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Oxygen Transfer from SO_2: Formation of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ from the Reaction of SO_2 with $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$

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Two soluble complexes, $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$ (1) and $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2), are formed in good yields from the addition of SO_2 to solutions of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$. We have previously reported the synthesis and crystal structure of 1.[1] Single-crystal X-ray studies of 2 revealed a dimeric complex containing terminal carbonyl ligands and a bridging thiosulfate ligand. $S^{18}O_2$-labeling studies have demonstrated that the SO_3H ligand in 1 is formed via oxygen transfer from SO_2;[1] $S^{18}O_2$-labeling studies for 2 have indicated that the extra oxygen required for the formation of the $\mu\text{-}S_2O_3$ ligand also originates from SO_2. Crystallographic data for $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$: $M_r = 696.76$; group space $Pc2_1n$; $a = 8.619$ (3) Å, $b = 14.530$ (4) Å, $c = 22.707$ (2) Å; $V = 2843$ (2) Å^3 at 295 K; $D_{calcd} = 1.63$ g cm^{-3} for $Z = 4$; anisotropic least-squares refinement converged at $R = 3.5\%$ and $R_w = 4.1\%$ for 2065 independent reflections with $I > 2\sigma(I)$ and $2\theta \leq 50°$.

Introduction

Reduction of SO_2 and its ultimate conversion to innocuous products such as S_8 and H_2O will be an increasingly important process as industrial use of high-sulfur fossil fuels increases. We have demonstrated[2] homogeneous catalytic hydrogenation of SO_2 (eq 1) using the complex

$$SO_2 + 2H_2 \xrightarrow[\text{75 °C}]{\text{(Mo–SH)}} S + 2H_2O \qquad (1)$$
$$\text{(350 turnovers/h)}$$

$[(\eta^5\text{-}C_5H_{5-n}Me_n)Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (n = 0, 1, 5) that was originally characterized by Rakowski DuBois and coworkers.[3] In an effort to understand more about the mechanistic aspects of this catalytic reduction of SO_2 and to further study the reduction/oxygen-transfer chemistry of SO_2, we have been investigating reactions of SO_2 with transition-metal hydride complexes.[1,4–8]

Addition of SO_2 to coordinately saturated transition-metal hydride complexes has yielded mostly sulfided metal systems. However, we have reported[7] the first examples of SO_2 insertion into metal–hydride bonds with the syntheses of $(\eta^5\text{-}C_5R_5)M(CO)_3SO_2H$ from the addition of SO_2 to solutions of $(\eta^5\text{-}C_5R_5)M(CO)_3H$ (M = Mo, W; R = H, Me). These SO_2H complexes are extremely reactive species that undergo autoredox reactions to form complexes that contain SO_2 reduction products.

We have also achieved partial reduction of SO_2 with the formation of water and the stable bidentate thiosulfate complexes $Cp_2M(\eta^2\text{-}S_2O_3)$ ($Cp = \eta^5\text{-}C_5H_5$) from reactions of SO_2 and Cp_2MH_2 (M = Mo, W).[5] In addition, the reaction of Cp_2WH_2 with SO_2 at −78 °C was found to yield a thermally unstable intermediate that decomposed at room temperature to give $Cp_2W(\eta^2\text{-}S_2O_3)$, H_2O, and several other Cp-containing species that were not identified. It was speculated that this intermediate might also be a metal–hydride SO_2 insertion product.

This project was extended by studies of addition of SO_2 to solutions of $Cp^*Ru(CO)_2H$ ($Cp^* = \eta^5\text{-}C_5Me_5$). This reaction has produced two new, stable complexes $Cp^*Ru(CO)_2SO_3H$ (1) and $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2). A single-crystal X-ray analysis of 1[1] revealed the presence of an insertion/oxygen-transfer $-SO_3H$ ligand rather than the $-SO_2H$ insertion ligand that might have been anticipated based on the products of the reactions of SO_2 with $(\eta^5\text{-}C_5R_5)M(CO)_3H$ (M = Mo, W; R = H, Me).[7] Labeling studies with $S^{18}O_2$ demonstrated that SO_2, rather than O_2 or adventitious water, provided the oxygen for the formation of the $-SO_3H$ ligand. A single-crystal X-ray study of 2 revealed a transition-metal complex containing a bridging thiosulfate ligand. Here also, labeling studies have demonstrated that the $\mu\text{-}S_2O_3$ ligand is formed by an oxygen-transfer process from SO_2. Formation of this bridged-thiosulfate complex via oxygen transfer is especially intriguing in view of the fact that a thiosulfate species formed by oxygen transfer from SO_2 is proposed[9] to be an intermediate in the catalytic reduction of SO_2 by $[(\eta^5\text{-}C_5H_{5-n}Me_n)Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (n = 0, 1, 5).[2]

In this paper, we present additional details of the synthesis and characterization of 1, along with the synthesis, $S^{18}O_2$-labeling study, and structural characterization of 2.

Experimental Section

Materials and Measurements. All sample transfers and sample manipulations were performed by using oven-dried solve-seal glassware under nitrogen on a preparative vacuum line or in a helium-filled Vacuum Atmospheres HE-43 drybox. Reactions with SO_2 were performed on a high-vacuum line. The following solvents were dried and distilled immediately before use; THF (NaK), hexane (NaK), heptane, (NaK), CH_3CN (CaH_2), toluene (NaK), CH_3OH (CaH_2), and CH_2Cl_2 (CaH_2). $Cp^*Ru(CO)_2H$ was synthesized either by the method of Humphries and

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Knox[10] or by the addition of HCl to $K^+[Cp^*Ru(CO)_2]^-$[11] and was purified by sublimation at 50 °C. $S^{18}O_2$ (95%) was prepared by heating stoichiometric amounts of S_8 and $N^{18}O$ (95%) at 450 °C for 24 h and was purified by trap-to-trap distillation. All other reagents were purchased from major chemical suppliers and were used without further purification.

Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer, and NMR spectra were recorded on a Varian EM-390 spectrometer. Residual gases from the reaction of $Cp^*Ru(CO)_2H$ with SO_2 were analyzed by using a Dycor Quadrupole gas analyzer with electron energy levels set at 70 eV.

Preparation and Physical Properties of $Cp^*Ru(CO)_2SO_3H$ (1) and $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2). $Cp^*Ru(CO)_2H$ (500 mg, 1.7 mmol) was dissolved in approximately 25 mL of dry, degassed CH_3CN. In the absence of air, an excess amount (2:1) of SO_2 was condensed into the solution containing the hydride. The solution was warmed to room temperature and was stirred for 2–3 h. During this time, the reaction mixture turned yellow and then orange.

A mass spectral analysis of gases over the frozen reaction mixture (−195 °C) revealed the presence of small amounts of CO and H_2. These reaction products were removed under vacuum; a subsequent mass spectral analysis of the volatiles over the same reaction mixture warmed to room temperature showed only those peaks associated with SO_2 and CH_3CN. In particular, there was no increase over background in the size of the peak associated with H_2O at $m/e = 18$.

A ^1H NMR spectrum of an aliquot of the orange solution ($CDCl_3$) displayed two resonances, one at δ 1.93 ppm and one at δ 1.91 ppm along with a small resonance at δ 6.67 ppm. Concentration of the reaction solution under vacuum resulted in the formation of a bright yellow precipitate (1) (~100 mg) that was separated from the orange filtrate and washed with hexane.

A solution IR spectrum of the yellow precipitate 1 ($CHCl_3$) exhibited carbonyl bands at 2025 and 2005 cm^{-1}; O–H bands at 2460 and 1243 cm^{-1}; and S–O bands at 1180, 1080, and 810 cm^{-1}. A ^1H NMR spectrum of 1 in $CDCl_3$ displayed a Cp* resonance at δ 1.93 ppm (15 H) and an –OH proton resonance at δ 6.67 ppm (1 H). This latter resonance shifted to δ 4.47 ppm upon the addition of water or more solid sample to the NMR tube.

Crystals of 1 were grown from $CDCl_3$ in an NMR tube. A structural analysis[1] of these crystals showed the yellow complex to be the insertion/oxygen-transfer species $Cp^*Ru(CO)_2SO_3H$.

A ^1H NMR spectrum ($CDCl_3$) of the orange filtrate 2 revealed a Cp* resonance at δ 1.91 ppm along with a small peak at δ 1.93 ppm indicative of 1. The orange 2 was separated more cleanly from 1 by chromatographic means. Solvent was stripped from the orange filtrate under vacuum. The products were redissolved in toluene and chromatographed on a Florisil column (80–200 mesh) that had been packed in toluene.

Two bands were removed from the column. The first, eluted with toluene, was identified from a ^1H NMR spectrum as 1 (~50 mg). An orange second band was removed from the column with a 50/50 toluene/THF mixture. The solvents were removed from the second-band eluent under a N_2 stream, and the product was identified as 2 (yield ~220 mg) from a ^1H NMR spectrum. Small amounts of insoluble material (presumably oxo or sulfido species) were left on the column. A solution IR spectrum of 2 ($CHCl_3$) exhibited terminal carbonyl bands at 2020 and 1985 cm^{-1} and S–O bands at 1228, 1190, 1045, 1020, and 505 cm^{-1}.

NMR Spectroscopic Studies of the Reaction of $Cp^*Ru(CO)_2H$ with Various Stoichiometries of SO_2. NMR scale reactions of $Cp^*Ru(CO)_2H$ in $CDCl_3$ and C_6D_6 with various ratios of the hydride to SO_2 were carried out to assess the dependence of the products and the yields of the products on solvent polarity and on the amount of SO_2 available for reaction. In a typical experiment, 10 mg (0.034 mmol) of $Cp^*Ru(CO)_2H$ was dissolved in the dry, degassed NMR solvent, and, on a vacuum line, a measured amount of SO_2 (1:1, 2:1, and excess) was condensed into an NMR tube containing the $Cp^*Ru(CO)_2H$ solution. The tube was then flame-sealed and allowed to warm to room temperature. After about 5 min, solutions of the hydride and SO_2 (for all stoichiometric ratios) showed new resonances corresponding to products 1 and 2. With time, these grew in intensity while the resonances associated with $Cp^*Ru(CO)_2H$ diminished. In each case, the reaction was complete in a matter of hours and the products 1 and 2 were formed in the same ratio as seen in previous reactions (as evidenced by ^1H NMR peak integrations). The reaction was slightly accelerated in the more polar $CDCl_3$.

