

# ACCOUNTS OF CHEMICAL RESEARCH®

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## Chemical Transformations and Disproportionation of Sulfur Dioxide on Transition Metal Complexes

GREGORY J. KUBAS

Los Alamos National Laboratory, Inorganic and Structural Chemistry Group (CST-3),  
MS-C346, Los Alamos, New Mexico 87545

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Aside from its renown as a source of acid precipitation, sulfur dioxide is remarkable in possessing physicochemical and coordination properties that are more diverse than those of any other small molecule. SO<sub>2</sub> is amphoteric, behaving as a Lewis acid or base, mild oxidant or reductant, or oxygen donor or acceptor. It is an excellent nonaqueous solvent<sup>1</sup> when liquefied at -10 °C and coordinates to many types of compounds, including metal complexes at both metal and ligand sites, strong Lewis acids, and virtually all nucleophiles, even halide ion (Figure 1). SO<sub>2</sub> can bind strongly to low-valent metals like CO or NO or completely reversibly like O<sub>2</sub> or H<sub>2</sub>. The diversity of metal-SO<sub>2</sub> bonding geometries is unmatched and has been reviewed by us and others.<sup>2</sup>

This Account will focus on the *reactivity* of SO<sub>2</sub>, e.g., S=O bond cleavage, some of which has been reviewed<sup>2</sup> but not in depth. We have been developing homogeneous catalytic processes for reducing SO<sub>2</sub> to sulfur to address the problem of SO<sub>2</sub> abatement. In our studies, SO<sub>2</sub> has revealed surprisingly facile oxygen transfer and disproportionation reactions that may be central to its chemistry and valuable for SO<sub>2</sub> conversion to useful/innocuous species. The richness of SO<sub>2</sub> chemistry has recently dramatically increased, and it appears that any transformation imaginable is possible. Although

Gregory Kubas was born in Cleveland, OH, in 1945. He obtained his B.S. in chemistry at Case-Western Reserve University and Ph.D. from Northwestern University under Duward Shriver. After postdoctoral positions at Princeton with Thomas Spiro and at Los Alamos, he joined the staff at Los Alamos National Laboratory in 1974. He was appointed a Laboratory Fellow in 1987 and was the recipient of the 1993 American Chemical Society Award in Inorganic Chemistry for his discovery of metal-dihydrogen coordination. His research includes binding and reactions of environmentally related and energy-related small molecules such as SO<sub>2</sub> and H<sub>2</sub> on metal complexes, particularly group 6 metals and sulfide clusters, as well as studies of metal σ-bond coordination.

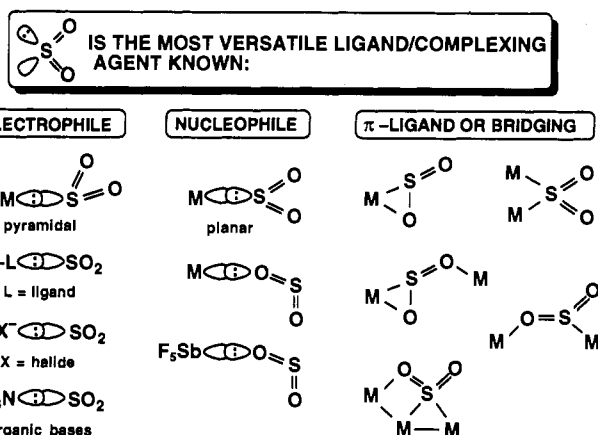
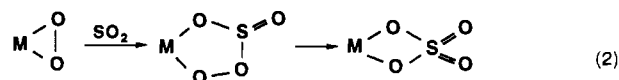
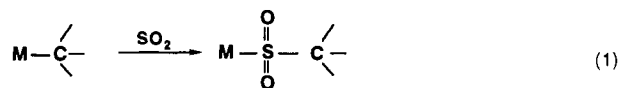


Figure 1. Coordination modes and geometries for SO<sub>2</sub>.

mechanistic studies of SO<sub>2</sub> reactions have been sparse, we have now begun to identify likely intermediates and pathways in SO<sub>2</sub> reduction and disproportionation.

### Insertion-Type Reactions of SO<sub>2</sub> and, Conversely, Attack at Bound SO<sub>2</sub>

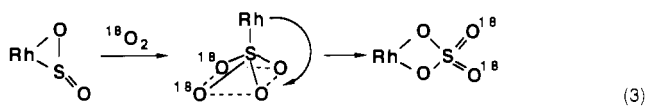
Historically, the first well-studied SO<sub>2</sub> reactions were insertion into M-C<sup>3</sup> and M-O:<sup>4,5</sup>



M-C insertion has been reviewed<sup>3</sup> and will not be

discussed further. The peroxysulfite intermediate in eq 2 was demonstrated by Collman<sup>4e</sup> by <sup>18</sup>O labeling and was supported theoretically.<sup>4h</sup> The sulfonate and bidentate<sup>4d</sup> ( $\eta^2$ ) sulfate groups generally could not easily be removed from the metal to regenerate starting complex, a common problem in designing catalytic conversions of SO<sub>2</sub> to, e.g., H<sub>2</sub>SO<sub>4</sub>. Little work has been done on reactions of sulfate complexes, but Atwood<sup>5a</sup> has recently found that  $\eta^2$ -SO<sub>4</sub> can be displaced from the coordination sphere of an iridium complex by CO. Also, novel reversible addition of SO<sub>2</sub> across *cis*-oxo bonds in L<sub>3</sub>Tc(=O)<sub>3</sub> to give L<sub>3</sub>Tc(=O)( $\eta^2$ -SO<sub>4</sub>) has now been observed.<sup>5b</sup> Insertions of SO<sub>2</sub> into the M-SO bond in Pd(PPh<sub>3</sub>)<sub>2</sub>(SO) to give S,O-bound *thiosulfate*<sup>6</sup> and into other metal-ligand bonds (M-OR, M-H) or internal ligand bonds<sup>7</sup> have been found, as discussed below.

The converse reaction of M-SO<sub>2</sub> with O<sub>2</sub> or SO<sub>6</sub> also forms  $\eta^2$ -SO<sub>4</sub> or -S<sub>2</sub>O<sub>3</sub> complexes.<sup>4a-d,8-10</sup> We identified at least two mechanisms by <sup>18</sup>O labeling: initial replacement of SO<sub>2</sub> in Pt(SO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> by O<sub>2</sub>,<sup>9</sup> followed by insertion as in eq 2, or attack of O<sub>2</sub> on sulfur in Rh(NO)( $\eta^2$ -SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> to form a Rh-SO<sub>4</sub> intermediate with square-pyramidal sulfur.<sup>10</sup>



Shift of Rh to the equivalent basal edges gave the expected 1:2:1 ratio of isotopomers. The former mechanism is generally more likely since usually complexes with labile M-SO<sub>2</sub> form sulfates<sup>2d</sup> and some sulfates are accessible from either M-O<sub>2</sub> or M-SO<sub>2</sub>.<sup>4a-d,9</sup>

Complexes with M=O bonds insert SO<sub>2</sub> to form

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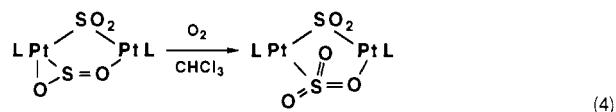
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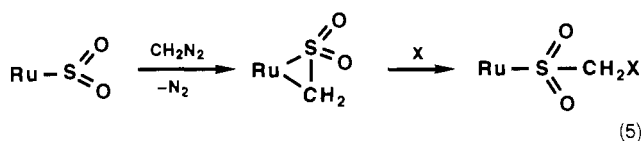
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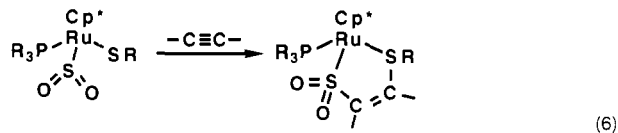
bidentate *sulfites*.<sup>11,12</sup> Reaction of (tmtaa)Ti( $\eta^2$ -SO<sub>2</sub>) (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldibenzo-[b,i][1,4,8,11]tetraazacyclotetradecine dianion) with NH<sub>4</sub>OH regenerated (tmtaa)Ti=O plus [NH<sub>4</sub>]<sub>2</sub>SO<sub>3</sub>, suggesting that M=O compounds could be useful as reusable SO<sub>2</sub> scavengers.<sup>11</sup> Farrar found a novel sulfite bridge formed from oxidation of  $\mu$ -SO<sub>2</sub>.<sup>13</sup>



