3. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*o* (4). 1 (2.0 g, 7.2 mmol) reacted with 7.2 mmol of *o*-$CH_3C_6H_4Li$[13] at −40 °C for 3 h followed by the alkylation and further treatment similar to the procedures described above for 2 gave 1.1 g (38%, based on 1) of orange-red crystals, mp 38 °C dec. Anal. Calcd for $C_{22}H_{28}O_3Fe$ (mol wt 396.31): C, 66.68; H, 7.12; Fe, 14.09. Found: C, 66.38; H, 7.30; Fe, 13.86. IR [ν(CO)]: 1955 vs, 1901 vs cm^{-1} (CH_2Cl_2); 1974 sh, 1960 vs, 1930 sh, 1915 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 396 $[M]^+$ (4.5), 368 $[M - CO]^+$ (7.0), 340 $[M - 2CO]^+$ (100).

4. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4OCH_3$-*p* (5). *n*-$C_4H_9Li$[14] (7.4 mmol) was mixed with a solution of 1.40 g (7.4 mmol) of *p*-$CH_3OC_6H_4Br$ in 15 mL of ether. The mixture was stirred at room temperature for 1 h. The resulting ether solution of *p*-$CH_3OC_6H_4Li$[15] reacted with 2.0 g (7.2 mmol) of 1 in 50 mL of ether at −50 °C for 3 h. Subsequent alkylation and treatment in a similar manner as described in preparation 1 afforded 1.2 g (40%, based on 1) of red oil. Anal. Calcd for $C_{22}H_{28}O_4Fe$ (mol wt 412.31): C, 64.09; H, 6.85; Fe, 13.54. Found: C, 64.02; H, 6.84; Fe, 13.25. IR [ν(CO)]: 1962 vs, 1895 vs cm^{-1} (CH_2Cl_2); 1977 vs, 1960 sh, 1915 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 412 $[M]^+$ (5.3), 384 $[M - CO]^+$ (14.3), 356 $[M - 2CO]^+$ (90.0).

5. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CF_3$-*p* (6). 1 (2.0 g, 7.2 mmol) reacted, in a manner similar to that described in preparation 1, with fresh *p*-$CF_3oC_6H_4Li$[16] prepared by reaction of 1.63 g (7.2 mmol) of *p*-$CF_3C_6H_4Br$ with 7.2 mmol of *n*-C_4H_9Li, in ether solution at −45 °C for 3 h to give 1.40 g (43%, based on 1) of red crystals, mp 82 °C dec. Anal. Calcd for $C_{22}H_{25}O_3F_3Fe$ (mol wt 450.28): C, 58.68; H, 5.60; Fe, 12.66. Found: C, 59.16; H, 5.63; Fe, 12.70. IR [ν(CO)]: 1980 vs, 1917 vs cm^{-1} (CH_2Cl_2); 1997 vs, 1940 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 450 $[M]^+$ (6.4), 422 $[M- CO]^+$ (41.5), 394 $[M- 2CO]^+$ (100).

Crystal Structure Determination. The single crystals of 3 and 4 suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether at −80 °C. A single crystal of approximate dimension of 0.20 × 0.30 × 0.30 mm for 3 and 0.20 × 0.30 × 0.40 mm for 4 were sealed in capillaries under N_2 atmosphere. The X-ray diffraction intensity data of 2476 and 2986 independent reflections, of which 1728 and 1755 with $F_o \geq 3\sigma(F_o)$ were observable, were collected with a R_3M/E four-circle diffractometer at −90 °C using Mo Kα radiation with a $\theta/2\theta$ scan mode within the ranges $3° \leq 2\theta \leq 42°$ and $3° \leq 2\theta \leq 45°$ for 3 and 4, respectively. The intensity data were corrected for Lorentz and Polarization factors, but no absorption correction was made.

3 and 4 crystallize in the monoclinic system. The space groups for 3 and 4 were determined to be $P2_1/c$ and $P2_1/a$, respectively, according to the following systematic absences: $h0l$ reflections, $l = 2n + 1$ for 3 and $h = 2n + 1$ for 4; $0k0$ reflections, $k = 2n + 1$ for 3 and 4.

