However, so far only six examples of complexes having linear M_4 geometries[38c] have been reported, which are tabulated in Table V.

Interestingly, the central two metal atoms in all complexes are second- or third-row metals, while nearly all the complexes exhibit a centrosymmetric symmetry. Besides, the presence of strongly bridging ligands seems to be a prerequisite for the stability of these species. It indicates that the R-DAB ligand may form a strong bridge between two metal centers, thereby stabilizing unusual geometries (see Introduction).

Another point worth mentioning is that the present Ru_4 cluster is isoelectronic with $H_2Os_4(CO)_{16}$, a species that was claimed to have a linear structure with two terminally bonded H atoms.[40]

Conclusions

$Ru_2(CO)_5$(R-DAB) reacts readily with molecular hydrogen to yield the oxidative addition product $H_2Ru_2(CO)_5$(R-DAB) in which both H ligands are presumably terminally bonded. This reaction proves that $Ru_2(CO)_5$(R-DAB) indeed reacts like an unsaturated species as has already been indicated by the facile reaction with CO. Further interesting reactions therefore can be expected.

$Ru_3(CO)_8$(neo-Pent-DAB) reacts with molecular hydrogen to yield $H_2Ru_4(CO)_8$(neo-Pent-DAB$)_2$. The observed change in geometry of the metal framework, i.e., from triangular to (unusual) linear, is unprecedented and can only be the result of a rather complex reaction mechanism. The hydrido ligands in the product are presumably terminally bonded which is very uncommon for such ligands bonded to a cluster. The geometry of the cluster indicates again that the R-DAB ligand is a strongly bridging ligand that may stabilize surprising cluster geometries.

Acknowledgment. The X-ray data were kindly collected by D. Heijdenrijk. We thank R. Bregman for recording the mass spectra and J. M. Ernsting for recording the 250-MHZ NMR spectra. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO).

Registry No. $H_2Ru_2(CO)_5$(*i*-Pr-DAB), 97877-19-5; $H_2Ru_2(CO)_5$(c-Hx-DAB), 97877-20-8; $H_2Ru_2(CO)_5$(*t*-Bu-DAB), 97860-65-6; $H_2Ru_2(CO)_5$(c-HxCH_2-DAB), 97860-66-7; $Ru_2(CO)_5$(*i*-Pr-DAB), 90219-26-4; $Ru_2(CO)_5$(c-Hx-DAB), 90219-27-5; $Ru_2(CO)_5$(c-HxCH_2-DAB), 97877-21-9; $Ru_2(CO)_6$(*i*-Pr-DAB), 74552-69-5; $Ru_2(CO)_6$(c-Hx-DAB), 74552-70-8; $Ru_2(CO)_6$(*t*-Bu-DAB), 74552-68-4; $H_2Ru_4(CO)_8$(neo-Pent-DAB$)_2$, 97877-22-0; $Ru_3(CO)_8$(neo-Pent-DAB), 78199-28-7; $Ru_2(CO)_5$(neo-Pent-DAB), 90219-29-7; $H_4Ru_4(CO)_{12}$, 34438-91-0; neo-Pent-DAB, 78198-90-0; H_2, 1333-74-0; Ru, 7440-18-8.

Supplementary Material Available: Table VI, elemental analysis, Table VII, all bond lengths and angles, Table VIII, structure factors, Table IX, anisotropic thermal parameters, and Table X, positional parameters of hydrogen and solvate atoms (15 pages). Ordering information is given on any current masthead page.

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Reduction of SO_2 by $(C_5R_5)M(CO)_3H$ (M = Mo, W; R = H, Me). Chemistry and Structures of $(C_5H_5)Mo(CO)_3(SO_2H)$, the First Example of Insertion of SO_2 into a M–H Bond, and $[(C_5Me_5)Mo(CO)_3]_2(\mu\text{-}S_2O_4)$, an S-Bonded Dithionite Complex

Gregory J. Kubas,* Harvey J. Wasserman, and R. R. Ryan

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

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Addition of SO_2 to solutions of $(C_5R_5)M(CO)_3H$ (R = H, Me; M = Mo, W) has produced the new complexes $(C_5R_5)M(CO)_3(SO_2H)$ and $[(C_5R_5)M(CO)_3]_2(\mu\text{-}S_2O_4)$, depending on reaction conditions. Single-crystal X-ray studies of $CpMo(CO)_3(SO_2H)$ revealed coordination of an unprecedented $-SO_2H$ ligand with the proton being bound to oxygen [Mo–S = 2.521 (2) Å; S–O(1) = 1.637 (6) Å; S–O(2) = 1.515 (6) Å]. The solid is thermally unstable at 20 °C, decomposing to SO_2 reduction products (e.g., metal–sulfide complexes and H_2O), and dissociates in solution to $CpMo(CO)_3H$ and SO_2. The Cp* (= C_5Me_5) analogues are more stable but can be thermolyzed at 75 °C to several oxo/sulfido complexes, e.g., $[Cp^*MO(\mu\text{-}S)]_2$. Prolonged solution reactions of $(C_5R_5)M(CO)_3H$ and SO_2 yield similar products, including the new complexes $[CpW(CO)_3]_2(\mu\text{-}S)$ and $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$. X-ray studies of $[Cp^*Mo(CO)_3]_2(\mu\text{-}S_2O_4)$, a solution-unstable possible intermediate in the above reactions, revealed the first structurally characterized example of a sulfur-bound dithionite ion (C_{2h} symmetry). It exhibits a S–S bond distance of 2.266 (1) Å which is 0.12 Å shorter than that in $Na_2S_2O_4$. Crystallographic data for $CpMo(CO)_3(SO_2H)$: space group $P2_1/c$, $a = 8.224$ (2) Å, $b = 9.902$ (3) Å, $c = 12.889$ (6) Å, $\beta = 100.61$ (3)°; $Z = 4$, $R = 0.049$ for 1618 independent reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 50°$. Crystallographic data for $[Cp^*Mo(CO)_3]_2(S_2O_4)$: space group *Pcab*, $a = 12.513$ (2) Å, $b = 14.000$ (3) Å, $c = 16.763$ (3) Å; $Z = 4$, $R = 0.034$ for 1641 independent reflections.

Introduction

Insertion of small molecules into metal–hydrogen bonds, while not uncommon, is limited to primarily carbon-containing species.[1] Prior to the work reported here, SO_2 insertion into metal–hydride bonds has not been observed despite the fact that insertion into M–R bonds[2] has been

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Table I. Infrared[a] and Proton NMR Data for New Complexes

compd	ν(CO), cm^{-1}	ν(SO), cm^{-1}	ν(OH), δ(OH), cm^{-1}	$\delta(^1H)$[b]
$CpMo(CO)_3(SO_2H)$	2015, 1944	990, 762	2540, 1320	
$CpW(CO)_3(SO_2H)$	2012, 1934	970, 760	2552, 1339	
$CpW(CO)_3(S^{18}O_2H)$	2012, 1934	937, 732	2544, 1336	
$CpW(CO)_3(SO_2D)$	2012, 1934	977, 753	*c*	
$Cp^*Mo(CO)_3(SO_2H)$	2016, 1948, 1924	1003, 753	2540, 1317	2.03 (s, Cp*), 3.89 (s, br, OH)[d]
$Cp^*W(CO)_3(SO_2H)$	2011, 1937, 1911	1000, 754	2550, 1321	~2.0 (s, Cp*), ~4.9 (s, br, O*H*)[e]
$[Cp^*Mo(CO)_3]_2(S_2O_4)$	2030, 1976, 1944	1207, 1027		1.57 (s, Cp*),[f] 2.01 (s, Cp*)[g]
$[Cp^*W(CO)_3]_2(S_2O_4)$	2026, 1964, 1932	1209, 1029		2.13 (s, Cp*)[h]

[a] Nujol mull samples. [b] Me_4Si reference, 300 MHz, unless stated otherwise. [c] Obscured. [d] In liquid SO_2 at -40 °C; intensity ratio, 15:1. [e] In liquid SO_2 at -40 °C, no internal reference. [f] In toluene-d_8 at 0 °C. [g] In liquid SO_2 at ~0 °C (90 MHz). [h] In $CDCl_3$ at 35 °C.

one of the most thoroughly studied areas of metal–SO_2 chemistry. We have been examining the reactions of SO_2 with transition-metal hydride complexes in exploring reductive schemes for conversion of this pollutant to innocuous products such as sulfur and water. Catalytic hydrogenation occurs readily under mild conditions (150 °C, 1 atm) using heterogeneous catalysts, e.g., Ru/Al_2O_3,[3] and we have recently discovered the first example of homogeneous catalysis of the SO_2–H_2 reaction.[4] However, homogeneous reduction of SO_2 with transition-metal hydrides usually terminates with the formation of sulfided metal complexes. This is not surprising in view of the ability of sulfur, SO_2,[2f] and sulfur oxyanions to strongly bind to metals. For example, stoichiometric reduction using Cp_2MH_2 (M = Mo, W) was found to terminate with the formation of a thiosulfate complex, $Cp_2M(S_2O_3)$, and H_2O, representing only partial SO_2 reduction.[5] Nonetheless, knowledge about elementary steps such as hydrogen transfer to an oxygen atom of SO_2 and subsequent elimination of H_2O is lacking, and the attainment of such mechanistic information represents a major aspect of our work.

The first definitively characterized product of insertion of SO_2 into a M–H bond, $CpMo(CO)_3(SO_2H)$, is reported here. This complex and its congeners $(C_5R_5)M(CO)_3(SO_2H)$ (M = Mo, W; R = H, Me) are of special interest since they are quite reactive, spontaneously undergoing auto-redox to SO_2 reduction products, including the new sulfur complexes[6] $[CpW(CO)_3]_2(\mu\text{-}S)$ and $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$ ($Cp^* = C_5Me_5$). A possible intermediate in the reduction, $[Cp^*Mo(CO)_3]_2(\mu\text{-}S_2O_4)$, has been characterized crystallographically and is the first example of a transition-metal dithionite structure. This complex also is unstable toward auto-redox.