Other examples of electrophilic and nucleophilic attack at metal-bound SO<sub>2</sub> are known.<sup>2c,14</sup> e.g., silylation at oxygen of Mo(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^1$ -SO<sub>2</sub>) to give S-bound O=S-O-SiMe<sub>3</sub> and alkylation at sulfur by LiR or ZnR<sub>2</sub> to give M-SO<sub>2</sub>R.<sup>14b</sup> CH<sub>2</sub>N<sub>2</sub> converts [CpRu(Ph<sub>2</sub>PCH<sub>2</sub>-PPh<sub>2</sub>)(SO<sub>2</sub>)]<sup>+</sup> to a  $\eta^2$ -sulfene reactive with X = Br<sup>-</sup>, CN<sup>-</sup>, PR<sub>3</sub>, or ROH.<sup>14c</sup>



Conversely, SO<sub>2</sub> had earlier been found to insert into M( $\mu$ -CH<sub>2</sub>)M and M=CH<sub>2</sub> to also form  $\eta^2$ -CH<sub>2</sub>SO<sub>2</sub>.<sup>15,16</sup> The versatility of SO<sub>2</sub> is further highlighted by a remarkable cycloaddition of activated acetylenes across S<sup>IV</sup> and S<sup>II</sup> centers:<sup>17</sup>



## SO<sub>2</sub> Reduction/Disproportionation by Transition Metal Hydride Complexes

About 20 years ago Taube<sup>18</sup> found the first example of reduction of metal-bound SO<sub>2</sub> by treating RuCl(NH<sub>3</sub>)<sub>4</sub>(SO<sub>2</sub>)<sup>2+</sup> with zinc in aqueous HCl to produce the S<sub>2</sub>-bridged dimer [RuCl(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>( $\mu$ -S<sub>2</sub>)<sup>4+</sup>. Meyer<sup>19</sup> recently showed stepwise 6e<sup>-</sup> electrochemical reduction of Ru(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)<sup>2+</sup> to Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>S)<sup>2+</sup> via the intermediacy of an S<sub>2</sub> dimer. Our initial efforts in SO<sub>2</sub> reactivity focused on its reduction by hydride complexes to devise new synthetic/catalytic methodologies and probe reduction mechanisms. Although H and SO<sub>2</sub> ligands can coexist,<sup>2b</sup> many hydrides should reduce SO<sub>2</sub>.

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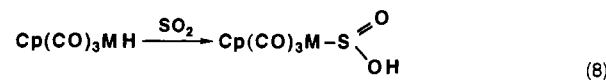
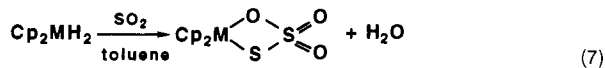
Table 1. IR and Structural Data for Metal-Coordinated Polyoxosulfido Ligands\*

complex	SO frequencies, cm <sup>-1</sup>	X-ray distances, Å <sup>b</sup>					ref
		M-S	M-O	S-S	S=O <sup>c</sup>	S-O <sup>d</sup>	
CpMo(CO) <sub>3</sub> (SO <sub>2</sub> H)	990, 762	2.521(2)			1.515(6)	1.637(6) <sup>e</sup>	23
CpW(CO) <sub>3</sub> (SO <sub>2</sub> H)	970, 760 (937, 732) <sup>f</sup>						23
Cp*Ru(CO) <sub>2</sub> (SO <sub>3</sub> H)	1180, 1080, 810	2.318(2)			1.459(3)	1.559(3) <sup>e</sup>	31
CpFe(CO) <sub>2</sub> (SO <sub>3</sub> H)	1184, 1084, 811						32a
[Ru(bpy) <sub>2</sub> (py)(SO <sub>3</sub> H)] <sup>+</sup>		2.286(2)			1.467(5)	1.586(5) <sup>e</sup>	33b
Ir(CO)(SO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (SO <sub>3</sub> H)	1213, <sup>g</sup> 1072, <sup>h</sup> 1053, <sup>g</sup> 918 <sup>h</sup>						25
Fe(TPP)(OSO <sub>3</sub> H)			1.919(4)		1.446(5)	1.492(4)	
						1.521(5) <sup>e</sup>	35
[CpMoO(S <sub>2</sub> )MoO(η <sup>2</sup> -SO <sub>3</sub> )] <sup>-</sup>	1166, 646, 571, 502		2.077(10) <sup>i</sup>		1.441(9)	1.586(9)	67
[CpMoO(S <sub>2</sub> )MoO(η <sup>2</sup> -SO <sub>4</sub> )] <sup>-</sup>	1307, 1172, 669, 612, 572, 540		2.077(10) <sup>i</sup>		1.43(1)	1.540(6)	67
[CpMoO(S <sub>2</sub> )MoO(η <sup>2</sup> -S <sub>2</sub> O <sub>3</sub> )] <sup>-</sup>	1277, 1172, 1150, 662, 542	2.302(6)	2.077(10) <sup>i</sup>	1.991(7)	1.429(10)	1.512(11)	67
Cp <sub>2</sub> Mo(η <sup>2</sup> -S <sub>2</sub> O <sub>3</sub> )	1247, 1137, 1128, 652, 545	2.450(2)	2.134(4)	2.051(2)	1.448(4)	1.536(4)	21
Ni(tu) <sub>4</sub> (η <sup>2</sup> -S <sub>2</sub> O <sub>3</sub> )·H <sub>2</sub> O	1152, 1090, 971, 665, 535	2.718(4)	2.107(9)	2.01(1)	1.45(1)	1.50(1)	22a,b
[Cp*Ru(CO) <sub>2</sub> ] <sub>2</sub> (μ-S <sub>2</sub> O <sub>3</sub> )	1228, 1190, 1045, 1020, 505	2.395(2)		2.135(3)	1.44(1)		31
Cp <sub>2</sub> Mo <sub>2</sub> (μ-S)(μ-S <sub>2</sub> )(μ-S <sub>2</sub> O <sub>3</sub> )	1242, 1205, 1010, 604	2.441(3)		2.166(4)	1.436(8)		62
Cp <sub>2</sub> Cr <sub>2</sub> (μ-S)(μ-S <sub>2</sub> )(μ-S <sub>2</sub> O <sub>3</sub> )	1228, 1204, 1012, 610	2.367(2)		2.152(2)	1.441(6)		65
[(S <sub>2</sub> )OMoS <sub>2</sub> MoO(η <sup>2</sup> -S <sub>3</sub> O <sub>2</sub> )] <sup>2-</sup> <sup>j</sup>	1255, 598, 557	2.417(5)		2.047(11)	1.401(15)		22e
[Cp*Mo(CO) <sub>3</sub> ] <sub>2</sub> (μ-S <sub>2</sub> O <sub>4</sub> )	1207, 1027	2.496(1)		2.266(1)	1.471(4)		23
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> (μ-S <sub>2</sub> O <sub>4</sub> )	1223, 1040						28a
[M(CO) <sub>3</sub> ] <sub>2</sub> (μ-S <sub>2</sub> O <sub>4</sub> ) (M = Mn, Re)	1224, 1037; <sup>k</sup> 1212, 1031 <sup>l</sup>						28a
CH <sub>2</sub> [CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (μ-S <sub>2</sub> O <sub>4</sub> )	1219, 1051						28c
Cp* <sub>2</sub> V(η <sup>2</sup> -[O,O]-S <sub>2</sub> O <sub>4</sub> )	1092, 942, 927		2.032(3) <sup>m</sup>	2.335(2)	1.472(4) <sup>m</sup>	1.534(3) <sup>m</sup>	29
Fe(dieneN <sub>4</sub> )(η <sup>2</sup> -[O,O]-S <sub>2</sub> O <sub>4</sub> ) <sup>j</sup>			2.173(9) <sup>m</sup>	2.222(7)	1.37(2) <sup>m</sup>	1.490(8) <sup>m</sup>	8g

