo-SSO<sub>x</sub> distances in **2** reflect the influence of the SO<sub>3</sub> group through the shorter and stronger S-S bond. We note also that the S-S distance for **2** is significantly longer than that for [Cp\*Ru(CO)<sub>2</sub>]<sub>2</sub>(μ-S<sub>2</sub>O<sub>3</sub>) (2.135 (3) Å),<sup>6</sup> consistent with the higher lability of the SO<sub>3</sub> moiety in **2** than in the Ru species (See Discussion).

If in **1**·SO<sub>2</sub> and **2**, S1 and S5 are described as the wingtip atoms of a Mo<sub>2</sub>S<sub>2</sub> butterfly core, the SO<sub>2</sub> group in **1**·SO<sub>2</sub> is endo to the butterfly and the SO<sub>3</sub> group in **2** is exo to the butterfly. The pertinent bond angles are in accord with the steric considerations of this difference in positioning; e.g., the S5-Mo-S1 angles for **1**·SO<sub>2</sub> (average 80.7°) are larger than the related angles in **2** (average 75.13°). The exo orientation of the SSO<sub>3</sub> ligand is the same as that in Wachter's structure,<sup>11a,b</sup> which, it should be emphasized, was obtained on a crystal formed by O<sub>2</sub> oxidation of **1**.

## Discussion

**Properties of Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-S-SO<sub>2</sub>) (**1**·SO<sub>2</sub>).** From SO<sub>2</sub> lability, IR, and X-ray evidence, the sulfide-SO<sub>2</sub> Lewis acid-base bond in **1**·SO<sub>2</sub> is much weaker than that previously found in [Cp\*W(CO)<sub>2</sub>(μ-S-SO<sub>2</sub>)<sub>2</sub>] and appears to be similar in strength to that in [Cp\*W(CO)<sub>3</sub>]<sub>2</sub>(μ-S-SO<sub>2</sub>).<sup>4</sup> SO<sub>2</sub> readily dissociates from both the latter and **1**·SO<sub>2</sub> at 25 °C, but the former does not lose SO<sub>2</sub> until 100 °C. This high lability renders <sup>18</sup>O labeling studies useless for obtaining mechanistic information on the oxygen-transfer process that converts **1**·SO<sub>2</sub> to **2**. Of the three adducts, the ν<sub>SO</sub> bands (Table I) are highest for **1**·SO<sub>2</sub>, consistent with the lowest degree of electron transfer to SO<sub>2</sub> and weakest interaction. The adduct Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>CH<sub>2</sub>)(μ-S)(μ-S-SO<sub>2</sub>) also contains a very weakly bound SO<sub>2</sub> and its ν<sub>SO</sub> frequencies are somewhat higher than those for **1**·SO<sub>2</sub>. Isomers **1'** and **1''** do not give stable adducts at 25 °C. It is difficult as yet to rationalize these stability differences because of the variability in coligands, metals, and formal metal oxidation states of the complexes studied thus far. It is clear however that relatively minor differences in structure can give large differences in μ-S-SO<sub>2</sub> stability.

**Reactions of Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)<sub>2</sub> (**1**) with SO<sub>2</sub> To Give Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>)(μ-S)(μ-SSO<sub>3</sub>) (**2**) and S<sub>8</sub>.** Isotopic labeling established that SO<sub>2</sub> is the sole oxygen source for formation of the μ-SSO<sub>3</sub> ligand in **2** according to eq 3, which, along with S<sub>8</sub> product formation, dictates that cleavage of SO<sub>2</sub> takes place on the Mo-S complexes. Oxygen transfer from one SO<sub>2</sub> to a second most likely occurs, giving SO<sub>3</sub> and SO, which in turn is unstable toward disproportionation to SO<sub>2</sub> and S<sub>8</sub>. The role of the Mo-S dimers in the mechanisms of eq 3 and other reactions described here are difficult to assess, however, primarily because of lack of observation of reaction intermediates. Judging on reactants and products alone, the reaction of **1** with SO<sub>2</sub> to give **2** appears to be based at the bridging sulfide ligand sites, but transformations taking place at metal centers of intermediates cannot be ruled out by the data. As is implied in eq 3, **2** may not necessarily be formed by direct intermolecular oxygen transfer to the SO<sub>2</sub> group in **1**·SO<sub>2</sub>. One must also consider the possibilities that **1**·SO<sub>2</sub> is not involved in the mechanism (i.e., the SO<sub>3</sub> moiety is fabricated at another site or even externally) or that intramolecular oxygen transfer from a second SO<sub>2</sub> coordinated to either the μ-S<sub>2</sub> or the other μ-S ligand takes place. Some evidence for involvement of the S<sub>2</sub> ligand is the finding that Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S<sub>2</sub>CH<sub>2</sub>)(μ-S)(μ-S-SO<sub>2</sub>), an analogue of **1**·SO<sub>2</sub>, does not react with SO<sub>2</sub> to give a thiosulfate. Aside from subtle electronic effects, the only major difference is the blocked reactivity of the μ-S<sub>2</sub>CH<sub>2</sub> ligand site compared to the μ-S<sub>2</sub> in **1**·SO<sub>2</sub>. Much stronger arguments can be made against intramolecular oxygen transfer however. The rate of formation of **2** is remarkably dependent on both solvent and the presence of base promoters. The lack of reaction in nonpolar media could even imply the presence of ionic intermediates in the mechanism. The rate of formation of **2** is so greatly