Experimental Section

All preparations were carried out in inert or SO_2-containing atmospheres. Metal carbonyls were purchased from Strem Chemicals, Newburyport, MA, and, along with solvents and SO_2, were generally used as received. Acetonitrile was dried over P_2O_5 and stored over molecular sieves. $S^{18}O_2$ was kindly supplied by Dr. David Moody of our group.

$CpM(CO)_3H$,[7] $CpW(CO)_3D$, $Cp^*Mo(CO)_3H$,[8,9] $Cp^*W(CO)_3H$,[9] and $CpM(CO)_2(PR_3)H$[10] were prepared by published procedures. Infrared, NMR, and mass spectra were recorded on Perkin-Elmer 521, Varian EM-390 or Bruker WM300, and Bendix MA-2 (time-of-flight) instruments, respectively. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $CpM(CO)_3(SO_2H)$ (M = Mo, W), $CpW(CO)_3(SO_2D)$, and $CpW(CO)_3(S^{18}O_2H)$. A concentrated solution of the hydride (or deuteride) in diethyl ether (about 2–3 mL/g) was treated at 0 °C with a stream of SO_2 gas for ca. 1–2 min. The solution initially turned red, soon followed by precipitation of yellow-orange $CpM(CO)_3(SO_2H)$ in 50–70% yield. The microcrystalline solid was collected by filtration, washed with several portions of 2:1 heptane–ether, and dried in vacuo. Because of the thermal instability of the complexes, the above procedures were carried out without excessive delays and the products were stored at -20 °C or lower. The ^{18}O-substituted complex was prepared by condensation of $S^{18}O_2$ into a flask containing $CpW(CO)_3H$ solution on a vacuum line and warming to 0 °C.

Preparation of $Cp^*M(CO)_3(SO_2H)$ (M = Mo, W). Synthesis of the Cp* analogue was similar to that above, except about 5 mL of solvent per gram of hydride was used and yields were 75–80%. The product was air stable for short periods and was also considerably more thermally stable than the Cp analogues. The solvent was found to be a crucial factor for M = W. Reasonably good results were attained by using 1:1 $MeCN$–Et_2O (20 mL) to dissolve the $Cp^*W(CO)_3H$ (2.333 g, 5.77 mmol). Addition of excess SO_2 at 0 °C gave a precipitate of $Cp^*W(CO)_3(SO_2H)$ within a few minutes, which was filtered off and washed with Et_2O after further stirring for 5 min. The bright orange product weighed 1.396 g (52% yield) and was stable in air at 20 °C for at least 5 days.

Preparation and Auto-Redox Reaction of $[Cp^*Mo(CO)_3]_2(S_2O_4)$. $Cp^*Mo(CO)_3H$ (1.08 g) in CH_3CN (55 mL) was treated at 0 °C with excess SO_2. The red solution was allowed to stand undisturbed for ca. 30 min at 0 °C then overnight at -20 °C. Orange prismatic crystals (0.40 g, 31% yield) of $[Cp^*Mo(CO)_3]_2(S_2O_4)$ formed and were filtered off, washed thoroughly with 1:1 Et_2O–CH_3CN, and dried in vacuo. A mixture of the dithionite crystals and thin flaky crystals of $Cp^*Mo(CO)_3(SO_2H)$ was obtained if the solution was higher in concentration or not kept at 0 °C for 30 min. Water was found to be formed in these reactions.

The dithionite is relatively air stable but rapidly converts in solution to new species. NMR in toluene-d_8 showed that the singlet Cp* peak (Table I) was replaced within minutes by two new peaks of equal intensity (δ 1.61, 1.81), which then were replaced (15 min, 35 °C) by seven new peaks, predominantly one due to $[Cp^*Mo(CO)_3]_2$. After 5 days, mainly $[Cp^*Mo(O)(\mu\text{-}S)]_2$ and A (see below) remained, but only trace amounts of $[Cp^*Mo(CO)_3]_2$ were present, indicating it is an intermediate and

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not a final product of the overall reaction.

A sample of $[Cp^*Mo(CO)_3]_2(S_2O_4)$ (57 mg, 0.075 mmol) was heated to 75–80 °C overnight, resulting in virtually complete conversion to a product mixture similar to the above final mixture. Analysis of the evolved gases showed 0.34 mmol of CO, 0.075 mmol of CO_2, and traces of COS and SO_2. Thus, about 92% of the CO originally present in the complex was evolved or oxidized to CO_2.

Preparation of $[Cp^*Mo(CO)_3]_2(S_2O_4)$ from $Na[Cp^*Mo(CO)_3]$ and SO_2. A slurry of 0.2 g (0.31 mmol) of $[Cp^*Mo(CO)_3]_2$ in 8 mL of dry THF was reacted with excess sodium (oil dispersion). Filtration and reaction of the $Na[Cp^*Mo(CO)_3]$ solution with excess SO_2 at 0 °C gave immediate deep red coloration. The reaction mixture was allowed to stand for 15 min at 0 °C and at −20 °C for 2 days. The precipitate that formed was collected, washed with benzene (2 × 10 mL), and found to consist of a mixture of 75 mg (32% yield) of $[Cp^*Mo(CO)_3]_2S_2O_4$ and 43 mg of a light gray, sandlike solid. The latter was water soluble and readily removable from the dithionite complex; it possessed IR bands consistent with $Na_2S_2O_4$.

Formation of $[Cp^*W(CO)_3]_2(S_2O_4)$ and $[CpMo(CO)_3]_2(S_2O_4)$. The filtrate from the preparation of $Cp^*W(CO)_3(SO_2H)$ was allowed to stand in a freezer overnight, yielding a small quantity (ca. 0.1 g) of orange crystals contaminated by dark brown crystals of unknown composition. The IR (Table I) of the orange crystals was nearly identical with that of $[Cp^*Mo(CO)_3]_2(S_2O_4)$. Attempts to prepare $[Cp^*W(CO)_3]_2(S_2O_4)$ in better yield failed. As for the Mo analogue, solutions decomposed (10 min, 35 °C, $CDCl_3$) to a mixture of products.

Small amounts of an orange complex with IR bands (Table I) appropriate for $[CpMo(CO)_3]_2(S_2O_4)$ were produced from reactions of $CpMo(CO)_3H$ and excess SO_2 in MeCN or toluene–heptane (1:1) at 0 to −20 °C. The reaction of $Na[CpMo(CO)_3]$ and SO_2 in THF gave no dithionite even at −45 °C.

Thermolysis of $CpMo(CO)_3(SO_2H)$. A sample of $CpMo(CO)_3(SO_2H)$ (0.49 g, 1.58 mmol) was placed into a 50-mL flask, which was evacuated, closed off, and allowed to stand overnight. The solid became dark red and released a mixture of volatile products (ca. 1.2 mmol), mass spectral analysis of which showed mostly CO, plus smaller quantities of SO_2, H_2O, CO_2, and COS. Passage of the gas through a −196 °C trap on a vacuum line allowed removal of CO; passage of the trap contents through a −95 °C trap allowed separation of water (0.3 mmol) from the SO_2, CO_2, and COS mixture (0.19 mmol total). Since a significant fraction of gas had been utilized for the initial mass spectral analysis, these quantities are proportionately low. The solid residue (0.395 g) contained primarily $[CpMo(CO)_3]_2$ from IR evidence; a 0.35-g sample was extracted with 5 mL of Me_2SO (in which the dimer is nearly insoluble), and the extract was found to contain ca. 0.1 g of Cp-containing complexes of uncharacterized composition. NMR in $Me_2SO\text{-}d_6$ showed Cp resonances at δ 5.80, 6.18, 6.27, and 6.46.

Thermolyses of $CpW(CO)_3(SO_2H)$, $CpW(CO)_3(SO_2D)$, and $CpW(CO)_3(S^{18}O_2H)$. The experiments were carried out as for the Mo species except that elevated temperatures (e.g., 55 °C overnight) were required. As an average for samples of all three isotopic species, 1.9 mmol of volatiles (CO, H_2O, SO_2, CO_2, COS) were released per millimole of complex, of which 0.24 mmol was determined to be H_2O and 0.25 mmol to be SO_2, CO_2, and COS. In the case of the SO_2D complex, D_2O (plus HDO from adventitious H_2O) was observed to be a product, while for the $S^{18}O_2H$ case, a ca. 70:30 $H_2{}^{18}O$–$H_2{}^{16}O$ mixture was produced. The CO_2 isotopes consisted primarily of $C^{16}O^{18}O$, but only negligible amounts of $C^{18}O$ and $C^{18}OS$ were found in the gaseous products. The major solid product was $[CpW(CO)_3]_2$ and minor products included species containing W═O bonds since IR bands observed at 916 and 933 cm^{-1} typical of $\nu_{W=O}$ shifted to 874 and 887 cm^{-1} for the ^{18}O analogues.

Reaction of $CpMo(CO)_3H$ with SO_2 in 4:1 Ratio in CH_3CN. A solution of 1.726 g (7.01 mmol) of $CpMo(CO)_3H$ in dry CH_3CN (5–6 mL) was treated with 1.75 mmol of SO_2 in a closed 25-mL flask on a vacuum line. The solution rapidly became deep red and began to deposit a crystalline precipitate within 0.5 h. After 18 h, the flask was cooled with liquid nitrogen for 15 min and opened to a manometer. Analysis of the gases showed ca. 0.93 mmol of CO and negligible H_2. Further fractionation of the products revealed 0.02 mmol of CO_2 and no unreacted SO_2 or $CpMo(CO)_3H$ (in the case of a 2:1 reaction, unreacted SO_2 was found). The amount of H_2O product was determined by Karl-Fischer titration to be 3.09 mmol, 88% of the amount expected from reduction of the SO_2.

