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_2 on $(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ To Form S_8 and a Thiosulfate Complex, $(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$. Possible Role in Homogeneous Hydrogenation of SO_2 Catalyzed by Mo–S Complexes

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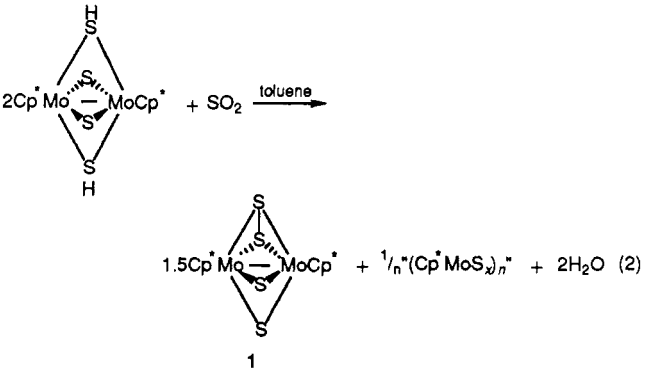
Abstract: Reaction of SO_2 with solutions of $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (**1**) initially yields **1**·SO_2, which is shown by crystallography to contain an SO_2 weakly bound to a μ-S (S–S = 2.60 Å). SO_2 further reacts with **1**·SO_2 to quantitatively give $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (**2**), which now contains an SO_3 bound to the μ-S (S–S = 2.17 Å). Effectively, a μ-S_2O_3 (thiosulfate) ligand is formed by an oxygen-transfer process, and *the source of the oxygen as established by* ^{18}O *labeling is* SO_2. S_8 is also produced, showing that SO_2 has undergone net disproportionation to SO_3 and S_8. The reaction rate is highly dependent on solvent polarity and base promoters such as Et_3N. 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_2 to S_8 and H_2O catalyzed by Mo–S complexes may involve **2** as an intermediate. Weak bases, e.g., Et_3N, strip off the SO_3 functionality in **2** to give primarily mixtures of isomers of **1** and products of base–SO_3 interaction. Crystallographic data for $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\text{·}SO_2)$: space group $P2_1/c$; a = 13.738 (2) Å, b = 10.581 (3) Å, c = 17.331 (4) Å, β = 92.41 (2)°; V = 2516.9 Å^3 at 296 K; D_{calc} = 1.73 g/cm^{-1} for Z = 4; R = 6.2% for 2017 independent reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 45°$. Crystallographic data for $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$: space group $P2_1/c$; a = 13.730 (5) Å, b = 10.635 (3) Å, c = 16.862 (2) Å, β = 93.17 (5)°; V = 2458.5 Å^3 at 296 K; D_{calc} = 1.81 g/cm^{-1} for Z = 4; R = 4.0% for 2612 reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 45°$.

The activation of S=O bonds in SO_2 by transition-metal complexes, particularly toward reduction by hydrides and hydrogen,[1-6] has been a major recent focus of our research. We have shown[1] that the complexes investigated by Rakowski DuBois and co-workers,[7] $[(Me_nCp)Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$, where n = 0, 1, or 5 (Cp*), catalyze homogeneous hydrogenation of SO_2 to S_8 and H_2O (eq 1) and react stoichiometrically with SO_2 as in eq 2:

$$SO_2 + 2H_2\ (2\text{–}3\ \text{atm}) \xrightarrow[350\ \text{turnovers/h}]{\text{PhCl–BuOH, 75°C}} \tfrac{1}{8}S_8 + 2H_2O \quad (1)$$

The disulfide-bridged product, $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (**1**), had previously been prepared and structurally characterized by Wachter's group,[8] and polymeric, insoluble $(Cp^*MoS_x)_n$ (x = ~3)[9] is the synthetic precursor to $[Cp^*MoS(SH)]_2$.[7] Both Mo



products of eq 2 react with H_2 under mild conditions similar to those in the catalytic reaction (eq 1) to regenerate the SH complex.[1,7,8b] Thus, eq 2 was believed to be a logical first step in the mechanism for catalytic reduction of SO_2.[1] 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_2 and other oxygen-containing small molecules (SO_3, O_2) and report the results here.[10]

The formation of an SO_2 adduct of **1**, $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\text{·}SO_2)$, **1**·$SO_2$, with the SO_2 bound to a μ-S ligand, was not

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surprising in view of our previous characterization of $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$.[4] However, further reaction with SO_2 to quantitatively give $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (**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[11] and our group,[10] formally contains a bridging thiosulfate (μ-SSO_3) ligand formed by *oxygen transfer from* SO_2. We have also observed oxygen transfer to give the SO_3 moiety in the reaction of SO_2 with $Cp^*Ru(CO)_2H$ to yield $Cp^*Ru(CO)_2(SO_3H)$ and $[Cp^*Ru(CO)_2]_2(\mu\text{-}SSO_3)$.[6] These facile $S^{IV} \rightarrow S^{VI}$ conversions and the oxygen-donating ability of SO_2 signal an important new area of SO_2 reactivity that merits further attention. Furthermore the S_2O_3 ligand in **2** displays novel reactivity, e.g., **2** can be hydrogenated back to **1** with elimination of H_2O and SO_2. This suggests that *2 may be an intermediate in the catalytic* SO_2 *hydrogenation (eq 1) and that thiosulfate species, which have now been found to be produced from* SO_2 *in several systems, may play an important role in* SO_2 *reduction.* The 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 SO_2 is disproportionated to sulfur and SO_3-containing derivatives under mild conditions.

Experimental Section

Materials and Instrumentation. Reactions were carried out under inert atmosphere using Schlenk techniques except for O_2 oxidations. Reagent-grade solvents, SO_2, SO_3 (Alfa Inorganics), and $Mo(CO)_6$ (Strem Chemical) were usually used as received, but for some reactions, solvents were dried by distillation from appropriate drying agents. Liquid SO_2 used as solvent was purified by passage through a −95 °C trap, and both it and SO_3 were manipulated on a vacuum line. The preparations of $[Cp^*MoS(SH)]_2$ were modifications of literature methods,[7a,12] and the synthesis of the MeCp analogue followed the published procedure.[7a] $S^{18}O_2$ (95%) was prepared by reaction of S_8 and $N^{18}O$; $^{18}O_2$ was also prepared from $N^{18}O$.[13]

Infrared and ^1H 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 $(Cp^*MoS_x)_n$ and $[Cp^*MoS(\mu\text{-}S)]_2$. The procedure described here is a modification of that reported[9b] and is carried out in one flask. A mixture of $Mo(CO)_6$ (9.0 g, 34 mmol) and 100 mL of propionitrile was refluxed for 24 h in a 500-mL flask to form $Mo(CO)_3(C_2H_5CN)_3$[14] (*Caution*: large amounts of CO are evolved). Solvent was completely removed in vacuo, 400 mL of THF and 5.3 mL of Cp^*H was added to the residue, and the mixture was refluxed for 30 min. This reaction nearly quantitatively formed $Cp^*Mo(CO)_3H$,[3] which is thermally unstable in solution at the reflux temperature and partially converts to $[Cp^*Mo(CO)_3]_2$, imparting a red color to the solution. After the solution was cooled to ~25 °C, 5.03 g of 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 $(Cp^*MoS_x)_n$ 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,[9b] $[Cp^*MoS(\mu\text{-}S)]_2$ (0.57 g of black microcrystals were obtained from a 3.5× smaller scale reaction upon solvent reduction to 10 mL). This complex can also be used as a precursor to $[Cp^*MoS(SH)]_2$.[7] The reaction sequence here produced proportionately more $(Cp^*MoS_x)_n$ than $[Cp^*MoS(\mu\text{-}S)]_2$ in comparison to the previously reported[9b] reaction of S_8 with $Cp^*Mo(CO)_3H$ purified by sublimation, possibly because of the in situ procedure and the 6-h longer reflux period for the final step.