enhanced by the presence of alcohols and small amounts of amines that one must assume that they are functioning as base promoters rather than increasing solvent polarity. The reaction rate in liquid SO<sub>2</sub> was found to be directly dependent on the amine:SO<sub>2</sub> ratio (Table II). A major question is whether the amines or alcohols act as Brønsted or Lewis bases. Because protons are not explicitly involved in eq 3, Brønsted behavior would seem to be ruled out, although the possibility of trace water as a proton source must always be considered (ionic salts such as [Et<sub>3</sub>NH<sup>+</sup>][HSO<sub>3</sub><sup>-</sup>]<sup>25</sup> can be isolated on SO<sub>2</sub> addition to Et<sub>3</sub>N in "wet" solvents). However, Lewis base promotion is more straightforward, and amines are known to coordinate<sup>26</sup> to SO<sub>2</sub>, a moderately strong Lewis acid, which also weakly interacts with alcohols and other donor solvents. As a test of whether the amine functions as a proton acceptor or as a Lewis base, a sterically hindered amine, 2,6-di-*tert*-butyl-4-methylpyridine, was tried as a promoter. This amine interacts only weakly, if at all, with SO<sub>2</sub>, but its proton accepting ability is similar to that of unhindered amines such as pyridine. Under identical reaction conditions (Table II), pyridine enhances the reaction rate much more than the hindered pyridine, implying Lewis base enhancement. Thus the S-O bonds in a Lewis base-SO<sub>2</sub> adduct could be more activated toward oxygen transfer in this system than the bonds in free SO<sub>2</sub> or ligand-bound SO<sub>2</sub>.

**Formation of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S<sub>2</sub>O<sub>3</sub>) (2) By Air Oxidation of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)<sub>2</sub> (1).** As for its formation from SO<sub>2</sub>, the formation of thiosulfate **2** on air oxidation of **1** (eq 4) is remarkable and could not have been predicted. Wachter and Pfauntsch<sup>11</sup> proposed a mechanism wherein **1** initially isomerizes to **1'** or **1''**, both of which have terminal Mo=S bonds that are presumably more capable of reacting with O<sub>2</sub> to give Mo=O-containing complexes (the primary products). The terminal sulfur ligands were theorized to be oxidized first to SO<sub>2</sub> and then to SO<sub>3</sub> by an unknown pathway, ultimately adding to unreacted **1** to give **2**. In view of our finding that SO<sub>2</sub> directly reacts with **1** to form **2**, one could also argue that eq 3 is the final step in eq 4.<sup>11c</sup> However, this mechanism appears unlikely because eq 3 occurs much too slowly in the solvent medium used in eq 4 and very little if any SO<sub>2</sub> was found to be present during the course of eq 4. It is possible that a highly activated, "nascent" form of SO<sub>2</sub> is generated from sulfide oxidation and either rapidly disproportionates to SO<sub>3</sub> on the complex or is oxidized to SO<sub>3</sub><sup>27</sup> by O<sub>2</sub> as initially suggested.

Competitive reactions of **1** with mixtures of SO<sub>2</sub> and <sup>18</sup>O<sub>2</sub> demonstrated that the SO<sub>3</sub> group in **2** is formed strictly from SO<sub>2</sub> oxygens and not O<sub>2</sub>. Even though SO<sub>2</sub> may be an intermediate in eq 4, the initial presence of excess SO<sub>2</sub> shuts down O<sub>2</sub> reaction with **1**, possibly for either of two reasons. The binding of SO<sub>2</sub> to **1** to give **1**·SO<sub>2</sub> may prevent isomerization to **1'** or **1''** (proposed above to be the initial step), or else the coordination of strongly electrophilic SO<sub>2</sub> to **1** lessens the susceptibility of **1** to electrophilic attack by O<sub>2</sub>.

