

## ACTIVATION OF H<sub>2</sub> AND SO<sub>2</sub> BY Mo AND W COMPLEXES: FIRST EXAMPLES OF MOLECULAR-H<sub>2</sub> COMPLEXES, SO<sub>2</sub> INSERTION INTO METAL-HYDRIDE BONDS, AND HOMOGENEOUS HYDROGENATION OF SO<sub>2</sub>

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**Abstract**—Our recent work on small-molecule activation by low-valent organometallic Mo and W complexes is summarized. Stereochemical control of Mo–SO<sub>2</sub> coordination geometry has been achieved since the SO<sub>2</sub> in Mo(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)(L) can bind as a  $\sigma$ -base ( $\eta^1$ ), as a  $\pi$ -acid ( $\eta^2$ ), or as an isomeric mixture of *both forms* merely by fine-tuning the donor-acceptor nature of the single *cis* ligand, L. Modification towards bulky phosphines led to a synthetic pathway to the formally 16-electron complexes, M(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> (R = Cy or Pr<sup>i</sup>), the structures of which show agostic M⋯H–C interaction. This weak interaction can readily be supplanted by others, including the first example of coordination of molecular H<sub>2</sub>. Neutron diffraction studies of W(CO)<sub>3</sub>(PPr<sup>i</sup>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>) show that W–H = 1.89(1) Å and H–H = 0.82(1) Å. <sup>1</sup>H NMR of the HD complex provides a useful spectroscopic diagnostic for molecular coordination ( $J_{\text{HD}} = 33.5$  Hz). Complete H–D isotopic exchange occurs for D<sub>2</sub> + H<sub>2</sub> complex, even in the solid state. Reductions of SO<sub>2</sub> by hydrides and H<sub>2</sub> have been studied. Addition of SO<sub>2</sub> to solutions of ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>3</sub>H [R = H (= Cp) or Me (= Cp\*)] produced ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>3</sub>(SO<sub>2</sub>H), the first example of SO<sub>2</sub> insertion into an M–H bond. The –S(O)(OH) complexes are thermally unstable, decomposing at 25–75°C to SO<sub>2</sub> reduction products, including water and sulfido–oxo cluster complexes. A dithionite-bridged complex, [Cp\*Mo(CO)<sub>3</sub>]<sub>2</sub>( $\mu$ -S<sub>2</sub>O<sub>4</sub>), has also been obtained from the hydride–SO<sub>2</sub> reaction. Homogeneous catalysis of SO<sub>2</sub> reduction by H<sub>2</sub> has been effected using [Cp\*Mo( $\mu$ -S)( $\mu$ -SH)]<sub>2</sub> catalyst. Clean conversion to sulfur and water occurs in chlorobenzene–butanol at 1–3 atm and 25–100°C at a rate of up to 350 catalyst turnovers h<sup>-1</sup>. Weak bases such as Et<sub>3</sub>N and ROH greatly increase the rate.

Our recent findings and those of others indicate that low-valent group 6 organometallic complexes are well-suited for studies of the activation of SO<sub>2</sub>, molecular H<sub>2</sub>,<sup>1</sup> C–H,<sup>2</sup> and O–H<sup>3</sup> bonds, and also of the stereochemical control of metal–ligand (e.g. Mo–SO<sub>2</sub>) coordination geometry.<sup>4</sup> Indeed, Cr(CO)<sub>5</sub> has been well recognized as a prototype mononuclear transition-metal fragment,<sup>5</sup> forming complexes with weak ligands such as methane in low-temperature matrices.<sup>6</sup> Formally 16-electron complexes, of which M(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> is an example,<sup>2,7</sup> have been found that offer a similar type of

chemistry with the advantage of room-temperature adduct stability conferred by the bulky phosphines. Because of this stability, the first examples of molecular-H<sub>2</sub> complexes have been characterized as isolable, crystalline solids.<sup>1</sup>

In this paper we summarize much of our recent work on small-molecule activation by Mo and W complexes. In general, both metals give similar chemistry, but, since the W complexes possess greater thermal and air stability, they often were more readily characterized. Our research has emphasized SO<sub>2</sub>–transition-metal chemistry, with recent work directed towards SO<sub>2</sub> reduction. The pursuit of this goal led to the recent serendipitous

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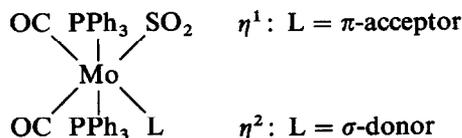
discovery of the W and Mo dihydrogen complexes. Little is known about the elementary steps of SO<sub>2</sub> reduction, and we have found that Mo complexes offer an excellent opportunity for studying stepwise reactions of SO<sub>2</sub> with hydrogen and hydride ligands. The overall goal of our efforts, in addition to understanding the mechanistic processes which occur during SO<sub>2</sub> reduction on heterogeneous catalysts, has been to develop a *homogeneous* catalytic SO<sub>2</sub> reduction cycle.

### COORDINATION OF SO<sub>2</sub> TO Mo(0) AND W(0) COMPLEXES

The primary focus of our research has been the synthesis, structure, bonding and reaction chemistry of transition-metal-SO<sub>2</sub> complexes.<sup>4(b)</sup> The diversity of bonding modes exhibited by SO<sub>2</sub>-metal complex interactions is unequalled by any other ligand, making SO<sub>2</sub> a remarkably versatile bonding probe for transition-metal complexes. Studies of octahedral *d*<sup>6</sup> complexes of the group 6 metals have contributed much to our understanding of SO<sub>2</sub> coordination. In particular, the ability of SO<sub>2</sub> to coordinate in an  $\eta^1$ -planar or  $\eta^2$  (S,O-bonded) fashion to Mo(0) and W(0) has been advantageous in regard to our understanding of the  $\pi$ -acceptor ability of SO<sub>2</sub>. Insight into the reactivity of coordinated SO<sub>2</sub>, for example the basicity of the uncoordinated oxygen atom in  $\eta^2$ -SO<sub>2</sub>, has also been obtained.

Interestingly, Mo(CO)<sub>3</sub>(phen)(SO<sub>2</sub>) and Mo(CO)<sub>2</sub>(bipy)(SO<sub>2</sub>)<sub>2</sub> contain  $\eta^2$ -SO<sub>2</sub> ligands,<sup>8</sup> whereas  $\eta^1$ -planar SO<sub>2</sub> was found in all previously structurally characterized SO<sub>2</sub> complexes of *d*<sup>6</sup>-metals.<sup>4(b)</sup> A large variety of *d*<sup>6</sup> Mo- and W-SO<sub>2</sub> complexes has since been systematically synthesized and characterized to determine the extent and nature of stereochemical control of the metal-SO<sub>2</sub> bonding geometry.<sup>4,9</sup> For *d*<sup>6</sup>-complexes in general, and Mo(0) and W(0) in particular, the  $\eta^1$ -planar and  $\eta^2$  geometries have been observed whereas the  $\eta^1$ -pyramidal has not and is not expected on the basis of simple orbital participation schemes, i.e.

$\eta^2$  fashion, depending upon the nature of L:<sup>4</sup>



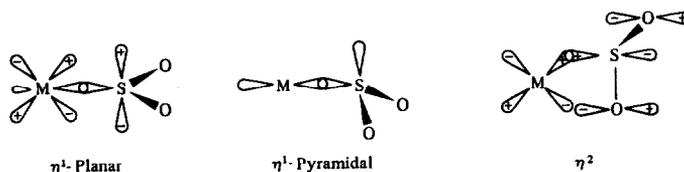
The bonding mode is remarkably sensitive to fine-tuning just *one* ligand and for the complex containing L = alkylisocyanide the coexistence of both an  $\eta^1$ -planar SO<sub>2</sub> isomer and an  $\eta^2$ -SO<sub>2</sub> isomer in apparent equimixture was observed. This is the first direct observation of spontaneous linkage isomerism of coordinated SO<sub>2</sub>, although it has been implicated in reactions of coordinated SO<sub>2</sub>. From these and related studies the following conclusions may be drawn:

(a) The  $\eta^2$ -geometry involves more M → SO<sub>2</sub>  $\pi$ -donation and less SO<sub>2</sub> → M  $\sigma$ -donation than does the  $\eta^1$ -planar case. The  $\eta^2$ -geometry is, therefore, generally discouraged by strongly  $\pi$ -accepting ligands and encouraged by strongly  $\sigma$ -donating ligands.