The residue from solvent removal weighed 1.675 g, consisting primarily (ca. 1.47 g) of $[CpMo(CO)_3]_2$. Elemental analysis of the residue showed 36.47% C, 2.30% H, 38.59% Mo, and 3.26% S. The amount of sulfur thus corresponded to 97.5% of the amount of sulfur originally present as SO_2, and the amount of Mo was 96% of that in the $CpMo(CO)_3H$. No elemental sulfur was present, but a mixture of Mo–S complexes (ca. 0.2 g) was separated from the $[CpMo(CO)_3]_2$ by dissolving away the latter in hot toluene (60 mL). The remaining brown solid was soluble in Me_2SO; NMR analysis showed Cp resonances identical with those found for the thermolysis of $CpMo(CO)_3(SO_2H)$. Infrared data indicated the presence of weak to medium bands due to Mo═O (913, 930 cm^{-1}) and CO (2020, 1955, 1885 cm^{-1}).

Reactions of $(C_5R_5)M(CO)_2(P)H$ ($P = P(OPh)_3$, $P\text{-}n\text{-}Bu_3$, PPh_2Me) with SO_2. A solution of $CpW(CO)_2[P(OPh)_3]H$ in CH_3CN saturated with SO_2 showed no reaction after 1 day. In liquid SO_2, immediate red coloration occurred and a red-brown precipitate formed overnight. IR indicated that the latter was a mixture and no further characterization was performed.

A benzene solution of $Cp^*Mo(CO)_2[P(OPh)_3]H$, formed by reaction of $Cp^*Mo(CO)_3H$ and $P(OPh)_3$ overnight, was treated with SO_2. No reaction occurred even after 3 days.

$CpW(CO)_2(PR_3)H$ ($PR_3 = P\text{-}n\text{-}Bu_3$, PPh_2Me), isolated as oils from reaction of the hydride and PR_3 in benzene at 65 °C for 2 days, were treated with SO_2 in MeCN (R = n-Bu) or toluene. Immediate red coloration resulted, followed by slow precipitation of reddish solids. In the $P\text{-}n\text{-}Bu_3$ case, the product was a small amount of an insoluble oxo species (ν(W═O) = 935, 926 cm^{-1}) shown by IR and elemental analysis to contain no phosphine or CO. IR and NMR of the product from the PPh_2Me complex indicated that it was a mixture of species containing phosphine and CO.

Reaction of $CpW(CO)_3H$ with SO_2 in 2:1 Ratio in CH_3CN. Isolation of $[CpW(CO)_3]_2(\mu\text{-}S)$. The hydride (1.618 g, 4.84 mmol) in CH_3CN (5 mL) was treated with 2.46 mmol of SO_2 in a similar manner to the $CpMo(CO)_3H$ reaction. About 2-mmol total of gas was found to be produced, mostly CO, some CO_2, but only a trace of COS. No unreacted SO_2 was found; a small amount of unreacted hydride was present, estimated to be less than 10% of the original amount. The crystalline precipitate was collected by filtration and weighed 1.24 g; extracted with 25 mL of SO_2-saturated CH_3CN[11] left 0.56 g of undissolved material identified to be primarily $[CpW(CO)_3]_2$. Solvent volume reduction to 5 mL and addition of CH_3OH (25 mL) yielded 0.54 g (32%) of a green solid identified to be $[CpW(CO)_3]_2(\mu\text{-}S)$. Minor amounts of several other complexes were also found to be present in the extract and the CH_3CN filtrate of the reaction mixture. Solvent removal from the latter gave 0.24 g of solid residue, consisting mostly of $[CpW(CO)_3]_2$ and smaller amounts of species containing W═O functionality (ν = 916, 933 cm^{-1}).

Thermolysis of $Cp^*Mo(CO)_3(SO_2H)$. A 0.426-g (1.12-mmol) sample was heated to 70 °C in a 50-mL flask overnight. Analysis as above showed that 2.85 mmol of volatiles were produced: approximately 2.1 mmol of CO, 0.34 mmol of H_2O, 0.37 mmol of CO_2 and COS, and only a trace of SO_2. NMR of the light brown residue in benzene displayed three predominant Cp* peaks (δ 1.78, 1.73, 1.71) and two minor resonances (δ 2.03 and 1.86). The 1.71 ppm peak was due to $[Cp^*Mo(CO)_3]_2$, confirmed to be present by IR data (ν_{CO} = 1927, 1897, 1871 cm^{-1}). IR also showed $\nu_{M=O}$ at 913 and 900 cm^{-1}.

The residue from a separate decomposition was chromatographed on alumina. A benzene solution (filtered to remove sparingly soluble $[Cp^*Mo(CO)_3]_2$) was placed onto the column, and elution with CH_2Cl_2 gave an initial orange band of $[Cp^*Mo(CO)_3]_2$ closely followed by a second orange band. Solvent removal from the latter and recrystallization from benzene-heptane yielded red-orange microcrystals identified to be

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[11] The precipitate contained dark green crystals of $[CpW(CO)_3]_2(\mu\text{-}S)$ which reversibly forms a more soluble red SO_2 adduct in SO_2-saturated CH_3CN. Solvent removal in vacuo removes the weakly bonded SO_2, which is believed to coordinate to the sulfide ligand.[6]

$[Cp^*MoO(\mu\text{-}S)]_2$ by IR ($\nu_{M=O}$ = 900 cm^{-1}; lit.[8] 900, 907 cm^{-1}), NMR ($\delta_{C_6H_6}$ 1.78), and elemental analysis (Table Is). An orange band near the top of the column was eluted with acetone. Solvent removal and recrystallization of the orange residue gave red-orange crystals, exhibiting two closely spaced Cp* resonances (δ 1.73, 1.72) of unequal intensity and $\nu_{M=O}$ at 913 and 904 (sh) cm^{-1}. No carbonyl absorptions were present. Elemental analysis and molecular weight measurement (Table Is) indicated that the complex A possessed the formula $Cp^*_3Mo_3O_4S_2$.

Thermolysis of $Cp^*W(CO)_3(SO_2H)$. A sample (0.452 g, 0.965 mmol) was heated to 75 °C overnight as above, giving 2.5 mmol of volatiles (H_2O, 0.34 mmol; CO_2 + COS + SO_2, 0.45 mmol; CO, 1.7 mmol). The amount of CO released as gas was ca. 75% of the amount originally present in the complex, the same as for the Mo analogue above. A small amount of $CpW(CO)_3H$ sublimed along the flask walls. NMR of the residue showed 16 bands due to Cp* at δ 1.87–2.19 in $CDCl_3$, none of which corresponded to that for $[Cp^*W(CO)_3]_2$ or $[Cp^*W(CO)_2]_2$.

Reaction of $Cp^*Mo(CO)_3H$ with SO_2 in 4:1 Ratio in Benzene. This experiment was carried out as for the Cp analogue, using 1.759 g (5.56 mmol) of complex, 1.39 mmol of SO_2, and 10 mL of benzene in a 100-mL flask. The initially homogeneous solution produced a crystalline precipitate, and after 3 days the flask contents were analyzed. At least 20% of the hydride was found to be unreacted (recovered by sublimation) and no unreacted SO_2 was present. Gases noncondensable at −196 °C totaled 2.7 mmol and were principally CO and a trace of H_2. CO_2 and COS (0.35-mmol total) were also recovered. Karl-Fischer titration revealed that 1.55 mmol of H_2O was recovered, 70% of the amount expected based on the observed $Cp^*Mo(CO)_3H$ consumption.

A sample of the solid residue (after being heated to 60 °C to sublime off $Cp^*Mo(CO)_3H$) gave NMR signals in benzene corresponding to mainly $[Cp^*Mo(CO)_3]_2$ plus several other species. Extraction of the residue with 4 mL of benzene left 0.79 g of undissolved $[Cp^*Mo(CO)_3]_2$. Solvent removal from the filtrate yielded 0.35 g of a mixture shown by NMR and IR to contain, in order of predominance, $[Cp^*MoO(\mu\text{-}S)]_2$, A, $[Cp^*Mo(CO)_3]_2$, and unidentified complexes.

Reaction of $Cp^*W(CO)_3H$ and SO_2 in MeCN–Et_2O. Preparation of $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$. The reaction of SO_2 with 2.1 g of $Cp^*W(CO)_3H$ in 35 mL of 1:1 MeCN–Et_2O for 5 days yielded large spear-shaped dark green crystals (0.806 g, 32%) along with a small amount of brown impurity. The latter was washed away with benzene and MeCN, leaving the elongated crystals, identified by X-ray crystallography to be $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$.[6] The impurity included the known complex $Cp^*_2W_2(CO)_2S_3$,[12] identified by comparison of IR and NMR spectra with an authentic sample, along with an oxo complex (δ_{CDCl_3} 2.11; ν(W=O) = 921 cm^{-1}).

Structure Determinations. Pertinent information concerning crystal data and intensity measurements is given in Table II. A needlelike crystal of $CpMo(CO)_3(SO_2H)$, approximately 0.3 mm long, was wedged into a 0.2-mm thin-walled glass capillary. Data collection for $[Cp^*Mo(CO)_3]_2(S_2O_4)$ was carried out by using a crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm, mounted in air on a thin glass fiber. The $Cp^*Mo(CO)_3(SO_2H)$ sample was cooled (−30 °C) with use of the Nonius Universal low-temperature device to arrest decomposition. All data were collected with use of the CAD4 automated diffractometer interfaced to a Digital Corp. PDP11/23 (LSI 11/23) computer. The diffractometer was equipped with a 0.3-mm diameter collimator and a 4.0-mm vertical detector slit. Cell constants were determined from a least-squares fit to the setting angles of 25 high-order reflections, located by an automatic search routine and centered at least two times. Scan speeds during data collection were variable and were determined by a fast (~6° min^{-1}) prescan. Final scan speeds ranged from 6 to 0.9° min^{-1}. The total scan range for each reflection was determined by the equation $\Delta\theta = A + B \tan\theta$, where A was set to 1.0° and B was set to 0.35°. The first and last 25% of each scan was taken as background. The intensity of two strong reflections were monitored after every 7200 s of X-ray exposure; only random (±2%) variations were observed. Additionally, an orientation check using two reflections was performed after every 200 reflections and automatic recentering was performed if the difference between calculated and observed scattering vector for either reflection exceeded 0.1°. Absorption corrections for both crystals were carried out by measuring a ψ scan of a strong, close-to-axial reflection.

