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Interconversion of Persulfido, Sulfur Hydride, and Hydride Ligands Coordinated to $CpRu(PPh_3)_2^+$

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The electron-rich metallothiol $CpRu(PPh_3)_2SH$ (**1**) has been prepared from the reactions of $CpRu(PPh_3)_2Cl$ with NaSH and $CpRu(PPh_3)_2H$ with elemental sulfur. Carbonylation of **1** gives $CpRu(PPh_3)(CO)SH$ whereas the carbonylation of $CpRu(PPh_3)_2Cl$ is thermodynamically unfavorable. Protonation of **1** gives $[CpRu(PPh_3)_2(SH_2)]^+$. Alkylation of **1** gives thiol complexes $[CpRu(PPh_3)_2(RSH)]^+$ ($R = CH_3$); such complexes were also prepared directly from $CpRu(PPh_3)_2OTf$ ($OTf = CF_3SO_3$) and RSH. The structure of the thiol complex $[CpRu(PPh_3)_2(n\text{-}PrSH)]BF_4{\cdot}CH_2Cl_2$ was determined by X-ray methods. Crystal data: triclinic space group $P\bar{1}$, with $a = 13.308$ (5) Å, $b = 14.641$ (7) Å, $c = 13.205$ Å, $\alpha = 113.64$ (3)°, $\beta = 110.01$ (4)°, $\gamma = 84.45$ (3)°, $V = 2212$ (2) Å^3, and $Z = 2$; structure solution and refinement based on 4091 reflections with $I > 2.58\sigma(I)$ to give $R = 0.054$. $[CpRu(PPh_3)_2(SH_2)]^+$ reacts reversibly with H_2 to give the dihydride $[CpRu(PPh_3)_2H_2]^+$. Analogous results were found for $[((2\text{-}SC_4H_3)CH_2C_5H_4)Ru(PPh_3)_2]^+$; the S-bound thiophene ligand can be displaced by H_2S, H_2, H^-, and SH^-. $[CpRu(PPh_3)_2(H_2S)]^+$ oxidizes in air to give $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ (**2**). Salts of **2** are formed in two-electron oxidations of **1** with Ph_3CBF_4, Cp_2Fe^+, and I_2 as well as electrochemically. A presumed intermediate in this oxidation is $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$. This mixed-valence compound disproportionates upon addition of HOTf to give **2** and $[CpRu(PPh_3)_2(SH_2)]^+$. The reaction of **1** with sulfur gave ruthenium polysulfides $[CpRu(PPh_3)]_2S_x$ ($x = 4, 6$).

Introduction

The hydrosulfide (SH) functionality recurs throughout sulfur chemistry. The chemistry of organic thiols is well recognized,[1] and metallothiols (MSH) have received considerable recent attention.[2] The SH^- ligand is the conceptual and often the actual link between the coordination chemistry of sulfido (S^{2-}) and mercapto (RS^-) complexes. MSH species are very likely involved in the formation of metal sulfides in aqueous solution since the pK_a of HS^- lies outside the aqueous range.[3] Additionally, MSH functionalities form upon hydrogenation of certain metal sulfide surfaces.[4]

While the MSH and MS^- fragments are obviously related, there are few MSH complexes that can withstand deprotonation. Two examples of protonated thiometalate anions are salts of $W_2(S_2)_4S_2(SH)^-$ [5] and $WS_3(SH)^-$.[6] The compound $WS_2(SH)_2$ has been claimed.[7] Additionally the protonation of $VO_xS_{4-x}^{3-}$ has been studied.[8] The protonation of MS^- species is related to the unusual redox processes that attend the acidification of tetrathiometalates. For example, protonation of WS_4^{2-} leads variously to $W_2S_{11}^{2-}$,[9] $W_3S_9^{2-}$,[10] $W_4S_{12}^{2-}$,[11] and polymeric $WS(S_2)$.[12,13] Such proton-induced transformations are related in poorly defined ways to other "induced redox" reactions of thiometalates, e.g. the conversion of MoS_4^{2-} to $MoS(S_4)_2^{2-}$ and $Mo_2S_4(S_2)_2^{2-}$.[14,15] These processes are characterized by net oxidation whereby persulfido bonds are forged, often[16] concomitant with formal reduction of the metal center. In order to gain some insight into these fundamental reactions, we have examined the oxidation of complexes containing a single SH ligand.

Oxidations of the MSH functionality have been little studied although the oxidation of organic thiols is well-known. Certain MSH complexes appear to oxidize somewhat like organic thiols resulting in "disulfides" (persulfides[17]). Sykes has described the 1e oxidation of $[Cr(H_2O)_5(SH)]^{2+}$, which gives a "$Cr_2S_2^{4+}$" product, probably $[Cr(H_2O)_5]_2(\mu\text{-}S_2)^{4+}$.[18] The oxidation of

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(9) $W_2S_{11}^{2-}$: Manoli, J.-M.; Potvin, C.; Sécheresse, F. *Inorg. Chem.* **1987**, *26*, 340. See also ref 6. $W_2O_2S_9^{2-}$: Manoli, J.-M.; Potvin, C.; Sécheresse, F. *Inorg. Chim. Acta* **1987**, *133*, 27.

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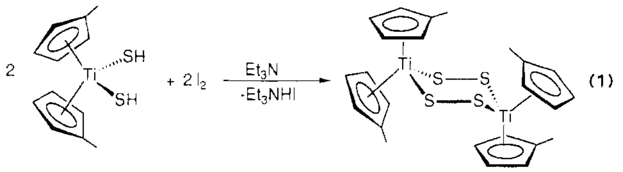
$(MeCp)_2Ti(SH)_2$ by I_2 gives a cyclic bis(persulfide) (eq 1).[19]



Treatment of $[Co(CN)_5]_2(\mu\text{-}O_2)^{6-}$ with H_2S gives $[Co(CN)_5]_2(\mu\text{-}S_2)^{6-}$.[20]

Kuehn and Taube implicated the 2e oxidation of $[Ru(NH_3)_5(SH)]^+$.[21] While the latter was not isolated in pure form, the oxidized product $[Ru(NH_3)_5]_2(\mu\text{-}S_2)^{4+}$ is stable.[22] We have previously remarked on the similarities of the coordination chemistry of the $[Ru(NH_3)_5]^{2+}$[23,24] and $CpRu(PPh_3)_2^+$ fragments.[25] In this report, we describe our studies on the oxidation of $CpRu(PPh_3)_2SH$ to $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$.

Several ruthenium SH complexes have been characterized, the first being $(PhMe_2P)_3Ru(\mu\text{-}SH)_3Ru(SH)(PMe_2Ph)_2$,[26] prepared from the reaction of $RuH_2(PMe_2Ph)_4$ and H_2S. The compounds $RuH(SH)(CO)_2(PPh_3)_2$ and $Ru(SH)_2(CO)_2(PPh_3)_2$ form sequentially in the reaction of $Ru(CO)_2(PPh_3)_3$ and H_2S.[27] $RuH_2(PPh_3)_4$ and H_2S react to give $RuH(SH)(PPh_3)_3$.[28] $(C_5Me_5)Ru(PMe_3)_2SH$ has been the subject of recent thermochemical studies.[29] Solid RuS_2[30] adds hydrogen at room temperature, giving surface SH groups.[4]

Results

$CpRu(PPh_3)_2SH$ and $CpRu(PPh_3)(CO)SH$. A slurry of $CpRu(PPh_3)_2Cl$ and excess NaSH in hot methanol react to give a good yield of $CpRu(PPh_3)_2SH$ (**1**). This neutral orange-brown air-sensitive material is soluble in polar organic solvents. Its ^1H NMR spectrum shows a single Cp resonance and a phenyl multiplet along with the S*H* resonance, which appears as a triplet at −3.15 ppm upfield of TMS (J_{PH} = 7 Hz).[31] The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a single line at 43.75 ppm downfield of the 85% H_3PO_4 standard. Compound **1** can also be prepared from the reaction of $CpRu(PPh_3)_2H$ with stoichiometric amounts of sulfur.