The crystal structures of 3 and 4 were solved by using the Patterson function method. After the position of the Fe atom was determined, the coordinates of the other non-hydrogen atoms were located by the Fourier synthesis. The coordinates of all hydrogen atoms of 3 were located at difference Fourier map and those of 4 were obtained by theoretical calculation. The coordinates and thermal parameters of all the atoms of 3 and 4 were refined by a block-diagonal-matrix least-squares method to give the final discrepancy indices $R = 0.0318$ and $R_w = 0.306$ and $R = 0.0847$ and $R_w = 0.0616$ for 3 and 4, respectively. The crystallographic data for 3 and 4 are listed in Table II. The atomic coordinates and temperature factors of non-hydrogen atoms for 3 and 4 are presented in Table III. The bond lengths and angles and the equations of the least-squares planes for 3 and 4 are given in Tables IV and V, respectively.

Acknowledgment. Financial support from the Science Foundation of the Chinese Academy of Sciences and the National Science Foundation of China is gratefully acknowledged.

Registry No. 1, 98212-66-9; 2, 114719-40-3; 3, 114719-41-4; 4, 114719-42-5; 5, 114719-43-6; 6, 114719-44-7; **a** (Ar = Ph), 114719-45-8; **a** (Ar = *p*-MeC_6H_4), 114719-46-9; **a** (Ar = *o*-MeC_6H_4), 114719-47-0; **a** (Ar = *p*-$MeOC_6H_4$), 114719-48-1; **a** (Ar = *p*-$CF_3C_6H_4$), 114719-49-2.

Supplementary Material Available: Table of H-atom coordinates and isotropic thermal parameters and anisotropic thermal parameters for complexes 3 and 4, the selected mass spectra of complexes 2–6, and the unit cell drawings of complexes 3 and 4 (7 pages); a listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on current masthead page.

Communications

Reaction of Sulfur Dioxide with $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$: Insertion of SO_2 into the Ru–H Bond and Oxygen Transfer To Form $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$

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Summary: The addition of SO_2 to $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$ yields $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$. Reaction of the starting hydride with $S^{18}O_2$ results in the formation of the product with a completely labeled SO_3H ligand, demonstrating that SO_2 provides the additional oxygen atom for the formation of this ligand.

Any process that will convert SO_2 in stack gases to inoffensive products such as sulfur and water will be based on the reduction/oxygen transfer chemistry of SO_2. To better understand this chemistry, we have been investigating reactions of SO_2 with transition-metal hydride complexes.[1,2] This work has now been extended to include the addition of SO_2 to $Cp^*Ru(CO)_2H$ ($Cp^* = \eta^5\text{-}C_5Me_5$).

Reactions of SO_2 with metal hydride species typically give products containing ligands formed from reduction of SO_2.[1-3] In particular, we have achieved partial reductions of SO_2 on Mo and W centers:[1,2]

$$CpM(CO)_3H + SO_2 \rightarrow CpM(CO)_3(SO_2H) \quad (1)$$

$$Cp_2MH_2 + 2SO_2 \rightarrow Cp_2M(S_2O_3) + H_2O \quad (2)$$

The SO_2H complexes are thermally unstable and undergo autoredox reactions to form oxo–sulfide clusters. In the $Cp^*Ru(CO)_2H$ case, however, a structural study revealed

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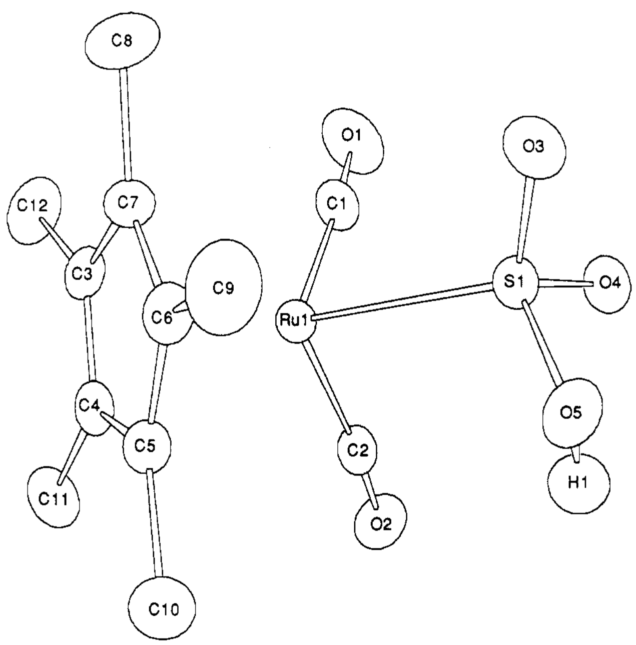