Addition of a stoichiometric amount of NEt_3 to the reaction in $CDCl_3$ accelerated the disappearance of the starting hydride even more; however, this interaction of $Cp^*Ru(CO)_2H$ and SO_2 in the presence of NEt_3 did not result in the formation of $Cp^*Ru(CO)_2SO_3H$. A ^1H NMR spectrum of the resultant products revealed Cp* resonances at δ 1.91 ppm (15 H) (2) and δ 1.94 ppm (15 H). ^1H resonances due to the products formed from NEt_3 consisted of a triplet centered at δ 1.15 ppm (3 H), a quartet centered at δ 2.73 ppm (2 H), and a broad peak at δ 10.35 ppm (1 H). The resonance associated with the SO_3H ligand of 1 at δ 6.67 ppm was not present in this spectrum. The spectrum is consistent with the formation of the species $[Et_3NH]^+[Cp^*Ru(CO)_2SO_3]^-$ which is based on the deprotonation of $Cp^*Ru(CO)_2SO_3H$. A similar reaction has been noted upon addition of secondary amines to $CpFe(CO)_2SO_3R$ and bases to $CpFe(CO)_2SO_3H$.[12]

Condensation of NEt_3 into the NMR tube without addition of SO_2 or condensation of NEt_3 into the NMR tube before SO_2 was condensed into the tube resulted in the formation of $[Cp^*Ru(CO)_2]_2$ along with other, unidentified products.

Addition of SO_2 to Solutions of $Cp^*Ru(CO)_2SO_3H$ and $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2). The possibility of further reaction of 1 and 2 with SO_2 under the same conditions used for the initial formation of 1 and 2 was investigated. Into an NMR tube containing $Cp^*Ru(CO)_2SO_3H$ (10 mg, 0.027 mmol, dissolved in $CDCl_3$) was condensed an excess of SO_2. The tube was flame-sealed and warmed to room temperature. The ^1H NMR resonance associated with the Cp* group of 1 at δ 1.93 ppm was monitored for a period of 2–3 h. No changes were observed in the NMR spectrum of 1.

Excess SO_2 was also condensed into an NMR tube containing $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2) (10 mg, 0.014 mmol, dissolved in $CDCl_3$). The tube was flame-sealed and warmed to room temperature. The ^1H NMR resonance associated with the Cp* group of 2 at δ 1.91 ppm was monitored for a period of 3–4 h. This resonance also exhibited no change.

Attempted Preparation of $Cp^*Ru(CO)_2SO_3H$ from Reaction of $Cp^*Ru(CO)_2H$ with SO_3. A stoichiometric amount (1:1) of SO_3 was condensed into an NMR tube containing $Cp^*Ru(CO)_2H$ (10 mg, 0.034 mmol in $CDCl_3$). No products that were soluble in $CDCl_3$ resulted from this reaction, and no identifiable products were isolated.

An NMR tube reaction of $Cp^*Ru(CO)_2H$ with the milder SO_3-donating agent $Me_3N\cdot SO_3$ (in a 1:1 ratio) in $CDCl_3$ resulted only in the formation of $[Cp^*Ru(CO)_2]_2$ along with some unidentified insoluble products.

Reaction of $[Cp^*Ru(CO)_2]_2$ with SO_2. An excess of SO_2 was condensed into a CH_3CN solution containing $[Cp^*Ru(CO)_2]_2$ (0.5 g, 0.8 mmol), and the reaction mixture was stirred at room temperature overnight. The CH_3CN was removed under vacuum. A Nujol IR spectrum of the resulting orange solid revealed only the presence of $[Cp^*Ru(CO)_2]_2$.

Reaction of $Cp^*Ru(CO)_2SO_3H$ (1) with CH_3OH To Give $Cp^*Ru(CO)_2SO_3CH_3$. $Cp^*Ru(CO)_2SO_3H$ was dissolved in dry, degassed CH_3OH, and the reaction mixture was stirred for several minutes. No color change occurred during this time period. The CH_3OH was removed under vacuum, and the resulting yellow solid was redissolved in $CDCl_3$. A ^1H NMR spectrum of this yellow solution displayed two resonances, one at δ 1.93 ppm (Cp*, 15 H) and one at δ 3.35 ppm (CH_3, 3 H). The –OH proton resonance of the starting 1 at δ 6.67 ppm was not visible in this spectrum. A Nujol mull IR spectrum of $Cp^*Ru(CO)_2SO_3CH_3$ exhibited teminal carbonyl bands at 2020 and 2010 cm^{-1} and S–O bands at 1205, 1090, and 630 cm^{-1}.

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Reaction of $Cp^*Ru(CO)_2H$ with $S^{18}O_2$. $Cp^*Ru(CO)_2H$ (100 mg, 0.341 mmol) was dissolved in 10 mL of dry, degassed CH_3CN. In the absence of air, an excess of $S^{18}O_2$ (95%) was condensed into the solution containing the hydride. The reaction mixture was warmed to room temperature and was stirred 2–3 h. A ^1H NMR spectrum of an aliquot of the orange solution ($CDCl_3$) again revealed the presence of products 1 and 2 in the same ratios as previously noted. The solvent was stripped from the reaction under an N_2 stream, and the orange solid was redissolved in $CHCl_3$. An IR spectrum of the orange solution (a mixture of labeled 1 and 2 in $CHCl_3$) was taken. This spectrum exhibited carbonyl bands at 2025 and 2005 cm^{-1} for 1 and 2020 and 1985 cm^{-1} for 2. S–O absorptions for 1 were observed at 1140 and 1020 cm^{-1}; those for 2 appeared at 1185, 1140, 1000, 960, and 497 cm^{-1}. The spectrum also contained an O–H band at 2450 cm^{-1} for 1. Strong solvent absorption bands obscured the shifted bands corresponding to the absorbances at 1243 and 810 cm^{-1} for 1.