Solutions of **1** undergo easy carbonylation at ambient temperatures to give the chiral metallothiol $CpRu(PPh_3)(CO)SH$. In contrast, $CpRu(PPh_3)_2Cl$ reacts incompletely with CO under these conditions (eq 2). The ^1H NMR spectrum of the carbonyl

$$CpRu(PPh_3)_2X + CO \rightleftarrows CpRu(PPh_3)(CO)X + PPh_3 \qquad (2)$$

$$X = Cl\text{: } K = 0.06$$

$$X = SH\ (\mathbf{1})\text{: } K > 20$$

shows an S*H* resonance at −3.57 ppm as a doublet (J_{PH} = 7 Hz). The ν_{CO} values for the SH and Cl[32] compounds are 1952 and 1960 cm^{-1} (KBr).

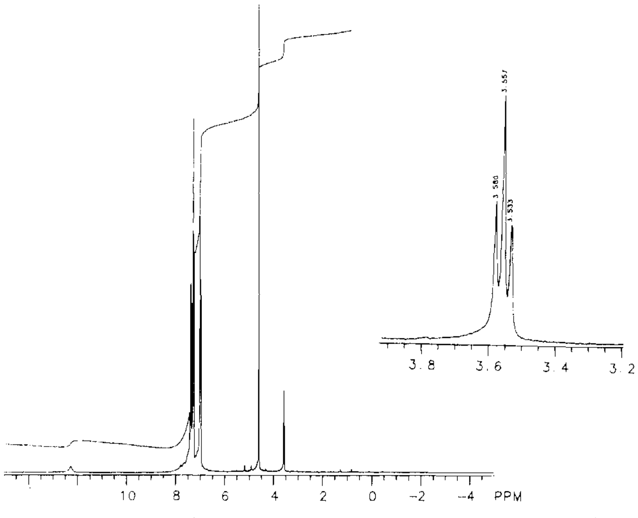


Figure 1. 300-MHz ^1H NMR spectrum of $[CpRu(PPh_3)_2(H_2S)]^+$ obtained by protonation of the thiol **1**. The low-field resonance is due to *H*OTf. The inset is an expansion of the S*H*$_2$ region.

$[CpRu(PPh_3)_2(SH_2)]OTf$. The protonation of **1** with 1 equiv of triflic acid (HOTf = $HOSO_2CF_3$) cleanly affords $[CpRu(PPh_3)_2(H_2S)]OTf$. In the ^1H NMR spectrum, the *H*$_2$S group appears as a triplet at 3.58 ppm (J_{PH} = 7.2 Hz), shifted 7 ppm downfield from δ_{SH^-} for **1** (Figure 1). In the presence of $[CpRu(PPh_3)_2(H_2S)]^+$, the Cp and S*H* resonances of $CpRu(PPh_3)_2SH$ disappear and the *H*$_2$S resonance is broad, indicating rapid equilibrium between **1** and its conjugate acid. The H_2S complex also forms upon treatment of $CpRu(PPh_3)_2OTf$ with H_2S. In the presence of excess H_2S, the coordinated *H*$_2$*S* resonance is broad. Attempts to isolate the H_2S complex were thwarted by its tendency to revert to $CpRu(PPh_3)_2OTf$.

Bruce observed that $CpRu(PMe_3)_2Cl$ can be protonated to give the ruthenium(IV) hydride $[CpRu(PMe_3)_2Cl(H)]^+$.[33] This suggested the possibility that $[CpRu(PPh_3)_2(SH_2)]^+$ exists in equilibrium with the ruthenium(IV) hydride $[CpRuH(PPh_3)_2SH]^+$. Variable-temperature ^1H NMR studies on the H_2S complex failed however to show new signals even at −80 °C.

Treatment of $[CpRu(PPh_3)_2(SH_2)]^+$ solutions with hydrogen rapidly establishes an equilibrium involving $[CpRu(PPh_3)_2H_2]OTf$. The ^1H NMR spectrum of the hydrogen complex shows a well resolved triplet at −3.55 ppm (J_{PH} = 24 Hz). In order to distinguish between the two isomeric possibilities, i.e., the dihydride and dihydrogen ($\eta^2\text{-}H_2$) formulations, T_1 of the high-field ^1H NMR signal (−7.3 ppm) of the complex was determined. The observed value of 470 ms is much higher than that for typical $\eta^2\text{-}H_2$ complexes (ca. 30 ms).[34] To assist in the structural assignment we examined the reaction of $CpRu(dppe)OTf$ with H_2. As indicated by Simpson et al., a mixture of two species is formed, one is characterized by a triplet at −8.60 (J_{PH} = 28 Hz) and the other exhibits a broad peak at −9.05 ppm ($w_{1/2}$ = 15 Hz). These results agree with Simpson's data for the *trans*-dihydride complex $[CpRu(dppe)H_2]PF_6$[35] and molecular dihydrogen cation $[CpRu(dppe)(\eta^2\text{-}H_2)]PF_6$ respectively. Accordingly, we assign the complex $[CpRu(PPh_3)_2H_2]^+$ as the *trans*-dihydride.[34,35] This dihydride species can also be prepared in good yields from $CpRu(PPh_3)_2OTf$ and H_2 as well as by protonation of $CpRu(PPh_3)_2H$ with HOTf. Interestingly we observe small amounts of $[CpRu(PPh_3)_2H_2]^+$ when solutions of **1** are treated with ca. 5 equiv of HOTf.

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Chemical Oxidations of $CpRu(PPh_3)_2SH$. Solutions of **1** are slowly oxidized in air to give intensely green solutions shown by optical spectroscopy to contain $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ (**2**). This oxidation is accelerated by protic acids. Thus solutions of the cationic H_2S complex are rapidly converted to **2** in air (eq 3). This

$$[CpRu(PPh_3)_2(H_2S)]^+ + \tfrac{1}{2}O_2 \rightarrow \underset{\mathbf{2}}{\tfrac{1}{2}[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}} + H_2O \quad (3)$$

reaction can also be conducted by adding the stoichiometric amount of O_2 and H_2S to a dichloromethane solution of $CpRu(PPh_3)_2OTf$. The order of the addition is not important. Salts of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ had been previously prepared from the reaction of elemental sulfur and sources of $CpRu(PPh_3)_2{}^+$.[25] Solutions of **2** are stable to dilute HOTf.

The aerial oxidation of **1** involves a net 2e oxidation per molecule. In order to investigate this point further we examined the oxidation of **1** with other reagents. Solutions of **1** and 1 equiv of Ph_3CBF_4 react to give almost quantitative yields of **2** together with Ph_3CH (eq 4). When **1** is treated with ca. 0.5 equiv of

$$CpRu(PPh_3)_2SH + Ph_3C^+ \rightarrow \tfrac{1}{2}[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + Ph_3CH \quad (4)$$

Ph_3CBF_4, we observe a complicated mixture comprised in part of $[CpRu(PPh_3)_2H_2]^+$ and $[CpRu(PPh_3)_2]_2(\mu\text{-}SH)^+$. Complex **1** reacts with 2 equiv of Cp_2Fe^+ in CD_2Cl_2 to give a 1:1 mixture of disulfur complex **2** and Cp_2Fe (eq 5). Lastly, 1 and $^1/_2$ equiv

$$2CpRu(PPh_3)_2SH + 4Cp_2Fe^+ \rightarrow [CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + 4Cp_2Fe + 2H^+ \quad (5)$$

of I_2 gave **2** and $CpRu(PPh_3)_2I$ in a 1:2 ratio as well as free H_2S. Our observations suggest the stoichiometry in eq 6. Oxidation of **1** with elemental sulfur gives the known dimetallic compounds $[CpRu(PPh_3)]_2S_x$ (x = 4, 6).[36]

$$4CpRu(PPh_3)_2SH + 2I_2 \rightarrow [CpRu(PPh_3)_2]_2(\mu\text{-}S_2)(I)_2 + 2\,CpRu(PPh_3)_2I + H_2S \quad (6)$$