Table II. Experimental Data for the X-ray Diffraction Analysis of $CpMo(CO)_3(SO_2H)$ and $[Cp^*Mo(CO)_3]_2(S_2O_4)$

	$CpMo(CO)_3$-(SO_2H)	$[Cp^*Mo(CO)_3]$-(S_2O_4)
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	$Pcab$
a, Å	8.224 (2)	12.513 (2)
b, Å	9.902 (3)	14.000 (3)
c, Å	12.889 (6)	16.763 (3)
β, deg	100.61 (3)	
V, Å^3	1031.6	2936.7
Z	4	4 (dimers)
ρ(calcd), g cm^{-3}	2.00	1.72
μ, cm^{-1}	14.3	10.2
T, °C	−30 (3)	+25
Measurement of Data		
diffractometer	Enraf-Nonius CAD-4	
radiatn	Mo Kα (λ = 0.709 30 Å)	
monochromator	highly oriented graphite	
reflctns measd	$+h,+k,\pm l$	
2θ range, deg	$\leqslant 50$	$\leqslant 45$
scan type	coupled θ(cryst)–2θ(counter)	
scan speed, deg min^{-1}	variable	
independent no. reflns, $I \geqslant 2.0\sigma(I)$	1618	1641
total no. of reflections	1861	2574

Standard Patterson, difference-Fourier and full-matrix least-squares refinement methods were used to solve both structures. The function $\sum w(F_o - F_c)^2$ was minimized where $w = 1/(\sigma_c(F) + 0.015F^2)^2$ and $\sigma_c(F)$ is based on counting statistics. Calculated structure factor amplitudes included analytical scattering factors for appropriate neutral atoms, modified by both real and imaginary components of anomalous dispersion.[13] Calculations were performed on a CDC 7600 computer utilizing an in-house package of programs developed by Dr. A. C. Larson.

$CpMo(CO)_3(SO_2H)$. All hydrogen atoms in this structure were located and refined. It was necessary to hold the thermal parameter for H(1) fixed (3.0). Convergence was reached with an unweighted R_1 value of 4.9%. The final model consisted of 160 parameters (anisotropic temperature factors for all non-hydrogen atoms) and included an isotropic correction for the effects of secondary extinction.[14] Final positional and thermal parameters are listed in Tables III and IIs.

$[Cp^*Mo(CO)_3]_2(S_2O_4)$. This structure was solved by using the MULTAN80 system. All hydrogen atoms were located from ΔF calculations but were fixed in the positions thus obtained and assigned isotropic thermal parameters of 3.5 Å^2. Refinement proceeded smoothly to convergence with an unweighted R value of 3.4%. Anisotropic thermal parameters were included for all non-hydrogen atoms (181 parameters). There was no evidence for secondary extinction. Final positional and thermal parameters may be found in Tables IV and IIIs.

Results

Reactions of $CpM(CO)_3H$ with SO_2. Formation and Thermolysis of $CpM(CO)_3(SO_2H)$. The hydride complexes, $CpM(CO)_3H$ (M = Mo, W), were found to react with SO_2, both in liquid SO_2 and organic solvents, to give rapid color changes (light yellow → red) followed by slow decomposition to $[CpM(CO)_3]_2$ and other products. Suf-

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[12] Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107.

[13] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Table 2.2A; Cromer, D. T., Table 2.3.1.

[14] (a) deMeulenaer, J.; Tompa, H. *Acta Crystallogr.* **1964**, *19*, 1014. (b) Templeton, L. K.; Templeton, D. H. "Abstracts of Papers", American Crystallographic Association Summer Meeting, Storrs, CT, June 1973, No. E10.

Table III. Fractional Coordinates and Thermal Parameters for $(\eta^5\text{-}C_5H_5)Mo(CO)_3(SO_2H)$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.29222 (7)	0.02130 (6)	0.25636 (5)		S(1)	0.0927 (2)	0.0353 (2)	0.3829 (2)	
O(1)	0.2113 (7)	0.0716 (6)	0.4959 (4)		O(2)	0.0222 (8)	−0.1040 (5)	0.3949 (4)	
C(1)	0.5352 (10)	0.0421 (8)	0.2679 (6)		O(3)	0.6797 (7)	0.0565 (6)	0.2752 (5)	
C(2)	0.3712 (10)	−0.1261 (8)	0.3647 (6)		O(4)	0.4124 (8)	−0.2079 (6)	0.4243 (5)	
C(3)	0.3348 (9)	0.2011 (8)	0.3252 (6)		O(5)	0.3560 (7)	0.3068 (5)	0.3628 (4)	
C(4)	0.1715 (13)	−0.1271 (9)	0.1181 (7)		C(5)	0.0446 (11)	−0.0480 (10)	0.1475 (7)	
C(6)	0.0746 (11)	0.0881 (9)	0.1245 (6)		C(7)	0.2197 (12)	0.0914 (9)	0.0821 (6)	
C(8)	0.2781 (12)	−0.0377 (10)	0.0788 (7)		H(1)	0.2534 (135)	−0.0104 (87)	0.5255 (79)	3.00 (0)
H(2)	0.1802 (137)	−0.2250 (106)	0.1336 (81)	4 (3)	H(3)	−0.0506 (123)	−0.0689 (94)	0.1657 (75)	3 (2)
H(4)	0.0181 (99)	0.1532 (77)	0.1313 (58)	1 (2)	H(5)	0.2097 (176)	0.1508 (130)	0.04 (99)	7 (4)
H(6)	0.3618 (161)	−0.0355 (121)	0.0573 (96)	6 (4)					

[a] Anisotropic thermal parameters are listed as Table IIs in the supplementary material.

Table IV. Fractional Coordinates for $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]_2S_2O_4$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.31342 (3)	0.49290 (3)	0.38467 (2)		S(1)	0.41191 (9)	0.50959 (11)	0.51340 (7)	
O(1)	0.3885 (3)	0.4329 (3)	0.5709 (2)		O(2)	0.4061 (3)	0.6066 (2)	0.5467 (2)	
C(1)	0.3714 (5)	0.4679 (4)	0.2769 (4)		O(3)	0.4018 (4)	0.4507 (4)	0.2140 (3)	
C(2)	0.3780 (4)	0.3607 (4)	0.3943 (3)		O(4)	0.4028 (3)	0.2819 (3)	0.3930 (3)	
C(3)	0.3995 (5)	0.6140 (4)	0.3652		O(5)	0.4330 (3)	0.6874 (3)	0.3494 (2)	
C(4)	0.1482 (5)	0.4442 (4)	0.3435 (4)		C(5)	0.1499 (4)	0.4330 (4)	0.4284 (4)	
C(6)	0.1596 (4)	0.5261 (4)	0.4620 (3)		C(7)	0.1659 (4)	0.5936 (3)	0.3993 (3)	
C(8)	0.1595 (5)	0.5437 (4)	0.3250 (4)		C(9)	0.1244 (6)	0.3658 (4)	0.2854 (5)	
C10)	0.1299 (5)	0.3434 (5)	0.4743 (4)		C(11)	0.1546 (4)	0.5487 (5)	0.5502 (3)	
C(12)	0.1668 (4)	0.7014 (4)	0.4096 (3)		C(13)	0.1530 (4)	0.5909 (4)	0.2450 (3)	
H(1)	0.0460 (0)	0.3550 (0)	0.2816 (0)	3.500 (0)	H(2)	0.1516 (0)	0.3857 (0)	0.2298 (0)	3.500 (0)
H(3)	0.1621 (0)	0.3056 (0)	0.3003 (0)	3.500 (0)	H(4)	0.1708 (0)	0.3416 (0)	0.5248 (0)	3.500 (0)
H(5)	0.0521 (0)	0.3339 (0)	0.4846 (0)	3.500 (0)	H(6)	0.1569 (0)	0.2953 (0)	0.4357 (0)	3.500 (0)
H(7)	0.1763 (0)	0.6179 (0)	0.5534 (0)	3.500 (0)	H(8)	0.0800 (0)	0.5386 (0)	0.5724 (0)	3.500 (0)
H(9)	0.2048 (0)	0.5066 (0)	0.5821 (0)	3.500 (0)	H(10)	0.2085 (0)	0.7167 (0)	0.4588 (0)	3.500 (0)
H(11)	0.2164 (0)	0.7262 (0)	0.3552 (0)	3.500 (0)	H(12)	0.0907 (0)	0.7165 (0)	0.3985 (0)	3.500 (0)
H(13)	0.1455 (0)	0.5410 (0)	0.2080 (0)	3.500 (0)	H(14)	0.0811 (0)	0.6163 (0)	0.2413 (0)	3.500 (0)
H(15)	0.2101 (0)	0.6508 (0)	0.2327 (0)	3.500 (0)					

[a] Anisotropic thermal parameters are listed as Table IIIs in the supplementary material.