(b) The existence of a D-M-A (D = donor or weak  $\pi$ -acceptor, A = acceptor) conformation *cis* to SO<sub>2</sub> promotes  $\eta^2$ -bonding and dictates the orientation of the S—O<sub>m</sub> bond: in all cases, the sulfur atom lies closest to the acceptor ligand (e.g. CO).

The latter can be attributed to a polarization of  $\pi$ -electron density toward the better  $\pi$ -accepting ligands in the plane *cis* to the SO<sub>2</sub>. The unsymmetrical  $\eta^2$ -SO<sub>2</sub> ligand is oriented to best compete for the  $\pi$ -electron density with the sulfur atom nearer the carbonyls since the *2b*<sub>1</sub> acceptor orbital is largely sulfur *p* in character with a smaller oxygen *p* contribution.

The coordinated SO<sub>2</sub> in the Mo complexes is neither reversibly bound nor reactive with oxygen to form sulfato complexes. For those complexes containing  $\eta^1$ -planar SO<sub>2</sub>, this behavior is consistent with the majority of known  $\eta^1$ -planar SO<sub>2</sub> complexes of all metal coordination types. The behavior of the  $\eta^2$ -complexes, however, is in contrast

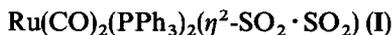


Control of the SO<sub>2</sub> bonding mode has been achieved by the proper choice of the  $\sigma$ -donating vs  $\pi$ -accepting ancillary ligands as well as their geometric disposition with respect to the SO<sub>2</sub>. For example, the SO<sub>2</sub> ligand in *cis,trans*-Mo(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)(L) has been found to coordinate in either  $\eta^1$ -planar or

to that of  $\eta^2$ -SO<sub>2</sub> in four- and five-coordinate complexes.<sup>4(b)</sup> One important difference between the octahedral  $\eta^2$ -SO<sub>2</sub> complexes and the lower-coordinate systems is the inaccessibility of the  $\eta^1$ -pyramidal SO<sub>2</sub> bonding mode in the octahedral complexes. In general, the  $\eta^1$ -pyramidal SO<sub>2</sub>

geometry is not far removed energetically from that of the  $\eta^2$ -geometry for the four- and five-coordinate  $\eta^2$ -SO<sub>2</sub> complexes. The great majority of  $\eta^1$ -pyramidal SO<sub>2</sub> complexes contain reversibly bound SO<sub>2</sub> and react with oxygen to give sulfato complexes.<sup>4(b)</sup> Thus, an intermediate species containing an  $\eta^1$ -pyramidal SO<sub>2</sub> might be involved in the reversible coordination of SO<sub>2</sub> and sulfato reaction of the four- and five-coordinate  $\eta^2$ -SO<sub>2</sub> complexes. For the octahedral  $\eta^2$ -SO<sub>2</sub> systems, such a reaction pathway would be blocked by the very high energy of the  $\eta^1$ -pyramidal species and, in general,  $d^6$   $\eta^2$ -complexes do not react with O<sub>2</sub> to form sulfates.

Since the discovery of  $\eta^2$ -SO<sub>2</sub> bonding in transition-metal complexes,<sup>10</sup> there has been considerable interest in this bonding mode and in the extent to which S—O bond activation actually occurs and whether it can be exploited in reaction chemistry studies. This form of coordinated SO<sub>2</sub> has shown some intriguing examples of reactivity quite different from that presently known for the  $\eta^1$ -planar,  $\eta^1$ -pyramidal or bridging SO<sub>2</sub> coordination modes. The bonding of  $\eta^2$ -SO<sub>2</sub> has been suggested to primarily involve  $\pi$ -donation from the metal to the LUMO of SO<sub>2</sub>, which is antibonding with respect to the S—O bond and bonding with respect to the O—O interaction.<sup>4(b)</sup> This type of interaction would be expected to lengthen S—O distances, increase the terminal oxygen basicity, and enhance coordination by Lewis acids. The complex



was found to contain a second SO<sub>2</sub> coordinated as a Lewis acid to the terminal oxygen of the  $\eta^2$ -SO<sub>2</sub>

(Fig. 1).<sup>11</sup> It exhibits the longest coordinated S—O bond and the lowest  $\nu(\text{SO})$  value of any of the reported  $\eta^2$ -SO<sub>2</sub> complexes.<sup>4(b)</sup> An unusual reactivity was observed: the complex slowly reacted with excess SO<sub>2</sub> in the absence of oxygen to generate the bidentate sulfate complex<sup>12</sup>  $\text{Ru}(\text{SO}_4)(\text{CO})_2(\text{PPh}_3)_2$  (the same complex that was obtained on reaction of I with molecular oxygen<sup>13</sup>) plus PPh<sub>3</sub>S and an unidentified ruthenium species which appeared to contain bridging carbonyls. The only products obtained in the presence of excess PPh<sub>3</sub> are  $\text{Ru}(\text{SO}_4)(\text{CO})_2(\text{PPh}_3)_2$  and PPh<sub>3</sub>S. In an attempt to explore the effect of enhanced basicity of the ancillary ligand, a variety of complexes of the type  $\text{Ru}(\text{CO})_2(\text{SO}_2)(\text{PR}_3)_2$  were prepared where PR<sub>3</sub> = (A) triphenylphosphine, (B) *p*-tolylidiphenylphosphine, (C) tribenzylphosphine, and (D) tricyclohexylphosphine. For A–C the reactivity is essentially identical with ~10% of the corresponding SO<sub>4</sub> complexes formed in 2 days in SO<sub>2</sub>-saturated benzene solutions. For D, a different complex was isolated after 1 day which analyzes for  $\text{Ru}(\text{CO})_2(\text{S}_2\text{O}_4)(\text{PCy}_3)_2$  and is monomeric by solution molecular weight studies. Since this species continues to react and generate the sulfato complex,  $\text{Ru}(\text{CO})_2(\text{SO}_4)(\text{PCy}_3)_2$ , it appears likely that this is an intermediate in the reaction and that the reaction should be depicted as  $\text{M}^0(\text{SO}_2 \cdot \text{SO}_2) \rightarrow \text{M}^{2+}(\text{S}_2\text{O}_4)^{2-} \rightarrow \text{M}^{2+}(\text{SO}_4)^{2-} + \frac{1}{8}\text{S}_8$  (the S<sub>8</sub> reacts with PR<sub>3</sub> to form SPR<sub>3</sub>). At this point there appears to be no clear trend in the reactivity that can be related to the phosphine basicity, but other factors such as steric effects could dominate.

Other studies of Mo–SO<sub>2</sub> complexes have produced well-defined illustrations of the basicity of

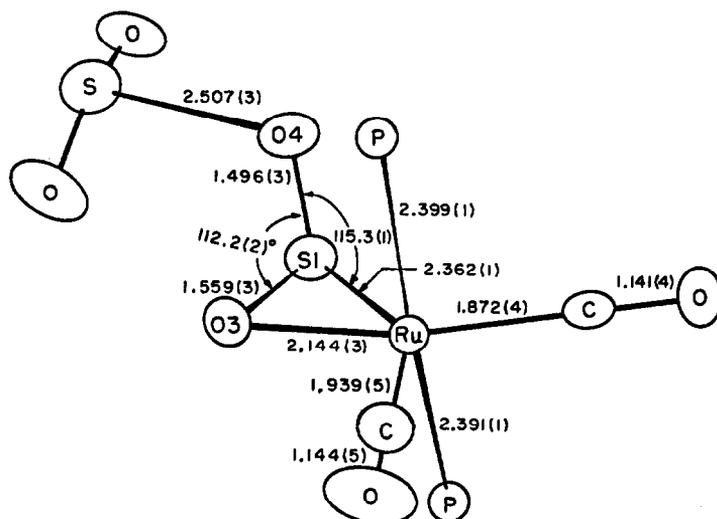


Fig. 1. Structure of  $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-SO}_2 \cdot \text{SO}_2)$ .