Protonation of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$. We reexamined some of the properties of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$ since it is presumably an intermediate in the conversion of **1** to **2**. This mixed-valence monocation is air-stable in solution.[23] We have found however that addition of 1 equiv of HOTf to the blue-green methylene chloride solutions of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$ gave, in the presence of oxygen, exclusively **2**, which was identified by its optical spectrum. When this reaction was monitored by ^1H NMR spectroscopy (in the absence of oxygen), we observed broadened signals assignable to **2** along with those for $[CpRu(PPh_3)_2(SH_2)]^+$ in an approximate ratio of 3:2. The broadness of this spectrum is attributed to the accelerated proton spin relaxation induced by fast electron exchange between **2** and residual $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$. Purging this solution with oxygen gave sharp peaks for the μ-S_2 dication **2**. In a separate experiment, addition of a 5-fold excess of HOTf to a solution containing both $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$ and the donor thiirane (SC_2H_4) afforded free H_2S, **2**, and the thiirane complex $[CpRu(PPh_3)_2(SC_2H_4)]^+$.[37] These experiments indicate that protons induce the disproportionation of the mixed valence compound according to eq 7. In contrast to its reaction with HOTf, the mixed-valence cation is unreactive toward CH_3OTf.

$$4[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+ + 4H^+ \rightarrow 3[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + 2CpRu(PPh_3)_2(SH_2)^+ \quad (7)$$

Electrochemical Oxidation of $CpRu(PPh_3)_2SH$. In methylene chloride solution, $CpRu(PPh_3)_2Cl$ undergoes a *single reversible* oxidation at 650 mV vs Ag/AgCl. On the other hand, the cyclic voltammogram of a 1 mM solution of **1** in acetonitrile on a glassy-carbon electrode shows *two irreversible* oxidation waves, one at 168 mV and a broad second wave at 350 mV vs Ag/AgCl. The reduction waves corresponding to these two oxidations were not observed even at scan rates up to 5 V/s. However during the reverse scan, *three* new reduction waves are observed at +200, −450, and −800 mV, all three of which have been assigned (Figure 2). The cyclic voltammogram of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ also shows waves at +200 and −800 mV, the first of which is reversible based on the linearity of a plot of i_p vs (scan rate)$^{1/2}$.[38] Solutions of **1** are electrochemically inactive in the range +100 to −1500 mV vs Ag/AgCl.

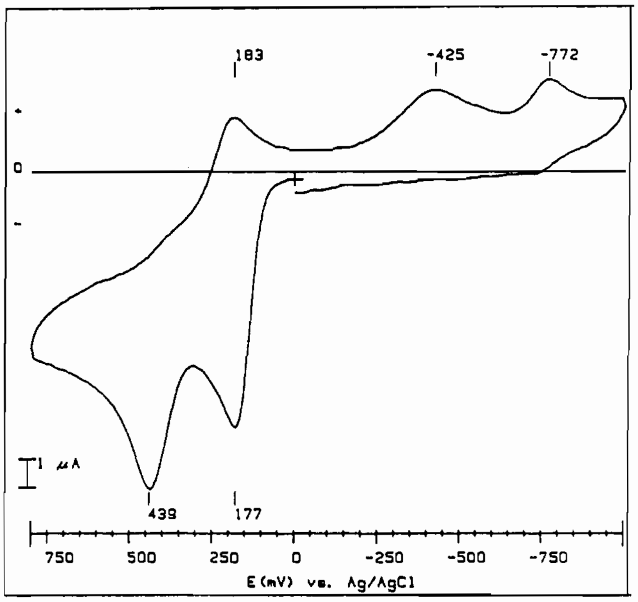

Figure 2. Cyclic voltammogram of a CH_3CN solution of $CpRu(PPh_3)_2SH$ (**1**) at a platinum electrode, 0.001 M in complex and 0.1 M in $n\text{-}Bu_4NPF_6$, at a sweep rate of 250 mV/s. Potentials are referenced to Ag/AgCl.

Controlled-potential electrolysis of $CpRu(PPh_3)_2SH$ at 600 mV releases 1.98e/Ru, concomitant with a color change from orange to green. The cyclic voltammogram of this resulting green solution showed waves at +200, −450, and −800 mV. Furthermore, the UV–vis spectrum of the electrolyzed solution matches that of **2**. The irreversible −450 mV wave is also observed in the cyclic voltammogram of HOTf in acetonitrile. Finally, the cyclic voltammogram of **2** in the presence of HOTf was very similar to that obtained after controlled-potential electrolysis at 600 mV. These experiments confirm that **1** undergoes 2e oxidation at 160 and 350 mV to give protons and the persulfide **2** (eq 8). Since

$$CpRu(PPh_3)_2SH \xrightarrow{>350\text{ mV}} \tfrac{1}{2}[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + H^+ + 2e^- \quad (8)$$

neither of the oxidation waves for **1** interrelate $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{n+}$, the intermediates in the electrochemical oxidation of **1** must differ from **2** in nuclearity and/or hydrogen content. The peak heights of the irreversible waves at 168 and 350 mV correspond to changes of ca. 1e/Ru whereas the i_p value for the reversible reduction of **2** indicates 0.5e/Ru. We have not been able to translate the clues provided by this electrochemical study into a definitive experiment that would clarify the nature of the intermediates.

We note that $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ is reduced by Et_3N/H_2S. Because of the reversibility of the reduction of **2**, the oxidation of H_2S can be made catalytic. Figure 3 shows the cyclic voltammetry trace which indicates the ability of **2** to catalyze the electrooxidation of H_2S.

Alkylation and Metalation of $CpRu(PPh_3)_2SH$. In order to assess the nucleophilic properties of **1**, we examined its reactions with electrophiles other than protons and oxidants. When solutions

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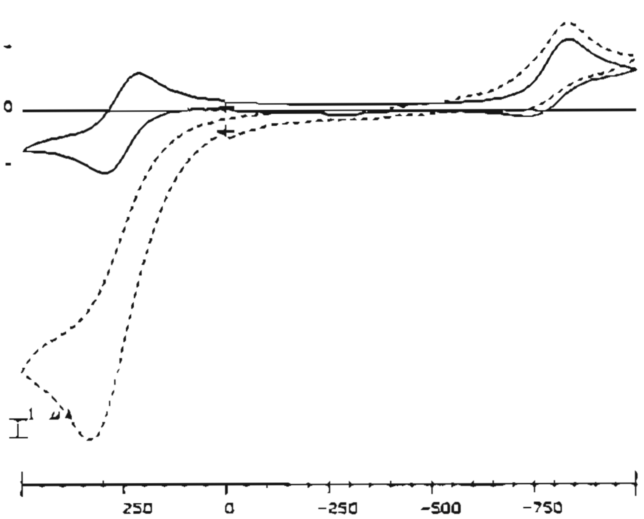


Figure 3. Cyclic voltammogram of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ (**2**) at a Pt electrode. The CH_3CN solution was 0.001 M in complex and 0.1 M in $n\text{-}Bu_4NPF_6$, at a sweep rate of 200 mV/s; potentials are referenced to Ag/AgCl. A few drops of H_2S-saturated CH_3CN had been added to the solution. The solid-line trace is before and the dashed trace is for after addition of 1 vol % Et_3N. The CV is unchanged by the addition of the Et_3N if the H_2S is not added first.

Table I. Selected Bond Distances (Å) and Bond Angles (deg)

Ru-S	2.377 (2)	Ru-P1	2.365 (2)
Ru-P2	2.365 (2)	Ru-Cp[a]	1.864 (7)
S-C7	1.84 (1)	C7-C8	1.46 (1)
C8-C9	1.50 (3)	S-H	1.25 (6)
S-Ru-P1	87.00 (7)	S-Ru-P2	91.97 (7)
S-Ru-Cp	126.8 (2)	P1-Ru-P2	103.17 (7)
Ru-S-H	97 (3)	C7-S-H	99 (3)

[a] Cyclopentadienyl ring centroid.

of $CpRu(PPh_3)_2SH$ and $CpRu(PPh_3)_2OTf$ are combined, the ^1H NMR spectrum shows a single C_5H_5 resonance and an SH quintet at −2.3 ppm. Solutions of this compound are stable only for a few minutes at room temperature, decomposing to what are apparently paramagnetic species. The metastable species is assigned as $[CpRu(PPh_3)_2]_2(\mu\text{-}SH)^+$.