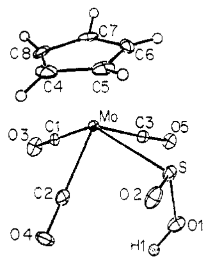


Figure 1. ORTEP projection of $CpMo(CO)_3(SO_2H)$.

ficiently concentrated solutions of the hydrides in toluene or diethyl ether initially yielded orange microcrystalline precipitates within seconds according to eq 1. This reaction

$$CpM(CO)_3H + SO_2 \xrightarrow{Et_2O} CpM(CO)_3(SO_2H) \quad (1)$$

action did not occur for the P-donor-substituted complexes $CpM(CO)_2(P)H$ (P = $P(OPh)_3$, P-*n*-Bu_3, or PPh_2Me). Prompt filtration allowed isolation of the insertion-type products, which gave Nujol mull IR spectra with bands indicative of a coordinated SO_2H ligand. X-ray crystallography of $CpMo(CO)_3(SO_2H)$ confirmed that an S-bound [1,2] insertion occurred (Figure 1). The SO_2 could be readily and completely extruded merely by dissolving the complexes in organic solvents. Unless excess SO_2 was present, proton NMR spectra of the resulting solutions showed peaks due only to $CpM(CO)_3H$ even at −50 °C. The solid complexes were thermally unstable, undergoing auto-redox within 1 day (25 °C for M = Mo; 55 °C for M = W) to products indicative of $S^{IV} \rightarrow S^{II-}$ reduction and metal oxidation (eq 2). In addition to predominant quantities of $[CpM(CO)_3]_2$, several uncharacterized sulfur- and/or oxo-containing complexes formed (represented by $[CpMS_xO_y]_n$), at least some of which were oligomeric on analogy with the characterized products of thermolysis of the Cp* congeners (see below). Mass spectral analysis and *P–V–T* measurements indicated the gaseous products consisted primarily of CO (0.5–1.5 mmol/mmol of complex), along with trace quantities of SO_2, CO_2, and COS. Isotopic substitution [$CpW(CO)_3(SO_2D)$ and $CpW(CO)_3(S^{18}O_2H)$] confirmed that the H_2O is derived from the SO_2H moiety and that the small quantities of CO_2 and COS formed result from oxidation of CO by SO_2 or SO_2H-derived species. Neither H_2 nor free sulfur were detected; the majority of the sulfur remained metal coordinated.

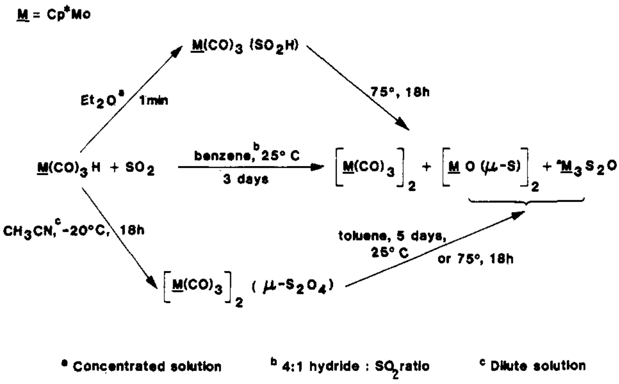
$$CpM(CO)_3(SO_2H) \xrightarrow{\Delta} [CpM(CO)_3]_2 + [CpMS_xO_y]_n + H_2O + CO \quad (2)$$

Stoichiometric reactions of the hydride complexes and SO_2 in acetonitrile solution were also carried out (eq 3), resulting in complete reduction of SO_2 for 4:1 ratios of hydride to SO_2.

$$4CpMo(CO)_3H + SO_2 \xrightarrow{CH_3CN} {}^7/_4[CpMo(CO)_3]_2 + {}^1/_2\text{“}CpMoS_2\text{”} + 2H_2O + CO \quad (3)$$

NMR evidence showed that the “$CpMoS_2$” was actually a mixture of several complexes similar in identity to those found in eq 2 for M = Mo. IR data indicated the presence of only minor amounts of Mo=O and carbonyl functionality in the products. Karl Fischer titration showed that the amount of water produced was nearly quantitative. In the case of reaction of $2CpM(CO)_3H$ per SO_2, nearly half of the SO_2 remained unreacted for M = Mo, but essentially complete disappearance of both reactants resulted for M = W. The products for M = W were similar to those observed in eq 2 and 3 although somewhat more oxo-

Scheme I. Summary of Reactions Involving Cp*Mo Complexes



containing products were formed than for M = Mo. One of the sulfur complexes was isolated in 32% yield and found to possess the structure $Cp(CO)_3W$-S-$W(CO)_3Cp$.[6] The analogous Se complex was reported by Jennings and Wojcicki.[15] The deep green sulfide complex is unusual in that it contains a bent, unsupported sulfide bridge (W-S-W = 127°). It is thermally unstable to CO loss at 90 °C and forms a weakly coordinated SO_2 adduct, $[CpW(CO)_3]_2(\mu\text{-}S\cdot SO_2)$.[6] The Mo analogue $[CpMo(CO)_3]_2(\mu\text{-}S)$ is unstable in solution at 20 °C which explains why it was not observed to be a product of eq 3. It undoubtedly is an intermediate since small quantities were observed to be produced when reaction 3 was carried out at −20 °C.

Reactions of $Cp^*M(CO)_3H$ with SO_2. Formation and Thermolysis of $Cp^*M(CO)_3(SO_2H)$. The insertion complexes were prepared as in eq 1 and were much more thermally stable than the Cp analogues. At room temperature, the solid tungsten complex was air stable for days. However, it still completely dissociated in solution to $Cp^*W(CO)_3H$ and SO_2. It was necessary to heat $Cp^*M(CO)_3(SO_2H)$ to 75 °C overnight to give decomposition according to eq 2. For M = Mo, only three principal complexes formed in roughly equal amounts: $[Cp^*Mo(CO)_3]_2$, the known oxo complex $[Cp^*MoO(\mu\text{-}S)]_2$,[8] and an oxo species, A, of composition $Cp^*_3Mo_3S_2O_4$ (Scheme I). Only a trace of SO_2 was evolved. In contrast, $Cp^*W(CO)_3(SO_2H)$ gave very little $[Cp^*W(CO)_3]_2$, along with several oxo complexes (four strong ν(W=O) bands at 900–940 cm^{-1}). Small amounts of the known complex $Cp^*_2W_2(CO)_2(\mu\text{-}S)_2S$[12] were also produced as was at least one other CO-containing complex (ν(CO) = 2003, 1924 sh, 1837 cm^{-1}).

Prolonged solution reactions of $Cp^*Mo(CO)_3H$ with SO_2 (4:1) were carried out in benzene since the complex reacts with CH_3CN.[9] Although the reaction was slower (3 days) and less complete (20% of the hydride was unreacted), the results were similar to those for the the Cp analogue. Proportionately more CO and oxo complexes, but less $[Cp^*Mo(CO)_3]_2$, were formed than in eq 3. As in the thermolysis of $Cp^*Mo(CO)_3(SO_2H)$, the major products were $[Cp^*MoO(\mu\text{-}S)]_2$, A, and $[Cp^*Mo(CO)_3]_2$. Karl Fischer titration showed that the yield of H_2O was approximately 70% of that expected based on the amount of hydride consumed.

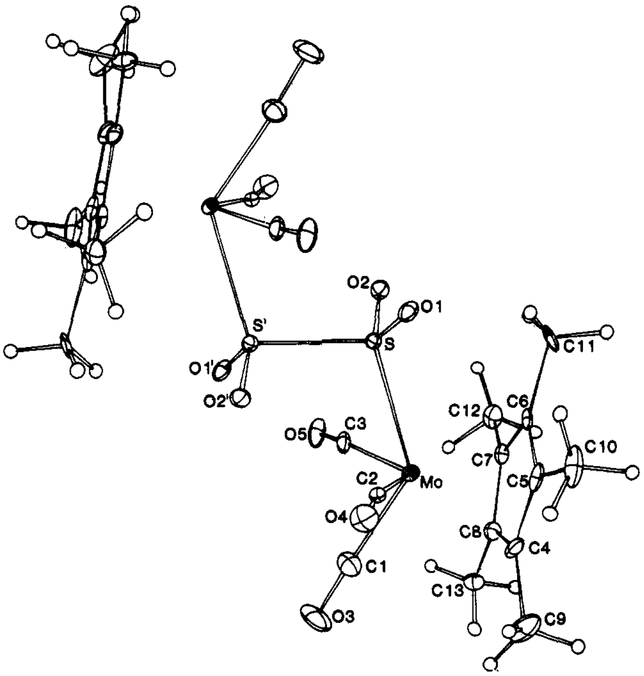
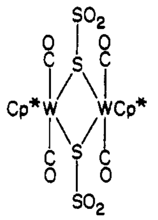


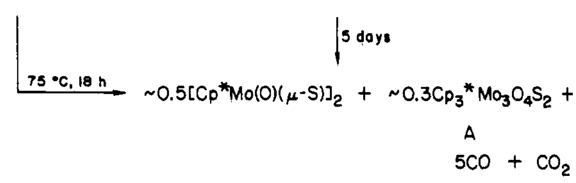
Figure 2. ORTEP projection of $[Cp^*Mo(CO)_3]_2(S_2O_4)$.