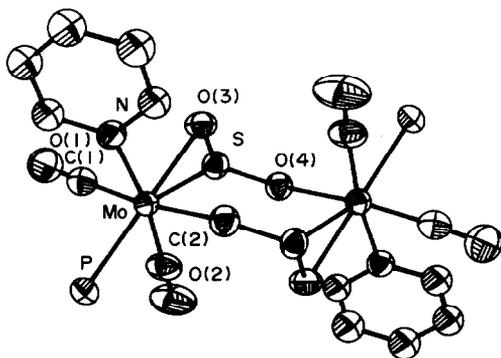
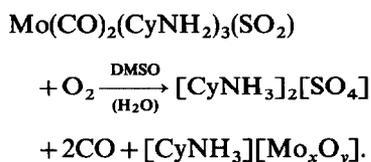


Fig. 2. Structure of  $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{py})(\text{SO}_2)]_2$ .

the terminal oxygen of  $\eta^2$ - $\text{SO}_2$ . The structure of  $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{py})(\text{SO}_2)]_2$  showed the first example of  $\text{SO}_2$  coordinated to metals by way of all three of its atoms (Fig. 2).<sup>4(a),14</sup> This complex was spontaneously formed in solution from  $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2(\text{pyridine})(\eta^2\text{-SO}_2)$  by loss of  $\text{PPh}_3$ . Thus, the terminal oxygen of the  $\eta^2$ - $\text{SO}_2$  ligand in this complex apparently possesses sufficient basicity to displace  $\text{PPh}_3$ , a surprising result since  $\text{PPh}_3$  is an excellent ligand. Even more striking is the finding that the dimer will precipitate in the presence of a large excess of pyridine, a strong competing ligand, and is not readily cleaved by pyridine and other strongly basic ligands. The low solubility of  $[\text{Mo}(\text{CO})_2(\text{pyridine})(\text{PPh}_3)(\mu\text{-SO}_2)]_2$  may provide some driving force for its formation, but nonetheless the Mo—O bond  $[\text{Mo—O}(4)]$  must be relatively strong (bond length = 2.24 Å) and indeed is only 0.05 Å longer than that for Mo—O(3). Further indication of the oxygen basicity in Mo— $\text{SO}_2$  complexes was given by Schenk and Baumann,<sup>9</sup> who reported O-silylation of both  $\eta^1$ - and  $\eta^2$ -complexes.

An interesting series of complexes of the type  $\text{Mo}(\text{CO})_2\text{L}_3(\text{SO}_2)$  ( $\text{L} = \text{PMePh}_2$  or  $\text{CyNH}_2$ ) has been synthesized and found to contain  $\eta^1$ -planar  $\text{SO}_2$ . The geometry was unexpected because the presence of three  $\sigma$ -donating ancillary ligands would appear to favor  $\eta^2$ -bonding. The X-ray crystal structure of  $\text{Mo}(\text{CO})_2(\text{CyNH}_2)_3(\text{SO}_2)$  revealed that the cyclohexylamine ligands coordinate in *facial* fashion.

The most intriguing feature of this complex was found to be its novel reactivity with oxygen:

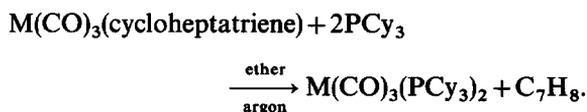


The production of *uncoordinated* sulfate from  $\text{SO}_2$  complexes has not been observed and a catalytic

method for  $\text{SO}_2$  oxidation to sulfate would be of considerable interest. However, the mechanism may involve reaction of dissociated ligands since  $\text{SO}_2$  and  $\text{CyNH}_2$  were found to give  $[\text{CyNH}_2][\text{HSO}_3]$  in DMSO, and air-oxidation of the bisulfite to sulfate was catalyzed by the molybdate coproduct of the reaction. Thus, it is probable that oxidation of the metal with concomitant ligand loss occurs initially, followed by reaction of  $\text{SO}_2$ ,  $\text{CyNH}_2$  and  $\text{H}_2\text{O}$  to give bisulfite and eventually sulfate.

#### ACTIVATION OF H—H AND C—H BONDS: MOLECULAR- $\text{H}_2$ COMPLEXES

The discovery<sup>2,7</sup> of a facile synthetic pathway to stable 16-electron complexes,  $\text{M}(\text{CO})_3(\text{PCy}_3)_2$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ), has provided an unparalleled opportunity to study small-molecule activation, in particular the first examples of molecular- $\text{H}_2$  complexes.<sup>1</sup> The complexes are the only ones of which we are aware that activate *both* H—H and C—H bonds. The synthesis evolved serendipitously from our work on Mo— $\text{SO}_2$  complexes, specifically *mer,trans*- $\text{Mo}(\text{CO})_3(\text{PR}_3)_2(\text{SO}_2)$ .<sup>4(a)</sup> During attempts to optimize their preparation from *fac*-tricarbonyl complexes containing labile ligands,  $\text{M}(\text{CO})_3(\text{cycloheptatriene})$  was found to be a viable precursor to formally coordinatively unsaturated species:



The observation of the striking deep blue-purple color of the 16-electron complexes was a key factor in their identification.

The stability of the complexes is largely a result of the well-known steric demands imposed by bulky phosphine ligands. The labile cycloheptatriene in the starting complex,  $\text{M}(\text{CO})_3(\text{cycloheptatriene})$ , occupies *three* coordination sites but is effectively displaced by only *two* phosphine ligands, thereby opening up the sixth coordination site. Because of the phosphine bulk, the cycloheptatriene is squeezed out of the coordination sphere of the metal. The phosphine size must, of course, be large enough such that three cannot easily fit around the metal in an octahedral array, but curiously the synthesis succeeds for  $\text{PCy}_3$ ,  $\text{PPr}^i$  and  $\text{PCy}_2\text{Pr}^i$ , but not for other phosphines with similar cone angles. The use of smaller phosphines results in the formation of  $\text{Mo}(\text{CO})_3(\text{PR}_3)_3$ .

The structure of  $\text{W}(\text{CO})_3(\text{PCy}_3)_2$  shows the addition of a distal phosphine hydrogen to the metal coordination sphere (Fig. 3). This agostic interaction

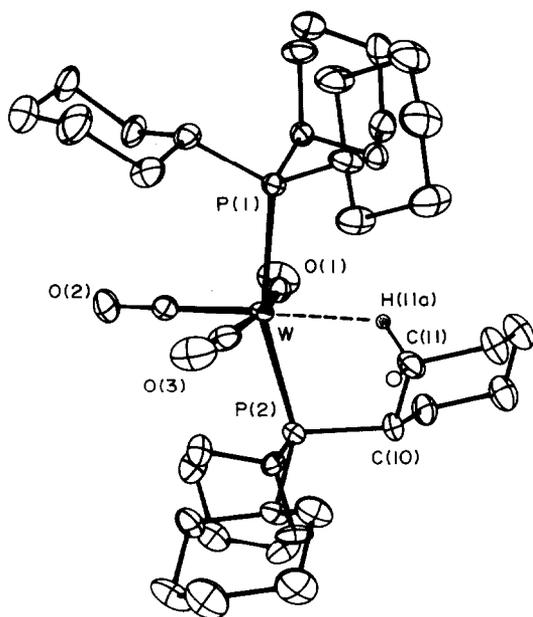


Fig. 3. Structure of  $W(CO)_3(PCy_3)_2$ .

$[\nu(CH) = 2552 \text{ cm}^{-1}]$  is the first well-defined example of its type for an alkylphosphine. Importantly the highly distorted geometry about P(2)

$$[W-P(2)-C(9) = 122.0(2)^\circ,$$

and

$$W-P(2)-C(10) = 99.0(2)^\circ]$$

is evidence that the tungsten atom exerts a strong *attractive* force upon the (11a) atom. Note that this is in distinct contrast with several other coordinatively unsaturated complexes in which hydrogen atoms from coordinated phosphine groups are located near the open site about the metal. For example, the triphenylphosphine ligands in both  $RhHCl(SiCl_3)(PPh_3)_2$ <sup>15</sup> and  $RuCl_2(PPh_3)_3$ <sup>16</sup> have normal, undistorted geometries. LaPlaca and Ibers<sup>16</sup> attribute the particular location of ring hydrogen atoms near the metal in these complexes to “geometric” effects, rather than any true metal–hydrogen bonding interactions. The same is apparently true in the case of the  $Mo(CO)(diphos)_2$  (diphos = diphenylphosphinoethane) molecule,<sup>17</sup> another example of a formally five-coordinate complex with a group 6 metal.

Although refinement of the hydrogen atom positions was unsuccessful, the idealized position of the activated hydrogen atom is *ca* 2.17 Å from the metal [ $W-C(11) = 2.943(6) \text{ \AA}$ ]. The overall structure of the  $PPR_3^i$  analogue is basically similar, although disorder hampers precise description of the crucial distorted portion of the molecule.

$M(CO)_3(PR_3)_2$  readily “add” donor ligands, which displace the C–H group from the metal center. The resultant *mer,trans*- $M(CO)_3(PR_3)_2L$  can contain reversibly bound donors (e.g. H<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O) or irreversibly bound groups (e.g. CO, SO<sub>2</sub> and pyridine).