\* Only representative examples of SO<sub>3</sub>, SO<sub>4</sub>, and SO<sub>3</sub>H ligands are listed. Abbreviations: Cp = C<sub>5</sub>H<sub>5</sub>; Cp\* = C<sub>5</sub>Me<sub>5</sub>; bpy = bipyridine; py = pyridine; TPP = tetraphenylporphyrinate; tu = thiourea; dieneN<sub>4</sub> = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. <sup>b</sup> Unless noted otherwise, average values are given for each bond type. <sup>c</sup> Terminal S=O. <sup>d</sup> S-O with oxygen bound to another atom. <sup>e</sup> S-OH distance. <sup>f</sup> <sup>18</sup>O isotopomer. <sup>g</sup> SO<sub>2</sub>. <sup>h</sup> SO<sub>3</sub>H. <sup>i</sup> In ref 67, an average M-O distance was given for all three Mo complexes listed here (range: 2.060(7)–2.090(4) Å). <sup>j</sup> η<sup>2</sup>-S<sub>3</sub>O<sub>2</sub> = S,S-bound dithiosulfate, η<sup>2</sup>-S<sub>2</sub>O<sub>5</sub> = O<sub>2</sub>SSO<sub>3</sub> bonded via one oxygen from each sulfur. <sup>k</sup> M = Mn. <sup>l</sup> M = Re. <sup>m</sup> Distances are symmetry-related.

However, we and others before were surprised to find that hydrides did not necessarily reduce SO<sub>2</sub> all the way to S<sup>0</sup> or S<sup>2-</sup> and sometimes gave S<sup>VI</sup> products indicative of sulfur oxidation. Several researchers<sup>2a,20</sup> reported perplexing SO<sub>2</sub> reactivity with RuH<sub>2</sub>(PR<sub>3</sub>)<sub>x</sub> (x = 3, 4) and related Ru species where sulfato complexes, e.g., Ru(SO<sub>4</sub>)(SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O),<sup>20c</sup> were identified to be among the products. At the time it was not clear whether traces of O<sub>2</sub> or H<sub>2</sub>O were involved, and SO<sub>2</sub> disproportionation was proposed.<sup>20c</sup> Our findings below support this idea, and what has evolved is exceptionally rich SO<sub>2</sub> reactivity involving both insertion and O transfer.

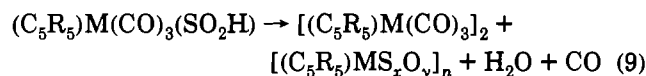
We chose group 6 metals as targets because of their low cost and use in hydrodesulfurization. Two important reactions occurred rapidly in good yield (M = Mo, W):



Equation 7 gave quantitative partial reduction to η<sup>2</sup>-thiosulfate rather than S<sub>8</sub> or sulfide, even with excess hydride.<sup>21</sup> As will be further shown, M-S<sub>2</sub>O<sub>3</sub><sup>22</sup> or similar M-S<sub>x</sub>O<sub>y</sub> species often form and seem to be thermody-

amic sinks (Table 1). Like ionic thiosulfates, Cp<sub>2</sub>M-(S<sub>2</sub>O<sub>3</sub>) reacted with strong acids, e.g., HBr, to give SO<sub>2</sub>, H<sub>2</sub>O, and Cp<sub>2</sub>M(S)(Br)<sub>2</sub>.<sup>21</sup> Equation 8 (in toluene or Et<sub>2</sub>O) demonstrated that SO<sub>2</sub> inserts into M-H bonds as in M-C bonds, except that the hydride attaches to oxygen rather than sulfur as in eq 1 to form the novel SO<sub>2</sub>H ligand.<sup>23</sup> This was proven crystallographically (Table 1) and spectroscopically (ν(OH) = 2552 cm<sup>-1</sup> in CpW(CO)<sub>3</sub>(SO<sub>2</sub>H)). Equation 8 is also unlike CO<sub>2</sub> insertion into M-H bonds, which gives η<sup>2</sup>-O-bound HCO<sub>2</sub>.<sup>24</sup> The solid SO<sub>2</sub>H complexes are remarkable in that they completely dissociate back to CpM(CO)<sub>3</sub>H and SO<sub>2</sub> upon redissolving in the solvents from which they were crystallized. A broad <sup>1</sup>H NMR signal (δ 3.89) for the SO<sub>2</sub>H in Cp\*Mo(CO)<sub>3</sub>(SO<sub>2</sub>H) was observable only at -40 °C in liquid SO<sub>2</sub>. The ephemeral nature of SO<sub>2</sub>H is reiterated by the only recent substantiation<sup>25</sup> of the tautomeric equilibrium IrH(SO<sub>2</sub>)(CO)(PR<sub>3</sub>)<sub>2</sub> ↔ Ir(SO<sub>2</sub>H)(CO)(PR<sub>3</sub>)<sub>2</sub> proposed<sup>8b</sup> 22 years ago.

Like RSO<sub>2</sub>H, M-SO<sub>2</sub>H complexes are thermally unstable toward auto-redox, even in the solid state where (C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>3</sub>(SO<sub>2</sub>H) gave a mixture of polynuclear sulfido and oxo-sulfido species in a day at 25 °C (M = Mo; R = H) or on mild heating (M = W).



It is thus possible that SO<sub>2</sub> inserts into the M-H bonds of Cp<sub>2</sub>MH<sub>2</sub> as the first step in eq 7, followed by elimination of H<sub>2</sub>O to give S<sub>2</sub>O<sub>3</sub>. In eq 9, however, a

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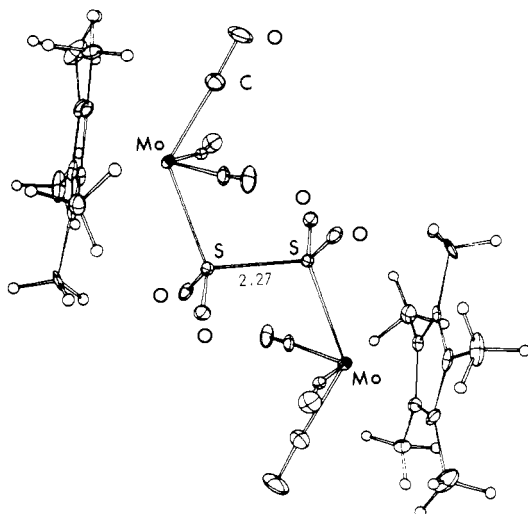
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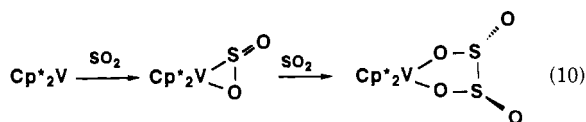
(22) Other examples of M-S<sub>2</sub>O<sub>3</sub>: (a) Gasparri, G. F.; Mangia, A.; Musatti, A.; Nardelli, M. *Acta Crystallogr. B* 1969, B25, 203. (b) Newman, G. A. *J. Mol. Struct.* 1970, 5, 61. (c) Gabelica, Z. *J. Mol. Struct.* 1980, 60, 131. (d) Freedman, A. N.; Straughan, B. P. *Spectrochim. Acta* 1971, 27A, 1455. M-dithiosulfate: (e) Muller, A.; Reinsch-Vogell, U.; Krickmeyer, E.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 796.