**Reactions of Cp\*<sub>2</sub>Mo<sub>2</sub>(S<sub>2</sub>)(S)(S<sub>2</sub>O<sub>3</sub>) with H<sub>2</sub> and Bases; Implications of Oxygen Transfer and Thiosulfate Intermediates in Reduction of SO<sub>2</sub>.** Although a variety of S-coordinated thiosulfate complexes have now been structurally characterized,<sup>6b,28</sup> none have been reported to possess the unique reactivity of **2**. Its facile reaction with H<sub>2</sub> to give **1** (eq 6) has led us to propose that **2** may be an intermediate in the homogeneous catalytic hydrogenation<sup>1</sup>

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(26) (a) van der Helm, D.; Childs, J. D.; Christian, S. D. *J. Chem. Soc., Chem. Commun.* **1969**, 887. (b) Santos, P. S.; Lieder, R. *J. Mol. Struct.* **1986**, *144*, 39, and references therein.

(27) Pt<sub>2</sub>(μ-SO<sub>2</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)<sub>2</sub> (C<sub>8</sub>H<sub>12</sub> = cycloocta-1,5-diene) has recently been found to be oxidized by atmospheric oxygen to Pt<sub>2</sub>(μ-SO<sub>3</sub>)(μ-SO<sub>2</sub>)(C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>, the first reported complex containing a μ-SO<sub>3</sub> ligand: Farrar, D. H.; Gukathasan, R. R. *J. Chem. Soc. Dalton Trans.* **1989**, 557.

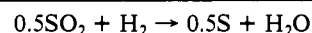
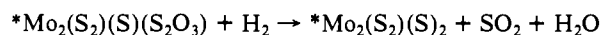
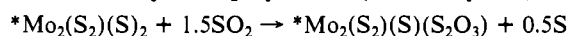
(28) (a) Ruben, H.; Zalkin, A.; Faltens, M. O.; Templeton, D. H. *Inorg. Chem.* **1974**, *13*, 1836. (b) Baggio, S. *J. Chem. Soc. A.* **1970**, 2384. (c) Restivo, R. J.; Ferguson, G.; Balahura, R. *J. Inorg. Chem.* **1977**, *16*, 167. (d) Baggio, S.; Amzel, L. M.; Becka, L. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1698. (e) Murdock, A. R.; Tyree, T.; Otterbein, W.; Kinney, L.; Carreras, M.; Cooper, J. N.; Elder, R. C. *Inorg. Chem.* **1985**, *24*, 3674.

**Table VI.** Comparison of Rate Dependencies on Solvent Media of Stoichiometric (eq 3) and Catalytic Reactions (eq 1)

solvent system <sup>a</sup>	reacn time (% compln) eq 3	rate eq 1 (turnovers/h) <sup>b</sup>
CHCl <sub>3</sub>	150 h (<5)	0.4
PhCl	96 h (22)	18
PhCl + amine <sup>c</sup>	12 min (50)	121
1:1 PhCl-ROH	10 min (100)	97
1:1 PhCl-ROH + py	6 min (100)	300
1:1 PhCl-ROH + ( <i>t</i> -Bu) <sub>2</sub> Mepy	11 min (100)	73

<sup>a</sup>R = Bu for eq 1 and Me for eq 3. <sup>b</sup>References 1 and 27. <sup>c</sup>Amine = Bu<sub>3</sub>N for eq 1 and py for eq 3.

of SO<sub>2</sub> (eq 1). The following cycle can be envisioned for formation of the observed S<sub>8</sub> and H<sub>2</sub>O products (\*Mo = Cp\*Mo):



This cycle based on SO<sub>2</sub> disproportionation to thiosulfate and sulfur may be occurring in addition to or even instead of that previously postulated<sup>1</sup> in which SO<sub>2</sub> was believed to be reduced by [Cp\*Mo(S)(SH)]<sub>2</sub> catalyst via eq 2 followed by regeneration of the SH complex via known reaction of H<sub>2</sub> with the Mo-S products of eq 2. Because **1** forms from reaction of the SH complex and SO<sub>2</sub>, it surely must be present in sufficient amounts in the catalytic system to be considered as an active catalyst component. We have now confirmed that **1** is as effective in catalyzing the SO<sub>2</sub> hydrogenation as [Cp\*Mo(S)(SH)]<sub>2</sub>.<sup>29</sup> However, it must be kept in mind that in the presence of H<sub>2</sub> the SH complex ultimately can be produced from all of the non-oxo containing Mo-S complexes studied here, including isomers **1'** and **1''**, which ensures a completely closed loop in the catalysis, regardless of mechanistic considerations. As long as oxygen is excluded from the system,<sup>30</sup> there are no "dead-end" reactions involving the Mo species, and both [Cp\*Mo(S)(SH)]<sub>2</sub> and **1** could independently function as catalysts.