The reduction of SO_2 by $Cp^*W(CO)_3H$ solutions gave several oxo sulfido clusters containing no CO ligands plus two CO-containing species. One of these, $Cp^*_2W_2(CO)_2(\mu\text{-}S)_2S$, formed in low yield while the other $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$ crystallized in 32% yield from MeCN-Et_2O containing excess SO_2. The crystal structure[6] of this dimer showed Lewis acid-base binding of SO_2 to the bridging sulfide ligands:



Preparation and Reactions of $[Cp^*M(CO)_3]_2(S_2O_4)$. An unexpected new complex formed during attempts to obtain single crystals of $Cp^*Mo(CO)_3(SO_2H)$. Cooling to −20 °C of dilute CH_3CN solutions of $Cp^*Mo(CO)_3H$ containing SO_2 gave orange prisms instead of (or in admixture with) the thin yellow plates characteristic of the SO_2H complex. The new crystals could be isolated in 31% yield under carefully controlled conditions, although only small yields of the W and Cp analogues could be obtained. X-ray crystallography revealed a dithionite-bridged structure, $[Cp^*Mo(CO)_3]_2(S_2O_4)$ (Figure 2), apparently produced by S-S coupling of two deprotonated $Cp^*Mo(CO)_3(SO_2H)$ fragments (see Discussion). This type of structure had been proposed for $[CpFe(CO)_2]_2(S_2O_4)$ as well as $[M(CO)_5]_2(S_2O_4)$ (M = Mn, Re).[16] The values of ν(SO) reported for these complexes are very similar to those of the group 6 complexes here (Table I).

The dithionite complex readily undergoes an interesting, complex auto-redox reaction:



Proton NMR evidence indicated that the resonance due

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(15) Jennings, M. A.; Wojcicki, A. *J. Organomet. Chem.* **1968**, *14*, 231.

(16) (a) Tennent, N. H.; Su, S. R.; Poffenberger, C. A.; Wojcicki, A. *J. Organomet. Chem.* **1975**, *102*, C46. (b) Poffenberger, C. A.; Tennent, N. H.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *191*, 107. (c) Reich-Rohrwig, P.; Clark, A. C.; Downs, R. L.; Wojcicki, A. *Ibid.* **1978**, *145*, 57.

to dithionite complex was rapidly replaced by several others, including primarily that for $[Cp^*Mo(CO)_3]_2$. After several days, only two major products remained, $[Cp^*MoO(\mu\text{-}S)]_2$ and A (or an isomer of A). Thermolysis of the solid dithionite gave similar products. Analysis of the gases evolved showed that nearly complete loss of carbonyl ligands occurred. About 1 mol of CO_2/mol of complex was produced, presumably by transfer of oxygen to CO. Thus it appears that the dithionite group, which is normally a reducing agent, behaves as an *oxidant*, oxidizing Mo^{II} to, for example, Mo^{V} in $[Cp^*MoO(\mu\text{-}S)]_2$. Concomitantly, S^{IV} is reduced to S^{II-}. In this context, it should be noted that SO_2 itself does not normally oxidize low-valent Mo complexes; Mo^0–SO_2 complexes are perfectly stable.[1f]

Interestingly, $[Cp^*Mo(CO)_3]_2(S_2O_4)$ could also be prepared in nearly identical yield to the above by the reaction of $Na[Cp^*Mo(CO)_3]$ and SO_2 in THF. This synthetic route is analogous to that reported for $[CpFe(CO)_2]_2(S_2O_4)$.[16] In general the group 6 Cp dithionites were quite elusive and could not be prepared by reactions of $[CpM(CO)_3]^-$ and SO_2 either by us or by Poffenberger,[16b] although $[CpWO(\mu\text{-}S)]_2$ was found[16b] to be a product of SO_2–$[CpW(CO)_3]^-$ reaction. Since we found $[Cp^*MoO(\mu\text{-}S)]_2$ to be a major product of solution decomposition of $[Cp^*Mo(CO)_3]_2(S_2O_4)$, the $[CpWO(\mu\text{-}S)]_2$ likewise could have resulted from decomposition of unstable $[CpW(CO)_3]_2(S_2O_4)$.

Infrared Spectroscopic Studies. Nujol mull infrared spectra of the SO_2H complexes are summarized in Table I. The positions of the SO stretching frequencies are consistent with attachment of the hydrogen atom to oxygen since the low-frequency band near 750 cm^{-1} is about 100 cm^{-1} lower than any previously observed[1f,17] $\nu(SO)$ in a transition metal–SO_2 complex and is comparable to bands for other compounds containing S–O–H (see below). This reflects a considerable lowering of the S–O bond order, in agreement with the 1.64 Å length of the S–OH bond (vs. 1.51 Å for the S–O bond). The broad weak band observed near 2550 cm^{-1} for each of the insertion complexes clearly results from a vibration involving the hydrogen atom originally bound to the metal in $CpM(CO)_3H$, as evidenced by the shift of this band to lower frequency for the product derived from $CpM(CO)_3D$. Since $\nu(SH)$ bands have previously been observed near 2550 cm^{-1} for metal-bound SH groups,[18] it was originally believed that the hydrogen in $CpM(CO)_3(SO_2H)$ could either be sulfur bound or oxygen bound. The ambiguity was resolved by isotopic substitution and later confirmed in the X-ray structure; the band shifted down 8 cm^{-1} (to 2544 cm^{-1}) for $CpW(CO)_3(S^{18}O_2H)$, in agreement with theory for $\nu(^{18}O\text{–}H)$. Also, a band at 1339 cm^{-1}, assigned to $\delta(OH)$, shifted to 1336 cm^{-1} (theory 1335 cm^{-1} for $\delta(^{18}O\text{–}H)$). The SO frequencies shifted appropriately also: 970 and 760 cm^{-1} in the normal species vs. 937 and 732 cm^{-1} in the ^{18}O species.

A relevant comparison of the IR bands of the SO_2H complexes to those of organic sulfinic acids, RSO_2H, can be made. Bands at 2340–2790 cm^{-1} and near 1280 cm^{-1} were assigned to $\nu(OH)$ and $\delta(OH)$, respectively, while $\nu(SO)$ occurred at 990–1090 and 810–870 cm^{-1} in RSO_2H.[19] These frequencies correspond well to those for metal-coordinated SO_2H. Comparison is also available with the organometallic sulfonic acid, $CpFe(CO)_2[S(O)_2OH]$,[20] which displays $\nu(OH)$ at 2940 cm^{-1} and $\nu(SO)$ at 1184, 1038, and 811 cm^{-1}.

Table V. Comparison of Important Distances (Å) within $CpMo(CO)_3(SO_2H)$ and $[Cp^*Mo(CO)_3]_2(S_2O_4)$

	$CpMo(CO)_3(SO_2H)$	$[Cp^*Mo(CO)_3]_2(S_2O_4)$
Mo–S	2.521 (2)	2.496 (1)
S–O1	1.637 (6)	1.472 (4)
S–O2	1.515 (6)	1.470 (4)
S–S′	3.692 (1)	2.266 (1)
Mo–C(1)	1.987 (8)	1.978 (7)
Mo–C(2)	2.041 (8)	2.027 (6)
Mo–C(3)	1.991 (8)	2.034 (6)
C(1)–O(3)	1.183 (10)	1.147 (7)
C(2)–O(4)	1.125 (10)	1.145 (6)
C(3)–O(5)	1.153 (9)	1.142 (7)
Mo–C(4)	2.381 (8)	2.283 (6)
Mo–C(5)	2.353 (8)	2.329 (6)
Mo–C(6)	2.325 (8)	2.367 (5)
Mo–C(7)	2.321 (8)	2.336 (5)
Mo–C(8)	2.345 (8)	2.284 (6)
Mo–Cp	2.00	1.98
O–H	0.94 (9)	

NMR Spectroscopic Studies. In order to observe the progress of the hydride–SO_2 reactions, proton NMR studies were carried out. After about 5 min, solutions of $CpW(CO)_3H$ and excess SO_2 showed new resonances corresponding to formation of $[CpW(CO)_3]_2(\mu\text{-}S)$ and H_2O, respectively. With time these peaks grew in intensity while the $CpW(CO)_3H$ peaks diminished and eventually disappeared. After 15 min, integration showed that most of the hydride ligand protons were converted to H_2O. Several weak Cp resonances also appeared, but the $[CpW(CO)_3]_2(\mu\text{-}S)$ peak was predominant, indicating that this complex is the major sulfide product (sparingly soluble $[CpW(CO)_3]_2$ precipitated out in the NMR tube).

Proton NMR of solutions of $(C_5R_5)M(CO)_3(SO_2H)$ in various organic solvents in all cases showed resonances arising only from the respective hydride complexes, indicating virtually complete dissociation of SO_2. This occurred even at −50 °C for $Cp^*Mo(CO)_3(SO_2H)$ in toluene-d_8, but the presence of excess SO_2 prevented SO_2 extrusion. For example, a solution of the latter complex in liquid SO_2 at −40 °C showed no hydride NMR peaks but rather a broad resonance for the OH proton at δ 3.89. Upon warming the sample to 0 °C for 20 min, the signal shifted to δ 2.93, reflecting exchange of the SO_2H proton with H_2O produced from partial decomposition of the complex (new Cp* peaks appeared). Similar results were obtained for the W congener, although some decomposition was already evident at −40 °C. The OH signal shifted from 4.9 to ca. 2.7 ppm (primarily now due to H_2O) after the solution was warmed to 35 °C for 20 min. Integration of total Cp* to OH area gave ~13:1 ratio, close to the expected 15:1 ratio. The SO_2H complexes proved to be less stable in mixtures of SO_2 and organic solvents. Although dissociation of SO_2 did not occur, solutions of $Cp^*Mo(CO)_3(SO_2H)$ in either CD_3CN (~1 M in SO_2) at −45 °C or 2:1 liquid SO_2–toluene-d_8 at −40 °C showed extensive decomposition.

NMR experiments indicated that insertion of SO_2 into the Mo–H bond in $Cp^*Mo(CO)_3H$ does not occur at low temperature (kinetically inhibited). A spectrum of

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$Cp^*Mo(CO)_3H$ in liquid SO_2 at −50 °C showed no reaction, but immediately after this solution was warmed to ambient temperature, an OH signal corresponding to SO_2H formation appeared at δ3.38 ppm. The latter then shifted and became unobservable within minutes because of rapid decomposition.