Preparation of $[Cp^*MoS(SH)]_2$. From H_2 Reduction. Into a heavy-walled glass 250-mL Fischer-Porter pressure vessel were placed 2.1 g of $(Cp^*MoS_x)_n$, 30 mL of chlorobenzene, 15 mL of ethanol, and 1 mL of Et_3N. The mixture was degassed by two freeze–pump–thaw cycles and 1 atm H_2 was added to the vessel while nearly totally immersed in liquid nitrogen, giving ~3 atm H_2 pressure on warming to 25 °C. The lower portion of the vessel containing the liquid phase was then immersed in an oil bath at 100 °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 °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 $[Cp^*MoS(SH)]_2$ 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 $(Cp^*MoS_x)_n$).

From $LiEt_3BH$ Reduction. $(Cp^*MoS_x)_n$ (4.14 g) was stirred with 45 mL of 1 M $LiEt_3BH$ in THF (Aldrich) for 2 h, as reported for the Cp analogue.[12] 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 H_2O. Addition of 50 mL of H_2O and reduction of solvent volume to ~80 mL in vacuo gave 2.84 g (76%) of $[Cp^*MoS(SH)]_2$, isolated as above (except initial wash with H_2O).

$NaEt_3BH$ was also used as a reducing agent in other reactions, but once again large excesses of the hydride (up to 10 equiv/equiv of $(Cp^*MoS_x)_n$) and 18-h reaction period were necessary. $[Cp^*MoS(\mu\text{-}S)]_2$ was also found to be reducible to $[Cp^*MoS(SH)]_2$ by $NaEt_3BH$ under similar conditions.

Preparation of $Cp^*_2Mo_2(S_2)(S)_2$ (1) from $[Cp^*MoS(SH)]_2$ and SO_2. $[Cp^*MoS(SH)]_2$ (2.57 g) in 150 mL of toluene was saturated with SO_2 and stirred for ~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 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 "$(Cp^*MoS_x)_n$" coproduct. Removal of most of the solvent and addition of hexane yielded 2.0 g of dark blue **1** containing ~5–10% **2**. The latter is difficult to remove by recrystallization but can be reduced to **1** by adding $[Cp^*MoS(SH)]_2$ (~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 $CHCl_3$–hexane yielded **1** pure enough for most purposes (*note*: CH_2Cl_2 should not be used as a solvent for **1** because of alkylation of sulfide ligands). Alternatively, chromatography[8a] 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 $(MeCp)_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ from $[(MeCp)MoS(SH)]_2$ and 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 $[(MeCp)MoS_x)]_n$. 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.[7b] Anal. Calcd for $C_{12}H_{14}S_4Mo_2$: C, 30.13; H, 2.95; S, 26.82. Found: C, 29.70; H, 2.85; S, 26.95.

Preparation of $Cp^*_2Mo_2(S_2)(S)(S{\cdot}SO_2)$ ($1{\cdot}SO_2$). Treatment of a saturated solution of **1** in toluene with excess SO_2 yielded a deep red crystalline precipitate of $1{\cdot}SO_2$, which was collected on a frit and dried in a stream of SO_2. Further crops can be obtained by addition of SO_2-saturated hexane or partial solvent removal followed by readdition of SO_2. $1{\cdot}SO_2$ readily loses SO_2 and must be stored in an 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 SO_2 indicated adduct formation.

Isomerization and Alkylation of 1. After several days in toluene or $CHCl_3$ solution at 25 °C under N_2, **1** began to isomerize to $[Cp^*MoS]_2(\mu\text{-}S_2)$ (**1′**) (δ_{CDCl_3} 1.97), and after 14 days, ~20% conversion occurred. In CH_2Cl_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 δ_{CDCl_3} 1.93–2.37, including a major signal at δ 2.01 due to another isomer of **1**, $[Cp^*MoS(\mu\text{-}S)]_2$, (**1″**). Major signals near δ 2.25 were apparently due to alkylated species, e.g., $[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$. In comparison, alkylation of **1** in CH_2Cl_2 with $MeSO_3F$ or EtI rapidly gave monoalkylated products with δ 2.28 and 2.24, respectively.

Reactions of 1 with $^{18}O_2$ and $H_2{}^{18}O$. Reaction of $^{18}O_2$ (0.3 mmol) with **1** (40 mg, 0.068 mmol) in 15 mL of $CHCl_3$ (undried) in a 50-mL flask overnight gave a mixture of **2** (~25%) and oxo–sulfido complexes, similar to the reaction carried out by Wachter and co-workers[8a] at 50 °C in toluene. IR showed that **2** was partially ^{18}O-labeled and that the oxo species were fully labeled. An identical reaction but with SO_2 (1 mmol) present gave negligible reaction overnight, but if Et_3N (20 μL) was present the reaction gave ~3:1 ratio of unlabeled **2** to labeled oxo complexes (~2:1 $^{18}O/^{16}O$).

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Table I. Spectroscopic Data for New Complexes and Related Sulfides

complex	ν_{SO}, cm^{-1} [a]	δ, ppm[b]
$Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (**1**)		2.14
$Cp^*_2Mo_2(\mu\text{-}S_2)(S)_2$ **1'**		1.97
$Cp^*_2Mo_2(\mu\text{-}S)_2(S)_2$ **1''**		2.02
$Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$ (**1**·SO_2)	1229, 1080, 533	2.13
$Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)_2$		2.25[c]
$Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$	1243, 1088, 535	2.21[d]
$[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$	1198, 1053	2.20
$[CpW(CO)_3](\mu\text{-}S{\cdot}SO_2)$	1213, 1074	5.04[e]
$Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ **2**	1242, 1205, 1010, 604, 523	2.31
$Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SS^{18}O_3)$	1204, 1172, 960, 594, 515	2.31
$MeCp_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$	1228, 1210, 1010, 600, 525	2.43

[a] Nujol mulls. [b] Resonance for Cp*; $CDCl_3$ solvent, 90 MHz (CW), TMS reference. [c] $\delta(CH_2)$ 2.40. [d] $\delta(CH_2)$ obscured. [e] Resonance for Cp, C_6D_6 solvent.