As with other unsaturated complexes, the ability to bind additional ligands is strongly influenced by steric factors. For example, as also found for  $Mo(CO)(diphos)_2$ ,<sup>17</sup> the complexes coordinate primary but not secondary or tertiary amines. Other ligands which fail to form isolable adducts include propylene, cyclohexene, butadiene, C<sub>2</sub>F<sub>4</sub> and furan. Nevertheless, certain strong ligands, such as phosphines (e.g. PPh<sub>3</sub>) and phosphites, will form adducts despite their relative bulkiness. Also, in spite of the strong Lewis acidity of the metal atom in  $M(CO)_3(PR_3)_2$ , it has been shown that CO<sub>2</sub> does not add, even in liquid CO<sub>2</sub>.<sup>3</sup> A hydrido-bicarbonate complex,  $W(CO)_3(PCy_3)_2(H)(HCO_3^-)$ , has been suggested as the result of reaction with “wet” CO<sub>2</sub>.<sup>3</sup> The same authors propose that the H<sub>2</sub>O complex is a precursor to the bicarbonate and contains hydrido–hydroxo ligands resulting from oxidative addition. This activation of O–H bonds by Mo and W is a promising area for exploration also.

#### Molecular-H<sub>2</sub> coordination

The activation of hydrogen by transition-metal complexes, i.e. oxidative addition to form hydride complexes, has been well studied because of its importance in catalysis. The geometry of approach of the H<sub>2</sub> molecule to the metal (“end-on” or “side-on”) has long been the subject of discussion,<sup>18</sup> and recent theoretical studies favored sideways addition to a 16-electron ML<sub>5</sub> center.<sup>5</sup> The existence of transient side-on molecular-H<sub>2</sub> coordination has been proposed, particularly in “direct hydrogen transfer” reaction processes,<sup>19</sup> but until our work a well-characterized molecular-H<sub>2</sub> complex had not been isolated. Spectroscopic evidence for  $Cr(CO)_5(H_2)$  (stable at low temperature but short-lived at 25°C) has recently been observed,<sup>20</sup> and, several years prior to this, we reported novel complexes,  $M(CO)_3(PCy_3)_2(H_2)$  (M = Mo or W), with unusual IR features.<sup>7</sup> These room-temperature stable complexes, along with  $W(CO)_3(PPR_3^i)_2(H_2)$ , were then shown to contain the  $\eta^2$ -H<sub>2</sub> ligand,<sup>1</sup> one of the last “holdouts” in the realm of small-molecule coordination. More importantly, the H<sub>2</sub> complexes (including newly reported examples<sup>21</sup>) represent incipient oxidative addition of a diatomic molecule, giving an unprecedented opportunity for study.

The complexes are readily synthesized in excellent yields from the 16-electron precursors,

$M(\text{CO})_3(\text{PR}_3)_2$ , or directly from  $M(\text{CO})_3$  (cycloheptatriene) and  $\text{PR}_3$  under  $\text{H}_2$ . As for  $M(\text{CO})_3(\text{PR}_3)_2$ , the complexes could be formed only for  $\text{R}_3 = \text{Cy}_3$ ,  $\text{Pr}_3^i$  or  $\text{Cy}_2\text{Pr}^i$ . The  $\text{H}_2$  ligand readily dissociates reversibly in solution although crystals of the complexes can be handled even in air for short periods. X-ray structural studies revealed an octahedral geometry for  $\text{W}(\text{CO})_3(\text{PPr}_3^i)_2(\text{H}_2)$  and the  $\text{H}_2$  molecular ligand was first observed by room-temperature neutron diffraction studies at the Los Alamos Pulsed Neutron Source. Subsequent low-temperature neutron studies<sup>21(d)</sup> at both the Brookhaven National Laboratory and Los Alamos were necessary in order to properly model a disorder in one of the phosphino ligands and resulted in the determination, with reasonable precision, of H—H and W—H distances of 0.82(1) and 1.89(1) Å (Fig. 4). The  $\text{H}_2$  is symmetrically bonded parallel to the  $i$ -W—P axis, and the overall coordination geometry is nearly octahedral. Similarly X-ray structural studies of  $M(\text{CO})_3(\text{PCy}_3)_2(\text{H}_2)$  demonstrated an octahedral geometry. Refinement of preliminary neutron diffraction data, despite a disorder of  $\text{H}_2$  and CO due to centrosymmetry at the metal, show the  $\text{H}_2$  to be bound in a similar fashion to that in the  $\text{PPr}_3^i$  analog. It should be noted that the structures of a series of group 6 hydride complexes, including  $\text{MoH}_2(\text{PMe}_3)_5$ , all showed non-octahedral phosphine positions.<sup>22</sup>

Spectroscopic studies confirmed the structural data, and a useful NMR diagnostic for molecular- $\text{H}_2$  coordination, was found to be the value of  $J_{\text{HD}}$  for the monodeuterated species, e.g.  $\text{W}(\text{CO})_3(\text{PPr}_3^i)_2(\text{HD})$ . The  $^1\text{H}$  spectrum (90 MHz) of the  $\text{H}_2$  complex showed only a single broad major\* resonance at  $ca$  -4 ppm from 70 to  $-80^\circ\text{C}$ , but the HD complex gave a 1:1:1 triplet with  $J_{\text{HD}} = 33.5$  Hz (Fig. 5). This value is an order of magnitude larger than that for, say, hydride and deuteride compounds and is 77% of that for HD gas (43.2 Hz).<sup>23</sup> Solid-state  $^2\text{H}$  NMR studies shows that, for  $\text{W}(\text{CO})_3(\text{PPr}_3^i)_2(\text{D}_2)$ , the  $\text{D}_2$  undergoes rotational motion about the metal- $\text{D}_2$  axis at a rate greater than 130 kHz at ambient temperature.

IR spectroscopy provided the first hint of molecular- $\text{H}_2$  coordination, and subsequent thorough IR and Raman examinations of the  $\text{H}_2$ , HD and  $\text{D}_2$  complexes located four of the six

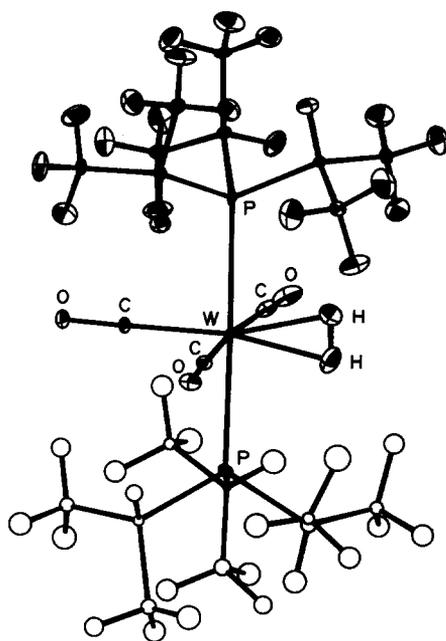
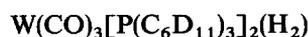


Fig. 4. Structure of  $\text{W}(\text{CO})_3(\text{PPr}_3^i)_2(\text{H}_2)$ .

fundamental modes expected for  $\eta^2\text{-H}_2$  (Table 1). The use of fully deuterated  $\text{PCy}_3$  enabled location of  $\nu(\text{HH})$  as a weak, broad band at  $2690\text{ cm}^{-1}$  in the Nujol mull IR spectrum of



(Fig. 6). This value is some  $1500\text{ cm}^{-1}$  lower than that of free  $\text{H}_2$ . Failure to observe  $\nu(\text{HH})$  in the Raman experiments may have been due to sample decomposition (even at 77 K). The electronic spectrum of  $\text{W}(\text{CO})_3(\text{PPr}_3^i)_2(\text{H}_2)$  shows a band at 364 nm.