Reaction of CH_3OTf and **1** gave the lime green compound $[CpRu(PPh_3)_2(CH_3SH)]OTf$. The ^1H NMR spectrum of this compound showed the SH resonance as a multiplet at 4.22 ppm and CH_3 resonances as doublet at 2.23 ppm. The proton–proton coupling constants for the CH_3SH fragment indicate that this ligand remains intact upon coordination, i.e. oxidative addition to give a mercapto hydride[39] has not occurred. The facile alkylation of **1** contrasts with the nonreactivity of the S_2 ligand in $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$. We attribute the diminished nucleophilicity of the mixed-valence compound to S to Ru π-donation and to the effect of the positive charge. Thiol complexes, $[CpRu(PPh_3)_2(RSH)]^+$, can also be prepared directly from the reactions of thiols and $CpRu(PPh_3)_2OTf$.[40]

The structure of $[CpRu(PPh_3)_2(HSPr^n)]BF_4$ has been established by single-crystal X-ray diffraction methods (Figure 4, Table I). The molecule adopts an approximate tetrahedral coordination geometry if the Cp is viewed as a mondentate ligand. The Ru-S distance of 2.377 (2) Å is unexceptional.[36,37,40] The SH atom was included in the refinement; the C-S-H and Ru-S-H angles are the same within experimental error at 98°.

Studies on Complexes with Pendant Thiophene Ligands. We briefly examined the analogues of $CpRu(PPh_3)_2X$ (X = H, SH) wherein the Cp group was replaced by 2-(thienylmethyl)cyclopentadienyl, $C_5H_4CH_2C_4H_3S$ (referred to as ThiCp). We had previously shown that the thiophene moiety in $[(ThiCp)Ru(PPh_3)_2]^+$ is coordinated via an Ru-S bond.[41]

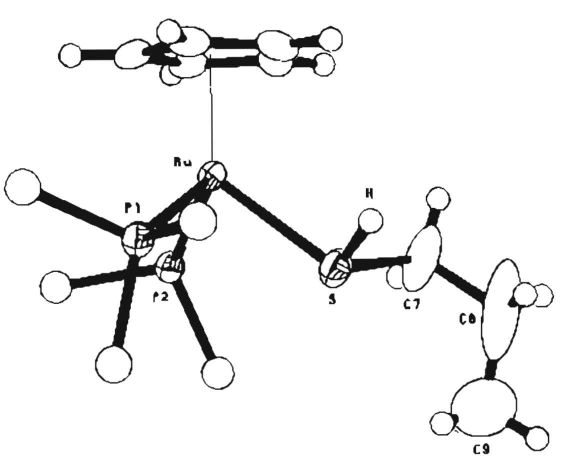
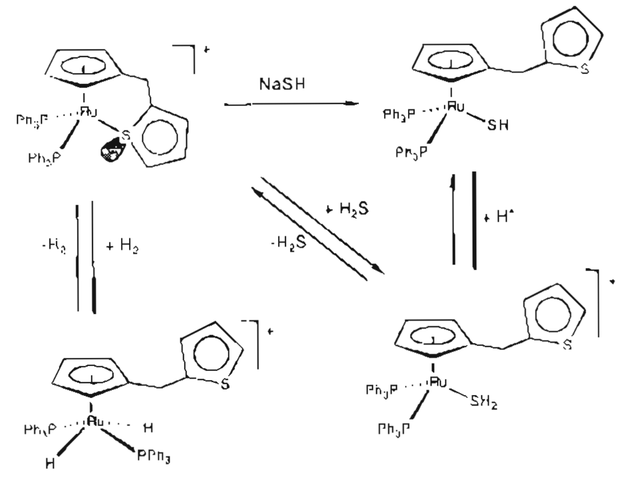


Figure 4. Molecular structure of the cation in $[CpRu(PPh_3)_2(n\text{-}PrSH)]BF_4$. Thermal ellipsoids are drawn at the 35% probability level. For clarity, only the ipso phenyl carbon atoms are shown.

Scheme I



The compound $(ThiCp)Ru(PPh_3)_2SH$ is quite similar to $CpRu(PPh_3)_2SH$ according to the ^1H NMR data. There are no indications that the pendant thiophene group interacts with the Ru-SH functionality. Protonation of solutions of $(ThiCp)Ru(PPh_3)_2SH$ with HOTf results in rapid displacement of H_2S by the thiophene group, giving the S-bound thiophene complex $[(ThiCp)Ru(PPh_3)_2]^+$ (Scheme I). An ^1H NMR measurement of this equilibrium gave

$$K_{eq} = [(ThiCp)Ru(PPh_3)_2(H_2S)]^+/[(ThiCp)Ru(PPh_3)_2^+]P_{H_2S} = 3.8$$

In this and related calculations of K_{eq}, the atmosphere over the solution was composed solely of the reacting gas and P_{gas} was assumed to be unity.

In the presence of H_2, the S-bound thiophene complex exists in equilibrium with $[(ThiCp)Ru(PPh_3)_2H_2]^+$ whose ^1H NMR spectrum resembles that for $[CpRu(PPh_3)_2H_2]^+$. Under our conditions, the coordinating power of both H_2 and H_2S are competitive with that of S-bound thiophene. Comparison of the affinities of $[(ThiCp)Ru(PPh_3)_2]^+$ for H_2 and H_2S provides a means to assess the relative binding constants for dihydrogen and hydrogen sulfide (eq 9). At the probe temperature of our NMR

$$K = [(ThiCp)Ru(PPh_3)_2(H_2)^+]P_{H_2S}/[(ThiCp)Ru(PPh_3)_2(H_2S)^+]P_{H_2} = 0.44 \quad (9)$$

spectrometer, which we estimate to be 30 °C, hydrogen sulfide

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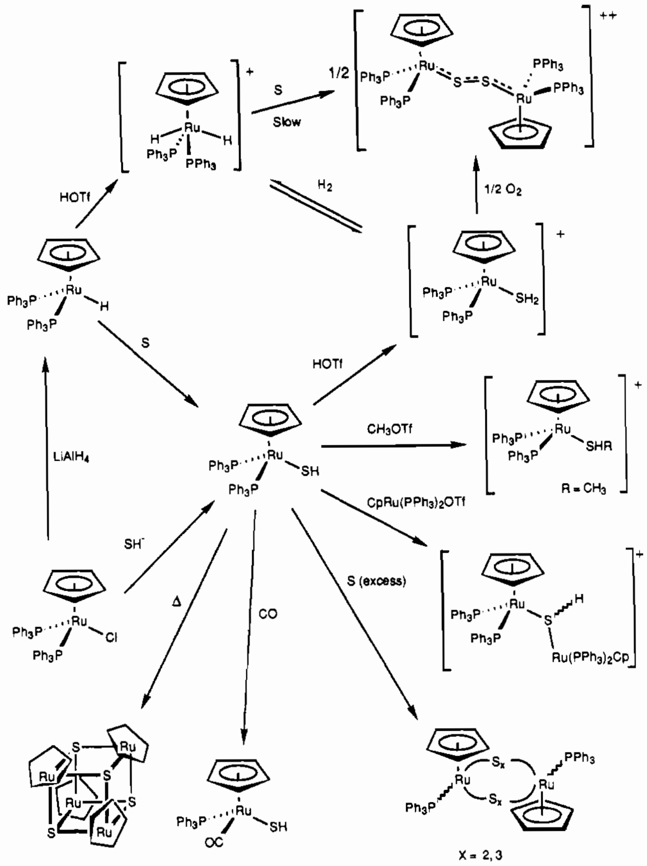
Scheme II



binds to the ruthenium center slightly better than dihydrogen, which in turn is able to displace S-bound thiophene. An advantage of determining the relative binding constants of these ligands by using the ThiCp complex is that its H_2S adduct is not sensitive to oxygen.

Discussion

The discussion is subdivided into four themes developed in this work.

1. $CpRu(PR_3)_2SH$, an Electron-Rich Species. $CpRu(PPh_3)_2SH$ is a compound that has an extensive reaction chemistry (Scheme II). Its behavior conforms to the general trend whereby two-coordinate sulfur ligands in electron-precise metal complexes are often highly nucleophilic. The electron-rich character of $CpRu(PPh_3)_2SH$ is signaled in three ways.