Figure 1. Molecular configuration of (η^5-C_5Me_5)Ru$(CO)_2SO_3H$ shown with 50% atomic probability ellipsoids. H1 is hydrogen bound to O4 on the neighboring symmetry-related molecule.

one of the products to be a stable insertion/oxygen transfer complex Cp*Ru$(CO)_2SO_3H$[4] which corresponds to an *oxidation* rather than a reduction of SO_2.

The SO_3H complex was prepared under rigorous exclusion of air by condensing SO_2 (excess *or* a 1:1 stoichiometric amount) into a CH_3CN solution of Cp*Ru$(CO)_2H$[5] (500 mg, 1.7 mmol). After being warmed to room temperature, the mixture was stirred for 2–3 h. Reduction of solvent volume in vacuo gave a bright yellow precipitate[6] that was collected and washed with hexane. The ^1H NMR spectrum of this species ($CDCl_3$) displayed a Cp* peak at δ 1.93 (15 H) and a resonance at δ 6.67 (–OH, 1 H). This latter resonance shifted (indicating exchange of the –OH) to δ 4.47 as either water or more solid complex was added to the NMR sample. The ^1H NMR spectrum ($CDCl_3$) of the orange filtrate exhibited a Cp* peak at δ 1.91 (a second product) along with a weak peak at δ 1.93 indicative of the isolated yellow product.

A structural analysis[7] of crystals of the yellow complex showed it to be Cp*Ru$(CO)_2SO_3H$. A view of the independent molecule, which contains no crystallographically imposed symmetry, is shown in Figure 1. The Ru–CO distances are 1.888 (5) and 1.895 (4) Å; the Ru–S distance is 2.318 (2) Å. The S–O distances are 1.431 (3), 1.487 (3) and 1.559 (3) Å where the longest S–O distance corresponds to the oxygen to which the hydrogen of the SO_3H ligand is bound. The difference of 0.056 Å in the two shorter S–O distances is a consequence of hydrogen bonding from a SO_3H ligand to the S–O(4) 1.487 Å oxygen on a center-of-symmetry related SO_3H ligand; the distances of 1.84 (4) Å for O(4)–H(1) and 2.629 (4) Å for O(4)–O(5) are within the ranges usually ascribed to hydrogen bonding.

Table I. Comparison of Infrared Data (cm^{-1}) for (η^5-C_5R_5)M$(CO)_2SO_3H$ (M = Ru, R = Me; M = Fe, R = H)

compound	ν(CO)	ν(OH)	ν(SO)
(η^5-C_5H_5)Fe$(CO)_2SO_3H$[15,a]	2062, 2018	2940	1184, 1084, 811
(η^5-C_5Me_5)Ru$(CO)_2SO_3H$[b]	2025, 2005	2460, 1243	1180, 1080, 810
(η^5-C_5Me_5)Ru$(CO)_2S^{18}O_3H$[b]	2025, 2005	2450, *c*	1140, 1020, *c*

[a] KBr. [b] $CHCl_3$. [c] Obscured.

Examples of alkyl sulfito (M–SO_2OR) complexes are known for Ni,[8] Pd,[9–11] Pt,[10–13] Co,[8] Ru,[14,15] and Fe.[16] These complexes are generally synthesized by reactions of the metal complex with SO_2 and ROH, which directly form the $SO_2(OR)$ group. Hydrolysis of these species to form an SO_3H group has only been demonstrated for the preparation of the related CpFe$(CO)_2SO_3H$ via hydrolysis of CpFe$(CO)_2SO_3R$.[16] The infrared spectrum of CpFe$(CO)_2SO_3H$ is compared with that of Cp*Ru$(CO)_2SO_3H$ in Table I.