In regard to the chemistry of the coordinated  $\text{H}_2$ , isotopic exchange has been found to occur between  $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$  and  $\text{D}_2$  gas in both solution and

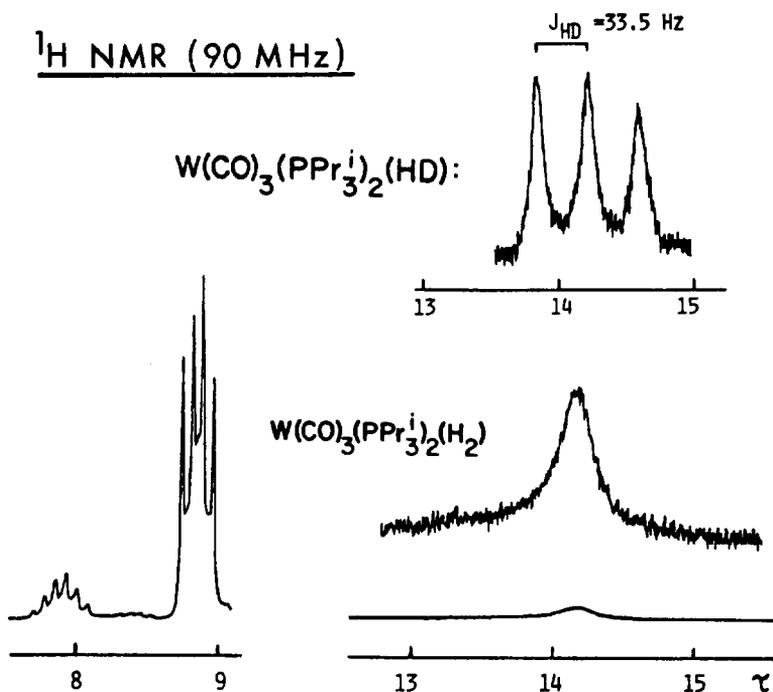
Table 1. Vibrational frequencies [ $\nu$  ( $\text{cm}^{-1}$ )] for solid  $\text{W}(\text{CO})_3(\text{PCy}_3)_2(\text{H}_2)$  and isotopically substituted species<sup>a</sup>

|                       | HH                           | HD                            | DD                            |
|-----------------------|------------------------------|-------------------------------|-------------------------------|
| $\nu(\text{HH})$      | 2690 (IR) <sup>b</sup>       | 2360 (IR)                     | $\sim 1900$ (R)               |
| $\nu_a(\text{WH}_2)$  | 1570 (IR)                    | $\sim 1350$ (IR) <sup>b</sup> | $\sim 1132$ (IR) <sup>b</sup> |
| $\nu_s(\text{WH}_2)$  | 953 (IR, R)                  | 791 (IR, R)                   | 703 (IR, R)                   |
| $\delta(\text{WH}_2)$ | $\sim 450$ (IR) <sup>b</sup> |                               | 319 (IR)                      |

\* A minor ( $ca$  15–20%) resonance appears on cooling or on changing to higher field (200 MHz). This resonance, which coalesces with the major peak at or above room temperature, is a triplet ( $J = 38$  Hz) in certain temperature ranges, suggesting P—H coupling and the possibility of a hydride form in equilibrium with the  $\text{H}_2$  form.<sup>21(c)</sup>

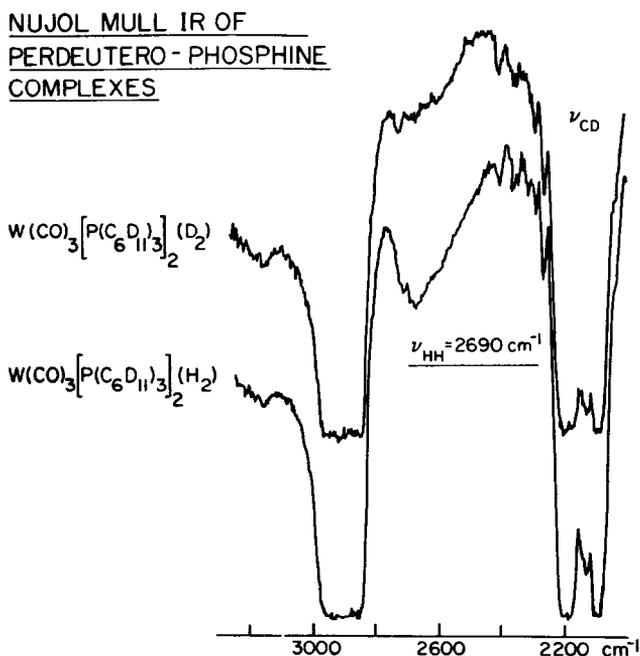
<sup>a</sup> IR samples were Nujol mulls; Raman samples were enclosed in capillaries and excited by the 5682-Å line of a Kr laser. Similar results were obtained for the P-*i*-Pr<sub>3</sub> analogues.

<sup>b</sup> Partially obscured.  $\nu(\text{HH})$  was relatively clear in the  $\text{P}(\text{C}_6\text{D}_{11})_3$  analogue.


 Fig. 5. <sup>1</sup>H NMR spectra in C<sub>6</sub>D<sub>6</sub> at 35°C.

solid states at 20°C, giving within days a statistical mixture of H<sub>2</sub>, HD and D<sub>2</sub> species. Neither the phosphine nor solvent hydrogen atoms exchange. At this point the mechanism for this process is unknown. The solid-gas scrambling is particularly interesting since transient phosphine dissociation

cannot be providing vacancies for coordination of a second H<sub>2</sub> and D<sub>2</sub> molecule. The H<sub>2</sub> complexes do not catalyze hydrogenation of ethylene under mild conditions (toluene, 1 atm, 20°C), presumably because of limited available coordination sites (i.e. steric crowding by the phosphines).


 Fig. 6. IR spectra of  $W(CO)_3[P(C_6D_{11})_3]_2(H_2)$  and D<sub>2</sub> species.

Theoretical calculations of  $H_2$  binding in the model complex,  $W(CO)_3(PH_3)_2(H_2)$ , indicate that the observed conformation of the complex is stable by  $16.8 \text{ kcal mol}^{-1}$  relative to  $W(CO)_3(PH_3)_2 + H_2$ .<sup>24</sup> The conformation with the H—H rotated by  $90^\circ$  was only  $0.3 \text{ kcal mol}^{-1}$  less stable, in agreement with the NMR results, indicating only a small barrier to rotation. The studies also indicated that the bonding of  $H_2$  to the metal involves primarily  $\sigma$ -donation to the metal, with very little backbonding into the  $\sigma^*$ -orbital of  $H_2$ . For the minimum-energy structure the H—H distance was  $0.79 \text{ \AA}$ , close to that observed ( $0.82 \text{ \AA}$ ) although the W—H distances were longer than those determined ( $2.15$  vs  $1.89 \text{ \AA}$ ).

Two obvious questions arise: do more  $H_2$  complexes exist and why do  $M(CO)_3(PR_3)_2(H_2)$  coordinate dihydrogen while  $MoH_2(PMe_3)_5$ <sup>22(a)</sup> and related complexes<sup>22</sup> proceed to the hydride? We now have evidence that the known 16-electron complex  $Mo(diphos)_2(CO)$ ,<sup>17</sup> which contains a weak  $M \cdots H-C$  interaction, gives very similar  $H_2$  complexes.<sup>21(c)</sup> Thus complexes which weakly coordinate a distal hydrogen atom are clearly excellent candidates for  $H_2$  coordination. While the bulkiness of the phosphine ligands is no doubt important in determining whether the  $H_2$  is arrested rather than cleaved by the metal, other factors are also involved. The electronic influence of the ligand *trans* to  $H_2$  may be crucial, judging by the fact that the  $H_2$  complexes [including  $Cr(CO)_5(H_2)$ ] contain *trans*-CO while none of the structurally-characterized group 6 polyhydrides<sup>22</sup> contain any CO ligands at all. These principles may not apply to other metal systems,<sup>21(b)</sup> and only the discovery of further examples of  $H_2$  coordination will provide understanding.

## REDUCTION OF $SO_2$ BY GROUP 6 METAL HYDRIDES AND HYDROGEN

### *Hydride reduction: insertion of $SO_2$ into a metal-hydride bond*

The reduction of  $SO_2$  with  $H_2$  or other agents such as CO to give sulfur and  $H_2O$  is an attractive method for  $SO_2$  conversion. In the objectives of our studies of transition-metal- $SO_2$  complexes, we include metal systems that will act as catalysts for the reduction of  $SO_2$  or will provide models for the elementary steps in a catalytic cycle. Transition-metal-hydride complexes have been shown to be important intermediates in catalytic cycles involving hydrogenation of organic substrates. Thus, in seeking homogeneous systems to catalytically or stoichiometrically hydrogenate  $SO_2$ , we are examining

the reactions of metal-hydride complexes with  $SO_2$ . Much of our work has focused upon molybdenum and tungsten complexes as these metals are abundant, nonstrategic, and contained in proven catalysts in industrial processes.