**Figure 2.** Structure of  $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2(\mu\text{-S}_2\text{O}_4)$ . Reprinted with permission from ref 23. Copyright 1985 American Chemical Society.

thiosulfate was not formed despite large variation in product composition depending on M and R.  $[(\text{C}_5\text{R}_5)\text{MO}(\mu\text{-S})]_2$  always formed, showing that total reduction of  $\text{S}^{\text{IV}}$  to  $\text{S}^{\text{II}}$  can occur even in the solid. Prolonged solution reactions of the W hydrides with  $\text{SO}_2$  in 4:1 ratio gave CO-containing sulfides such as  $[\text{Cp}^*\text{W}(\text{CO})_2(\mu\text{-S}\cdot\text{SO}_2)]_2$ ,<sup>23</sup> further illustrating the diversity of pathways. Tight binding of  $\text{SO}_2$  to  $\mu\text{-S}$  apparently stabilized the latter since attempts to remove  $\text{SO}_2$  thermally gave decomposition. Ligand- $\text{SO}_2$  binding is normally reversible, e.g., in  $\text{L}_n\text{Cu}^{\text{I}}(\text{SR}\cdot\text{SO}_2)$ , which can form a basis for  $\text{SO}_2$  sensors.<sup>27</sup>

At  $-20^\circ\text{C}$  in  $\text{SO}_2$ -saturated  $\text{CH}_3\text{CN}$ ,  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$  unexpectedly gave instead of the  $\text{SO}_2\text{H}$  complex a 31% yield of a dithionite-bridged complex (protons eliminated as water).  $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2(\text{S}_2\text{O}_4)$  (Figure 2) is the first example of S-bound  $\text{S}_2\text{O}_4^{2-}$  and a rare case of  $\text{C}_{2h}\text{S}_2\text{O}_4$ .<sup>23</sup> The S-S distance (2.266 Å) is shorter than in  $\text{Na}_2\text{S}_2\text{O}_4$  and other  $\text{C}_{2v}\text{S}_2\text{O}_4^{2-}$  ions (2.35–2.39 Å).<sup>28</sup> The dithionite is solution unstable, giving the same oxo-sulfido clusters as from  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}\text{-SO}_2$  reaction. Reaction of  $\text{SO}_2$  with  $\text{Na}[\text{Cp}^*\text{M}(\text{CO})_3]_2$  also gave the dithionite in 31% yield (plus  $\text{Na}_2\text{S}_2\text{O}_4$ ), analogous to an iron system<sup>28a,b</sup> for which a mechanism involving coupling of  $\text{M}(\text{SO}_2)^{\cdot}$  radicals was proposed. We subsequently found that O-bonded dithionite can be produced by coupling of two  $\text{SO}_2$  at a vanadium center:



$\text{Cp}^*_2\text{V}(\eta^2\text{-SO}_2)$  had the lowest  $\nu_{\text{SO}}$  bands ever observed for  $\eta^2\text{-SO}_2$  (1076, 819  $\text{cm}^{-1}$ ), indicating activation of  $\text{SO}_2$  via metal-ligand back-bonding, and indeed reacted

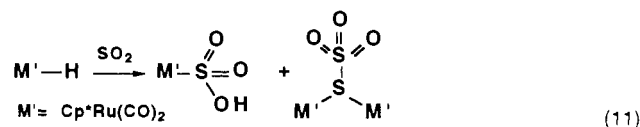
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(27) (a) Eller, P. G.; Kubas, G. J. U.S. Patent 4,152,118 (May 1, 1979). (b) Cook, R. L.; MacDuff, R. C.; Sammells, A. F. *Anal. Chim. Acta* 1989, 217, 101; 226, 153.

(28) See ref 23. Non structurally characterized metal-dithionites: (a) Poffenberger, C. A.; Tennent, N. H.; Wojcicki, A. J. *Organomet. Chem.* 1980, 191, 107. (b) Reich-Rohrwig, P.; Clark, A. C.; Downs, R. L.; Wojcicki, A. *Ibid.* 1978, 145, 57. (c) Bitterwolf, T. E. *Ibid.* 1987, 320, 121.

further with  $\text{SO}_2$  to yield the less soluble  $\text{S}_2\text{O}_4$  complex.<sup>29</sup> The staggered coordination mode of the dithionite is unprecedented, and whether it is a kinetic product formed in the coupling of  $\text{SO}_2$  ligands or the preferred coordination mode for dithionite is unknown. A similarly bonded disulfite ligand,  $\text{O}_2\text{S}\text{-SO}_3^{2-}$ , was prepared from an Fe macrocycle and  $\text{HSO}_3^-$ , possibly via  $2\text{HSO}_3^- \leftrightarrow \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$ .<sup>8g</sup> To complete the series of  $\text{S}_2\text{O}_x^{2-}$  formations, a redox/disproportionation reaction of  $\text{SO}_2$  with  $\text{Cr}(\text{C}_6\text{H}_6)_2$  gave  $[(\text{C}_6\text{H}_6)_2\text{Cr}]_2[\text{S}_2\text{O}_6\cdot 2\text{SO}_2]$  containing  $\text{SO}_2$ -solvated dithionate anion.<sup>30</sup>

A ruthenium analogue of the above hydrides,  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{H}$ , gave yet different reactivity with  $\text{SO}_2$ , yielding two soluble, crystallographically-characterized complexes,  $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{SO}_3\text{H})$  (25%) and dinuclear  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2(\mu\text{-S}_2\text{O}_3)$  (37%), plus unidentified species, in a variety of solvents.<sup>31</sup> In this case,  $\text{SO}_3\text{H}$  and



bridging thiosulfate ligands are created by oxygen transfer. The source of the third oxygen in these ligands was confirmed to be  $\text{SO}_2$  by  $\text{S}^{18}\text{O}_2$  labeling and IR (Table 1). As for the Mo/W systems, varying the  $\text{SO}_2$ :hydride ratio of eq 11 did not change product ratios, indicating thermodynamic control. A mechanism is difficult to propose, but it is noteworthy that polar solvents and bases such as  $\text{NET}_3$  accelerated the reaction, a common feature of  $\text{SO}_2$  disproportionations discussed later.

$\text{SO}_3\text{R}$  ligands<sup>32</sup> are commonly formed by  $\text{SO}_2$  insertion into  $\text{M-OR}^{32c}$  or  $\text{RO}^-$  attack on  $\text{M-SO}_2$ .<sup>14a</sup> Usually they are S-bound,<sup>32b</sup> but an O-bound form has recently been shown in  $\text{Ir}(\text{CO})[\text{OSO}_2\text{Me}](\text{SO}_2)(\text{PPh}_3)_2$ .<sup>25</sup>  $\text{SO}_3\text{H}$  ligands<sup>25,32c,33</sup> are rare (Table 1) and prior to our work had not been made directly from  $\text{SO}_2$  ( $\text{CpFe}(\text{CO})_2\text{-}(\text{SO}_3\text{H})$  was synthesized by hydrolysis of the  $\text{SO}_3\text{R}$  species<sup>32a</sup>). X-ray<sup>28a,31</sup> and IR<sup>31</sup> studies showed attachment of the proton to oxygen ( $\nu(\text{OH})/\nu(^{18}\text{OH}) = 2460/2450$ ) in  $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{SO}_3\text{H})$ , which can readily be deprotonated by  $\text{Et}_3\text{N}$ . Theoretical work showed that the bisulfite isomers  $\text{HSO}_3^-$  and  $\text{SO}_3\text{H}^-$  are comparable in energy, with the latter containing a long S-OH bond (1.716 Å) suggesting assembly from weakly interacting  $\text{SO}_2$  and  $\text{OH}^-$ .<sup>34</sup> Insertion of  $\text{SO}_2$  into  $\text{M-OH}$  to form  $\text{M-SO}_3\text{H}$  has indeed been found for  $\text{Rh}^{32c}$  and  $\text{Ir}$ .<sup>25</sup> The experimental S-OH distance in  $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{SO}_3\text{H})$ , 1.559 Å, is much shorter than the theoretical, indicating that metal binding may stabilize  $\text{SO}_3\text{H}$ . To complete the  $\text{SO}_x\text{H}$  series, O-bonded *bisulfate* is formed in Fe-

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(30) Elschenbroich, C.; Gondrum, R.; Massa, W. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 967.

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(32) Examples: (a) Poffenberger, C. A.; Wojcicki, A. *Inorg. Chem.* 1980, 19, 3795. (b) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* 1977, 16, 2377. (c) Green, L. M.; Meek, D. W. *Organometallics* 1989, 8, 659.

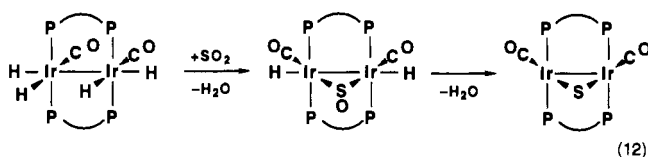
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(34) Stromberg, A.; Gropen, O.; Wahlgren, U.; Lindqvist, O. *Inorg. Chem.* 1983, 22, 1129.