Structural Determination of $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2). Crystals of 2 suitable for X-ray diffraction analysis were grown by dissolving the complex in THF followed by a careful layering of hexane over the THF solution. An orange wedge-shaped crystal (0.5 × 0.4 × 0.3 mm) was mounted in air in a thin-walled glass capillary. Intensity data for this complex were collected at room temperature with graphite-monochromated Mo Kα radiation on an Enraf-Nonius CAD4 automated diffractometer using a variable speed θ–2θ scan mode. Unit-cell parameters were derived from a least-squares analysis of 25 reflections in the range $10° < \theta < 20°$. The intensities and orientations of two standard reflections were monitored every 2 h of X-ray exposure time and every 200 reflections, respectively. The standard reflections showed no significant intensity fluctuations; reorientation was not required. Intensity data were corrected for Lorentz and polarization factors. Data were corrected for absorption by using the relative intensity of a low-angle reflection measured as a function of Ψ (corrected to ϕ) multiplied by a spherical correction using a radius calculated from the average distance between the three most prominent directions of crystal development.

The structure was solved by using standard Patterson and difference Fourier methods and was refined with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.[13] The Los Alamos crystal structure codes were used for all calculations.[14] The function minimized was $R = \sum w^2[F_o - F_c]^2$ and weights were calculated as $w^2 = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\sigma_c(I)$ is the error based on counting statistics. Although most hydrogen atoms were identified in an electron density map, they were not included in the refinement. All other atoms were refined with anisotropic thermal parameters. A final difference Fourier map did not reveal any features beyond those associated with the hydrogen atoms from the Cp* rings. Lattice constants, data collection parameters, and final refinement parameters for the structure are presented in Table I. Coordinates for the atoms from the least-squares cycle are presented in Table II. Selected distances and bond angles are listed in Table III. Tables of anisotropic thermal parameters along with a listing of observed and calculated structure factor amplitudes are given as supplementary material.

Table I. Experimental Data for X-ray Diffraction Analysis of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S\bullet SO_3)$

chem formula	$C_{24}H_{30}O_7S_2Ru$
cryst system	orthorhombic
space group	$Pc2_1n$
a, Å	8.619 (5)
b, Å	14.530 (5)
c, Å	22.707 (5)
V, Å^3	2843 (3)
Z	4
d(calcd), g/cm^3	1.63
λ(Mo Kα_1), Å	0.709 30
temp, °C	25
cryst color	orange
abs coeff, cm^{-1}	12.18
abs corr type	ϕ × sphere
sphere radius, mm	0.4
transmissn range	0.85, 0.74
av peak width (ω), deg	0.8
scan range (2θ max), deg	0–50
scan type	θ–2θ
scan rate	variable
scan range	$\pm h, \pm k, l$
total no. of reflctns collected	5043
no. of unique reflctns	2602
no of reflctns with $I > 2\sigma(I)$	2065
R_F equiv reflctns	1.7%
R_F obsd reflctns	3.5%
R_{wF} obsd reflctns	4.1%
GOF	1.9

Results

General Data. Solutions of $Cp^*Ru(CO)_2H$ in various organic solvents turn yellow and then orange upon exposure to SO_2. Two soluble complexes, $Cp^*Ru(CO)_2SO_3H$ (1)[1] and $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2), can be isolated from the reaction. However, the presence of CO in a mass spectral analysis of the headspace gases over a frozen (−195 °C) reaction mixture indicates that other products besides these two are formed in this reaction. This is also confirmed by the yields of products 1 and 2 (25% for 1 and 37% for 2, based on Ru). The other Ru-containing products may be insoluble oxo or sulfido species as no other Cp*-containing products are observed in the NMR. Varying the SO_2/metal–hydride stoichiometry of the reaction mixture does not change the ratios of formation of the products, and 1 and 2 undergo no further reaction with SO_2. The reaction is accelerated in more polar solvents, and addition of NEt_3 to the reaction system under certain conditions accelerates the formation of 2 even more. However, in the presence of NEt_3, $[Et_3NH]^+[Cp^*Ru(CO)_2SO_3]^-$ rather than 1 is formed.

Oxygen Transfer from SO_2. The source of extra oxygen for the formation of the SO_3H ligand in 1 and the $\mu\text{-}S_2O_3$ ligand in 2 was explored by means of a $S^{18}O_2$-labeling study. The IR bands for the labeled 1 (^{18}1) show no overlap with the IR bands for the unlabeled 1 (Table IV). The complete disappearance of S–O and O–H stretching frequencies associated with 1 and their replacement by new S–O and O–H bands in ^{18}1 clearly demonstrated that SO_2 is the sole source of oxygen for the formation of the $-SO_3H$ ligand.

An analysis of the IR band shifts between the labeled 2 (^{18}2) and unlabeled 2 is made difficult by the overlap of some ν(SO) peaks between ^{18}2 and 2. In particular, it is not entirely clear whether the S–O band at 1190 cm^{-1} in 2 is the same absorbance which appears at 1185 cm^{-1} in ^{18}2. The other frequency shifts are fairly clear. After the labeling experiment, the S–O bands at 1045, 1020, and 505 cm^{-1} in 2 completely disappear and are replaced by bands at 1000, 960, and 497 cm^{-1} in ^{18}2. We presume that the 1228 and 1190 cm^{-1} bands in 2 are shifted to 1185 and 1140 cm^{-1} in ^{18}2. If this is true, the sole source of oxygen for the formation of the $\mu\text{-}S_2O_3$ ligand in 2 is SO_2.