A solution of **1** (30 mg, 0.05 mmol) in 5 mL of dried toluene containing $H_2{}^{18}O$ (50 μL, 2.5 mmol) was stirred 18 h in the presence of atmospheric O_2 (~0.8 mmol) in a closed 100-mL flask. After solvent removal, NMR and IR of the residue showed nearly fully ^{18}O-labeled **2** and primarily unlabeled oxo complexes ($\nu_{Mo=O}$ at 905–909 cm^{-1}) (**2** does not undergo oxygen exchange with $H_2{}^{18}O$ under the reaction conditions here). A similar reaction in CH_2Cl_2 gave primarily unlabeled **2**, essentially unlabeled oxo complexes, and some unreacted **1**. Similar 2-day reactions in CH_2Cl_2 under N_2 using unlabeled H_2O or no added H_2O gave mainly isomerization and alkylation products plus ~10% **2**.

Preparation of $Cp^*_2Mo_2(S_2)(S)(S_2O_3)$ (2) from $[Cp^*MoS(SH)]_2$. A solution of $[Cp^*MoS(SH)]_2$ (0.253 g) and 0.1 mL of Et_3N (promoter) in 20 mL of $CHCl_3$ was treated with excess SO_2. 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 $C_{20}H_{30}S_5O_3Mo_2$: 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_2, 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_3NH^+ salts (ν_{NH} = 2500 cm^{-1}; δ 3.1 (q, CH_2), 1.3 (t, CH_3)).

Preparation of 2 from 1: Preparation of MeCp Analogue of 2. In CH_2Cl_2. **1** (0.50 g) in 8 mL of CH_2Cl_2 containing 0.1 mL of Et_3N was reacted with SO_2 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_3N^+ salts. Extraction of this residue with H_2O yielded an oily solid (~60 mg) with ν_{SO} bands and NMR Et resonances consistent with the presence of Et_3NH^+ 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_2Cl_2–hexane.

The MeCp analogue of **2** was prepared by allowing a saturated solution of $(MeCp)_2Mo_2(S_2)(S)_2$ in toluene–$CHCl_3$ to stand for ~64 h in a closed flask in the presence of excess SO_2 (not rigorously anaerobic). Crystals of the desired complex formed and exhibited physical and spectral properties similar to **2** (Table I).

In Liquid SO_2. Identification of S_8 as a Product. Into a 250-mL heavy-wall glass Fischer & Porter pressure vessel was placed 0.50 g of **1**. SO_2 was condensed into the flask on a vacuum line, and the solution (~10 mL of liquid SO_2) was allowed to stand overnight at 25 °C. Removal of SO_2, extraction of the residue with CS_2 (5 mL), filtration, and removal of CS_2 yielded a rose-colored residue. Washing the latter with ~1 mL of $CHCl_3$ left a small amount (~5 mg) of a light-colored solid that was sparingly soluble in CH_2Cl_2 and toluene but very soluble in CS_2. 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_8. The total yield of **2** (mainly recovered from the original extraction residue) was 0.57 g (92%).

Preparation of $Cp^*_2Mo_2(S_2)(S)(S_2{}^{18}O_3)$ from 1 and $S^{18}O_2$ (But Not SO_2 + $^{18}O_2$ or $H_2{}^{18}O$). A solution of **1** (40 mg, 0.068 mmol) in dry CH_2Cl_2 (3 mL) containing Et_3N (50 mL, 0.36 mmol) in a 15-mL flask was treated with 2 equiv of $S^{18}O_2$ (95%) on a vacuum line. After 3 h, addition of ethanol and partial solvent removal precipitated nearly fully ^{18}O-labeled **2**, characterized by IR (Table I). Analogous closed-flask reactions using normal SO_2 (>2 equiv) in the presence of either $^{18}O_2$ (90 Torr, 0.1 mmol) or $H_2{}^{18}O$ (50 μL, 2.5 mmol) gave little or no incorporation of ^{18}O into **2**.

NMR Studies of Rates of Reaction of 1 with SO_2 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_2 in 5-mm NMR tubes or small volume flasks and 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_2. For the reaction of **1** (purified by chromatography) in liquid SO_2, 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_2, and extracting **2** from the residue with $CHCl_3$.

Table II. Summary of Reactions of SO_2 with **1**[a]

solvent	promoter, mmol		SO_2, mmol	reactn time	% compln[b]
liquid SO_2			11.0	30 min	50
				45 min	66
				120 min	100
	Et_3N	1.00	11.0	5 min	100
		0.72	11.0	5 min[c]	75
		0.04	11.0	8 min[c]	15
	py	1.00	11.0	8 min[c]	33
	$(t\text{-}Bu)_2Mepy$	0.65	11.0	8 min[c]	0
$CDCl_3$			0.7	7 days	<5
	Et_3N	0.14	0.7[d]	4 h	50
				24 h	85
				45 h	100
	py	0.14	0.7	10 min	50
				20 min	75
				60 min	93
				120 min	95[e]
	$(t\text{-}Bu)_2Mepy$	0.14	0.7	1 h	<5
				5 h	65
				8 h	87
$CDCl_3$–CD_3OD (10:1)			satd	3 h	100
CH_3NO_2			satd	60 min	100
	py	0.25	satd	10 min	100
CD_3CN			satd	6 h	100
benzene	Et_3N	0.10	0.4	months	<5
PhCl			satd	4 days	22
	py	0.07	0.7	12 min	50
				4 h	100
PhCl–CD_3OD (1:1)			0.7	5 min	50[f]
				10 min	100
	Et_3N	0.07	0.7	2.5 min	50
				8 min	100
	py	0.07	0.7	2.5 min	75
				6 min	100
	$(t\text{-}Bu)_2Mepy$	0.07	0.7	4 min	70
				11 min	100

[a] 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_2. [b] As judged by relative intensities of Cp* NMR resonances of **1** and **2**. [c] At 0 °C. [d] Reaction used 15 mg of **1** and measured amount of SO_2 (other $CDCl_3$ reactions utilized SO_2-saturated solutions, which correspond to approximately 0.7 mmol SO_2 in 0.5 mL of $CDCl_3$). [e] Reaction appeared to reach an equilibrium. [f] Reaction was relatively slow initially (10% complete after 2.25 min), but rate increased rather than decreased as for most of the other reactions.

Reaction of 2 with $[Cp^*MoS(SH)]_2$ to Give 1. **2** (18 mg, 0.027 mmol) and $[Cp^*MoS(SH)]_2$ (16 mg, 0.027 mmol) were placed into an NMR tube, $CDCl_3$ was added, and the solution was degassed. ^1H NMR

Table III. Summary of Reactions of **2** with H_2 and Weak Bases

solvent/reactant[a]	condns[b]	time, h	product ratios, ~% unreact **2**	**1**	**1'**	oxo[c]	other
$CDCl_3$ + **H_2** (1 atm)	A, 25 °C	18	30	65			5[d]
$CDCl_3$ + **H_2** (1 atm)	B, 25 °C	96	70				30[d]
$CDCl_3$ + Et_3N + **H_2** (1 atm)	B, 25 °C	4					100[d]
BuOH–PhCl (1:1) + Et_3N + **H_2** (3 atm)	A, 75 °C	0.15					100[d]
$CHCl_3$–H_2O (20:1)	A, reflux	48	100				
PhCl	A, 75 °C	18	100				
BuOH–PhCl (1:1)	A, 75 °C	2	10		45	25	20[e]
BuOH	A, 75 °C	1	30		60	10	
MeOH	A, 75 °C	1.5	15	10	30	25	10[e]
MeOH + **Et_3N**	A, 75 °C	1	44	44	12		
BuOH–PhCl (1:1) + **Et_3N**	A, 75 °C	0.67	28	44	28		
MeOH–$CHCl_3$ (1:1) + **Et_3N**	A, 75 °C	5	10	40	50		
$CDCl_3$ + **Et_3N**	B, 25 °C	96	50	40	10		
$CDCl_3$–**Et_3N** (1:4)	A, 25 °C	18	2	90	5	3	
MeOH–$CHCl_3$ (4:1) + H_2O	A, 75 °C	17		25	50	25	
DMSO-d_6–$CDCl_3$ (3:1) + H_2O	B, 75 °C	1.5			100		
DMSO-d_6–$CDCl_3$ (1:1) + H_2O	B, 25 °C	120	50		30	20	
DMSO–$CHCl_3$–H_2O (8:6:1)	A, 75 °C	0.75		5	95		
acetone–$CHCl_3$–H_2O (8:6:1)	A, 75 °C	18		15	70	15	