Description of the Crystal Structures of $CpMo(CO)_3(SO_2H)$ and $[Cp^*Mo(CO)_3]_2(S_2O_4)$. Interatomic distances and angles for these two species are compared in Tables V and VI, respectively. The geometry of the $CpMo(CO)_3(SO_2H)$ molecule is illustrated in Figure 1, and the $[Cp^*Mo(CO)_3]_2(S_2O_4)$ molecule is shown in Figure 2.

The structure of $CpMo(CO)_3(SO_2H)$ contains no crystallographically imposed symmetry, nor is there any approximate molecular symmetry, as shown in Figure 1. However, $[Cp^*Mo(CO)_3]_2(S_2O_4)$ is a dimeric species, which contains two $Cp^*Mo(CO)_3$ moieties linked together by a bridging $O_2S-SO_2^{2-}$ group and lies on a crystallographic center of symmetry which coincides with the midpoint of the S–S bond. Additionally, each half of the $[Cp^*Mo(CO)_3]_2(S_2O_4)$ molecule exhibits approximate mirror, or C_s, symmetry.

The $CpMo(CO)_3S$ portion of both molecules takes up the usual four-legged piano-stool geometry. The trans S–Mo–C(1) angle is slightly larger in the insertion product [135.4 (2)°] than in the dimer [128.7 (2)°]. An even larger difference between the two molecules appears in the other trans angle, with C(2)–Mo–C(3) = 109.1 (3)° in the $CpMo(CO)_3(SO_2H)$ and 124.2 (2)° in $[Cp^*Mo(CO)_3]_2(S_2O_4)$. The former value is close to that commonly observed in some other $CpM(CO)_3X$ molecules, e.g., 109.8 (2)° in $CpMo(CO)_3Cl$.[21] Both differences in trans angles are likely due to the increased spatial requirements of the Cp* ligand.

Discussion

Structure of $[Cp^*Mo(CO)_3]_2(S_2O_4)$ and $CpMo(CO)_3(SO_2H)$. The structure of the dithionite ion has long been a subject of discussion.[22-24] The first structure reported was that of $Na_2S_2O_4$[22] with an S–S bond distance of 2.39 Å, some 0.13–0.19 Å longer than the distances predicted from comparison of the S–S bonds in dithionate[25] ($S_2O_6^{2-}$) and disulfite[26] ($S_2O_5^{2-}$). Approximate C_{2v} symmetry was found for the $S_2O_4^{2-}$ ion in studies prior to the present one, i.e., $Na_2S_2O_4$,[22] $ZnS_2O_4{\cdot}py$,[23a] and $Sn_2(S_2O_4)_2$,[23b] and in all three cases the S–S bond was noted to be unexpectedly long (2.35–2.39 Å). In these three structures the oxygen atoms are involved in the first coordination sphere of the metal atom. Although the C_{2v} geometry of $S_2O_4^{2-}$ has been rationalized in terms of d orbital participation[22] or direct O–O bonding,[23a] approximate MO calculations favor a C_{2h} geometry[27] and recent solution spectroscopic studies[24] have been interpreted to be inconsistent with C_{2v} symmetry. The long S–S bond (C_{2v} geometry) has been suggested to be due to dπ antibonding interactions[22] or VSEP repulsions[24] but has generally eluded attempts at theoretical description.

The present structure is interesting in that it represents the first example of a sulfur-bound (to a metal) dithionite ion and contains C_{2h} S_2O_4. The S–S bond distance of 2.266 (1) Å is within the range suggested by the dithionate and disulfite structures. This distance is significantly longer than that found for diphenyl disulfone,[28] $Ph_2S_2O_4$ (2.193 (1) Å), the only other structure we know of for which the S_2O_4 moiety is found in approximate C_{2h} symmetry. Clearly the nature of the bonding in $S_2O_4^{2-}$ remains anomalous and deserves a detailed theoretical treatment.

The primary point of interest for $CpMo(CO)_3(SO_2H)$ is the structure of the $M-SO_2H$ moiety which represents, at least formally, the insertion of SO_2 into the Mo–H bond to form an *S*-sulfinate. Although both S–O distances are significantly longer than that normally found in SO_2 complexes (ca. 1.45 Å),[17b] the difference in the two distances is sufficient to indicate that the H atom is bound to O(1) (Table IV). 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 structurally characterized for *S*-sulfinates or *O*-sulfinates[29,30] with an alkyl or aryl bound to the sulfur, and spectroscopic evidence exists for *O,O*-sulfinate and those of the type M–S(0)–OR.[31] The present study affords the first structural characterization of the latter type.

Inspection of the packing diagram for $CpMo(CO)_3SO_2H$ shows two molecules related by a center of symmetry with a S–S distance of 3.692 (2) Å and approximate C_{2h} symmetry similar, except for the S–S distance, to the structure for the dithionite complex. In spite of the fact that the insertion complex represents a conceivable point on the reaction pathway to the dithionite complex, attempts to thermally induce the transition in the solid state lead to decomposition products.

Properties and Reactions of the Insertion and Dithionite Complexes. The complexes $(C_5R_5)M(CO)_3(SO_2H)$ can be considered to be metallo analogues of sulfinic acids,[19] RSO_2H. A metallo *sulfonic* acid, $CpFe(CO)_2[S(O)_2OH]$, is known[20] but is not a result of an insertion reaction. There appears to be no well-characterized precedent for the SO_2H^- ligand (or free anion) although a sulfinate structure, $Ru(SO_2H)_2(PPh_2Me)_3$, was tentatively formulated for the product of $RuH_2(PPh_2Me)_4-SO_2$ reaction.[32] In contrast with SO_2, insertion of CO_2 into metal–hydride bonds is well-known and results in metal oxygen coordination, M–O–C(O)H or $\overline{\text{M–O–C(H)–O}}$; definitive identification of a metallocarboxylic acid, M–C(O)–OH, derived by CO_2 insertion is lacking.[33]

The mechanism of the SO_2 insertion may be a concerted process, involving attack on the coordinated hydride, analogous to the attack on α-carbon proposed for the alkyl analogues $CpM(CO)_3R$.[34] In the latter case, the end product is the *S*-sulfinate $CpM(CO)_3S(O)_2R$. It is reasonable to assume that SO_2 initially coordinates to the hydride much as it does to metal-bound halides and pseudohalides.[17b] Rearrangement to coordinated SO_2H could then occur. Mechanistic studies to support this

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Table VI. Comparison of Important Interatomic Angles (deg) within $CpMo(CO)_3(SO_2H)$ and $[Cp^*Mo(CO)_3]_2(S_2O_4)$

	$CpMo(CO)_3(SO_2H)$	$[Cp^*Mo(CO)_3]_2(S_2O_4)$
Mo–S–S′	159.17 (5)	107.33 (3)
Mo–S–O(1)	103.6 (2)	113.6 (2)
Mo–S–O(2)	108.8 (2)	112.9 (2)
O(1)–S–S′	65.3 (2)	103.7 (1)
O(2)–S–S′	61.4 (2)	103.5 (2)
O(1)–S–O(2)	106.6 (3)	114.5 (2)
S–Mo–C(1)	135.4 (2)	128.7 (2)
S–Mo–C(2)	76.1 (2)	79.6 (2)
S–Mo–C(3)	75.2 (2)	78.4 (2)
S–Mo–Cp	107.5	115.4
Cp–Mo–C(1)	116.6	115.9
Cp–Mo–C(2)	129.8	119.4
Cp–Mo–C(3)	120.4	116.4
C(1)–Mo–C(2)	80.5 (3)	76.4 (2)
C(1)–Mo–C(3)	77.4 (3)	78.8 (3)
C(2)–Mo–C(3)	109.1 (3)	124.2 (2)
Mo–C(1)–O(3)	179.0 (7)	177.2 (6)
Mo–C(2)–O(4)	179.0 (7)	170.2 (5)
Mo–C(3)–O(5)	178.0 (7)	169.2 (5)
S–O(1)–H(1)	107 (6)	

proposal are hindered by (a) the remarkably facile and complete dissociation of the complexes to $(C_5R_5)M(CO)_3H$ and SO_2 in solution and (b) the instability of the system toward reduction of SO_2.

The thermal instability of $(C_5R_5)M(CO)_3(SO_2H)$ at 25–75 °C is in line with the instability of RSO_2H. The latter readily disproportionates at 25–100 °C to give thiolsulfonates and sulfonic acids.[19] In the case of both metallo and organo derivatives, water is found to be a product. Both MSO_2H thermolysis and prolonged solution reaction of $(C_5R_5)M(CO)_3H$ with SO_2 results in reduction of sulfur(IV) to sulfur(II–) and, to a varying extent, the formation of metal–oxo bonds. The similarity of the products suggests that solution SO_2 reduction by $(C_5R_5)M(CO)_3H$ proceeds by initial insertion of SO_2 into the metal–hydride bond. Also, we have evidence for an insertion process as an intermediate step in the reduction of SO_2 by $Os_3(\mu\text{-}H)_2(CO)_{10}$.[35] In this case, SO_2 initially coordinates to the metals as a bridging ligand since the cluster is electronically unsaturated.[36] Insertion of SO_2 into $[Cp_2FeH]^+$ had been proposed as a step in the reaction of Cp_2Fe with SO_2 in acid solutions to give Cp_2Fe^+, H_2O, and S_8.[37]

The reactive, solution-unstable dithionites $[Cp^*M(CO)_3]_2(S_2O_4)$ apparently are further intermediates in the SO_2 reduction. The oxo sulfido clusters produced from the dithionite are identical with those from prolonged SO_2–$Cp^*M(CO)_3H$ reaction. The addition of SO_2 to $Na[Cp^*M(CO)_3]$ also was found to yield the dithionite complexes, plus $Na_2S_2O_4$. A radical-coupling mechanism has been proposed[16b,c] for the formation of the iron analogue $[CpFe(CO)_2]_2(S_2O_4)$ from $Na[CpFe(CO)_2]$ (eq 4).