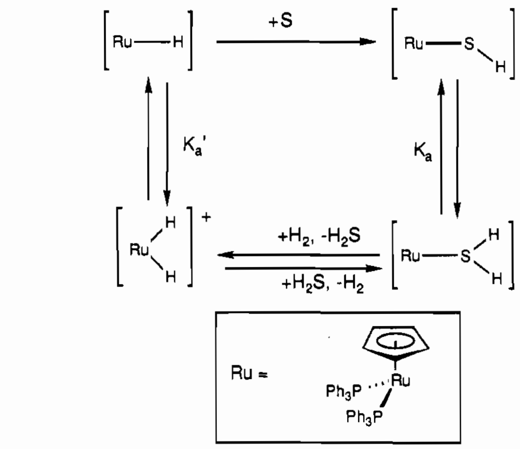
(i) Basicity and Nucleophilicity of the SH Ligand.[42] Compound **1** undergoes facile protonation, metalation, and alkylation, all at sulfur. The thiol complexes are more stable than the H_2S complex, reflecting the relative pK_a's of alkanethiols and H_2S, which are ca. 10 and 7, respectively.[1]

(ii) Carbonylation of the Ruthenium Center. The replacement of Cl by SH changes the K_{CO} by a factor of at least 20. This is an equilibrium effect but indications are the phosphines in **1** are highly labile: when solutions of **1** are heated all of the phosphine ligands are liberated giving a good yield of $Cp_4Ru_4S_4$.[43]

(iii) Oxidation Potential. Replacement of Cl by SH decreases the $E_{1/2}$ by ca. 500 mV. The irreversibility of the electrochemical oxidation of **1** precludes quantitative interpretation, but the effect is large.

The reason that the thiol **1** undergoes 2e oxidation is that the product of 1e oxidation, the neutral persulfide $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)$, is itself an even a stronger reductant than the starting thiol. In our previous report,[25] we estimated its first oxidation couple at −868 mV vs Ag/AgCl. So the question is then, why is the neutral persulfide so reducing? We suggest that this effect exists because of unfavorable interactions between the π-symmetry electrons on ruthenium and sulfur; this effect is exacerbated by nonbonding interactions between the adjacent sulfur atoms.[44,45] It is well-known that the group $CpRu(PR_3)_2^+$ is an excellent π-donor because it possesses a full complement of nonbonding electrons in orbitals of π symmetry and it lacks strong acceptor ligands. The π-donor property of this ruthenium center is well illustrated by the stability of its vinylidene complexes $[CpRu(PPh_3)_2C_2RH]^+$.[46] These arguments explain certain fundamental differences between the chemical behavior of organic and transition-metal SH derivatives.

Scheme III



2. Comparative Coordination Chemistry of H_2 and H_2S. The experiments described in this paper highlight chemical connections between dihydrogen, sulfur, and sulfur hydrides. The following four-step cycle was demonstrated: insertion of sulfur into an Ru–H bond, protonation of the resulting SH ligand, displacement of coordinated H_2S by H_2, and regeneration of the ruthenium hydride (Scheme III). Under appropriate conditions, each of these steps is rapid at room temperature. We were surprised by the similarity of the equilibrium constants for the binding of H_2S and the oxidative addition of H_2.

Our results are in accord with studies on catalytic hydrodesulfurization where, at low hydrogen pressures, the rate is first order in hydrogen and inhibited by hydrogen as well as arenes (including thiophene).[47] We also showed that conversion of coordinated SH to H_2S provides a plausible means to open a coordination site for other weak ligands such as thiophenes.[48] Metal complexes of H_2S remain rare, we are only aware of derivatives of metals with the $(t_{2g})^6$ configuration and even these are labile.[49,50]

3. Oxidation of $[CpRu(PPh_3)_2SH_2]^+$. The oxidation of H_2S is conducted on a large scale industrially by using ferric amino carboxylate chelates followed by regeneration of the oxidant with molecular oxygen.[51] The oxidation of H_2S by oxygen using

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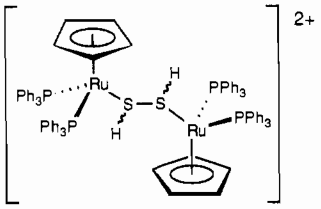
$CpRu(PPh_3)_2OTf$ is not catalytic because $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ is unreactive toward further H_2S. In the presence of base, however, **2** oxidizes H_2S (probably as BH^+/SH^-). The resulting mixed-valence diruthenium cation can be regenerated electrochemically (eq 10 and 11).

$$2[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + H_2S + 2R_3N \rightarrow 2[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+ + S + 2R_3NH^+ \quad (10)$$

$$[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+ \xrightarrow{200\text{ mV}} [CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + e^- \quad (11)$$

The lability of the H_2S ligand generated upon protonation of **1** suggests that its acid-catalyzed oxidation may proceed via the reaction of free H_2S with an oxygenated derivative of $CpRu(PPh_3)_2^+$. Consistent with this proposal, the conversion of $CpRu(PPh_3)_2OTf$, O_2, and H_2S to the persulfide proceeded in high yield regardless of the order of the addition. Outer-sphere oxidation of H_2S by ruthenium (III) ammines has been described previously,[52] but the relevance of this process to our results is not established.

4. Oxidation of $CpRu(PPh_3)_2SH$. The oxidation of **1** is a 2e/Ru process; the product is $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$. Precedents from the chemistry of organic mercaptans[53] would suggest the intermediacy of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2H_2)^{2+}$.



This proposal is also supported by the synthesis of $[CpFe(PR_3)_2]_2(\mu\text{-}S_2Ph_2)^{2+}$ by the oxidation of $CpFeL_2SR$ species.[54] We were not able to isolate or even definitively detect an H_2S_2 complex although the free ligand is known.[55]

The oxidative coupling of the two RuSH fragments is envisioned as occuring via the combination of sulfur-centered radical $CpRu(PPh_3)_2SH^+$. Fenske–Hall calculations and photoelectron spectroscopic measurements on $CpFe(CO)_2SH$ indicate that the HOMO is largely sulfur in character.[56] Experimental results on complexes with terminal mercaptides repeatedly highlight the importance of M–S π interactions. Isoelectronic with $CpFe(CO)_2SR^+$ is $Cp^*Mn(CO)_2(S\text{-}t\text{-}Bu)$, a stable 17e complex characterized by a short Mn–S bond of 2.187 (5) Å.[57] Metal–sulfur π-bonding can also be invoked to explain the extremely short Cu–S(mercaptide) bond length in the blue copper proteins.[58,59]

We have obtained no evidence in support of a thioruthenyl(IV) intermediate in the oxidation of **1**. A thioruthenyl(IV) species is not plausible because it would be two oxidation steps beyond **2**, and we know that the oxidation of $[CpRu(PMe_3)_2](\mu\text{-}S_2)^{2+}$ occurs at 700 mV (vs Ag/AgCl). In contrast, the 2e oxidation of coordinated water to oxo is established in the case of $[(terpy)(bpy)RuO]^{2+}$.[60]

A specific model for the dehydrogenation of the putative $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2H_2)^{2+}$ is provided by Sellmann's conversion of an $Ru_2(\mu\text{-}N_2H_4)$ to an $Ru_2(\mu\text{-}N_2H_2)$ species.[61] In fact, dehydrogenation of ligands coordinated to ruthenium is common. Studies on the oxidation of $[Ru(NH_3)_5(NH_2CHR_2)]^{2+}$ to $[Ru(NH_3)_5(NHCR_2)]^{2+}$ consistently point to cycles of oxidation followed by deprotonation.[62] Oxidation enhances the acidity of ligand protons while deprotonation enhances ligand to metal π-donation. The effects are mutually reinforcing.

One of our most unusual results is the proton-induced disproportionation of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$. Obviously the protonated mixed-valence persulfide $H[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ must be involved, but the site of protonation remains undetermined; it could be at either ruthenium or sulfur. It appears that $H[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ possesses the unusual ability to oxidize its own conjugate base (see eq 7). Protonation of a π-donor ligand would be expected to diminish its π-donor ability; the protonated complex would therefore be expected to be a better oxidant than its conjugate base. This interesting effect is probably the basis of the ability of protons to induce redox condensations for the tetrathiometalates, as described in the Introduction.