[a] 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_3N and H_2O addends typically were 2–5% of the solvent volume. [b] A, flask reaction; B, NMR tube reaction. [c] Primarily $Cp^*_2Mo_2O_2S_2$ with lesser amounts of $Cp^*_2Mo_2OS_3$. [d] $[Cp^*Mo(S)(SH)]_2$. [e] **1''**.

showed approximately equal intensity peaks due to Cp* of each complex. Et_3N 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_3N shifted downfield by ~0.1 ppm, indicative of protonation to Et_3NH^+.

A larger scale reaction (0.843 g of **2**, 0.736 g of SH complex in 20 mL CH_2Cl_2, plus 0.5 mL of Et_3N) 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 $CHCl_3$ is used as solvent.

Reductions of 2 with H_2 to Give 1 and Ultimately $[Cp^*MoS(SH)]_2$. A solution of **2** (60 mg) in 1:1 PhCl–BuOH (20 mL) and Et_3N (50 μL) was pressurized with H_2 (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 $[Cp^*MoS(SH)]_2$. NMR of the residue from solvent removal showed pure SH complex.

A solution of **2** (~5 mg) in $CDCl_3$ in an NMR tube under 1 atm H_2 at 35 °C gave very slow reaction (only 30% conversion after 4 days). However, when Et_3N (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_2 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_2 and H_2O as Products of Above Reaction. A 0.556-g (0.83 mol) aliquot of **2** in 13 mL of dry PhCl was placed into a reaction vessel with a total volume of 40 mL. Bu_3N (20 μL, 0.084 mmol) was added, and the solution was degassed on a vacuum line. H_2 (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_2, and after 17 h the red solution color indicated substantial amounts of **1**·SO_2. The vessel was cooled to −196 °C and found to contain no unreacted H_2 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_2 and a residual solvent mixture containing immiscible H_2O 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_2 (at least 0.2 mmol) went into a side reaction with **1** to form $[Cp^*MoS(SH)]_2$, which then reacted with SO_2 via eq 2 to give back most of the **1** plus $(Cp^*MoS_x)_n$. 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 $CHCl_3$ 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_2 and 0.68 mmol of H_2O should have been produced. These are consistent with the experimental results (some SO_2 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_3. Formation of 2. Solutions of **1** (30 mg) in 2 mL of dry CH_2Cl_2 were reacted on a vacuum line with various ratios of SO_3 (measured in the gas phase by *PVT* methods). The SO_3 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_3 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_3 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_3NO_3) but decomposed rapidly in aqueous solution or if air was present.

Preparation of $Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)_2$. Reactions with SO_2 and SO_3. The synthesis was analogous to that of the Cp analogue.[15] To a solution of $[Cp^*MoS(SH)]_2$ (0.888 g, 1.5 mmol) in 15 mL of dry THF was added CH_2Br_2 (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_2Cl_2. 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 ^1H NMR revealed the presence of ~10% impurities (two Cp* peaks near δ 2.1). These were removed by recrystallization from CH_2Cl_2–MeOH to give 0.55 g (60%) of pure $Cp^*_2Mo_2(S_2CH_2)(S)_2$. Anal. Calcd for $C_{21}H_{32}S_4Mo_2$: C, 41.72; H, 5.34; S, 21.21. Found: C, 41.17; H, 5.41; S, 21.57.

The deep blue $Cp^*_2Mo_2(S_2CH_2)(S)_2$ formed a red, reversible SO_2 adduct analogous to **1**·SO_2. However, no further reaction to a thiosulfate occurred. Reaction with 1.5 equiv of SO_3 in CH_2Cl_2 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_2O_3.

Structural Determination of $Cp^*_2Mo_2(S_2)(S)(S\text{·}SO_2)$ (1·SO_2) and $Cp^*_2Mo_2(S_2)(S)(SSO_3)$ (2). Crystals of **1**·SO_2 suitable for X-ray diffraction were grown by slowly cooling a saturated solution of the complex in SO_2-saturated toluene–acetone. Crystals of **2** (synthesized from SO_2) were grown in $CHCl_3$ by slow cooling.

(15) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

Table IV. X-ray Data for $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\text{-}SO_2)$ and $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S_2O_3)$

chem formula	$C_{20}H_{30}O_2S_5Mo$	$C_{20}H_{30}O_3S_5Mo$
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
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^3	2516.9	2458.5
Z	4	4
D_{measd}, g/cm^3	1.73	1.81
λ (Mo Kα_1)	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^{-1}	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	$\pm h,+k,+l$	$\pm h,\pm k,+l$
no. measd reflcns	3476	6722
no. of unique reflcns	3285	3218
R_F equiv reflcns, %	3.2	2.1
$I \geq 2\sigma(I)$	2017	2612
no. of refined params	263	272
R_F obs reflcns, %	6.2	4.0
$R_{\omega F}$ obs reflcns, %	6.5	6.2

Room-temperature data were collected by variable speed θ–2θ scans on an Enraf Nonius CÁD-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 ($I \geq 2\sigma(I)$) with full-matrix least-squares methods using appropriate neutral scattering factors and anomolous scattering terms.[16] Refinements included anisotropic thermal parameters for all atoms and a correction for secondary extinction.[17] Final Fourier difference maps failed to show peaks that could be interpreted as hydrogen atoms. The Los Alamos Crystal Structure Codes[18] 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 $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\delta_c(I)$ 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_2 reaction with $[(CpMe_n)MoS(SH)]_2$ used to catalyze SO_2 hydrogenation (eq 1). Two procedures for synthesis of this SH complex[7a] or its Cp analogue[7a,12] have been reported, both of which we have used and found to have some minor disadvantages. Reaction of the immediate precursor, $(Cp^*MoS_x)_n$, with H_2 (~3 atm, 75–100 °C) in $CHCl_3$ required 3–4 days,[7a] and reduction of $(Cp^*MoS_x)_n$ with $LiHBEt_3$ or $NaHBEt_3$ analogous to that reported[12] 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 of hydride per gram of $(Cp^*MoS_x)_n$ (~1.5 mmol based on $x = 3$,[1] $n = 2$) was required in some cases, possibly because of variable composition of the $(Cp^*MoS_x)_n$ or the presence of impurities (H_2O, S_8). In comparison to the conditions reported for the Cp case, longer reaction periods (18 h) were also necessary. This was particularly true for $NaHBEt_3$ addition to $[Cp^*MoS(\mu\text{-}S)]_2$, a coproduct of the $(Cp^*MoS_x)_n$ synthesis, which was also found to be reducible to the SH complex. Overall we found that H_2 reduction of $(Cp^*MoS_x)_n$ is the more reliable procedure and can be improved time-wise by using 2:1 chlorobenzene–ethanol containing Et_3N (~1 mL) as solvent, which is similar to the solvent mixture used in eq 1. Good yields of $[Cp^*MoS(SH)]_2$ 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.