$$[CpFe(CO)_2]^- \xrightarrow{SO_2} [CpFe(CO)_2(SO_2)]^- \xrightarrow{[O]} [CpFe(CO)_2(SO_2)]\cdot \rightarrow {}^1/_2[CpFe(CO)_2]_2(S_2O_4) \quad (4)$$

A similar mechanism can be envisioned for the group 6 species. The oxidizing agent [O] is believed to be SO_2 in this case since oxygen is not present.[16] Our observation of $Na_2S_2O_4$ as a product of $Na[Cp^*Mo(CO)_3]_2$–SO_2 reaction is consistent with this since reduction of SO_2 to $S_2O_4^{2-}$ salts is well established.[38] In the reaction of $Cp^*Mo(CO)_3H$ and SO_2 to form $[Cp^*M(CO)_3]_2(S_2O_4)$ (and other products), several mechanistic possibilities exist, the most obvious being deprotonation of either $Cp^*Mo(CO)_3H$ or $Cp^*Mo(CO)_3(SO_2H)$ to $[Cp^*Mo(CO)_3]^-$ or $[Cp^*Mo(CO)_3(SO_2)]^-$. The proton would most likely transfer to an oxygen atom of, for example, an SO_2H group to split off water, one of the observed products. Loss of H· to directly form $[Cp^*M(CO)_3(SO_2)]\cdot$ radicals could also generate the dithionite via eq 4. The fact that very little or no H_2 gas is formed in the dithionite preparations, or in any other reaction studied here, favors H^+ rather than H· transfer. Furthermore, $(C_5R_5)M(CO)_3(SO_2H)$ would be expected to be a strong acid, on analogy with $CpFe(CO)_2(SO_3H)$[20] and sulfinic acids such as $p\text{-}ClC_6H_4SO_2H$ ($pK_a = 1.14$ in H_2O).[19] The precursor hydrides themselves are surprisingly strong acids in CH_3CN solution; the pK_a of $CpMo(CO)_3H$ has been measured to be 13.9, in between that of CH_3SO_3H ($pK_a = 10.0$) and 2,4-dinitrophenol ($pK_a = 16.0$).[39] The acidity of $Cp^*Mo(CO)_3H$ was determined to be significantly lower than that of $CpMo(CO)_3H$[40] in line with the greater redox reactivity of the latter with SO_2.

The *prolonged solution reactions* of SO_2 and $(C_5R_5)M(CO)_3H$ in all cases eventually yield a mixture of sulfido and/or oxo metal complexes and water as a result of SO_2 reduction. The nature of the final products depends heavily on metal, R group, solvent, temperature, and hydride:SO_2 ratio. For example, whereas $[CpW(CO)_3]_2(\mu\text{-}S)$ is both the major as well as initially observed sulfur-containing product for M = W, the Mo analogue is unstable and rapidly decomposes in solution with CO loss to a *mixture* of sulfide products. Complexes of the type $[Cp^*M(CO)_3]_2S$ are *not* observed as products for the Cp* systems, but rather *oxo-containing* products such as $[Cp^*MO(\mu\text{-}S)]_2$ are prevalent on hydride–SO_2 reaction. Perhaps a reaction pathway involving the dithionite complex as an intermediate predominates here, since the dithionite is known to proceed nearly exclusively to oxo sulfido complexes. For M = W, a *double* sulfide-bridged complex, $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$, can be isolated. The different products isolated in these reactions may thus merely reflect different stabilities rather than major differences in mechanisms.

The versatility of sulfur and oxysulfur ligands is well illustrated in the systems studied here, especially in regard to the surprisingly facile spontaneous auto-redox transformations that take place. The apparent intrinsic instability of the SO_2H moiety certainly bears further study in relation to its role in SO_2 reduction.

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Registry No. $CpMo(CO)_3(SO_2H)$, 94024-82-5; $CpW(CO)_3(SO_2H)$, 98105-16-9; $CpW(CO)_3(S^{18}O_2H)$, 98105-17-0; $CpW(CO)_3(SO_2D)$, 98105-18-1; $Cp^*Mo(CO)_3(SO_2H)$, 98105-19-2; $Cp^*W(CO)3(SO_2H)$, 98105-20-5; $[Cp^*Mo(CO)_3]_2(S_2O_4)$, 98126-16-0; $[Cp^*W(CO)_3]_2(S_2O_4)$, 98126-17-1; $CpMo(CO)_3H$, 12176-06-6; $CpW(CO)_3H$, 12128-26-6; $CpW(CO)_3D$, 65915-50-6; $Cp^*Mo(CO)_3H$, 78003-92-6; $Cp^*W(CO)_3H$, 32839-62-6; $[Cp^*Mo(CO)_3]_2$, 56200-14-7; $[Cp^*Mo(O)(\mu\text{-}S)]_2$, 98168-87-7; $Na[Cp^*Mo(CO)_3]$,

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Supplementary Material Available: Elemental analyses (Table Is), anisotropic thermal parameters (Tables IIs and IIIs), interatomic C–C distances and angles (Tables IVs and Vs), and structure factor amplitudes (Tables VIs and VIIs) (17 pages). Ordering information is given on any current masthead page.

(Trimethylphosphine)cobalt(I) Complexes. 4. Reaction with Acyclic Dienes and Crystal Structure of (Butadiene)tris(trimethylphosphine)cobalt(I) Tetraphenylborate

L. C. Ananias de Carvahlo,[1a,c] Yolande Pérès,[1a] Michèle Dartiguenave,*[1a] Yves Dartiguenave,[1a] and André L. Beauchamp*[1b]

Laboratoire de Chimie de Coordination du CNRS, 31400 Toulouse, France, and the Département de Chimie, Université de Montréal, Montréal, Canada H3C 3V1

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Reaction of $CoBr(PMe_3)_3$ with butadiene, isoprene, and 2,3-dimethylbutadiene in presence of $NaBPh_4$ yielded $[Co(diene)(PMe_3)_3]BPh_4$ complexes. The crystal structure of $[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]BPh_4$ has been determined by X-ray diffraction techniques. The complex crystallizes in the monoclinic system, $C2/c$, with $a = 46.71$ (2) Å, $b = 15.93$ (4) Å, $c = 34.21$ (2) Å, $\beta = 118.69$ (4)°, $Z = 24$, and $R = 0.083$ (5587 "observed" reflections). The structure consists of a perfectly ordered framework of BPh_4^- anions, in which large cavities are occupied by $[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]^+$ cations. In only one-third of these cavities are the cations ordered. Two different kinds of disorder are found for the remaining cations. In the ordered cations, cobalt is in a distorted square-pyramidal environment. One of the PMe_3 molecules is apical, whereas two PMe_3 molecules and the butadiene ligand occupy the basal sites. The difference between the apical (2.192 (5) Å) and basal (average 2.221 (4) Å) Co–P bond lengths is significant but small. The butadiene ligand is planar within 0.5σ, and its plane makes an angle of 84.5° to the basal plane. It is symmetrically coordinated and the cobalt atom is located 0.60 Å above the basal plane. In one of the disordered cations, two isomeric forms related by a 120° rotation of the butadiene ligand about the pseudo C_3 axis of the $Co(PMe_3)_3$ fragment are observed, suggesting the possibility of fluxionality in the crystal. Multinuclear NMR studies (187–295 K) show that in solution the $[Co(\eta^4\text{-}diene)(PMe_3)_3]BPh_4$ compounds do not exist as η^3-allyl complexes with $\sigma\text{-}CH_2$ ligand-to-cobalt interactions but retain the η^4-diene structure observed in the solid state.

Introduction

As part of our continuing research involving the chemistry of first-row d^8 nickel and cobalt complexes with trimethylphosphine, we recently reported the reaction of $CoBr(PMe_3)_3$ with ethylene and diphenylacetylene,[2] which gave rise to the new complexes $[Co(C_2H_4)(MeCN)(PMe_3)_3]BPh_4$, **1**, $[Co(C_2Ph_2)(MeCN)(PMe_3)_3]BPh_4$, **2**, and $[Co(C_2Ph_2)(PMe_3)_3]BPh_4$, **3**. They can be envisioned as constituted from the 14-electron $[Co(PMe_3)_3]^+$ fragment accepting four electrons (either from two 2-electron species like ethylene, diphenylacetylene, acetonitrile, etc. or from one 4-electron species like diphenylacetylene) in order to fill the metal coordination sphere and reach the 18-electron configuration.[3] Unfortunately, this interpretation gives little information on the nature of the bond between Co and the organic ligand. This aspect is of interest since such complexes possess a reduced Co(I) metal center which could induce internal oxidative addition and thus activate the organic ligand, giving rise to new chemical reactions.

In order to get more information, we are currently investigating the reactions of $CoBr(PMe_3)_3$ with other 4-electron donor ligands: conjugated and nonconjugated dienes. In the present study, the $[Co(\eta^4\text{-}diene)(PMe_3)_3]BPh_4$ complexes of butadiene (I), isoprene (II), and 2,3-dimethylbutadiene (III) were synthesized in good yields by reacting $CoBr(PMe_3)_3$ with the diene in presence of $NaBPh_4$.[4] Their behavior in solution was examined by means of ^1H, ^{13}C, and ^{31}P NMR. To our knowledge, there are no crystallographic data on Co(I) compounds of this type. The crystal structure of the butadiene complex $[Co(\eta^4\text{-}C_4H_6)(PMe_3)_3]BPh_4$ (I) is reported here.

Experimental Section

Procedure, Reagents, and Solvents. All operations were carried out under purified argon atmosphere in a conventional vacuum system or in a Jaram glovebox. The solvents were distilled before use, transferred under argon, and degassed in vacuum line. PMe_3 was prepared following an improved variation of Wolfsberger and Schmidbaur's method[5] and stored under argon.

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