Experimental Section

Materials. All reactions and workups were performed under an atmosphere of purified nitrogen unless indicated otherwise. All solvents were dried by standard methods under nitrogen. $CpRu(PPh_3)_2Cl$,[63] $CpRu(PPh_3)_2H$,[32] NaSH,[64] Ph_3BF_4,[65] $Cp_2Fe(PF_6)$,[66] $C_5H_4CH_2C_4H_3S$ (2-(thienylmethyl)cyclopentadiene, referred to as ThiCp),[41] and $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2Cl$[41] were prepared according to the literature methods. Tetrabutylammonium hexafluorophosphate was prepared from NH_4PF_6 and tetrabutylammonium iodide and recrystallized from water. Triethylamine was redistilled from KOH. Other reagents were purchased from Aldrich.

Instrumentation. All standard ^1H NMR spectra were recorded on a GE Nicolet QE-300 instrument. $^{31}P\{^1H\}$ NMR spectra were obtained on a GE Nicolet GN-300NB spectrometer using an internal D_2O lock with 85% H_3PO_4 as an external reference (downfield shifts are positive). All NMR chemical shifts are quoted in ppm. IR spectra were obtained on a Perkin-Elmer Model 1750 spectrometer; IR absorptions are reported in cm^{-1}. UV/vis spectra were recorded with a Varian 2300 spectrometer; absorption maxima are reported in nm. Electron paramagnetic resonance spectra were recorded on a Varian E-9 X-band spectrometer employing an E101 microwave bridge with a 6-in. (10-kG) magnet.

All electrochemical measurements were performed with a BAS-100 electrochemical analyzer. A three-electrode system was used for all cyclic voltammetry measurements. This consisted of a Pt working electrode (BAS-MF2013), a Pt-wire counter electrode, and an Ag/AgCl reference electrode (BAS-MF2020). Many of these experiments required that the electrodes be cleaned between uses due to adsorption of the metal–sulfur complex; nonetheless, the results with Pt electrodes were preferred to those with glassy-carbon electrodes because the latter gave broader peaks. Constant-potential electrolysis experiments were performed by using a two-component U cell fitted with a medium frit. A Pt plate of area 300 mm^2 was used as the working electrode, and a smaller Pt-plate electrode (area 200 mm^2) was used as the auxiliary electrode. Solutions contained

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0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte for all of the electrochemical experiments. Solvents were degassed with N_2 for about 10 min before the electrochemical experiments, which were conducted under a positive N_2 atmosphere. The potentials are reported with reference to the Ag/AgCl electrode.

Microanalyses were performed by the School of Chemical Sciences microanalytical laboratory.

$CpRu(PPh_3)_2SH$. A slurry of $CpRu(PPh_3)_2Cl$ (1.17 g, 1.6 mmol) and NaSH (0.15 g, 2.6 mmol) in 40 mL of methanol was refluxed for ca. 18 h. The cold slurry was filtered, and the orange microcrystalline product was washed with two 10-mL portions of methanol. The product was recrystallized from toluene–methanol. After the product was in vacuo overnight, we obtained 0.75 g (1.04 mmol, 65%) of product. Anal. Calcd for $C_{41}H_{36}P_2SRu$: C, 68.04; H, 4.98; S, 4.45. Found: C, 67.72; H, 4.82; S, 4.43. ^1H NMR (benzene-d_6): 7.0–7.8 (m, 30 H), 4.28 (s, 5 H), −3.15 (t, J_{PH} = 7 Hz, 1 H). $^{31}P\{^1H\}$ NMR (benzene-d_6): 43.75.

Reaction of $CpRu(PPh_3)_2H$ with $^1/_8S_8$. To a solution of $CpRu(PPh_3)_2H$ (0.010 g, 1.45×10^{-5} mol) in ca. 0.3 mL of C_6D_6 was added S_8 (0.5 mg, 1.8×10^{-6} mol). The ^1H NMR spectrum, recorded after all the sulfur had dissolved (ca. 18 H), showed that $CpRu(PPh_3)_2SH$ had formed contaminated with small amounts (ca. 5%) of $[CpRu(PPh_3)]_2S_6$ as well as H_2S (0.85 ppm) (the expected $[CpRu(PPh_3)]_2S_4$ is insoluble).

$CpRu(PPh_3)(CO)SH$. Carbon monoxide gas was bubbled through a solution of $CpRu(PPh_3)_2SH$ (0.20 g, 0.28 mmol) in 20 mL of toluene for 3 h, during which time the color of the solution changed from orange to yellow. The solution was stirred for a further 16 h under 1 atm of CO. Addition of hexanes gave a yellow precipitate, which was recrystallized from toluene/hexanes to give yellow microcrystals, yield 0.082 g (0.168 mmol, 60%). Anal. Calcd for $C_{24}H_{21}ORuSP$: C, 58.90; H, 4.29; S, 6.54. Found: C, 59.30; H, 4.41; S, 6.60. ^1H NMR ($CDCl_3$): 7.2–7.5 (m, 15 H), 4.84 (s, 5 H), −3.58 (d, J_{PH} = 7 Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): 54.34. IR (CH_2Cl_2): 1964 (strong, ν_{CO}).

Reaction of $CpRu(PPh_3)_2SH$ with HOTf. HOTf (1.7 μL, 1.7×10^{-5} mol) was added to a solution of $CpRu(PPh_3)_2SH$ (0.012 g, 1.66×10^{-5} mol) in ca. 0.3 mL of $CDCl_3$ in an NMR tube. The color of the solution immediately turned from orange to yellow. The product was identified by ^1H NMR as $[CpRu(PPh_3)_2(SH_2)]OTf$. ^1H NMR ($CDCl_3$): 7.0–7.5 (m, 30 H), 4.58 (s, 5 H), 3.58 (t, J_{PH} = 7 Hz, 2 H).

Reaction of $CpRu(PPh_3)_2OTf$ with H_2S. A 15-mg sample of $CpRu(PPh_3)_2OTf$ in ca. 0.3 mL of CD_2Cl_2 in a NMR tube was purged with H_2S gas and sealed under 1 atm of H_2S. The ^1H NMR spectrum of this yellow solution was identical with that obtained above, except that the peak at 3.5 ppm was broadened.

$[CpRu(PPh_3)_2H_2]OTf\cdot CH_2Cl_2$. Solid AgOTf (0.075 g, 0.29 mmol) was added to a stirred solution of $CpRu(PPh_3)_2Cl$ (0.20 g, 0.28 mmol) in 20 mL of CH_2Cl_2. After 3 h, the slurry was filtered, and the filtrate was purged with H_2 and stirred under an H_2 atmosphere for about 15 min. The color of the solution immediately changed from orange to pale yellow. After 1 h the solution was concentrated to ca. half of the original volume and diluted with hexanes to give a pale yellow precipitate. The solid was washed with hexanes and dried in vacuo overnight. Yield: 0.163 g (60%). Anal. Calcd for $C_{43}H_{39}Cl_2F_3O_3P_2Ru$: C, 55.73; H, 4.24. Found: C, 56.01; H, 4.54. ^1H NMR ($CDCl_3$): 7.1–7.3 (m, 30 H), 5.32 (s, 2 H for CH_2Cl_2), 4.84 (s, 5 H), −7.32 (t, J(PH) = 14.7 Hz, 2 H). $^{31}P\{^1H\}$ ($CDCl_3$): 58.13. Above 60 °C, this compound is unstable with respect to $CpRu(PPh_3)_2OTf$.

Reaction of $[CpRu(PPh_3)_2(SH_2)]OTf$ with O_2. Oxygen gas was bubbled through the above solution, and ^1H NMR and UV/vis spectra were recorded on the resulting green solution. The product was identified as $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[OTf]_2$. ^1H NMR (CD_2Cl_2): 7.0–7.8 (m, 60 H), 4.90 (s, 10 H), 2.5 (br, H_2O?). UV/vis (CD_2Cl_2): 820 sh, 718, 445 sh, 362. Similar results were obtained when a CH_2Cl_2 solution of $CpRu(PPh_3)_2OTf$ was treated sequentially with O_2 (10/Ru) and H_2S (1 or 2 equiv) followed by stirring for 12 h.

Reaction of $CpRu(PPh_3)_2SH$ with Ph_3CBF_4. A solution of Ph_3CBF_4 (0.05 g, 0.14 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a solution of $CpRu(PPh_3)_2SH$ (0.11 g, 0.15 mmol) in 20 mL of CH_2Cl_2 to give an immediate color change from orange to deep green. The stirred solution was exposed to air for 2 h and evaporated to dryness. By ^1H NMR and UV/vis spectroscopies, this product was shown to be $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$. On the basis of the UV/vis extinction coefficient of 32 000 M^{-1} cm^{-1} at 718 nm, the yield was calculated to be 95%.