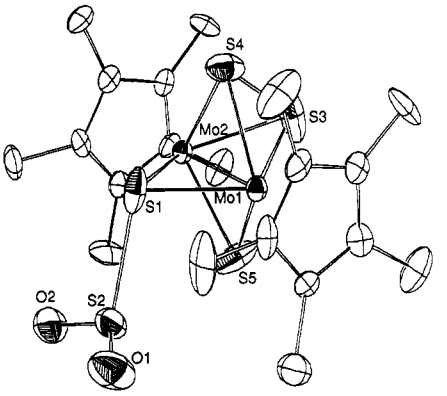
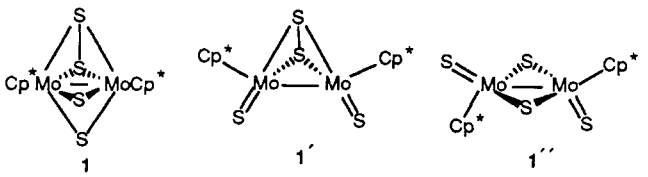


Figure 1. Molecular geometry and atom-labeling scheme for $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\text{-}SO_2)$ (**1**·SO_2; 35% ellipsoids).

Because of thermal instability, $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (**1**) must be synthesized under mild conditions such as those employed in Wachter's[8a] original preparation ($[Cp^*Mo(CO)_2]_2$ and S_8 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_2 with $[Cp^*MoS(SH)]_2$ according to eq 2 without need for chromatography. Complex **1** is novel in that it has two isomers that are thermally and photochemically[17] interconvertible at 25 °C: **1** is the least stable thermally while



$[Cp^*MoS(\mu\text{-}S)]_2$ (**1″**) is the most stable (see below), and photolysis[17] 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^{IV} to Mo^{V} on isomerization to **1″**. Chemical oxidation with I_2 and cyclic voltammetry shows that **1** can be oxidized to an apparent dicationic species in reversible or quasi-reversible fashion.[20] 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 $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (1) with SO_2 and SO_3. SO_2 Adduct Formation and Cleavage of SO_2 to S_8 and $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (2). In the presence of SO_2, **1** reversibly forms an adduct, **1**·SO_2, from which the SO_2 readily dissociates at 25 °C. Crystalline **1**·SO_2 can be isolated under an SO_2-enriched atmosphere, and X-ray crystallography (see below and Figure 1) shows that one SO_2 is bound to a bridging sulfide and that a very long S–S bond consistent with the high lability is present. IR ν_{SO}

(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.

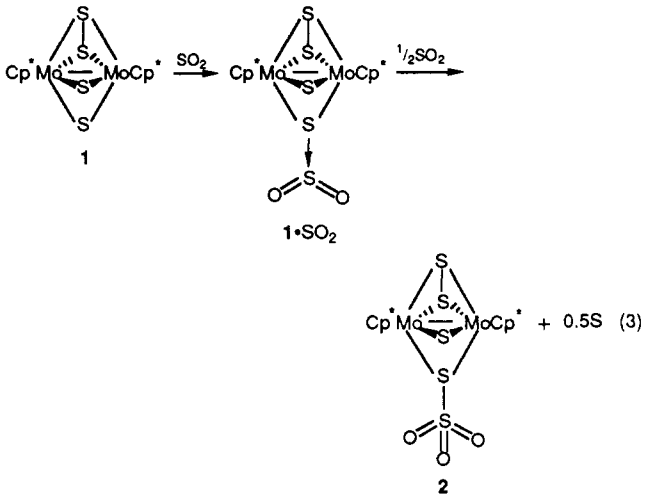
(17) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664.

(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 SO_2.[21] The spectacular color change from bright blue to bright red on adduct formation is noteworthy considering that the SO_2 is weakly bound to a ligand rather than the metal. **1**·SO_2 was found to undergo a further, irreversible reaction with SO_2 in various organic solvents and liquid SO_2 (eq 3). The product is $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (**2**), which possesses an SO_3 rather than an SO_2 bound to sulfide. Effectively a μ-S_2O_3 ligand (S-bound thiosulfate) is created by an oxygen-transfer process, and *the source of the oxygen as established by ^{18}O labeling is clearly SO_2* (see below) and not adventitious O_2 or H_2O. No other Mo-containing product is formed and elemental sulfur is also produced, indicating that SO_2 has effectively been disproportionated to S_8 and coordinated SO_3. Complex **2** can also be prepared from $[Cp^*MoS(SH)]_2$ by coupling eq 2 and 3. The less soluble MeCp analogues exhibit chemistry similar to the 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 ^1H NMR.[22] No intermediates are observed, and the reaction rate shows dependence upon SO_2 concentration and a high dependence on solvent polarity and the presence of organic base promoters such as Et_3N, 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 SO_2–Et_3N) 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 (~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)$_2$Mepy) were much less effective than unhindered amines, and the rate of reaction showed dependence on amine:SO_2 ratio. The amine was always present in large excess (>10:1) in relation to **1** but usually <1:5 with respect to SO_2. In liquid SO_2 containing Et_3N (amine:SO_2 = 0.07), conversion of **1** to **2** was complete in 8 min but only 15% conversion occurred in this time for amine: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 ~95% conversion (Table II). Solid state conversion of **1**·SO_2 to **2** occurs very slowly ($t_{1/2}$ ~month) at 25 °C in a closed vessel under 1 atm SO_2.

$Cp^*_2Mo_2(S_2)(S)(SSO_3)$ is air stable, does not release sulfur oxides on heating, and also forms on treatment of **1** with SO_3 in CH_2Cl_2 below 25 °C. The reaction is less clean than eq 3 however, and use of SO_3:**1** ratios > 2 give mostly unidentified products. Transfer of SO_3 to **1** from Me_3NSO_3 does not occur, although Pfauntsch[11c] obtained 49% yields of **2** by treating **1** with pyridine–SO_3 in CH_3CN. Thus, it appears that the strength of the donor–acceptor S–SO_3 bond in **2** falls in between that of the two amine–SO_3 complexes (see Discussion).

A complex closely related to **1**, $Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)_2$, which also is deep blue in color, formed a red, reversibly bound SO_2 adduct but did not react further with SO_2. Reaction of this complex, which contains a methanedithiolate ligand instead of S_2, with SO_3 also failed to give a thiosulfate. The SO_2 adduct gives ν_{SO} bands (Table I) similar to **1**·SO_2 and presumably contains μ-S–SO_2 binding.