The ability of SO_2 to function as an oxygen-transfer agent has been established in main-group chemistry with the reaction of SO_2 and $(Me_3Si)_2NH$ to give $(Me_3Si)_2O$, Me_3SiNSO, and $NH_4[Me_3SiOSO_2]$.[15] Oxygen transfer from SO_2 in organometallic systems has been demonstrated with the oxidation of CS_2 in $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ by SO_2 to

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Table II. Fractional Coordinates and Isotropic Thermal Parameters for $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$

atom	*x*	*y*	*z*	$U_{eq}{}^a$, Å^2	atom	*x*	*y*	*z*	$U_{eq}{}^a$, Å^2
Ru(1)	0.05853 (8)	0.25000 (0)	0.23367 (3)	4.75	C(1)	0.2434 (18)	0.1836 (9)	0.2285 (7)	9.4
O(1)	0.3639 (12)	0.1481 (9)	0.2304 (6)	14.2	C(2)	0.1596 (13)	0.3449 (8)	0.1910 (6)	7.1
O(2)	0.2250 (12)	0.4033 (7)	0.1680 (5)	11.5	C(3)	−0.1608 (13)	0.2941 (6)	0.2769 (4)	4.7
C(4)	−0.0369 (14)	0.3467 (7)	0.3017 (5)	6.1	C(5)	0.0680 (14)	0.2880 (9)	0.3283 (5)	6.9
C(6)	0.0057 (18)	0.1952 (10)	0.3244 (6)	7.9	C(7)	−0.1376 (18)	0.1986 (7)	0.2919 (6)	7.0
C(8)	−0.2490 (19)	0.1203 (9)	0.2764 (6)	9.6	C(9)	0.0697 (23)	0.1107 (14)	0.3520 (8)	14.6
C(10)	0.2072 (16)	0.3130 (15)	0.3647 (7)	13.2	C(11)	−0.0260 (17)	0.4515 (8)	0.3015 (6)	9.4
C(12)	−0.3055 (13)	0.3322 (9)	0.2472 (5)	7.0	S(1)	−0.0738 (3)	0.1843 (1)	0.1510 (1)	4.4
S(2)	0.0517 (5)	0.0615 (2)	0.1311 (2)	9.1	O(3)	0.2014 (13)	0.0916 (8)	0.1104 (6)	13.4
O(4)	−0.0404 (14)	0.0168 (7)	0.0870 (5)	13.5	O(5)	0.0563 (15)	0.0175 (6)	0.1884 (5)	14.9
Ru(2)	−0.12076 (8)	0.26591 (7)	0.06105 (3)	5.00	C(13)	0.0819 (13)	0.2652 (17)	0.0352 (5)	11.3
O(6)	0.2013 (11)	0.2607 (20)	0.0141 (4)	20.2	C(14)	−0.0975 (17)	0.3823 (8)	0.0974 (6)	9.3
O(7)	−0.1021 (15)	0.4545 (7)	0.1180 (6)	13.4	C(15)	−0.2977 (17)	0.3237 (9)	0.0032 (7)	8.2
C(16)	−0.2143 (11)	0.2666 (10)	−0.0299 (4)	6.2	C(17)	−0.2292 (14)	0.1743 (9)	−0.0063 (5)	6.7
C(18)	−0.1705 (21)	0.0886 (11)	−0.0319 (7)	10.9	C(19)	−0.3323 (15)	0.1815 (10)	0.0421 (6)	7.7
C(20)	−0.3756 (13)	0.2767 (11)	0.0494 (5)	7.2	C(21)	−0.4916 (17)	0.3143 (16)	0.0978 (7)	13.7
C(22)	−0.3941 (18)	0.1017 (11)	0.0799 (7)	11.1	C(23)	−0.1225 (18)	0.2913 (13)	−0.0849 (5)	11.4
C(24)	−0.3205 (24)	0.4313 (11)	−0.0095 (9)	13.8					

[a] $(U_{11} + U_{22} + U_{33})/3$.

Table III. Selected Distances and Angles for $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$

	Distances (Å)		
Ru1–S1	2.395 (2)	C3–C4	1.43 (1)
Ru2–S1	2.396 (2)	C4–C5	1.38 (2)
Ru1–C1	1.87 (1)	C5–C6	1.45 (2)
Ru1–C2	1.90 (1)	C6–C7	1.44 (2)
Ru2–C13	1.84 (2)	C7–C3	1.44 (2)
Ru2–C14	1.89 (1)		1.43 (av)
S1–S2	2.135 (3)	C3–C12	1.52 (2)
S2–O3	1.44 (1)	C4–C11	1.53 (2)
S2–O4	1.432 (9)	C5–C10	1.50 (2)
S2–O5	1.45 (1)	C6–C9	1.49 (2)
		C7–C8	1.53 (2)
C1–O1	1.16 (2)		1.51 (av)
C2–O2	1.14 (1)		
C13–O6	1.14 (1)	C15–C16	1.33 (2)
C14–O7	1.15 (2)	C16–C17	1.45 (2)
		C17–C19	1.42 (2)
Ru1–C3	2.22 (1)	C19–C20	1.44 (2)
R1–C4	2.243 (9)	C20–C15	1.42 (2)
Ru1–C5	2.22 (1)		1.41 (av)
Ru1–C6	2.25 (1)		
Ru1–C7	2.27 (1)	C15–C24	1.60 (2)
	2.24 (av)	C16–C23	1.52 (2)
		C17–C18	1.46 (2)
Ru2–C15	2.18 (1)	C19–C22	1.54 (2)
Ru2–C16	2.216 (8)	C20–C21	1.58 (2)
Ru2–C17	2.23 (1)		1.54 (av)
Ru2–C19	2.24 (1)		
Ru2–C20	2.22 (1)		
	2.22 (av)		
	Angles (deg)		
C1–Ru1–C2	87.2 (6)	Ru2–C13–O6	173 (1)
C13–Ru2–C14	92.5 (8)	Ru2–C14–O7	172 (1)
C1–Ru1–S1	98.7 (4)	S1–S2–O3	105.6 (4)
C2–Ru1–S1	96.2 (4)	S1–S2–O4	104.2 (4)
C13–Ru2–S1	96.3 (5)	S1–S2–O5	101.0 (4)
C14–Ru2–S1	93.0 (4)	O3–S2–O4	114.0 (8)
Ru1–C1–O1	173 (1)	O3–S2–O5	113.6 (8)
Ru1–C2–O2	176 (1)	O4–S2–O5	116.2 (8)