A wide variety of reaction types have been found depending on the nature of steric and electronic factors. The system  $Cp_2MH_2$  ( $M = Mo$  or  $W$ ) cleanly and rapidly reduced  $SO_2$  to  $Cp_2M(S_2O_3)$  and  $H_2O$ , representing partial reduction of the  $SO_2$ .<sup>25</sup> Strong acids such as HCl convert  $Cp_2M(S_2O_3)$  to  $H_2O$ ,  $SO_2$  and new types of cationic metal-sulfur complexes<sup>25</sup> in a manner similar to the conversion of ionic thiosulfate to  $H_2O$ ,  $SO_2$  and  $S_8$ . We speculate that a well-defined color change upon the addition of  $SO_2$  to  $Cp_2MoH_2$  may be due to adduct formation which is then followed by  $SO_2$  insertion into the Mo—H bond.  $SO_2$  inserts into the metal-hydride bond in  $C_5H_5M(CO)_3H$  ( $R = H$  or  $Me$ ;  $M = Mo$  or  $W$ ) to form  $(C_5R_5)M(CO)_3(SO_2H)$ .<sup>26</sup> The reaction occurs readily at room temperature, and the insertion product precipitates upon addition of  $SO_2$  to a concentrated solution of  $(C_5R_5)M(CO)_3H$  in organic solvents. X-ray crystallography of  $CpMo(CO)_3(SO_2H)$  confirmed that an S-bound insertion occurred (Fig. 7). Although both S—O distances are significantly longer than that normally found in  $SO_2$  complexes (*ca*  $1.45 \text{ \AA}$ )<sup>4(b)</sup> the difference in the two distances [S—O(1) =  $1.637(6)$ , S—O(2) =  $1.515(6)$ ] is sufficient to indicate that the H atom is bound to O(1). A peak appeared in the difference maps near O(1) and refined to a chemically reasonable position for an H-atom if the thermal parameter was fixed. Sulfinate ligands bound to transition metals have been

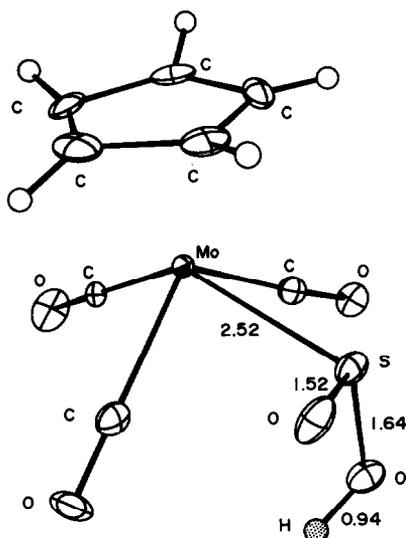
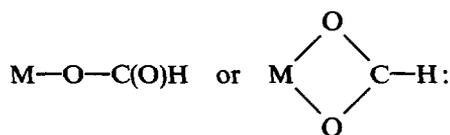


Fig. 7. Structure of  $CpMo(CO)_3(SO_2H)$ .

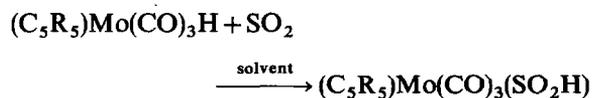
structurally characterized for *S*-sulfinates or *O*-sulfinates<sup>27,28</sup> with an alkyl or aryl bound to the sulfur and spectroscopic evidence exists for *O,O*-sulfinates and those of the type M—S(O)—OR.<sup>29</sup> The present study affords the first structural characterization of the latter type as well as the first direct evidence for insertion into a M—H bond.

The complexes (C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>3</sub>(SO<sub>2</sub>H) can be considered to be metallo analogues of organic sulfinic acids, RSO<sub>2</sub>H.<sup>30</sup> A metallo *sulfonic* acid, CpFe(CO)<sub>2</sub>[S(O)<sub>2</sub>OH], is known,<sup>31</sup> but is not a result of an insertion reaction. There appears to be no well-characterized precedent for the SO<sub>2</sub>H<sup>-</sup> ligand (or free anion) although a sulfinate structure, Ru(SO<sub>2</sub>H)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>3</sub>, was tentatively formulated for the product of the RuH<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>-SO<sub>2</sub> reaction.<sup>32</sup> In contrast with SO<sub>2</sub>, insertion of CO<sub>2</sub> into metal-hydride bonds is well known and results in metal-oxygen coordination,



definitive identification of a metallocarboxylic acid, M—C(O)—OH, derived by CO<sub>2</sub> insertion is lacking.<sup>33</sup>

For the reaction:

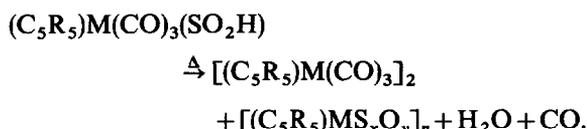


the solution equilibrium lies far to the left; NMR shows that SO<sub>2</sub> readily extrudes on dissolution, unless excess SO<sub>2</sub> is present. Cp\*Mo(CO)<sub>3</sub>(SO<sub>2</sub>H) (Cp\* = C<sub>5</sub>Me<sub>5</sub>) in liquid SO<sub>2</sub> at -40°C shows a broad resonance for the OH proton at δ 3.89, which

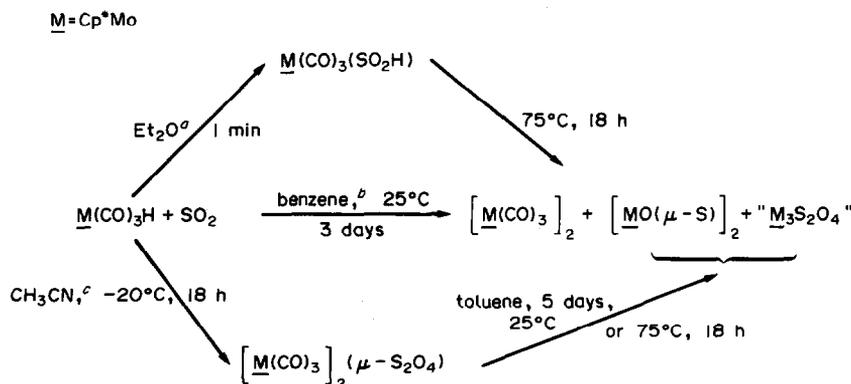
shifts on addition of H<sub>2</sub>O, reflecting proton exchange. A weak, broad IR stretch near 2550 cm<sup>-1</sup> is assigned to ν(OH), on the basis of <sup>2</sup>H and <sup>18</sup>O substitution.

The mechanism of the SO<sub>2</sub> insertion may be a *concerted* process, involving attack on the coordinated hydride, analogous to the attack on α-carbon proposed for the alkyl analogues, CpM(CO)<sub>3</sub>S(O)<sub>2</sub>R.<sup>34</sup> It is reasonable that SO<sub>2</sub> initially coordinates to the hydride much as it does to metal-bound halides and pseudohalides.<sup>4(b)</sup>

A significant finding in terms of SO<sub>2</sub> reduction is the thermal instability of the solid complexes, which undergo auto-redox within 1 day [25°C for CpMo(CO)<sub>3</sub>(SO<sub>2</sub>H), and 55–75°C for the W and Cp\* analogues] to products indicative to S(IV) → S(II-) reduction and metal oxidation:



A complex mixture of sulfido and oxo-sulfido complexes generally resulted, although for R = Me and M = Mo, the reaction was cleaner, yielding [(C<sub>5</sub>Me<sub>5</sub>)MoO(μ-S)]<sub>2</sub><sup>35</sup> and a species analyzing as "(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Mo<sub>3</sub>S<sub>2</sub>O<sub>4</sub>" (see Fig. 8). Prolonged reactions of solutions of (C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>3</sub>H with SO<sub>2</sub> in 4:1 stoichiometry also gave reduction of SO<sub>2</sub>, and for R = Me and M = Mo the products were nearly identical to those for thermolysis of the SO<sub>2</sub> complex. Thus it would appear that the insertion complexes are logical intermediates in the SO<sub>2</sub> reduction. A possible further (or alternate) intermediate has also been isolated and structurally characterized. A solution-unstable dithionite-bridged complex, [(C<sub>5</sub>Me<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub>(μ-S<sub>2</sub>O<sub>4</sub>)



<sup>a</sup>Concentrated solution, <sup>b</sup>4:1 hydride:SO<sub>2</sub> ratio, <sup>c</sup>dilute solution

Fig. 8. Reactions of Cp\*Mo(CO)<sub>3</sub>H with SO<sub>2</sub>.