In a separate experiment, Ph_3CBF_4 (4.4 mg, 1.4×10^{-5} mol) was added to a solution of $CpRu(PPh_3)_2SH$ (9 mg, 1.31×10^{-5} mol) in ca. 0.5 mL of $CDCl_3$ to give an immediate green solution. The ^1H NMR spectrum of this solution showed the presence of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ and ca. 80% of $(C_6H_5)_3CH$ (5.56 ppm; yield based on integration relative to internal $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$).

Reaction of $CpRu(PPh_3)_2SH$ with 2 Equiv of $Cp_2Fe(PF_6)$. A solution of $Cp_2Fe(PF_6)$ (0.043 g, 0.15 mmol) in 10 mL of CH_2Cl_2 was added to a solution of $CpRu(PPh_3)_2SH$ (0.05 g, 0.07 mmol) in 10 mL of CH_2Cl_2, resulting in an immediate color change from orange to green. The solution was stirred for 3 h and evaporated to dryness. The green residue was washed with toluene and recrystallized from CH_2Cl_2/ether. The product was identified as $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ by ^1H NMR and UV/vis spectroscopy; yield 0.045 g (0.026 mmol, 75%). A related experiment whereby solid Cp_2FePF_6 was added to a CD_2Cl_2 solution of **1** in an NMR tube gave similar results.

In a separate experiment, a solution of $CpRu(PPh_3)_2SH$ (0.016 g, 2.2×10^{-5} mol) in ca. 0.3 mL of CD_2Cl_2 was treated with $Cp_2Fe(PF_6)$ (0.015 g, 5×10^{-5} mol) to give a green solution. A ^1H NMR spectrum showed the presence of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ and a new compound, whose Cp resonance appeared at 4.52 ppm and whose S*H* resonance appeared at 2.75 ppm (t, J_{PH} = 7 Hz) that which could be assigned to $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2H_2)^{2+}$. When this solution was treated with O_2 gas, the ^1H NMR peaks assigned to $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2H_2)^{2+}$ disappeared, to give exclusively $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$.

Reaction of $CpRu(PPh_3)_2SH$ with I_2. A mixture of $CpRu(PPh_3)_2SH$ (0.01 g, 1.38×10^{-5} mol) and I_2 (2.0 mg, 0.78×10^{-5} mol) in an NMR tube was dissolved in ca. 0.5 mL of CD_2Cl_2. Initially, the solution was green but then turned dark brown. The ^1H NMR spectrum of this solution showed peaks at 7.0 − 7.8, 4.84 (s, Cp resonance of $[CpRu(PPh_3)_2]_2S_2^{2+}$), 4.21 (s), and 0.87 (s, H_2S). The peak at 4.21 was confirmed as the Cp resonance of $CpRu(PPh_3)_2I$ by independent synthesis from 1 equiv of *n*-Bu_4NI and $CpRu(PPh_3)_2OTf$.

Reaction of $[CpRu(PPh_3)_2](\mu\text{-}S_2)[OTf]$ with HOTf. A solution of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[OTf]$ (0.090 g, 0.057 mmol) in 20 mL of CH_2Cl_2 was treated with HOTf (5.6 μL, 0.062 mmol) to give a immediate color change from blue-green to green. The solution was stirred for 1 h, concentrated to ca. 5 mL, and diluted with ether to give a green precipitate. The product was washed with ether and dried in vacuo. This product was identified as $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[OTf]_2$ by ^1H NMR and UV/vis spectroscopies. Yield: 0.082 g (0.047 mmol, 83%).

The same experiment was carried out in the presence of thiirane. A solution of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[OTf]$ (0.017 g, 1.07×10^{-5} mol) and thiirane (3 μL, 5×10^{-5} mol) in ca. 0.5 mL of CD_2Cl_2 was treated with HOTf (5 μL, 5.3×10^{-5} mol). The ^1H NMR of the resulting solution showed the presence of free H_2S as well as $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ and $CpRu(PPh_3)_2(SC_2H_4)^+$ in the approximate ratio of 3:2.

Reaction of $CpRu(PPh_3)_2SH$ and $CpRu(PPh_3)_2OTf$. A mixture of $CpRu(PPh_3)_2SH$ (0.020 g, 2.7×10^{-5} mol) and $CpRu(PPh_3)_2OTf$ (0.21 g, 2.7×10^{-5} mol) was dissolved in ca. 0.3 mL of CD_2Cl_2 in a NMR tube to give a red solution. The ^1H NMR spectrum, recorded after ca. 10 min., showed only one Cp singlet assigned to $[CpRu(PPh_3)_2]_2(\mu\text{-}SH)^+$. ^1H NMR (CD_2Cl_2): 6.9–7.2 (m, 60 H), 4.57 (s, 10 H), −2.17 (quint, J_{PH} = 7 Hz, 1 H).

$[CpRu(PPh_3)_2(HSCH_3)]OTf$. A solution of CH_3OTf (35 μL, 0.3 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a stirred solution of $CpRu(PPh_3)_2SH$ (0.2 g, 0.28 mmol) in 20 mL of CH_2Cl_2. The solution color immediately changed from orange to yellow-green. After 2 h, the solution was concentrated to about 10 mL and diluted with hexanes to give a yellow-green microcrystalline product. The product was washed with hexanes and dried in vacuo; yield, 0.175 (0.2 mmol, 72%). Anal. Calcd for $C_{43}H_{39}P_2RuS_2O_3F_3$: C, 58.17; H, 4.40;, S, 7.22. Found: C, 58.72; H, 4.58; S, 7.36. ^1H NMR ($CDCl_3$): 7.0–7.5 (m, 30 H), 4.67 (s, 5 H), 4.12 (m, 1 H), 2.23 (d, *J* = 7 Hz, 3 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 41.20.

$[(ThiCp)Ru(PPh_3)_2]OTf$. Solid AgOTf (0.10 g, 0.38 mmol) was added to a stirred solution of $(ThiCp)Ru(PPh_3)_2Cl$ (0.25 g, 0.30 mmol) in 20 mL of CH_2Cl_2. The slurry was stirred for 3 h and filtered, and the filtrate was diluted with 20 mL of toluene and concentrated to about 10 mL to give orange crystals. These were washed with toluene and dried in vacuo; yield 0.20 g (0.2 mmol, 67%). Anal. Calcd for $C_{47}H_{39}P_2RuS_2O_3F_3$: C, 60.32; H, 4.17; S, 6.84. Found: C, 60.15; H, 4.23; S, 6.83. ^1H NMR ($CDCl_3$): 6.9–7.5 (m, 30 H), 6.8 (m, 3 H), 4.82, 3.60 (d, 4 H), 3.39 (s, 2 H). $\{^1H\}^{31}P$ NMR (CH_2Cl_2/C_6D_6): 40.6.

$(ThiCp)Ru(PPh_3)_2SH$. To a solution of $(ThiCp)Ru(PPh_3)_2OTf$ (0.14 g, 0.14 mmol) in 20 mL of methanol was added solid NaSH (0.2 g, 0.35 mmol) to give an immediate brown precipitate. The slurry was stirred for 2 h, filtered, and recrystallized from toluene/methanol to give 0.69 g (0.87 mmol, 60%) of product. Anal. Calcd for $C_{46}H_{40}P_2S_2Ru$: C, 67.40; H, 4.88; S, 7.81. Found: C, 67.10; H, 4.55; S, 8.52. ^1H NMR ($CDCl_3$): 7.1–7.6 (m, 30 H), 6.73, 6.85 (d, 3 H), 4.07, 3.67 (d, 4 H), 3.65 (s, 2 H), −3.37 (s, 1 H). $^{31}P\{^1H\}$ NMR (toluene/C_6H_6): 44.46.