form $Pt(\eta^2\text{-}CS_2O)(PPh_3)_2$, S_8, and SO_3.[16]

Oxidation of SO_2 to SO_4 has been noted in several systems where the reactions of SO_2 with Ru–H complexes were carried out. Eisenberg and co-workers[17] structurally characterized $RuCl(SO_4)(NO)(PPh_3)_2$, a complex that can be formed from the addition of SO_2 to $RuH(NO)(PPh_3)_3$[18] in chlorinated solvents. Addition of SO_2 to $RuCl(NO)(PPh_3)_2$ yielded the same product, and it was surmised that hydride ligand was exchanged with a chlorine of the solvent during the course of the reaction. The source of oxygen for the formation of the sulfate ligand was not discussed.

Table IV. Comparison Infrared Data for $[(\eta^5\text{-}C_5R_5)M(CO)_2]_2(\mu\text{-}S_2O_3)$ and $(\eta^5\text{-}C_5R_5)M(CO)_2]_2(\mu\text{-}S_2O_3)$

compound	ν(CO), cm^{-1}	ν(OH), cm^{-1}	ν(SO), cm^{-1}
$Cp^*Ru(CO)_2SO_3H$[a]	2025, 2005	2460, 1243	1180, 1080, 810
$Cp^*Ru(CO)_2S^{18}O_3H$[a]	2025, 2005	2450, *b*	1140, 1020, *b*
$Cp^*Ru(CO)_2SO_3CH_3$[c]	2020, 2010		1205, 1090, 630
$[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$[a]	2020, 1985		1228, 1190, 1045, 1020, 505
$[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2{}^{18}O_3)$[a]	2020, 1985		1185, 1140, 1000, 960, 497

[a] $CHCl_3$ solution. [b] Obscured. [c] Nujol.

The formation of the coordinated sulfate in $[Ru(SO_4)(SO_2)(PPh_3)_2]_2$ from the reaction of $RuH_2(PPh_3)_4$ with SO_2 was attributed by Mingos and co-workers to traces of O_2 or disproportionation of SO_2;[19] however, labeling studies have not been reported.

$Cp^*Ru(CO)_2SO_3H$ (1). Transition-metal complexes containing S-bonded $-SO_3R$ groups have been synthesized and are fairly common. These systems typically have been prepared via addition of SO_2 to an alcoholic solution or suspension of a transition-metal complex.[12,20] Compounds containing the $-SO_3R$ ligand have also been formed by insertion of SO_2 into metal–alkoxy bonds.[21] Complexes containing the $-SO_3H$ ligands are known but are less common. Johnson, Jeter, and Cordes have carried out a structural characterization of $Na_4[Ru(SO_3)_2(SO_3H)_2(NH_3)_2]\cdot 6H_2O$,[22] and Poffenberger and Wojcicki have synthesized and characterized $CpFe(CO)_2SO_3H$.[12] The latter was formed by the hydrolysis of $CpFe(CO)_2SO_3R$ (R =

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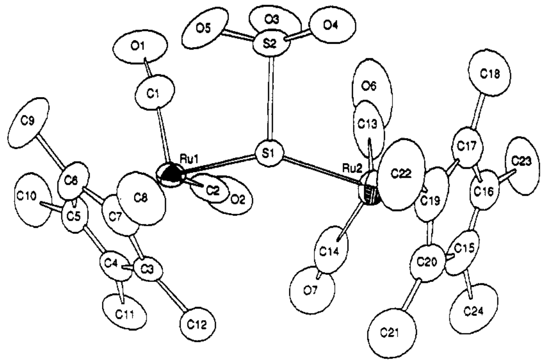

Figure 1. Molecular geometry and atom-labeling scheme for $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2, 40% ellipsoids).

CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$), where the original $-SO_3R$ complex was synthesized via reaction of $[CpFe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ ($R = CH_3$, C_2H_5), using an appropriate alcohol as the solvent. It was noted that the products could be interconverted by use of various alcohols at reflux; we have also observed that treatment of 1 with CH_3OH forms $Cp^*Ru(CO)_2SO_3CH_3$. In the case of the Ru complex, however, the reaction is complete within minutes at room temperature rather than the 24 h required for the conversion $CpFe(CO)_2SO_3H$ to $CpFe(CO)_2SO_3CH_3$. Addition of NaOH to $CpFe(CO)_2SO_3H$ was found to yield $Na^+[CpFe(CO)_2SO_3]^-$. A similar deprotonation process probably takes place upon the addition of the base NEt_3 to the reaction mixture of $Cp^*Ru(CO)_2H$ and SO_2, where the acidity of the $-SO_3H$ ligand[12] promotes the formation of $NEt_3H^+[Cp^*Ru(CO)_2(SO_3)]^-$ rather than 1.