(TPP)(OSO<sub>3</sub>H) from Fe(TPP) and SO<sub>2</sub> (TPP = tetraphenylporphyrinate), where trace O<sub>2</sub> is the oxidant.<sup>35</sup>

M-SO<sub>2</sub>H may often be unobserved intermediates in SO<sub>2</sub> reduction. Prior to our work, reaction of Cp<sub>2</sub>Fe with CF<sub>3</sub>SO<sub>3</sub>H in liquid SO<sub>2</sub> to give Cp<sub>2</sub>Fe<sup>+</sup>, H<sub>2</sub>O, and S<sub>8</sub> had been proposed to occur via insertion of SO<sub>2</sub> into Cp<sub>2</sub>Fe-H<sup>+</sup> followed by loss of unstable "HSO<sub>2</sub> radical".<sup>36</sup> A well-studied hydride which we also believe activates SO<sub>2</sub> by insertion is Os<sub>3</sub>(CO)<sub>10</sub>(μ-H)<sub>2</sub>. The latter forms an SO<sub>2</sub>-bridged complex, Os<sub>3</sub>(CO)<sub>10</sub>(μ-H)<sub>2</sub>(μ-SO<sub>2</sub>), as the first observable product, which gradually converts in solution to an unisolated species believed to be Os<sub>3</sub>(CO)<sub>10</sub>(μ-H)(SO<sub>2</sub>H) based on NMR and isolation of the salt [Bz<sub>3</sub>NH][Os<sub>3</sub>(CO)<sub>10</sub>(μ-H)(μ-SO<sub>2</sub>)] on addition of Bz<sub>3</sub>N.<sup>37</sup> Reduction of SO<sub>2</sub> to H<sub>2</sub>O and unidentified Os-SO species then occurs after several days in liquid SO<sub>2</sub>.

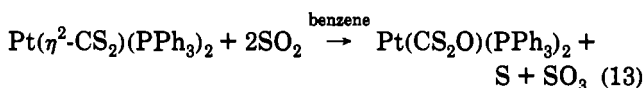
An iridium polyhydride reduces SO<sub>2</sub> stepwise, initially to an unstable μ-SO complex and then to μ-S, which can later be protonated off as H<sub>2</sub>S:<sup>38</sup>



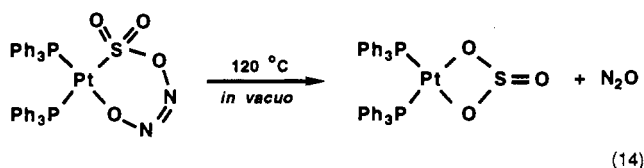
This is a rare example of complete reduction of SO<sub>2</sub> to sulfide and H<sub>2</sub>O by hydrides.

### Oxygen-Transfer Reactions of SO<sub>2</sub> on Metal Centers

Prior to our work, oxygen transfer to or from SO<sub>2</sub> had been rarely observed under mild conditions. Bennett found that reaction of SO<sub>2</sub> and (Me<sub>3</sub>Si)<sub>2</sub>NH gave (Me<sub>3</sub>Si)<sub>2</sub>O, Me<sub>3</sub>SiNSO, and NH<sub>4</sub>[Me<sub>3</sub>SiOSO<sub>2</sub>],<sup>39</sup> while Mingos demonstrated that SO<sub>2</sub> is able to function as both an oxygen donor and receptor on metal complexes:<sup>8c,40</sup>

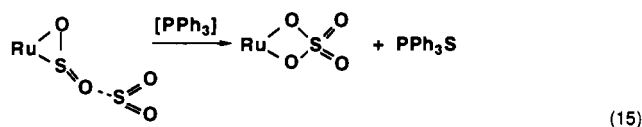


SO<sub>2</sub> addition to Pt(N<sub>2</sub>O<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> gave a product proposed on the basis of IR <sup>15</sup>N-labeling studies to have the cyclic insertion-type structure shown below, which decomposed on heating to a sulfite complex.<sup>8c</sup>



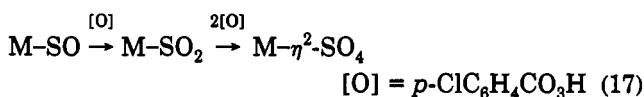
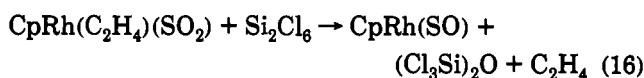
At about the same time, we noted that Ru(CO)<sub>2</sub>(η<sup>2</sup>-SO<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>, PPh<sub>3</sub>S, and unidentified Ru species slowly formed from Ru(CO)<sub>2</sub>(η<sup>2</sup>-SO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> in toluene con-

taining excess SO<sub>2</sub> even with careful exclusion of O<sub>2</sub>.<sup>41</sup> The structure at -60 °C revealed a second SO<sub>2</sub> weakly bonded to the terminal O of SO<sub>2</sub>.



This suggested that *self-association of SO<sub>2</sub> molecules* was the first step in an O-transfer process to give SO<sub>4</sub> plus sulfur, scavenged by PPh<sub>3</sub> (free or coordinated), an important theme echoed by our later work on SO<sub>2</sub> disproportionation on sulfide complexes.

Several single oxygen-atom transfer reactions are known,<sup>42</sup> e.g., removal of oxygen from bound SO<sub>2</sub> to give bound SO<sup>42a</sup> and vice-versa (M = Fe, Ru, Rh, Ir):<sup>42b-d</sup>



RuCl(NO)(PPh<sub>3</sub>)(SO) in eq 17 converted all the way to sulfate.<sup>42d</sup> On M = [CpRu(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, SO disproportionated to give MSO<sub>2</sub> and MSSM.<sup>42c</sup> Many more examples of O transfer and disproportionation-type reactions are emerging, and in a sense all SO<sub>2</sub> bond-breaking reactions can be considered O transfer.

### Activation of SO<sub>2</sub> on Metal Clusters To Give Sulfido and Oxo Ligands

Although reactions of SO<sub>2</sub> on metal clusters would be a good model for SO<sub>2</sub> reactions on surfaces,<sup>43</sup> little such work has been done.<sup>44</sup> While investigating potential catalysts for SO<sub>2</sub> reduction, we found that Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> catalyzed SO<sub>2</sub>/H<sub>2</sub> reaction (10–100 atm of H<sub>2</sub>, 100 °C, toluene) to give primarily S<sub>8</sub> and H<sub>2</sub>O. Under 1 atm, reduction was not observed, and the same Mo-containing products resulted with or without H<sub>2</sub>. Analysis of the products indicated that CO from Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> reduced SO<sub>2</sub> to give CO<sub>2</sub> and sulfido complexes. One early product that disappeared on longer reaction was characterized to be the first homonuclear butterfly cluster of a group 6 metal (Figure 3).<sup>45</sup> The complex contained the elements of reduced SO<sub>2</sub>, and an overall reaction can be written:

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(43) Oxidation to sulfate has been studied: (a) Outka, D. A.; Madix, R. J.; Fisher, G. B.; DiMaggio, C. *J. Phys. Chem.* 1986, 90, 4051. (b) Burke, M. L.; Madix, R. J. *Ibid.* 1988, 92, 1974.

(44) Pd and Pt clusters with a variety of SO<sub>2</sub> geometries have been characterized by Mingos but have shown little reactivity: Burrows, A. D.; Mingos, D. M. P.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* 1992, 261 and references therein. Mingos, D. M. P.; Oster, P.; Sherman, D. J. *J. Organomet. Chem.* 1987, 320, 257.

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(36) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* 1972, 40, C29.

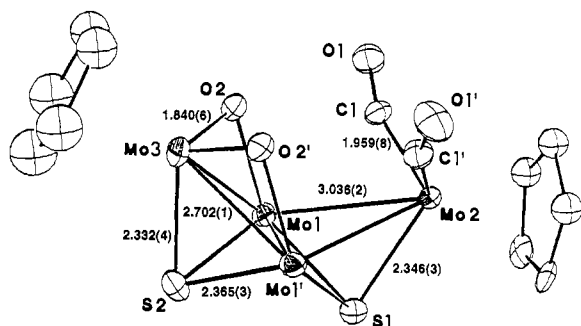
(37) (a) Jarvinen, G. D.; Ryan, R. R. *Organometallics* 1984, 3, 1434.