Reactions of 1 with O_2, SO_2–O_2, SO_2–H_2O, and O_2–H_2O Mixtures. ^{18}O Labeling Experiments. In order to verify that SO_2 rather than adventitious O_2 or H_2O is the source of the third oxygen in **2** produced in eq 3, ^{18}O labeling studies were carried out. Reaction of 2 equiv of $S^{18}O_2$ (95%) with **1** in CH_2Cl_2 containing Et_3N promoter gave primarily fully labeled $Cp^*_2Mo_2(S_2)(S)(S_2{}^{18}O_3)$ (Table I gives IR isotopic shift data), indicating that the oxygen originates exclusively from SO_2. When normal SO_2 was reacted with **1** in the presence of either $^{18}O_2$ or $H_2{}^{18}O$, ^{18}O was not incorporated into **2**, further corroborating that *the SSO_3 ligand is formed by oxygen transfer from SO_2 in preference to O_2.*

1 does slowly react with atmospheric oxygen *in the absence of SO_2* to form **2** in low yield (25%) along with a mixture of oxo–sulfido dimers in their various isomeric forms:

$$\underset{\mathbf{1}}{Cp^*_2Mo_2(S_2)(S)_2} \xrightarrow[CHCl_3,\ 18\ h]{O_2} Cp^*_2Mo_2(S_2)(S)(S_2O_3) + Cp^*_2Mo_2O_2S_2 + Cp^*_2Mo_2OS_3 \quad (4)$$
$$\underset{\mathbf{2}\ (25\%)}{}$$

Proton NMR showed that eq 4 was complete in 18 h at 25 °C in $CHCl_3$. Brunner et al.[11] independently found that air oxidation of **1** under somewhat different conditions (50 °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 SO_2 were present after either partial or complete reaction. Thus it would appear that insufficient amounts of SO_2 (potentially generable via sulfide ligand oxidation, see Discussion) were present to convert **1** to **2** according to eq 3. When excess SO_2 was included as a reactant in eq 4 (SO_2:O_2 = 4), very little reaction beyond formation of **1**·SO_2 occurred in 18 h. Thus, coordination of SO_2 to the sulfide in **1** apparently blocks reactivity with O_2 (see Discussion). It is also important to note that very little conversion of **1**·SO_2 to **2** via eq 3 occurs in this system in 18 h because this reaction is very slow in $CHCl_3$ without promoter (see Table II). Reaction of **1** with $^{18}O_2$ in $CHCl_3$ (16 h) according to eq 4 gave, as expected, the ^{18}O isotopomers of both **2** and the oxo dimers (as shown by ~40 cm^{-1} isotopic shifts in $\nu_{Mo=O}$[11b] near 900 cm^{-1}). When SO_2 was present in the latter reaction (SO_2:$^{18}O_2$ = 4) *along with Et_3N* promoter, it proceeded to completion in 18 h and the product distribution was now *unlabeled* **2** (75%) and partially ^{18}O-labeled oxo dimers (25%). Only a small amount of presumably the $SS^{16}O_2{}^{18}O$ isotopomer was present, as indicated by a weak ν_{SO} band at 992 cm^{-1}. The absence of significant ^{18}O-labeled **2** showed that formation of **2** occurred via amine-promoted disproportionation of SO_2 (eq 3) rather than the $^{18}O_2$ 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 O_2 does not become incorporated into the thiosulfate ligand and provides a check that isotopic exchange of $^{18}O_2$ and SO_2 is not occurring prior to any reaction with **1**. The formation of oxo species containing ^{18}O indicates that some reaction of $^{18}O_2$ with Mo sulfide complex occurred. Because the oxo ligands were only partially labeled (~2:1 $^{18}O/^{16}O$),^{16}O originating from 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 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 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 $CDCl_3$ solutions. (b) We find that the Cp* resonances occur ~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 $H_2{}^{18}O$, solutions of **1** ($H_2{}^{18}O$:**1** = ~30–50) reacted with atmospheric oxygen ($H_2{}^{18}O$:O_2 = ~3) in a closed flask for 16 h to give **2** predominantly *labeled* with ^{18}O and oxo complexes that were predominantly *unlabeled*.

$$\mathbf{1} \xrightarrow[CH_2Cl_2 \text{ or toluene}]{O_2/H_2{}^{18}O} \text{labeled } \mathbf{2} + \text{unlabeled } Cp^*{}_2Mo_2S_xO_y \qquad (5)$$

Water alone showed no significant reaction with **1** in this time frame, and the nonincorporation of ^{18}O into the oxo clusters showed that they formed from O_2 and not H_2O. The unexpected incorporation of ^{18}O into **2** points to an intermediate that rapidly exchanges its oxygen with oxygen in H_2O. One possibility is SO_2, which was verified by IR to undergo rapid exchange (minutes or less) with $H_2{}^{18}O$ in organic solvents. However the lack of a detectable steady-state concentration of SO_2 in O_2 oxidation of **1** indicates either noninvolvement of SO_2 or very fast reaction of an SO_2 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[19]). 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[8a]). In $CHCl_3$ or toluene, solutions of **1** are stable for days before NMR evidence for **1′** formation appears, but *in* CH_2Cl_2 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_2Cl_2 to give $[Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$, 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 $MeSO_3F$ or EtI to **1** (δ 2.24–2.28) and to that of $[Cp^*{}_2Mo_2(S_2)(S)(SMe)]PF_6$ (δ 2.33[22b]) isolated by Wachter and coworkers.[8b] Similar alkylation of μ-S by CH_2Cl_2 and also $CHCl_3$ was previously reported for $Pt_2(\mu\text{-}S)_2(PPh_3)_4$.[23] A solution of **1** in CH_2Cl_2 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_2Cl_2 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_2Cl_2 before this problem was discovered, although the level of alkylation here (<5%) did not significantly effect the outcome. It is unclear why $CHCl_3$, which usually is more reactive toward nucleophiles than CH_2Cl_2, 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_3SO_3H and HPF_6. The color of the protonated complex in $CHCl_3$ 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_2.

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_2 are

$$\underset{\mathbf{2}}{Cp^*{}_2Mo_2(S_2)(S)(SSO_3)} \xrightarrow[CHCl_3,\ R_3N]{H_2,\ 25\text{–}75\ ^\circ C} \underset{\mathbf{1}}{Cp^*{}_2Mo_2(S_2)(S)_2} + SO_2 + H_2O \qquad (6)$$

coproducts, and the SO_2 may partially associate with **1** in relatively concentrated solutions in a closed system (dilution favors SO_2 dissociation). Whether H_2 reduction directly gives **1** or **1**·SO_2 cannot be readily ascertained, in the same manner that it is not known whether **1** or **1**·SO_2 directly reacts with SO_2 to give **2** (eq 3). Equation 6 is accelerated by Et_3N: at 25 °C, reduction with

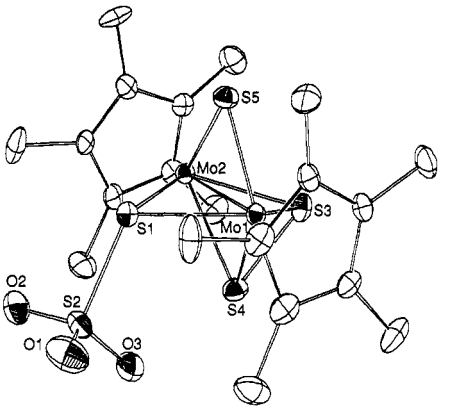


Figure 2. Molecular geometry and atom-labeling scheme for $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (**2**; 35% ellipsoids).