(Fig. 9), crystallized slowly at  $-20^{\circ}\text{C}$  from dilute  $\text{CH}_3\text{CN}$  solutions of  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$  containing excess  $\text{SO}_2$ . No  $\text{H}_2$  was produced in this or any other of the hydride- $\text{SO}_2$  reactions; the hydride protons transfer to an oxygen atom to form  $\text{H}_2\text{O}$ . Conceivably, the dithionite species is produced by S-S coupling of two deprotonated  $\text{Cp}^*\text{Mo}(\text{CO})_3(\text{SO}_2\text{H})$  fragments (an oxidation step is also required). The dithionite decomposes in solution, converting within minutes to a series of products. After several days, only two major products formed (plus  $\text{CO}$  and  $\text{CO}_2$ ): the same two oxo-sulfido complexes produced from thermolysis of the insertion product or prolonged solution reaction of  $(\text{C}_5\text{Me}_5)\text{Mo}(\text{CO})_3\text{H}$  and  $\text{SO}_2$ . Thermolysis of the solid dithionite at  $75^{\circ}\text{C}$  for 18 h gave the same complexes, along with  $\text{CO}$  and  $\text{CO}_2$  (from transfer of oxygen to  $\text{CO}$ ).

The S-bound dithionite represents the first structurally characterized example of its type although this geometry had been proposed for  $[\text{CpFe}(\text{CO})_2]_2(\text{S}_2\text{O}_4)$  and  $[\text{M}(\text{CO})_5]_2(\text{S}_2\text{O}_4)$  ( $\text{M} = \text{Mn}$  or  $\text{Re}$ ).<sup>36</sup> The S-S bond distance of  $2.266(1)\text{ \AA}$  for the  $\text{C}_{2h}$   $\text{S}_2\text{O}_4$  is shorter than that found in  $\text{Na}_2\text{S}_2\text{O}_4$  and other structures with  $\text{C}_{2v}$   $\text{S}_2\text{O}_4^{2-}$  ion ( $2.35\text{--}2.39\text{ \AA}$ ).<sup>37</sup> These unexpectedly long distances have generally eluded attempts at theoretical description. The S-S distance in the Mo complex is significantly longer than that in diphenyl disulfone

$[2.193(1)\text{ \AA}]$ ,<sup>38</sup> the only other structure we know of for which the  $\text{S}_2\text{O}_4$  moiety is found in approximate  $\text{C}_{2h}$ -symmetry.

As previously mentioned, the prolonged solution reactions of  $\text{SO}_2$  and  $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_3\text{H}$  in all cases eventually yield a mixture of sulfido and/or oxo metal complexes and water as a result of  $\text{SO}_2$  reduction. The nature of the final products depends on the metal, R group, solvent, temperature and hydride: $\text{SO}_2$  ratio. For example, whereas  $[\text{CpW}(\text{CO})_3]_2(\mu\text{-S})$ <sup>39</sup> is found to be both the major as well as the initially observed sulfur-containing product for  $\text{M} = \text{W}$ , the Mo analogue is unstable and rapidly decomposes in solution with  $\text{CO}$  loss to a mixture of sulfide products. Complexes of the type  $[\text{Cp}^*\text{M}(\text{CO})_3]_2\text{S}$  are not observed for the  $\text{Cp}^*$  systems, but rather oxo-containing products such as  $[\text{Cp}^*\text{MO}(\mu\text{-S})]_2$  are prevalent in hydride- $\text{SO}_2$  reactions. However, for  $\text{M} = \text{W}$ , a double sulfide-bridged complex,  $[\text{Cp}^*\text{W}(\text{CO})_2(\mu\text{-S}\cdot\text{SO}_2)]_2$ , with a strong sulfide- $\text{SO}_2$  interaction can also be isolated (Fig. 10).<sup>39</sup> The different products isolated in these reactions may thus merely reflect different stabilities rather than major differences in mechanisms.

Summarizing, the  $\text{SO}_2\text{H}$  unit appears to be inherently unstable, certainly when coordinated to transition metals [reduction of  $\text{SO}_2$  by  $(\mu\text{-H}_2)\text{Os}_3(\text{CO})_{10}$  is also believed to proceed via an  $\text{SO}_2\text{H}$  complex]<sup>40</sup> and also in sulfinic acids,  $\text{RSO}_2\text{H}$ ,

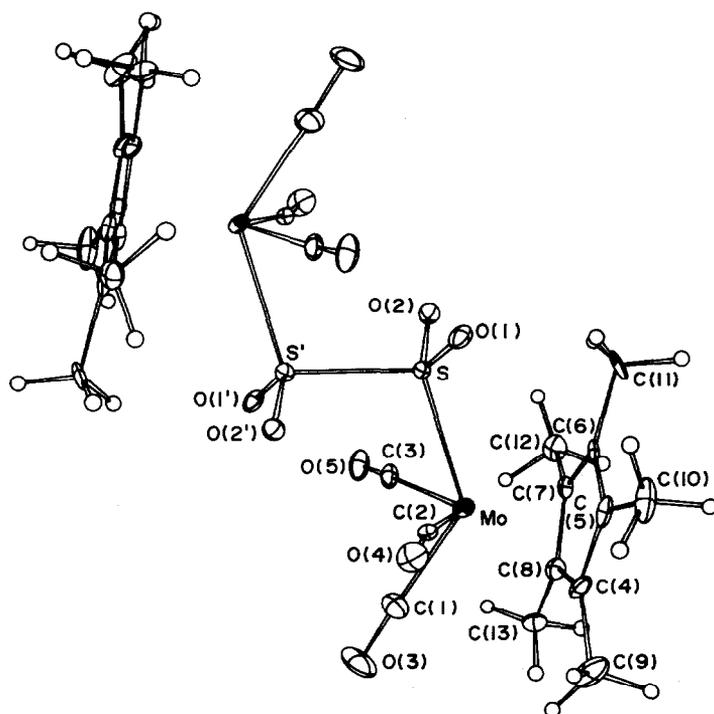


Fig. 9. Structure of  $[\text{Cp}^*\text{Mo}(\text{CO})_3]_2(\text{S}_2\text{O}_4)$ .

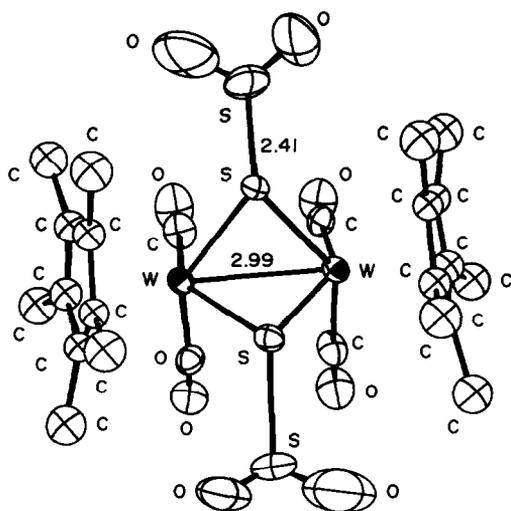


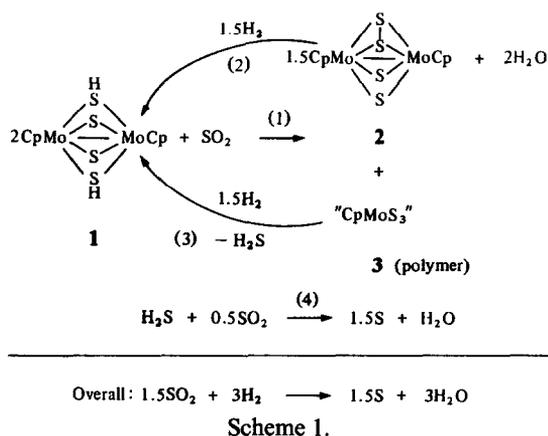
Fig. 10. Structure of  $[\text{Cp}^*\text{W}(\text{CO})_2(\mu\text{-S}\cdot\text{SO}_2)]_2$ .

which readily disproportionate at 25–75°C.<sup>30</sup> One can conclude that the SO<sub>2</sub>H ligand is even more reactive in solution since it could not be observed spectroscopically except at low temperature, where its reactivity was suppressed. Thus, the SO<sub>2</sub>H species would appear to be a key intermediate in the reduction of SO<sub>2</sub> by hydrogen-containing complexes.

