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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 $Cp^*Ru(CO)_2SO_3H$.

Acknowledgment. This research was performed under the auspices of the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

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

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

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.

(2) Such ions, however, are known in the gas phase, e.g., Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982,** *104,* 4329-4332.

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increases to 4400 Hz (δ -13) at 0.146 M. From these values, we calculated that the amount of free ion varies for Me_3GeClO_4 from 99% at 0.001 53 M to 6.4% at 0.584 and for Ph_3GeClO_4 from 99% at 0.001 555 M to 4.4% at 0.146 M. By comparison, the line width of $HClO_4$ in sulfolane is 10-25 Hz in the concentration range 0.00225-0.146 M.

Charge distribution within the phenyl ring was explored by comparison of the ^{13}C chemical shifts of Ph_3GeH and Ph_3Ge^+. The ipso and ortho shifts are not useful because of the normal α and β effects. The meta resonance moves from δ 128.33 to δ 128.27 on cation formation in CH_2Cl_2 and the para resonance from δ 129.14 to δ 131.9. Such shifts are consistent with the modest charge buildup expected of ion pairs at high concentrations.

These results are interpretable only in terms of monomeric, ionic germylenium ions in dilute sulfolane solution: high conductance, two-particle molecular weight, and sharp ^{35}Cl line width. Association occurs at higher concentrations in sulfolane and in less polar solvents such as dichloromethane.

Registry No. Me_3Ge^+, 76568-90-6; Ph_3Ge^+, 41099-51-8.

Unprecedented Transformation of a Vinylidene Ligand. Synthesis and ESR Characterization of a Paramagnetic σ-Acetylide Complex of Rhodium(II)

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Summary: Thermal decomposition in THF of the diamagnetic vinylidene complex $[(np_3)RhC{=}C(H)Ph]^+$, obtained by protonation of $[(np_3)RhC{\equiv}CPh]$, affords H_2 and the paramagnetic σ-acetylide complex of rhodium(II) $[(np_3)RhC{\equiv}CPh]^+$ which has been characterized by chemical, electrochemical, and ESR techniques [$np_3 = N(CH_2CH_2PPh_2)_3$].

The key role of the vinylidene group in many catalytic processes involving carbon monoxide or unsaturated hydrocarbons is certainly one of the reasons for experimental[1] and theoretical[2] studies presently carried out on vinylidene complexes of transition metals. In this communication we report on an unprecedented transformation of the vinylidene ligand in $[(np_3)RhC{=}C(H)Ph]BPh_4$[3] (1) [$np_3 = N(CH_2CH_2PPh_2)_3$].

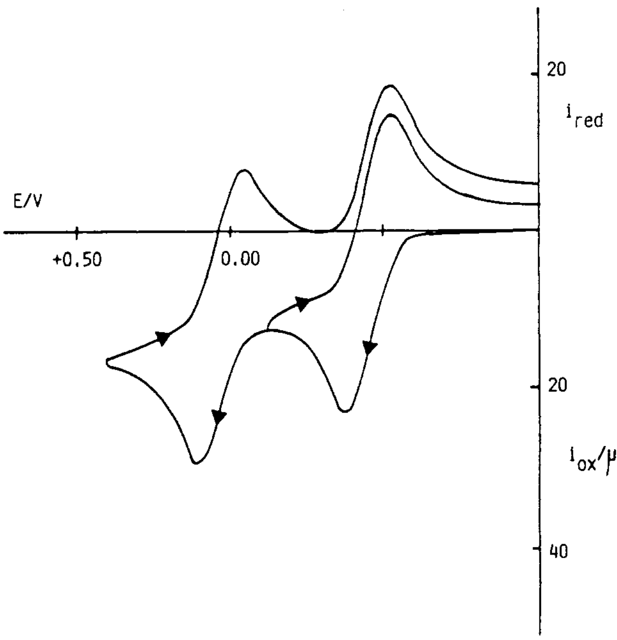
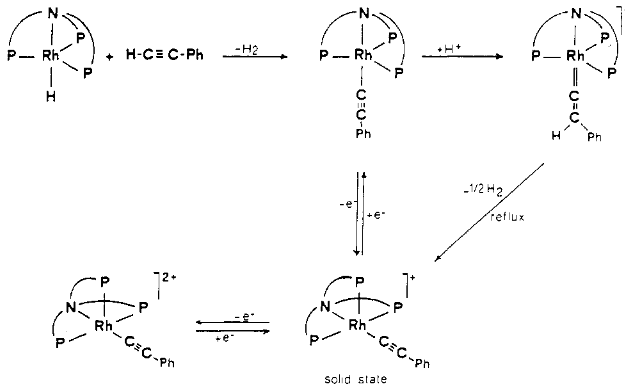


Figure 1. Cyclic voltammogram recorded at a platinum electrode on a THF solution containing $[(np_3)RhC{\equiv}CPh]$ (1.70×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Scheme I



Compound 1 is synthesized as deep red crystals by protonation of $[(np_3)RhC{\equiv}CPh]$[4] (2) in THF by $HOSO_2CF_3$, followed by addition of $NaBPh_4$ in ethanol (yield 70%) (Scheme I). The neutral σ-acetylide 2 is prepared quantitatively by treatment of $[(np_3)RhH]$[5] (3) in THF with a twofold excess of $HC{\equiv}CPh$.[6] The vinylidene complex 1 is trigonal-bipyramidal (TBP) as deduced by analysis of the ^{31}P and ^1H NMR spectra. In particular, the $^{31}P\{^1H\}$ NMR spectrum exhibits an A_3X spin system

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(3) Anal. Calcd (Found): C, 75.07 (75.45); H, 5.93 (5.82); N, 1.10 (1.19); Rh, 8.52 (8.74). IR (Nujol): $\nu(C{=}C)$ 1640 (m), phenyl-reinforced vibration 1590 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz, TMS, 298 K): δ 4.93 [qd, 1 H, $^4J(HP) = 13.8$ Hz, $^3J(HRh) = 1.1$ Hz, $=CH$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 32.19 MHz, H_3PO_4 85%, 298 K): A_3X pattern, $\delta(P_A)$ 37.86 [$J(PRh) = 136.8$ Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.43 MHz, TMS, 298 K): δ 316.82 [dq, $J(CRh) = 44.2$ Hz, $^2J(CP) = 20.0$ Hz, C_α of the vinylidene ligand]; the β-carbon resonance was not conclusively identified as it lies under the phenyl multiplets. Like many vinylidene complexes, 1 is deprotonated by a base such as NEt_3 to form the starting σ-acetylide and $[NEt_3H]^+$.

(4) Anal. Calcd (Found): C, 69.79 (70.01); H, 5.63 (5.52); N, 1.59 (1.63); Rh, 11.87 (12.00). IR (Nujol): $\nu(C{\equiv}C)$ 2080 (s), phenyl-reinforced vibration 1590 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): A_3X pattern, $\delta(P_A)$ 24.68 [$J(PRh) = 160.7$ Hz].

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