Additional evidence for a thiosulfate-based catalytic scheme was obtained by comparison of reaction rate data in various solvent media. Both the overall catalytic conversion and the stoichiometric reactions (eq 3 and 6) of the above cycle are promoted by organic bases such as amines. Increasing the solvent polarity, particularly with alcohols (which also are weak bases), enhanced conversion of **1** to **2** in the same order that was observed<sup>1</sup> for the catalytic reductions (Table VI). The organic solvent mixture that gave the fastest rate was 1:1 PhCl-ROH plus amine, exactly as found for the catalytic reaction. Solvents not containing organic bases gave very slow reactions for both eq 3 and the catalytic reaction. In these cases, the predominant mechanism for the catalysis may be that previously proposed,<sup>1</sup> while the thiosulfate route dominates for solvent mixtures containing Lewis bases. Interestingly, just as found for eq 3, the use of the hindered pyridine in the catalytic reaction has been found to give slower conversion rates (73 turnovers/h, which is similar to that for no added amine) than reaction mixtures containing pyridine or Bu<sub>3</sub>N (>300 turnovers/h).<sup>29</sup> Thus the similar rate dependencies of eq 1 and 3 on the nature of the solvent and amine suggest that eq 3 might be the rate-determining step in the catalysis.

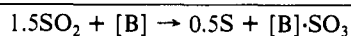
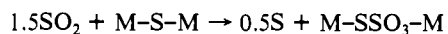
Mechanisms of SO<sub>2</sub> reduction involving oxygen transfer to give S<sub>2</sub>O<sub>3</sub> and S<sub>8</sub> have received little attention. Thiosulfate complexes have now been found to be produced on reduction of SO<sub>2</sub> with metal hydrides in several cases<sup>2,6b,31</sup> and may be key intermediates in SO<sub>2</sub> reduction. Sulfur-sulfur bond activation by metal complexes has been the subject of increasing study, and the relatively long S-S distance in the S<sub>2</sub>O<sub>3</sub> ligand in **2** suggested proclivity toward cleavage. Wachter,<sup>11</sup> for example, found that **2** reacted

(29) Kubas, G. J.; Ryan, R. R.; Sauer, N. N., manuscript in preparation.

(30) When oxygen was present in the catalytic reaction, oxo species (primarily green Cp\*<sub>2</sub>Mo<sub>2</sub>OS<sub>3</sub>) were formed, which shut down the catalysis.

(31) Li<sub>2</sub>S<sub>2</sub>O<sub>3</sub> has been reported to be formed on reaction of SO<sub>2</sub> with LiH.

with  $\text{Cr}(\text{CO})_5(\text{THF})$  with loss of the  $\text{SO}_3$  unit to give a hetero-trimetallic sulfido cluster. We in turn have found that the  $\text{SO}_3$  moiety can be stripped off even by weak organic bases such as amines and alcohols to regenerate **1** under mild conditions. This suggests the possibility of a catalytic cycle wherein  $\text{SO}_2$  is brought to react with bases [B] to give  $\text{S}^0$  and  $\text{S}^{\text{VI}}$  products:



Assuming that [B] is an inexpensive organic compound (e.g., ROH), conversion of  $\text{SO}_2$  to useful sulfonylated organics may be a feasible  $\text{SO}_2$  recovery method. The chemistry of **2** will be investigated further to determine whether the above cycle can be catalytic and to survey the reactivity of **2** with hydride reducing agents and strong acids.

Summarizing, the oxygen-transfer chemistry of  $\text{SO}_2$  and related thiosulfate formation is a promising area for future development. The facile reactions of  $\text{Cp}^*_2\text{Mo}_2(\text{S}_2)(\text{S})(\text{S}_2\text{O}_3)$  demonstrate that the thiosulfate ligand possesses versatile reactivity and is not merely a terminal end product of partial  $\text{SO}_2$  reduction. The role of the

metal center in this chemistry is undefined and conceivably the reaction sites are entirely ligand-based. Further examination of small molecule reactivity with the numerous known metal-sulfide clusters could lead to rich chemistry and excellent systems for catalytic conversion of  $\text{SO}_2$  and other noxious small molecules (e.g.,  $\text{NO}_x$ <sup>32</sup>).