#### Hydrogen reduction of SO<sub>2</sub>: the first example of a catalytic homogeneous system

Reduction of SO<sub>2</sub> by H<sub>2</sub> over heterogeneous catalysts is known. An effective heterogeneous catalyst has been found to be Ru–Al<sub>2</sub>O<sub>3</sub> which readily and cleanly promoted hydrogenation to sulfur and H<sub>2</sub>O under mild conditions (150°C, 1 atm), without catalyst poisoning.<sup>41</sup> Catalysis of SO<sub>2</sub> reduction by transition-metal species is a difficult problem in homogeneous systems because of catalyst poisoning by sulfur. As seen in the previous section, metal sulfides and oxysulfides readily form and no well-defined homogeneous systems catalyzed by transition-metal complexes have been reported. However, a possible means to circumvent the sulfiding problem was suggested by a reaction of SO<sub>2</sub> with a metallithiol complex,  $[\text{W}(\text{CO})_5(\text{SH})]^-$ , in which elemental sulfur was found to be produced. Instead of using metal-bound hydrogen to reduce SO<sub>2</sub>, one could conceivably use the active hydrogen contained in SH groups ligated to a sulfur-saturated metal center. Furthermore, a remarkable addition of hydrogen to a dinuclear sulfur-bridged molybdenum complex to form a metallithiol  $[(\text{Me}_n\text{Cp})\text{MoS}(\text{SH})]_2$  (1) has been described in the literature.<sup>42</sup> This SH complex has been found<sup>42</sup>

to homogeneously catalyze the reaction of sulfur with H<sub>2</sub> in CHCl<sub>3</sub> solution to form H<sub>2</sub>S, and one could easily envision extension to SO<sub>2</sub> reduction. Experiments have indeed confirmed room-temperature reaction of SO<sub>2</sub> + H<sub>2</sub>, in a closed flask, to give elemental sulfur and H<sub>2</sub>O under mild conditions (25–75°C, 1–3 atm of H<sub>2</sub>). The stoichiometric reaction of SO<sub>2</sub> with 1 (no H<sub>2</sub>) produces  $(\text{Me}_n\text{Cp})_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-S}_2)$  (2), an insoluble sulfur-rich species  $(\text{Me}_n\text{CpMoS}_3)_x$  (3), and H<sub>2</sub>O. Both 2 and 3 readily react with H<sub>2</sub> to regenerate 1, and H<sub>2</sub>S is also generated from the excess sulfur in 3. In the catalytic system, H<sub>2</sub>S is produced but rapidly reacts with unconsumed SO<sub>2</sub> via the Claus reaction to give the observed products, sulfur and H<sub>2</sub>O. The mechanism of the catalysis conceivably involves the above reactions (see Scheme 1) but is obviously quite complex in nature.



If the catalysis is terminated at or before complete SO<sub>2</sub> consumption, sulfur is the product. If the reaction is allowed to continue (assuming excess H<sub>2</sub> is present), the S<sub>8</sub> is hydrogenated to H<sub>2</sub>S as the final product. Actually, a parallel catalytic cycle based on SO<sub>2</sub> reduction by H<sub>2</sub>S produced from the S<sub>8</sub>–H<sub>2</sub> reaction undoubtedly occurs in addition to the cycle shown in the Scheme 1. Importantly, the catalyst is stable to oxygenation by SO<sub>2</sub>, although the presence of atmospheric oxygen results in  $(\text{Me}_5\text{Cp})_2\text{Mo}_2(\text{O})\text{S}_3$ <sup>43</sup> being formed.

Both reaction (1) and the overall catalysis have been carefully studied in regard to variations in reaction conditions (Table 2). In both instances, SO<sub>2</sub> reduction proceeds at a slow rate if CHCl<sub>3</sub> is used as solvent. However, the rate of catalysis increases several hundred fold (e.g. from 0.4 to 355 turnovers h<sup>-1</sup>) if weakly basic solvents such as alcohols and/or catalytic amounts of Bronsted bases such as amines are present in the catalyst solution. For example, using only 0.04 mmol of 1, 6.1 mmol of SO<sub>2</sub> is cleanly reduced by H<sub>2</sub> (27 mmol, ~3 atm) in 34 min at 75°C in 1:1 butanol–chlorobenzene (25 cm<sup>3</sup>) containing

Table 2. Summary of catalytic reactions of SO<sub>2</sub> (3–8 mmol) and H<sub>2</sub> (12–17 mmol) to give sulfur and H<sub>2</sub>O<sup>a</sup>

| Solvent  | Catalyst<br>[Me <sub>n</sub> CpMoS(SH)] <sub>2</sub> | Temperature<br>(°C) | P <sub>H<sub>2</sub></sub><br>(atm) | Reaction<br>time<br>(h) | Catalyst<br>turnovers<br>h <sup>-1</sup> (average) <sup>b</sup> |
|--|--|---------------------|-------------------------------------|-------------------------|---|
| Toluene  | n = 0  | 60                  | 1.2                                 | 64                      | 0.3   |
| CHCl <sub>3</sub>                              | n = 1  | 65                  | 1.2                                 | 240                     | 0.2   |
| CHCl <sub>3</sub>                              | n = 5  | 75                  | 2.8                                 | 144                     | 0.4   |
| PhCl   | n = 5  | 100                 | 2.8                                 | 5.8                     | 18.4  |
| 4:1 PhCl–BzOH                                  | n = 5  | 20                  | 1.2                                 | 15.5                    | 1.8   |
| 4:1 PhCl–BzOH                                  | n = 5  | 100                 | 1.2                                 | 1.0                     | 34.0  |
| 4:1 PhCl–BuOH                                  | n = 5  | 75                  | 2.8                                 | 1.4                     | 110   |
| 1:1 PhCl–BuOH                                  | n = 5  | 75                  | 2.8                                 | 1.0                     | 203   |
| PhCl + Bu <sub>3</sub> N <sup>c</sup>          | n = 5  | 75                  | 2.8                                 | 1.2                     | 121   |
| 1:1 PhCl–BuOH + Bu <sub>3</sub> N <sup>d</sup> | n = 5  | 75                  | 2.8                                 | 0.6                     | 355   |

<sup>a</sup> Magnetically-stirred in a closed 250- or 500-cm<sup>3</sup> flask, using 0.04–0.1 mmol catalyst in 25–50 cm<sup>3</sup> of solvent.

<sup>b</sup> Based on SO<sub>2</sub> consumption (assuming 2 mmol of catalyst converts 1.5 mmol SO<sub>2</sub>).

<sup>c</sup> 0.1 cm<sup>3</sup> (0.42 mmol).

<sup>d</sup> 0.025 cm<sup>3</sup> (0.105 mmol).

0.1 mmol of Bu<sub>3</sub>N. Similar rate enhancements by weak bases occur for reaction (1) and the Claus reaction [(4)], which also is very slow in CHCl<sub>3</sub> but is known<sup>44</sup> to be promoted by donor solvents (e.g. H<sub>2</sub>O and alcohols) and weak bases. If CHCl<sub>3</sub> is the solvent for the catalysis, the Claus reaction occurs inefficiently mainly along the upper flask walls (sulfur deposition is observed) where H<sub>2</sub>O (from SO<sub>2</sub> reduction) condenses and acts to promote it. If alcohols or small amounts of amines are present in the catalyst solution, the H<sub>2</sub>S–SO<sub>2</sub> reaction [(4)] occurs rapidly and completely in the solution phase. In this context, the reactivities of (μ-SH)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> and Cp<sub>2</sub>Ti(SH)<sub>2</sub>Mo(CO)<sub>4</sub> have been found to be also promoted by bases such as amines.<sup>45</sup> The mechanism for base promotion of reaction (1) may be proton abstraction followed by electrophilic attack of SO<sub>2</sub> on S<sup>-</sup>. In this regard, the complex μ-SH[W(CO)<sub>5</sub>]<sub>2</sub><sup>-</sup> was found to be much more reactive to heterocumulenes (e.g. MeN=C=O) in its deprotonated form,<sup>46</sup> and SO<sub>2</sub> is a type of heterocumulene. Alternatively, initial coordination of SO<sub>2</sub> to the sulfur atom of the SH ligand, similar to Lewis acid coordination of SO<sub>2</sub> to SR ligands in L<sub>n</sub>CuSR,<sup>47</sup> could occur. In both cases, base-assisted proton transfer to an oxygen atom could result in formation of an MSSO<sub>2</sub>H group, giving what amounts to insertion of SO<sub>2</sub> into the S–H bond. Since, as discussed above, the SO<sub>2</sub>H unit is unstable in both RSO<sub>2</sub>H and the MSO<sub>2</sub>H complexes, the proposed MSSO<sub>2</sub>H group would likewise be expected to decompose with eventual formation of H<sub>2</sub>O and polysulfide (S<sub>n</sub><sup>2-</sup>). This is precisely what is

observed [reaction (1) of Scheme 1], since the sulfur-rich product, 3, almost certainly contains polysulfide. The implications of the above chemistry, which has recently been reported,<sup>48</sup> could extend to heterogeneous sulfide catalysts such as hydrodesulfurization catalysts. Thus, we plan to investigate such catalysts for SO<sub>2</sub> reduction and to determine whether bases promote reaction.

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