(b) Jarvinen, G. D.; Larson, E. M.; Wasserman, H. J.; Burns, C. J.; Ryan, R. R. *Acta Crystallogr.* 1988, C44, 1701. (c) Jarvinen, G. D.; Kubas, G. J. Unpublished results.

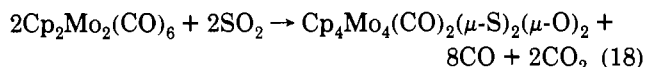
(38) Neher, A.; Lorenz, I.-P. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1342.

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**Figure 3.** Structure of  $\text{Cp}_4\text{Mo}_4(\text{CO})_2(\mu\text{-S})_2(\mu\text{-O})_2$  (Cp rings on Mo1 and Mo1' omitted). Distances not shown: Mo1–Mo1' = 2.845(2) Å; Mo1–O2 = 2.051(5) Å; Mo1–S1 = 2.364(2) Å; Mo1–C1 = 2.718(8) Å; dihedral angle between wings: 123°.



The average Mo oxidation state changed from +1 to +3 (and sulfur from +4 to –2), but examination of the Mo environments individually led to assignments of +3 for Mo1 and Mo1', +2 for Mo2, and +4 Mo3. The presence of three different metal oxidation states is rare in homonuclear clusters. More importantly, the structure provides a model for some of the intermediates that have been proposed for metal-catalyzed reduction of  $\text{SO}_2$  with CO.  $\text{SO}_2$  can be envisioned to coordinate to a metal surface or unsaturated cluster and dissociate into sulfido and oxo ligands (terminal or bridging). The oxo species could then react with nearby M–CO to give  $\text{CO}_2$ . In the Mo cluster, each oxo is 2.58 Å away from the carbon atom of a semibridging CO. This distance is less than the sum of the van der Waals radii (~3.0 Å), suggesting a weak interaction between the CO and oxo ligands.

Recently Shriver<sup>46</sup> found that cluster-bound  $\text{SO}_2$  is reduced by  $\text{NaPh}_2\text{CO}$  to sulfido or SO ligands in  $[\text{HFe}_3(\text{CO})_9(\text{SO}_2)]^-$ , where prior acetylation is necessary for reductive cleavage of both oxygens from  $\text{SO}_2$  (Figure 4). Both cluster-bound SO and formation of a stable SO complex by oxygen removal from bound  $\text{SO}_2$  are rare.<sup>38</sup> Reaction with AcCl initially formed unstable  $[\text{HFe}_3(\text{CO})_9(\text{SO}_2\text{Ac})]$ , which then was reduced via a complex, multistep mechanism not involving  $[\text{HFe}_3(\text{CO})_9\text{S}]^-$  or  $[\text{Fe}_3(\text{CO})_9\text{SO}]^{2-}$  as intermediates.

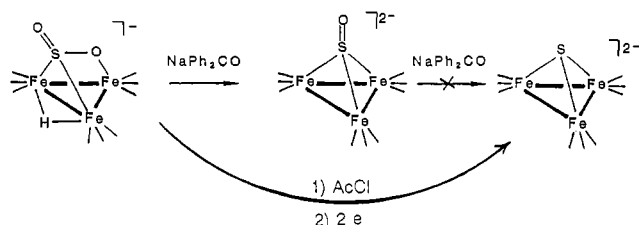
Other examples reiterating the usefulness of  $\text{SO}_2$  as a S/O-ligand source include Taube's Ru– $\text{S}_2$ –Ru dimer<sup>18</sup> and  $[\text{Rh}_{17}(\text{S})_2(\text{CO})_{32}]^{3-}$  from reduction of  $\text{Rh}(\text{CO})_2(\text{acac})$  and  $\text{SO}_2$  with  $\text{H}_2/\text{CO}$  (300 atm, 160 °C).<sup>47</sup> Reactions of  $\text{SO}_2$  with the dithiocarbamate  $\text{W}(\text{CO})_3(\text{LL})_2$  (LL =  $\text{S}_2\text{-CNR}_2$ ) formed a mixture of  $\text{WO}(\text{S}_2)(\text{LL})_2$ ,  $\text{WS}(\text{S}_2)(\text{LL})_2$ , and  $\text{W}_2\text{O}_2\text{S}_2(\text{LL})_2$ , and with  $\text{MoCl}(\text{LL})_3$  reduced with Zn/Hg gave  $\text{Mo}(\text{SOCl}_2)(\text{LL})_3$ , claimed to be the first  $\text{SOCl}_2$  complex.<sup>48</sup> Noncluster building examples include Lorenz's reaction of  $\text{SO}_2$  with *trans*- $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$  to give *trans*- $\text{Mo}(=\text{S})(=\text{O})(\text{dppe})_2$  containing lattice  $\text{H}_2\text{-SO}_4$  (dppe =  $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ ).<sup>49</sup> It was speculated that

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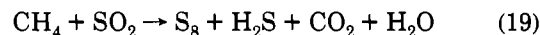


**Figure 4.** Structure and reactions of  $[\text{HFe}_3(\text{CO})_9(\text{SO}_2)]^-$  (three CO ligands on each iron; Ac = acetyl).

$\text{SO}_2$  disproportionated to  $\text{SO}_3$  (the source of  $\text{H}_2\text{SO}_4$ ) and SO, which oxidatively added to a  $14e^-$   $\text{Mo}(\text{dppe})_2$  fragment. However, the mechanism and origin of  $\text{H}_2\text{-SO}_4$  were not well defined. A related system is  $\text{MoH}_4(\text{dppe})_2$  protonated with  $\text{HBF}_4$  in THF that reacted with  $\text{SO}_2$  to form *trans*- $[\text{MoF}(\text{O})(\text{dppe})_2]^+$  and *trans*- $[\text{MoF}(\text{S})(\text{dppe})_2]^+$ .<sup>50</sup> These are rare examples of total cleavage of  $\text{SO}_2$  to separate O/S ligands. We recently found novel removal of the oxygens of  $\text{SO}_2$  at 25 °C by  $\text{U}(\text{OR})_3$  to give  $(\text{OR})_3\text{U-S-U}(\text{OR})_3$  as the major uranium product.<sup>51a</sup> The fate of the oxygens is as yet unknown. Conversely,  $\text{W}(\text{CO})(\text{phenanthroline})(\text{SPh})_2(\eta^2\text{-SO}_2)$  spontaneously converts in solution to *cis*- $\text{W}(=\text{O})_2(\text{phenanthroline})(\text{SPh})_2$  and  $\text{S}_8$ .<sup>51b</sup>

### Catalytic Reduction and Disproportionation-Type Reactions of $\text{SO}_2$

Aside from commonly used limestone scrubbing,  $\text{SO}_2$  abatement schemes can involve either oxidation to  $\text{H}_2\text{-SO}_4$  or reduction to sulfur, which is of greater research interest because methodology is less established and  $\text{S}_8$  is often a more desirable product.<sup>52</sup> Numerous papers and patents have appeared on this subject, and a variety of reducing agents have been used including  $\text{H}_2$ ,  $\text{CH}_4$ , and CO. An early concept for  $\text{SO}_2$  removal from combustion gases was to reduce it with CO already present, but formation of toxic COS was a problem.<sup>53</sup> However, natural gas is currently employed to reduce  $\text{SO}_2$  scrubbed from the flue gas of certain coal-fired utilities:



Vanadium–alumina<sup>54</sup> or metal sulfide<sup>52</sup> catalysts at 620–720 K can be used to produce sulfur and/or  $\text{H}_2\text{S}$ , which is then reacted with further  $\text{SO}_2$  to give  $\text{S}_8$  as the final product.