H_2 is complete within 4 h if amine (~3% of solvent volume) is present but otherwise is incomplete after days. $[Cp^*MoS(SH)]_2$ is the final product if excess H_2 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_3N. This is an excellent synthetic method for recycling **2** back to **1** because the $[Cp^*MoS(SH)]_2$ is also converted to **1**, which is thereby the sole organometallic product of the reaction.

Significantly, organic bases such as Et_3N have been found to react with **2** *without reducing agent being present.* The SO_3 functionality is stripped off to give primarily mixtures of isomers of **1** and products of base–SO_3 interaction (eq 7, where B = R_3N,

$$\underset{\mathbf{2}}{Cp^*{}_2Mo_2(S_2)(S)(SSO_3)} \xrightarrow{[B],\ 25\text{–}75\ ^\circ C} Cp^*{}_2Mo_2S_4 + [B]SO_3 \{+\text{oxo complexes}\} \qquad (7)$$

ROH, DMSO). As shown in Table III, solutions of **2** containing Et_3N 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 ($t_{1/2}$ ~ 4 days) and **1** was the predominant organometallic product. The reaction rate also depended on Et_3N concentration and **2** converted to **1** in 4:1 $CHCl_3$–Et_3N 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_3 to give mainly **1′**, but varying amounts of oxo species were also formed. Presumably the SO_3 reacts with alcohols to give an alkylsulfuric acid, $ROSO_3H$,[24] which then may be a source of oxo ligand. When both Et_3N and ROH were present in the reaction, no oxo species formed, indicating that R_3N reacts preferentially. In an attempt to determine whether H_2O would react with **2** to possibly give H_2SO_4, a $CHCl_3$ solution of **2** containing excess H_2O was refluxed for 2 days. However, no reaction occurred. A mixture of DMSO, $CHCl_3$, and water did give a reaction in which **1′** was found to be formed nearly quantitatively in 1.5 h at 75 °C. $BaCl_2$ 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_3 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 $Cp^*{}_2Mo_2(S_2)(S)(S\text{·}SO_2)$ (1·SO_2) and $Cp^*{}_2Mo_2(S_2)(S)(SSO_3)$ (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_2 and **2** (synthesized via eq 3) contain discrete molecular units separated by normal van der Waals distances.

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(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 $[(\eta^5\text{-}C_5Me_5)Mo]_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}X)$ (X = SO_2, SO_3)

	SO_2	SO_3
	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 $1{\cdot}SO_2$ and **2** consists of two Cp*Mo groups, which are bridged by a S_2 group, a S atom, and a SSO_x group (x = 2 for $1{\cdot}SO_2$ and 3 for **2**). The metal–sulfur cores of each molecule are structurally analogous, with each system possessing roughly C_{2v} 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 $1{\cdot}SO_2$ and 2.302 to 2.442 Å for **2**.

We have observed formation of the μ-S·SO_2 ligand in several other reaction systems, the most recent involving addition of SO_2 to $Cp^*W(CO)_3H$ to form $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$.[4] The longer S–S distance observed for $Cp^*_2Mo_2(S_2)(S)(S{\cdot}SO_2)$ (2.601 vs 2.408 Å) is consistent with the high lability of the SO_2 group.

$Cp^*_2Mo_2(S_2)(S)(SSO_3)$ (**2**) has been independently synthesized by air oxidation of **1** and structurally characterized by Wachter and co-workers.[11a,b] Our structure of **2** prepared via SO_2 reaction with **1** is identical.

A significant difference between $1{\cdot}SO_2$ and **2** is the 0.435-Å longer S–S bond associated with the μ-SSO_2 ligand. As noted by Brunner et al., the metal–metal and metal–sulfur distances are very dependent on the nature of the sulfur bridges.[8a] The longer Mo–Mo distance and Mo–SSO_x distances in **2** reflect the influence of the SO_3 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 $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2.135 (3) Å),[6] consistent with the higher lability of the SO_3 moiety in **2** than in the Ru species (See Discussion).

If in $1{\cdot}SO_2$ and **2**, S1 and S5 are described as the wingtip atoms of a Mo_2S_2 butterfly core, the SO_2 group in $1{\cdot}SO_2$ is endo to the butterfly and the SO_3 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 $1{\cdot}SO_2$ (average 80.7°) are larger than the related angles in **2** (average 75.13°). The exo orientation of the SSO_3 ligand is the same as that in Wachter's structure,[11a,b] which, it should be emphasized, was obtained on a crystal formed by O_2 oxidation of **1**.

Discussion

Properties of $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$ ($1{\cdot}SO_2$). From SO_2 lability, IR, and X-ray evidence, the sulfide–SO_2 Lewis acid–base bond in $1{\cdot}SO_2$ is much weaker than that previously found in $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$ and appears to be similar in strength to that in $[CpW(CO)_3]_2(\mu\text{-}S{\cdot}SO_2)$.[4] SO_2 readily dissociates from both the latter and $1{\cdot}SO_2$ at 25 °C, but the former does not lose SO_2 until 100 °C. This high lability renders ^{18}O labeling studies useless for obtaining mechanistic information on the oxygen-transfer process that converts $1{\cdot}SO_2$ to **2**. Of the three adducts, the ν_{SO} bands (Table I) are highest for $1{\cdot}SO_2$, consistent with the lowest degree of electron transfer to SO_2 and weakest interaction. The adduct $Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$ also contains a very weakly bound SO_2 and its ν_{SO} frequencies are somewhat higher than those for $1{\cdot}SO_2$. 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_2 stability.

Reactions of $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (1) with SO_2 To Give $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ (2) and S_8. Isotopic labeling established that SO_2 is the sole oxygen source for formation of the μ-SSO_3 ligand in **2** according to eq 3, which, along with S_8 product formation, dictates that cleavage of SO_2 takes place on the Mo–S complexes. Oxygen transfer from one SO_2 to a second most likely occurs, giving SO_3 and SO, which in turn is unstable toward disproportionation to SO_2 and S_8. 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_2 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_2 group in $1{\cdot}SO_2$. One must also consider the possibilities that $1{\cdot}SO_2$ is not involved in the mechanism (i.e., the SO_3 moiety is fabricated at another site or even externally) or that *intramolecular* oxygen transfer from a second SO_2 coordinated to either the μ-S_2 or the other μ-S ligand takes place. Some evidence for involvement of the S_2 ligand is the finding that $Cp^*_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$, an analogue of $1{\cdot}SO_2$, does not react with SO_2 to give a thiosulfate. Aside from subtle electronic effects, the only major difference is the blocked reactivity of the μ-S_2CH_2 ligand site compared to the μ-S_2 in $1{\cdot}SO_2$. 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_2 was found to be directly dependent on the amine:SO_2 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 $[Et_3NH^+][HSO_3^-]$[25] can be isolated on SO_2 addition to Et_3N in "wet" solvents). However, Lewis base promotion is more straightforward, and amines are known to coordinate[26] to SO_2, 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_2, 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_2 adduct could be more activated toward oxygen transfer in this system than the bonds in free SO_2 or ligand-bound SO_2.