Although we have successfully formed $-SO_3$-containing complexes via the addition of SO_3 to suitable precursor species[9] and SO_3 has been shown to insert into the M–R bond of $RRe(CO)_5$ (R = alkyl or aryl),[23] attempts to produce the $-SO_3H$ complex via direct addition of SO_3 to $Cp^*Ru(CO)_2H$ results in the formation of insoluble products rather than 1. Use of the milder SO_3-donating agent $Me_3N{\cdot}SO_3$ gives $[Cp^*Ru(CO)_2]_2$ along with an insoluble tar.

$[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (2). The molecular structure of $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ and its atomic numbering scheme are depicted in Figure 1. The crystal contains discrete molecules of $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ separated by normal van der Waals distances. $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ consists of two $Cp^*Ru(CO)_2$ fragments bridged by a thiosulfate ligand. The two CO ligands and the $\mu\text{-}S_2O_3$ ligand are disposed in a nearly orthogonal fashion around each Ru center with carbonyl C–Ru–S bond angles ranging from 93.0 (4)° to 98.7 (4)° and OC–Ru–CO bond angles ranging from 87.2 (6)° to 92.5 (8)°. The Ru(1)–CO distances are 1.87 (1) and 1.90 (1) Å; the Ru(2)–CO distances are 1.84 (1) and 1.89 (1) Å. The bridging sulfur atom is equidistant from the two Ru atoms (2.395 (2) and 2.396 (2) Å); the S(1)–S(2) distance is 2.135 Å. The S(2) atom of the thiosulfate ligand is bent approximately 1.7 Å out of the plane described by Ru(1), Ru(2), and S(1). The average S(2)–O bond distance is 1.44 (1) Å, and the S(2) atom is roughly tetrahedral with O–S–O bond angles ranging from 113.6 (7)° to 116.2 (8)° and S(1)–S(2)–O bond angles ranging from 101.1 (4)° to 106.5 (5)°. Other selected interatomic distances and angles are collected in Table III.

Bridging thiosulfate ligands have been found in other complexes. Reaction of $CuCl_2$ with S_7NH in a methanol solution eventually yields $[(S_3N)Cu(\mu\text{-}S_2O_3)Cu(S_3N)]$.[24] Like 2, this complex contains two metal centers linked only by a thiosulfate bridge. The complex $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S_2O_3)$, which was prepared by Brunner and co-workers[25] via air oxidation of $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, also contains a bridging thiosulfate ligand. We have indepently synthesized this complex from the reaction of $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ and SO_2.[9]

A comparison of the bond angles and lengths between the $\mu\text{-}S_2O_3$ ligands in the Mo and Ru complexes reveals an interesting detail. The average S–S–O and O–S–O bond angles of the two systems are similar (103.6 vs 104.1 and 114.6 vs 114.3, respectively, for the Ru complex vs the Mo complex); however, there is a slight difference between the S–S bond lengths for $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S_2O_3)$[9,25] and $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$. The Mo complex exhibits a longer S–S distance than the Ru complex (2.168 vs 2.135 Å). Both of these distances are longer than those previously observed for complexes containing either terminal or bridging S-coordinated thiosulfate ligands.[24,26] Unusual lability of the SO_3 fragment in $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S_2O_3)$ has been observed (i.e. loss of SO_3 in weakly basic solvents[9]); this could be a consequence of the longer S–S bond distance.[9,25] The thiosulfate ligand in $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$, which has a slightly shorter S–S distance, is not as reactive as the ($\mu\text{-}S_2O_3$) in the Mo system; $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ is stable under vacuum and in the presence of the base NEt_3.

Discussion

As stated in the Introduction, an ultimate goal of our study of the interaction of SO_2 with transition-metal hydride compounds is the elucidation of possible mechanisms for the catalytic reduction of SO_2. Previously from these reactions, we have isolated complexes containing sulfide, dithionite, or thiosulfate ligands that are formed from the reduction of SO_2.[5,7–9]

The net reduction of SO_2 and ultimate formation of a stable thiosulfate-containing species from the reaction of SO_2 with $Cp^*Ru(CO)_2H$ is not inconsistent with our earlier studies. There remains, however, the need to address the mechanistic aspects of SO_3H and $-S_2O_3$ ligand formation in this and previously studied reactions. The previous work suggests possible routes for the synthesis of 1 and 2 that can be based on intermediates that contain either an unstable SO_2H ligand or an –S bridging ligand.

The feasibility for formation of an unstable insertion product $Cp^*Ru(CO)_2SO_2H$ can be supported by our earlier preparation of the complexes $(\eta^5\text{-}C_5R_5)M(CO)_3SO_2H$ (M = Mo, W; R = H, Me) via SO_2 insertion into M–H bonds.[7] In addition, Wojcicki and co-workers have extensively documented simple SO_2 insertion into metal–alkyl and –aryl bonds.[27]

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[26] Other systems containing S-coordinated thiosulfate ligands: $Na_3[Au(S_2O_3)_2]$, (S–S distances = 2.051 (5) and 2.069 (5) Å) (Ruben, H.; Zalkin, A.; Faltens, M. O.; Templeton, D. H. *Inorg. Chem.* **1974**, *13*, 1836–1839); $[(NH_3)_5Co(S_2O_3)_3)]Cl$, (S–S distance = 2.048 (2) Å) (Baggio, S. *J. Chem. Soc. A* **1970**, 2384–2387. Restivo, R. J.; Ferguson, G.; Balahura, R. J. *Inorg. Chem.* **1977**, *16*, 167–172); $[Pd(en)(S_2O_3)_2]^{2-}$ (where en = $-H_2NCH_2CH_2NH_2$) (S–S distance = 2.066 (6) Å) (Baggio, S.; Amzel, L. M.; Becka, L. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1698–11705); and *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$ (S–S distance = 2.053 (3) Å) (Murdock, A. R.; Tyree, T.; Otterbein, W.; Kinney, L.; Carreras, M.; Copper, J. N.; Elder, R. C. *Inorg. Chem.* **1985**, *24*, 3674–3679.