We chose to study  $\text{SO}_2$  reduction by  $\text{H}_2$ , initially using very active heterogeneous catalysts such as 0.5% Ru/alumina under mild conditions (150–300 °C) to minimize formation of byproducts such as  $\text{H}_2\text{S}$ .<sup>55</sup> Typical experiments involved flask-heating of catalyst pellets and  $\text{SO}_2/\text{H}_2$  in 1:2 ratio at ~1 atm. The only products obtained were  $\text{S}_8$  and  $\text{H}_2\text{O}$ . Turnovers/h ranged up to 65 at 300 °C with no catalyst poisoning. Mixtures of

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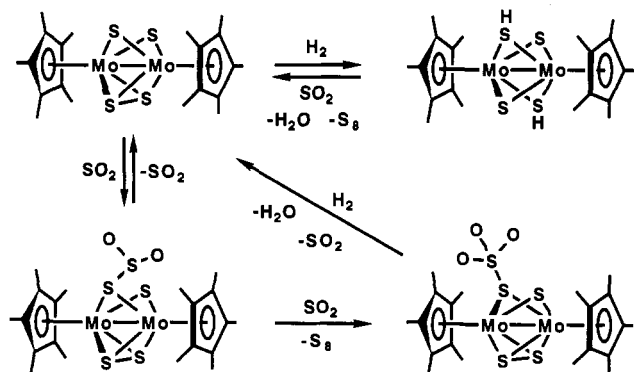
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**Figure 5.** Reactions relating to catalytic SO<sub>2</sub> hydrogenation and disproportionation on Mo-S complexes. The S<sub>8</sub> produced from SO<sub>2</sub> reduction in the top reaction becomes incorporated into the clusters to form [Cp\*MoS<sub>3</sub>]<sub>n</sub> (ref 58).

SO<sub>2</sub> and NO were simultaneously reduced to N<sub>2</sub>, S<sub>8</sub>, H<sub>2</sub>O, and a trace of N<sub>2</sub>O.

The next goal was to establish *homogeneous* catalytic reduction. As mentioned above, Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> catalyzed hydrogenation but decomposed. Clearly the major obstacle is sulfur poisoning, so we looked into sulfido complexes as catalysts. [CpMoS(SH)]<sub>2</sub> (Figure 5, top right) stood out because it catalyzed S<sub>8</sub> and H<sub>2</sub> to H<sub>2</sub>S and contained reducing SH ligands uniquely regenerable from H<sub>2</sub>.<sup>56</sup> Hydrogenation of SO<sub>2</sub> to S<sub>8</sub> and H<sub>2</sub>O was found to occur cleanly at 25 °C in a closed flask containing a solution of [CpMoS(SH)]<sub>2</sub>.<sup>57</sup> Optimization of conditions, including use of more soluble Cp\* analogues in 1:1 PhCl-BuOH solvent with 0.1% Bu<sub>3</sub>N promoter and ~3 atm of H<sub>2</sub> gave 350 turnovers/h at 75 °C. A 10-fold rate increase in the presence of weak bases such as alcohols and amines was a critical clue in postulating a mechanism for the catalysis, which initially was believed to include the top reactions in Figure 5, plus reduction of SO<sub>2</sub> by H<sub>2</sub>S formed from H<sub>2</sub> reaction with [Cp\*MoS<sub>3</sub>]<sub>n</sub><sup>58</sup> and/or S<sub>8</sub> product. It is important that the system be totally regenerable, i.e., that there be no dead-end species. Indeed Cp\*<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub><sup>59</sup> formed from SO<sub>2</sub>-[Cp\*MoS(SH)]<sub>2</sub> reaction (Figure 5, top) was an equally good catalyst.

Further research led to fascinating new chemistry where SO<sub>2</sub> was found to disproportionate on the clusters to S<sub>8</sub> and SO<sub>3</sub>, forming the basis for new catalytic pathways. We found that reaction of SO<sub>2</sub> with Cp\*<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub> initially yielded an adduct containing SO<sub>2</sub> weakly bound to μ-S (Figure 5, S-SO<sub>2</sub> = 2.60 Å).<sup>60</sup> Reversible Lewis acid binding of SO<sub>2</sub> to sulfur ligands is common,<sup>61</sup> but in this case further reaction with SO<sub>2</sub> unexpectedly occurred in solution to quantitatively give sulfur and Cp\*<sub>2</sub>Mo<sub>2</sub>(μ-S)(μ-S<sub>2</sub>)(μ-SSO<sub>3</sub>) containing an SO<sub>3</sub> fragment bound to the μ-S (Figure 5). <sup>18</sup>O labeling

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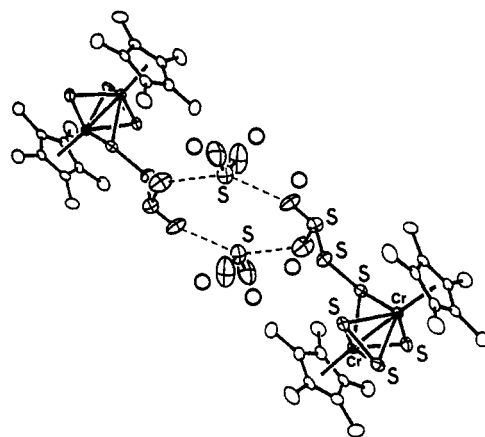
(57) Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6138.

(58) An insoluble species that incorporates the S<sub>8</sub> produced from SO<sub>2</sub> reduction by [CpMoS(SH)]<sub>2</sub> and reacts with H<sub>2</sub> to re-form [CpMoS(SH)]<sub>2</sub>: (a) Schunn, R. A.; Fritchie, C. J., Jr.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892. (b) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Ibid.* **1981**, *20*, 3064.

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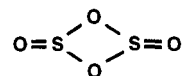
(61) See refs 23, 27, 68, and 69. A cooperative bonding effect between metal-bonded and S-bonded SO<sub>2</sub> has been proposed: Shaver, A.; Plouffe, P.-Y. *Inorg. Chem.* **1992**, *31*, 1823.



**Figure 6.** Structure of 2Cp\*<sub>2</sub>Cr<sub>2</sub>(μ-S)(μ-η<sup>2</sup>-S<sub>2</sub>)(μ-η<sup>1</sup>-SS-SO<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>, showing cyclic aggregation of SO<sub>2</sub>. Reprinted with permission from ref 63. Copyright 1992 American Chemical Society.

established that the SO<sub>3</sub> is formed from SO<sub>2</sub> by oxygen transfer. The SSO<sub>3</sub> can be regarded as a reactive thiosulfate ligand (S-S = 2.17 Å) and is readily hydrogenated at 25–75 °C to regenerate Cp\*<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub> (Figure 5). The relationship to the catalytic hydrogenation of SO<sub>2</sub> became apparent: rates of the disproportionation and catalytic reactions were similar, and both processes were promoted by Lewis bases nearly identically. A new mechanism for catalysis based on Figure 5 was proposed, where the rate-determining step is SO<sub>2</sub> disproportionation to sulfur and S-bound SO<sub>3</sub>.<sup>60</sup>

We then found that Cp\*<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub>, with both η<sup>1</sup>-S<sub>2</sub> and η<sup>2</sup>-S<sub>2</sub> ligands,<sup>62</sup> is more active than the Mo sulfides in cleaving SO<sub>2</sub>.<sup>63</sup> It initially bonded SO<sub>2</sub> at the η<sup>1</sup>-S<sub>2</sub>, and crystallography revealed a crucial finding: the oxygens of each bound SO<sub>2</sub> interacted further with the sulfurs of two *associated* SO<sub>2</sub> molecules to form a ring (Figure 6). In solution disproportionation then occurred to Cp\*<sub>2</sub>Cr<sub>2</sub>S<sub>4</sub>SO<sub>3</sub> with one less core sulfur, isostructural with the Mo analogue. The structure of the SO<sub>2</sub> adduct suggested an oxygen-transfer mechanism initiated by *self-aggregation of SO<sub>2</sub> via weak Lewis acid-base interactions induced by electron donation from sulfide* (Figure 7). In support of this mechanism, reaction of <sup>34</sup>S-labeled Cp\*<sub>2</sub>Cr<sub>2</sub>S<sub>5</sub> with SO<sub>2</sub> produced labeled S<sub>8</sub> and unlabeled SO<sub>3</sub>. The role of base promoters (B) is perhaps to stabilize transients, i.e., SO<sub>3</sub> and unstable S<sub>2</sub>O<sup>64</sup> (bases also catalyze SOCl<sub>2</sub>-SO<sub>2</sub> exchange<sup>1</sup>). SO<sub>2</sub> itself is slightly associated in liquid and gas,<sup>1</sup> although an X-ray<sup>65</sup> of the solid showed no close interactions. Self-exchange of oxygens occurs within minutes, possibly via a cyclic intermediate:<sup>1</sup>