In view of the above reactions, the question of the source of the extra oxygen for the formation of the SO_3H ligand becomes important. As we surmised this oxygen to come from a second SO_2, reaction of Cp*Ru$(CO)_2H$ with $S^{18}O_2$[17] was carried out. Under the same conditions as previous reactions, $S^{18}O_2$ was condensed into a solution of the hydride and the reaction products were monitored by IR. Solution IR ($CHCl_3$) showed no shifts between the C–O bands for the unlabeled product and the labeled product. The O–H and S–O bands shifted as detailed in Table I. These shifts demonstrate that the source of the oxygen for the formation of the SO_3H ligand is SO_2. On the basis of eq 1, we presume that SO_2 inserts into the Ru–H bond to form an unstable Ru–SO_2H species that then acquires an extra oxygen from SO_2.

SO_2H species have also been postulated as intermediates in the homogeneous hydrogenation of SO_2 to S_8 and H_2O catalyzed by [Cp*Mo(μ-S)(μ-SH)]$_2$ or Cp*$_2Mo_2$(μ-S)$_2$(μ-S)$_2$ under mild conditions.[18] Interestingly we have found

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(4) A portion of this research has been previously presented: Kubat-Martin, K. A.; Kubas, G. J.; Ryan, R. R. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, 1987.

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(6) Yield: 100 mg. Anal. Calcd for $C_{12}H_{16}O_5SRu$: C, 38.60; H, 4.32; S, 8.59. Found: C, 39.23; H, 4.06; S, 9.20.

(7) Ru(η^5-C_5Me_5)$(CO)_2SO_3H$ (fw = 373.38): yellow parallelopiped-shaped crystals (0.1 × 0.2 × 0.2 mm) obtained by cooling a $CDCl_3$ solution containing the complex; monoclinic, $P2_1/a$; a = 8.654 (5) Å, b = 21.930 (5) Å, c = 8.901 (5) Å, β = 119.53 (5)°; V = 1469.8 (3) Å^3 at T = 295 K; d_{calcd} = 1.69 g/cm^3 for Z = 4; linear absorption coefficient μ = 11.9 cm^{-1} for Mo Kα (λ = 0.709 30 Å) radiation. An empirical absorption correction (based on a ψ scan of a strong close-to-axial reflection) was carried out. The structure was determined by standard Patterson and difference Fourier methods using neutral atoms scattering factors and appropriate anomalous scattering terms.[21] A correction was made for secondary extinction.[22] Anisotropic thermal parameters were refined for non-hydrogen atoms. All hydrogen atoms were located in an electron density map and were refined with B fixed at 4.0. Least-squares refinements did not converge if B of H1 was not fixed. Full-matrix least-squares refinement converged at R = 2.3% and R_w = 3.1% for 1629 independent reflections with $I > 2\sigma(I)$ obtained with a Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation. Calculations were performed on a CDC 7600 computer utilizing an in-house package of programs developed in part by Dr. A. C. Larson.

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(17) $S^{18}O_2$ (<95%) was prepared from the reaction of $N^{18}O$ and S_8 at 450 °C and was purified by trap-to-trap distillation.

oxygen transfer from SO_2 also readily takes place on the latter complex, cleanly forming the thiosulfate complex $Cp^*Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SSO_3)$ and S_8.[19] The Mo catalyst can be regenerated by reaction of the thiosulfate species with H_2, suggesting a role for oxygen transfer in the catalytic cycle.

Formation of stable SO_3H moieties in the d^6 Ru–H system is intriguing, especially in view of the fact that reactions of SO_2 with transition-metal hydrides generally form SO_2 reduction products (i.e. S_2O_3, S_2O_4, and SO_2H).[1-3] However, it has been previously noted by Mingos and co-workers[20] that reactions of SO_2 with low-valent Ru compounds are likely to form sulfate complexes. An example of this is the reaction of SO_2 and $RuH_2(PPh_3)_4$ that forms $[Ru(SO_4)(SO_2)(PPh_3)_2]_2$.[20] The formation of coordinated sulfate at the d^6 Ru center has been attributed to either traces of O_2 or to disproportionation of SO_2; however, labeling studies have not been reported.

Future work will involve identification of the other product formed in the $Cp^*Ru(CO)_2H/SO_2$ reaction along with a study of the reactivity patterns of $Cp^*Ru(CO)_2SO_3H$.

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Registry No. $Cp^*Ru(CO)_2SO_3H$, 114737-80-3; SO_2, 7446-09-5; $Cp^*Ru(CO)_2H$, 82728-97-0.