Formation of $Cp^*_2Mo_2(S_2)(S)(S_2O_3)$ (2) By Air Oxidation of $Cp^*_2Mo_2(S_2)(S)_2$ (1). As for its formation from SO_2, the formation of thiosulfate **2** on air oxidation of **1** (eq 4) is remarkable and could not have been predicted. Wachter and Pfauntsch[11] 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_2 to give Mo=O-containing complexes (the primary products). The terminal sulfur ligands were theorized to be oxidized first to SO_2 and then to SO_3 by an unknown pathway, ultimately adding to unreacted **1** to give **2**. In view of our finding that SO_2 *directly* reacts with **1** to form **2**, one could also argue that eq 3 is the final step in eq 4.[11c] 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_2 was found to be present during the course of eq 4. It is possible that a highly activated, "nascent" form of SO_2 is generated from sulfide oxidation and either rapidly disproportionates to SO_3 on the complex or is oxidized to SO_3[27] by O_2 as initially suggested.

Competitive reactions of **1** with mixtures of SO_2 and $^{18}O_2$ demonstrated that the SO_3 group in **2** is formed strictly from SO_2 oxygens and not O_2. Even though SO_2 may be an intermediate in eq 4, the *initial* presence of *excess* SO_2 shuts down O_2 reaction with **1**, possibly for either of two reasons. The binding of SO_2 to **1** to give **1**·SO_2 may prevent isomerization to **1′** or **1″** (proposed above to be the initial step), or else the coordination of strongly electrophilic SO_2 to **1** lessens the susceptibility of **1** to electrophilic attack by O_2.

Reactions of $Cp^*_2Mo_2(S_2)(S)(S_2O_3)$ with H_2 and Bases; Implications of Oxygen Transfer and Thiosulfate Intermediates in Reduction of SO_2. Although a variety of S-coordinated thiosulfate complexes have now been structurally characterized,[6b,28] none have been reported to possess the unique reactivity of **2**. Its facile reaction with H_2 to give 1 (eq 6) has led us to propose that ***2* may be an intermediate in the homogeneous catalytic hydrogenation** of SO_2 (*eq 1*). The following cycle can be envisioned for formation of the observed S_8 and H_2O products (*Mo = Cp*Mo):

$$*Mo_2(S_2)(S)_2 + 1.5SO_2 \rightarrow *Mo_2(S_2)(S)(S_2O_3) + 0.5S$$

$$*Mo_2(S_2)(S)(S_2O_3) + H_2 \rightarrow *Mo_2(S_2)(S)_2 + SO_2 + H_2O$$

$$0.5SO_2 + H_2 \rightarrow 0.5S + H_2O$$

This cycle based on SO_2 disproportionation to thiosulfate and sulfur may be occurring in addition to or even instead of that previously postulated[1] in which SO_2 was believed to be reduced by $[Cp^*Mo(S)(SH)]_2$ catalyst via eq 2 followed by regeneration of the SH complex via known reaction of H_2 with the Mo–S products of eq 2. Because **1** forms from reaction of the SH complex and SO_2, 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_2 hydrogenation as $[Cp^*Mo(S)(SH)]_2$.[29] However, it must be kept in mind that in the presence of H_2 *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,[30] there are no "dead-end" reactions involving the Mo species, and both $[Cp^*Mo(S)(SH)]_2$ 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[1] 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,[1] 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_3N (>300 turnovers/h).[29] 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-determing step in the catalysis.

Mechanisms of SO_2 reduction involving oxygen transfer to give S_2O_3 and S_8 have received little attention. Thiosulfate complexes have now been found to be produced on reduction of SO_2 with metal hydrides in several cases[2,6b,31] and may be key intermediates in SO_2 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_2O_3 ligand in **2** suggested proclivity toward cleavage. Wachter,[11] for example, found that **2** reacted

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

solvent system[a]	reacn time (% compln) eq 3	rate eq 1 (turnovers/h)[b]
$CHCl_3$	150 h (<5)	0.4
PhCl	96 h (22)	18
PhCl + amine[c]	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 + $(t\text{-Bu})_2$Mepy	11 min (100)	73

[a] R = Bu for eq 1 and Me for eq 3. [b] References 1 and 27. [c] Amine = Bu_3N for eq 1 and py for eq 3.

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(30) When oxygen was present in the catalytic reaction, oxo species (primarily green $Cp^*_2Mo_2OS_3$) were formed, which shut down the catalysis.

(31) $Li_2S_2O_3$ has been reported to be formed on reaction of SO_2 with LiH.

with $Cr(CO)_5(THF)$ with loss of the SO_3 unit to give a heterotrimetallic sulfido cluster. We in turn have found that the 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 SO_2 is brought to react with bases [B] to give S^0 and S^{VI} products:

$$1.5SO_2 + M\text{-}S\text{-}M \rightarrow 0.5S + M\text{-}SSO_3\text{-}M$$

$$M\text{-}SSO_3\text{-}M + [B] \rightarrow M\text{-}S\text{-}M + [B]\cdot SO_3$$

$$1.5SO_2 + [B] \rightarrow 0.5S + [B]\cdot SO_3$$

Assuming that [B] is an inexpensive organic compound (e.g., ROH), conversion of SO_2 to useful sulfonylated organics may be a feasible 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 SO_2 and related thiosulfate formation is a promising area for future development. The facile reactions of $Cp^*_2Mo_2(S_2)(S)(S_2O_3)$ demonstrate that the thiosulfate ligand possesses versatile reactivity and is not merely a terminal end product of partial 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 SO_2 and other noxious small molecules (e.g., NO_x[32]).

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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[29] show that $[Cp^*MoS(SH)]_2$ also catalyzes reduction of NO by H_2 to give N_2, N_2O, and H_2O, but at a much slower rate than for SO_2 reduction (amines did not appear to promote the reaction significantly). Equimolar NO-SO_2 mixtures were reduced to the latter products plus S_8 at a rate halfway between NO and 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 ($Mn(CO)_6^+$, $Re(CO)_6^+$, $Mn(CO)_5PPh_3^+$, $Mn(CO)_4(PPh_3)_2^+$, $Mn(CO)_5PEt_3^+$, $Mn(CO)_5PPh_2Me^+$, $Re(CO)_5PPh_3^+$, and $CpFe(CO)_3^+$) with metal carbonyl anions ($Co(CO)_3PPh_3^-$, $Co(CO)_4^-$, $Mn(CO)_5^-$, $Mn(CO)_4PPh_3^-$, $Mn(CO)_4PEt_3^-$, $Mn(CO)_4PPh_2Me^-$, $Mn(CO)_3(PPh_3)_2^-$, $CpFe(CO)_2^-$, $Re(CO)_5^-$, and $Re(CO)_4PPh_3^-$) 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 CO^{2+} transfer with the more nucleophilic of the two anions retaining the 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.[1,2] Through elegant studies, outer-sphere electron transfer,[1] inner-sphere electron transfer,[1] long-range electron transfer,[3] and single-electron-transfer reactions[2] 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 CO^{2+} group).[4] 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,[5] 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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