**Acknowledgment.** This research was sponsored by the Department of Energy, Basic Energy Sciences, Office of Chemical Sciences. We are very grateful to Dr. Elizabeth Larson for substantial contributions to the X-ray crystallographic work.

**Supplementary Material Available:** Fractional coordinates (Tables Is and IIs) and anisotropic thermal parameters (Tables IIIs and IVs) (4 pages); observed and calculated structure factors (Tables Vs and VIs) (23 pages). Ordering information is given on any current masthead page.

(32) Preliminary results<sup>29</sup> show that  $[\text{Cp}^*\text{MoS}(\text{SH})]_2$  also catalyzes reduction of NO by  $\text{H}_2$  to give  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$ , but at a much slower rate than for  $\text{SO}_2$  reduction (amines did not appear to promote the reaction significantly). Equimolar NO- $\text{SO}_2$  mixtures were reduced to the latter products plus  $\text{S}_8$  at a rate halfway between NO and  $\text{SO}_2$  reduction.

## Steric and Electronic Factors That Control Two-Electron Processes between Metal Carbonyl Cations and Anions

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**Abstract:** Reactions of metal carbonyl cations ( $\text{Mn}(\text{CO})_6^+$ ,  $\text{Re}(\text{CO})_6^+$ ,  $\text{Mn}(\text{CO})_5\text{PPh}_3^+$ ,  $\text{Mn}(\text{CO})_4(\text{PPh}_3)_2^+$ ,  $\text{Mn}(\text{CO})_5\text{PEt}_3^+$ ,  $\text{Mn}(\text{CO})_5\text{PPh}_2\text{Me}^+$ ,  $\text{Re}(\text{CO})_5\text{PPh}_3^+$ , and  $\text{CpFe}(\text{CO})_3^+$ ) with metal carbonyl anions ( $\text{Co}(\text{CO})_3\text{PPh}_3^-$ ,  $\text{Co}(\text{CO})_4^-$ ,  $\text{Mn}(\text{CO})_5^-$ ,  $\text{Mn}(\text{CO})_4\text{PPh}_3^-$ ,  $\text{Mn}(\text{CO})_4\text{PEt}_3^-$ ,  $\text{Mn}(\text{CO})_4\text{PPh}_2\text{Me}^-$ ,  $\text{Mn}(\text{CO})_3(\text{PPh}_3)_2^-$ ,  $\text{CpFe}(\text{CO})_2^-$ ,  $\text{Re}(\text{CO})_5^-$ , and  $\text{Re}(\text{CO})_4\text{PPh}_3^-$ ) are reported. Peak potentials are reported for all ions, and nucleophilicities (as measured by reaction with MeI) are reported for the anions. Reaction of any metal carbonyl cation with any metal carbonyl anion leads ultimately to binuclear products, which are the thermodynamic products. The binuclear products are formed by a single-electron transfer. In over half of the reactions between metal carbonyl cations and anions, a two-electron change results in a new metal carbonyl cation and anion. The two-electron change may be considered mechanistically as a  $\text{CO}^{2+}$  transfer with the more nucleophilic of the two anions retaining the  $\text{CO}^{2+}$ . The kinetic and thermodynamic driving forces and the suggested mechanism are examined.

Electron transfer is one of the fundamental reaction types in chemistry.<sup>1,2</sup> Through elegant studies, outer-sphere electron transfer,<sup>1</sup> inner-sphere electron transfer,<sup>1</sup> long-range electron transfer,<sup>3</sup> and single-electron-transfer reactions<sup>2</sup> are well understood. In our research, aimed at defining the mechanistic possibilities for organometallic electron-transfer reactions, we have found that in some cases reactions of metal carbonyl cations with metal carbonyl anions result in a single-event two-electron transfer

(or a transfer of a  $\text{CO}^{2+}$  group).<sup>4</sup> In this manuscript we examine the scope of this reaction and the kinetic and thermodynamic driving forces for such a reaction.

The thermodynamic parameters for electron-transfer reactions are most easily assessed from the standard potential for the reaction. Most of the simple metal carbonyl cations and anions have been electrochemically examined a number of times,<sup>5</sup> but since the electrochemical reactions are irreversible, reliable values for  $E_0$  are not known for most metal carbonyl complexes.

In some cases inner-sphere electron-transfer reactions are accompanied by transfer of an atom between the redox-active centers. This often results when the substitutional reactivity of the two centers is markedly affected by the oxidation or reduction as in

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