Supplementary Material Available: Tables of selected listings of bond distances and angles, fractional coordinates, and anisotropic thermal parameters (3 pages); a listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Trivalent Germanium Cations in Solution

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Summary: Reaction of R_3GeH (R = Me, Ph) with trityl perchlorate produces free germylenium cations (R_3Ge^+) in dilute sulfolane solution. Conductivities, cryoscopic molecular weights, ^{35}Cl line widths, and ^{35}Cl chemical shifts are interpretable only in terms of ionic materials. Association with perchlorate occurs in sulfolane at concentrations above 0.01 M and in dichloromethane at all concentrations studied.

Germanium(III) cations (germylenium ions) have not heretofore been prepared in solution.[2] The recent preparation of the first silicon(III) cations in solution[3] prompts us to report that long-lived germylenium ions may be prepared in polar, nonnucleophilic solvents. Because of the higher polarizability of germanium, the situation may be somewhat more favorable than for silicon. Indeed, the divalent state of germanium is more readily accessible than that of silicon.[4]

We have prepared the germylenium ions Me_3Ge^+ and Ph_3Ge^+ with perchlorate as the anion by hydride abstraction from the corresponding germane in dichloromethane or sulfolane. These solvents are of extremely low nucleophilicity but still are highly polar. The abstracting agent is trityl cation, and the equilibrium is well on the side of the germylenium ion (eq 1). The ^1H and ^{13}C

$$R_3GeH + Ph_3C^+ClO_4^- \rightarrow R_3Ge^+ClO_4^- + Ph_3CH \qquad (1)$$

spectra of both Me_3GeClO_4 and Ph_3GeClO_4 indicate that the Ge–H resonance is gone and that there is on the average only one species in solution, with the gross structure R_3GeClO_4.

The major structural question that must be addressed concerns association of the germylenium ion with itself (dimerization), with solvent, or with perchlorate anion (to form a covalent or ion-paired species). The materials produced by eq 1 are highly conducting in sulfolane (equivalent conductance $\Lambda = 10.07\ \Omega^{-1}\ cm^2\ eq^{-1}$ at about 1 mM for R = Me and 9.98 $\Omega^{-1}\ cm^2\ eq^{-1}$ for R = Ph, compared with 10.0 $\Omega^{-1}\ cm^2\ eq^{-1}$ for trityl perchlorate). Solvents were dried to a level well below that of the substrate in all of these experiments. In dichloromethane, which is less polar than sulfolane, the equivalent conductance is 0.0053 $\Omega^{-1}\ cm^2\ eq^{-1}$ for R = Me and 0.0191 $\Omega^{-1}\ cm^2\ eq^{-1}$ for R = Ph, the lower values reflecting substantial association of the germylenium ion with perchlorate.

The molecular weights were measured cryoscopically in dilute sulfolane. If the materials are ionic monomers (two particles), the measured molecular weights are 196 for R = Me (9.7% different from the theoretical value of 217.1) and 423 for R = Ph (error of 4.9% from 403.3). If the species were covalent or tightly ion paired, there would be only one particle. With this model, the observed molecular weights are 98 for R = Me (55% different from theory) and 211.5 for R = Ph (47.5% error). Thus both conductance and molecular weight measurements confirm the ionic nature of both Me_3GeClO_4 and Ph_3GeClO_4 in dilute sulfolane. Dimers also are excluded by these measurements.

Even more sensitive probes for the ionicity of these species are the ^{35}Cl line width and chemical shift.[3] Because ^{35}Cl has a large quadrupole moment, line widths tend to be extremely broad, except in a tetrahedral environment such as that offered by free perchlorate ion. Thus ionic germylenium perchlorates should have narrow line widths, and associated forms should have broad line widths. *In dilute solution we observe the narrow line widths expected for the ionic form.* Thus the ^{35}Cl line width for Me_3GeClO_4 is only 20 Hz (chemical shift 4.4 ppm downfield from dilute aqueous $HClO_4$) at 0.00153 M, and for Ph_3GeClO_4 it is 40 Hz (δ 4.1) at 0.001 555 M. Both lines broaden as the concentration increases, and the resonance positions move upfield. For Me_3GeClO_4, the line width increases to 1030 Hz (δ −11) at 0.584 M. For Ph_3GeClO_4, the line width

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(1) (a) Supported by the National Science Foundation (Grant CHE-8609899). (b) On leave from the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.

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