Raman studies of SO<sub>2</sub> at high pressure indicated formation of a cyclic trimer at 25 kbar which produced free sulfur on photolysis.<sup>66</sup> The bimolecular dispro-

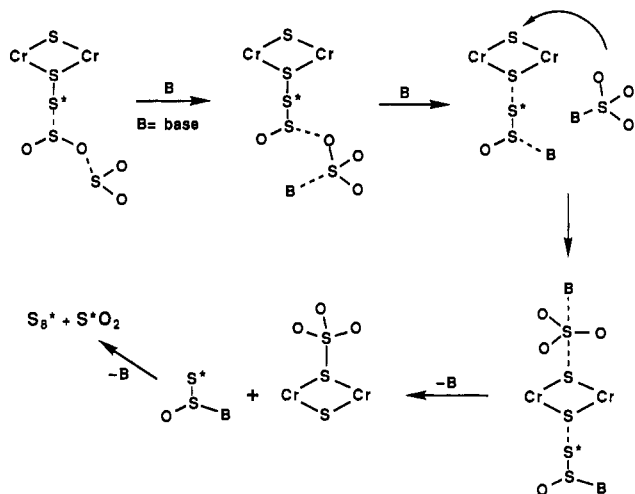
(62) (a) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765. (b) Wachter, J.; Brunner, H.; Meier, W. *Inorg. Synth.* **1990**, *27*, 69.

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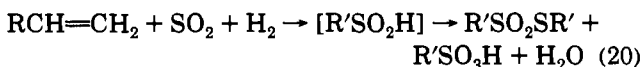
(66) Swanson, B. I.; Babcock, L. M.; Schiferl, D.; Moody, C. C.; Mills, R. L.; Ryan, R. R. *Chem. Phys. Lett.* **1982**, *91*, 393.



**Figure 7.** Possible mechanism for the disproportionation of  $\text{SO}_2$  to sulfur and  $\text{SO}_3$  on  $\text{Cp}^*_2\text{Cr}_2(\mu\text{-S})(\mu\text{-}\eta^2\text{-S}_2)(\mu\text{-}\eta^1\text{-SS-SO}_2)$ , where B is a Lewis base such as  $\text{Et}_3\text{N}$ .  $\text{S}^*$  indicates positions of  $^{34}\text{S}$  in the labeling experiment (metal-bound core sulfides also contained  $^{34}\text{S}$ ). The  $\mu\text{-}\eta^2\text{-S}_2$  ligand is not shown for clarity. Reprinted with permission from ref 63. Copyright 1992 American Chemical Society.

portionation  $2\text{SO}_2 \rightarrow \text{SO}_3 + \text{SO}$  is thermodynamically unfavorable<sup>63</sup> and complicated by the instability of  $\text{SO}_3$ <sup>64</sup> and the strong oxidizing ability of  $\text{SO}_3$ . However, the latter can be stabilized by binding to bases, e.g., sulfide to give thiosulfate, and the resulting binding energy can then make the overall process thermodynamically favorable. The fact that  $\text{SO}$  and  $\text{S}_2\text{O}$  quickly go to  $\text{S}_8$  (and  $\text{SO}_2$ ) gives an easy kinetic pathway for attrition of  $\text{SO}_2$  to sulfur. Thus, disproportionation may be a disguised mechanistic feature of many  $\text{SO}_2$  reactions, and even apparent reduction of  $\text{S}^{\text{IV}}\text{O}_2$  may actually go via  $\text{S}^{\text{VI}}\text{O}_3$ -containing intermediates from oxygen transfer between  $\text{SO}_2$  (as in eq 11). It is important to note that the disproportionation is directly facilitated by the sulfide ligand rather than the spectating metal, and that sulfate was not formed as in the metal-bound case (eq 15).

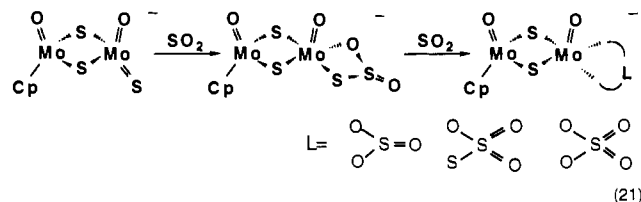
Facile disproportionation of  $\text{SO}_2$  has potential for use in  $\text{SO}_2$  scavenging. A product such as  $\text{Cp}^*_2\text{Mo}_2\text{S}_4\text{SO}_3$  can be considered to be a source of stabilized  $\text{SO}_3$  (nucleophiles such as amines strip it off under mild conditions<sup>60</sup>). It is conceivable that catalytic cycles can be designed where  $\text{SO}_3$  species are directly utilized to form organosulfonates or  $\text{H}_2\text{SO}_4$ . Indeed rapid hydro-sulfonation catalyzed by  $[\text{Pd}(\text{dppp})(\text{MeCN})_2]^{2+}$  at  $80^\circ\text{C}$  has recently been found,<sup>67</sup> analogous to hydro-formylation:



Unstable sulfinic acids<sup>26</sup> formed via  $\text{H}_2$  reaction with  $\text{Pd-SO}_2\text{R}'$  were postulated as intermediates, but overall, many pathways to useful compounds may be possible.

A recent flurry of activity has occurred in the area of  $\text{SO}_2$  disproportionation/oxygen transfer. Coucouvanis<sup>68</sup> showed even more diverse reactivity with a Mo oxo-sulfido cluster leading to formation of crystallo-

graphically-characterized sulfite, thiosulfate, or sulfate species depending on temperature and time:



The initial step was believed to be addition of  $\text{SO}_2$  across the terminal  $\text{Mo}=\text{S}$  bond to give an unisolated  $\eta^2$ -thiosulfite complex, followed by further multistep reactions with  $\text{SO}_2$ . A related Mo oxo-sulfido dimer also produced sulfate ligands from  $\text{SO}_2$  in the absence of oxygen in DMF at  $100^\circ\text{C}$ , including an unprecedented  $\mu_4\text{-SO}_4$  linking two  $[(\text{SO}_4)\text{Mo}(\text{O})(\mu\text{-S})_2\text{Mo}(\text{O})(\text{SO}_4)]^{2-}$  subunits. In another remarkable variation on the same theme, *anionic* sulfate has been formed from reaction of  $\text{O}_2$  with *ligand-bound*  $\text{SO}_2$  in a nickel(II)-dithiolate.<sup>69</sup> Ligands also may participate in exposure of  $\text{MnX}_2(\text{OPPh}_3)_n(\text{SO}_2)$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ ) to moist air to give  $\text{H}_2\text{SO}_4$ , isolated as  $(\text{PPh}_3\text{O})(\text{PPh}_3\text{OH})(\text{HSO}_4)$ .<sup>70</sup>

## Epilogue

There appear to be endless possibilities for  $\text{SO}_2$  activation at both metal and ligand sites, both with and without oxygen present, to give either free or coordinated sulfur and oxysulfur species.  $\text{SO}_2$  disproportionation to primarily thiosulfate-containing species is ubiquitous and may be the central step in much of known  $\text{SO}_2$  reactivity, including catalytic hydrogenation or even reduction by methane on sulfide catalysts such as  $\text{Re}_2\text{S}_7$  and  $\text{MoS}_2$ .<sup>52,71</sup> Indeed  $\text{FeS}$  is known to react with  $\text{SO}_2$  in water to produce thiosulfate ion,<sup>72</sup> perhaps analogously to the  $\text{Cp}^*_2\text{Mo}_2\text{S}_4$  system. Even well-established but mechanistically undefined processes not involving metals, such as Claus reaction of  $\text{SO}_2$  and  $\text{H}_2\text{S}$ , may initially involve O transfer among  $\text{SO}_2$  molecules to form unstable intermediates such as  $\text{H}_2\text{-SSO}_3$ . A major question is, How susceptible are  $\text{SO}_2$  and other amphoteric molecules such as  $\text{NO}_x$  to disproportionation processes? Further study of the conditions which promote this reactivity may lead to new strategies for chemical synthesis and abatement technology.

*The author is deeply grateful to his colleagues at Los Alamos, especially to Dr. Robert R. Ryan for providing inspiration and expertise that made possible a comprehensive study of  $\text{SO}_2$  activation. The research was funded by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.*

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