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Decomposition of an unstable $Cp^*Ru(CO)_2SO_2H$ could conceivably lead to the formation either **1** or **2**. A possible route for the synthesis of $Cp^*Ru(CO)_2SO_3H$ (**1**) parallels the decomposition pathway of organic sulfinic acids (RSO_2H). These acids are known to disproportionate to give the corresponding sulfonic acids (RSO_3H).[28] Also, an unstable $-SO_2H$ insertion product has been proposed as an intermediate in the synthesis of the thiosulfate-containing $Cp_2MoS_2O_3$ from the reaction of Cp_2MoH_2 with SO_2.[5]

A comparison with the known reaction chemistry of $-SO_2H$ systems, however, reveals that the unstable organometallic-SO_2H compounds that we have isolated[7] undergo autoredox reactions to give complexes containing bridging dithionite and sulfide ligands rather than $-SO_3H$ and $-S_2O_3$ ligands. The ultimate formation of S-bridged products, and especially the formation of the SO_2 adduct compound $[Cp^*W(CO)_2(\mu\text{-}S{\cdot}SO_2)]_2$ from the reaction of $Cp^*W(CO)_3H$ and SO_2,[7] suggests that complexes such as $[Cp^*Ru(CO)_2]_2(\mu\text{-}S)$ or $[Cp^*Ru(CO)_2]_2(\mu\text{-}SO)$ could also be intermediates in the formation of $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$.

Formation of a $\mu\text{-}S_2O_3$ system from a bridging sulfide is not without precedent. We have noted that the S-bridged $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, which we had previously studied as a catalyst for the reduction of SO_2 by hydrogen,[2] also mediates oxygen transfer from SO_2 under mild conditions.[9] Initial reaction of $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ with SO_2 leads to the formation of $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_2)$. In the continued presence of SO_2, a new complex, $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S{\cdot}SO_3)$, is formed. In this reaction system also, labeling studies have confirmed that the oxygen for the formation of the thiosulfate ligand comes from SO_2.[9]

Our future work in this area, which will focus on understanding how the oxygen transfer ligands are formed in $M\text{–}H/SO_2$ reaction systems, will, no doubt, lead to a clearer understanding of the Mo–SH catalysis system,[2] where oxygen transfer from SO_2 and the formation of a reactive thiosulfate may be the basis of the catalytic cycle (eq 1).

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Registry No. 1, 114737-80-3; ^{18}1, 121124-64-9; 2, 121124-61-6; ^{18}2, 121124-65-0; $Cp^*Ru(CO)_2H$, 82728-97-0; SO_2, 7446-09-5; $[Et_3NH]^+[Cp^*Ru(CO)_2SO_3]^-$, 121124-62-7; SO_3, 7446-11-9; $Me_3N{\cdot}SO_3$, 3162-58-1; $[Cp^*Ru(CO)_2]_2$, 70669-56-6; $Cp^*Ru(CO)_2SO_3CH_3$, 121124-63-8; $S^{18}O_2$, 24262-77-9.

Supplementary Material Available: A table with anisotropic thermal parameters for $[Cp^*Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ (1 page); a listing of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Indium(III) Compounds Containing the Neopentyl Substituent, $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $In(CH_2CMe_3)Cl_2$, and $In(CH_2CMe_3)_2CH_3$. Crystal and Molecular Structure of Dichloroneopentylindium(III), an Inorganic Polymer

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The neopentylindium(III) derivatives $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $In(CH_2CMe_3)Cl_2$, and $In(CH_2CMe_3)_2Me$ have been prepared and characterized by elemental analyses, cryoscopic molecular weight studies in benzene, IR and ^1H NMR spectroscopic data, and Lewis acidity studies. Molecular weight studies suggest that $In(CH_2CMe_3)_3$ and $In(CH_2CMe_3)_2Me$ are monomeric molecules whereas $In(CH_2CMe_3)_2Cl$ is dimeric in benzene solution. The dichloro derivative $In(CH_2CMe_3)Cl_2$, which has insufficient solubility in benzene for molecular weight studies, crystallizes in the acentric space group $P2_12_12_1$ with $a = 6.717$ (4) Å, $b = 12.217$ (4) Å, $c = 22.658$ (7) Å, $V = 1859$ Å^3, and $Z = 8$ (formula units). Diffraction data (Mo Kα, $2\theta = 2\text{–}50°$) were collected with a Enraf-Nonius CAD-4/$\theta\text{–}2\theta$ diffractometer. Full-matrix least-squares refinement led to a final R value of 0.062 for 1584 observed [$F_o \geq 5\sigma(F_o)$] reflections. Dichloroneopentylindium(III) is a one-dimensional polymer with no short contacts between strands. Each indium has distorted trigonal-bipyramidal geometry.

Introduction

Organometallic chemical vapor deposition (OMCVD) is one of the most useful techniques for making compound semiconductors[2] such as InP. The most desirable organometallic sources for OMCVD should be easily prepared, readily purified volatile liquids with excellent stability at room temperature. A number of homoleptic organoindium(III) compounds (InR_3, R = Me,[3] Et,[4,5] *n*-Pr,[5]

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