$(ThiCp)Ru(PPh_3)_2H$. To a slurry of $(ThiCp)Ru(PPh_3)_2Cl$ (0.20 g, 0.24 mmol) in 20 mL of diethyl ether was added a filtered solution of $LiAlH_4$ (0.18 g, 0.47 mmol) in 10 mL of ether. The slurry was stirred for ca. 3 h to give a pale yellow solution. Dry ethanol (10 mL) was added to destroy the excess $LiAlH_4$, and the solution was evaporated to dryness. The residue was extracted with hexanes, and the extract was evaporated

Table II. Crystal and Experimental Data for X-ray Diffraction Study of $[CpRu(PPh_3)_2(HSPr)]BF_4{\cdot}CH_2Cl_2$

formula	$[Ru(C_5H_5)(P(C_6H_5)_3)_2(SC_3H_8)][BF_4]{\cdot}CH_2Cl_2$
cryst syst	triclinic
space group	$P\bar{1}$
T, °C	24 °C
λ, Å	0.710 69 (Mo Kα)
a, Å	13.308 (5)
b, Å	14.641 (7)
c, Å	13.205 (7)
α, deg	113.64 (3)
β, deg	110.01 (4)
γ, deg	84.45 (3)
V, Å^3	2212 (2)
Z	2
d (calcd), g/cm^3	1.409
color, habit	yellow, prismatic
dimens {form} or (face), mm	{0,−1,1}, 0.10; {1,0,−1}, 0.15; (1,1,1), 0.34; (−1,0,−1), 0.34
diffractometer	Syntex $P2_1$
monochromator	graphite
μ, cm^{-1}	6.32
transm factor range	0.897–0.814 (numerical)
2θ limit, deg (octants)	46.0 ($\pm h,\pm k,\pm l$)
no. of intens (unique, R_i)	7429 (6196, 0.018)
no. of intens $>2.58\sigma(I)$	4091
R	0.054
R_w (for $w = 1/\sigma^2(F_o) + pF_o^2$)	0.062 (p = 0.03)
max density in ΔF map, e/Å^3	0.74 (<0.7 Å from C34 and C35)

Table III. Refined Atomic Coordinates for $[CpRu(PPh_3)_2HSPr]BF_4{\cdot}CH_2Cl_2$

	x/a	y/b	z/c
Ru	0.22581 (5)	0.18477 (5)	0.17321 (5)
S	0.4112 (2)	0.2230 (2)	0.2811 (2)
P1	0.2020 (2)	0.3585 (1)	0.2498 (2)
P2	0.2010 (1)	0.1331 (1)	0.3117 (2)
C1	0.1494 (6)	0.1885 (6)	−0.0031 (6)
C2	0.0773 (6)	0.1392 (6)	0.0203 (6)
C3	0.1275 (6)	0.0527 (6)	0.0324 (6)
C4	0.2275 (6)	0.0486 (6)	0.0171 (6)
C5	0.2410 (7)	0.1318 (6)	−0.0042 (6)
C7	0.4911 (7)	0.1120 (8)	0.270 (1)
C8	0.6061 (9)	0.134 (1)	0.330 (2)
C9	0.635 (1)	0.188 (1)	0.460 (1)
C11	0.0624 (6)	0.3909 (5)	0.1903 (6)
C12	0.0348 (7)	0.4622 (6)	0.1430 (8)
C13	−0.0748 (8)	0.4809 (7)	0.1001 (9)
C14	−0.1525 (8)	0.4289 (7)	0.1040 (8)
C15	−0.1264 (7)	0.3585 (6)	0.1491 (7)
C16	−0.0181 (6)	0.3395 (6)	0.1940 (7)
C21	0.2371 (6)	0.4338 (5)	0.4083 (6)
C22	0.1620 (7)	0.4574 (6)	0.4646 (7)
C23	0.1931 (8)	0.5107 (7)	0.5862 (9)
C24	0.2984 (8)	0.5397 (7)	0.6502 (9)
C25	0.3737 (7)	0.5169 (6)	0.5947 (8)
C26	0.3455 (7)	0.4649 (6)	0.4757 (7)
C31	0.2773 (6)	0.4322 (5)	0.2110 (7)
C32	0.3252 (6)	0.3867 (6)	0.1265 (7)
C33	0.3746 (6)	0.4438 (6)	0.0926 (7)
C34	0.3767 (6)	0.5461 (6)	0.1428 (7)
C35	0.3322 (6)	0.5920 (6)	0.2288 (7)
C36	0.2831 (6)	0.5370 (6)	0.2650 (7)
C41	0.3071 (6)	0.1596 (5)	0.4542 (6)
C42	0.3594 (6)	0.0841 (6)	0.4887 (7)
C43	0.4395 (7)	0.1098 (7)	0.5975 (8)
C44	0.4667 (7)	0.2070 (6)	0.6726 (8)
C45	0.4162 (7)	0.2818 (7)	0.6389 (8)
C46	0.3387 (6)	0.2578 (6)	0.5296 (7)
C51	0.0799 (6)	0.1756 (5)	0.3498 (6)
C52	0.0772 (7)	0.2412 (6)	0.4571 (7)
C53	−0.0189 (8)	0.2747 (7)	0.4782 (9)
C54	−0.1137 (8)	0.2375 (7)	0.3872 (8)
C55	−0.1156 (7)	0.1709 (6)	0.2798 (8)
C56	−0.0191 (6)	0.1394 (6)	0.2603 (7)
C61	0.1824 (6)	−0.0041 (5)	0.2625 (6)
C62	0.2413 (6)	−0.0692 (6)	0.1964 (7)
C63	0.2290 (7)	−0.1717 (6)	0.1599 (7)
C64	0.1584 (7)	−0.2087 (7)	0.1913 (7)
C65	0.1019 (7)	−0.1464 (7)	0.2588 (8)
C66	0.1138 (6)	−0.0428 (6)	0.2964 (7)
H[a]	0.434 (5)	0.247 (5)	0.211 (6)
B	0.561 (1)	0.212 (1)	0.011 (1)
F1	0.5870 (6)	0.2957 (5)	−0.0031 (7)
F2a[b]	0.628 (2)	0.149 (2)	−0.001 (3)
F3a[b]	0.457 (1)	0.194 (2)	−0.056 (2)
F4a[b]	0.556 (2)	0.252 (1)	0.122 (1)
F2b[b]	0.555 (4)	0.136 (2)	−0.093 (2)
F3b[b]	0.475 (2)	0.210 (2)	0.034 (4)
F4b[b]	0.641 (3)	0.198 (5)	0.089 (4)
Cl1[c]	0.1759 (3)	0.2756 (3)	0.7754 (3)
Cl2[c]	0.1453 (4)	0.0631 (3)	0.6542 (5)
C[c]	0.229 (1)	0.163 (1)	0.718 (1)

[a] Mercapto hydrogen atom positions was independently refined. [b] The BF_4^- anion was rotationally disordered in two positions about the F1–B vector designated F2,3,4 "a" and "b"; the relative site occupancy for group "a" was 0.61 (3). [c] Methylene chloride solvate molecule.

to afford a yellow solid. Yield: 0.110 g (0.14 mmol, 60%). Anal. Calcd for $C_{46}H_{40}P_2RuS$: C, 70.14; H, 5.12; S, 4.07. Found: C, 70.43; H, 5.28; S, 4.14. ^1H NMR (C_6D_6): 6.8–7.8 (m, 30 H), 6.66 (m, 3 H), 4.54, 3.61 (d, 4 H), 4.11 (s, 2 H), −10.94 (t, J_{PH} = 34 Hz, 1 H). $^{31}P\{^1H\}$ NMR (toluene/benzene-d_6): 68.64.

Reaction of $[(ThiCp)Ru(PPh_3)_2]BF_4$ and H_2S. A solution of $[(ThiCp)Ru(PPh_3)_2]BF_4$ (3 mg, 3.4 × 10^{-6} mol) in ca. 0.5 mL of $CDCl_3$ was saturated with H_2S, and the ^1H NMR spectrum was recorded. A new species had formed that was assigned as $[(ThiCp)Ru(PPh_3)_2(SH_2)]^+$, which exists in a directly observable equilibrium with $[(ThiCp)Ru(PPh_3)_2]^+$. The equilibrium constant for was calculated (P_{H_2S} = 1 atm) to be 3.8 in favor of $[(ThiCp)Ru(PPh_3)_2(H_2S)]^+$. ^1H NMR ($CDCl_3$) for $[(ThiCp)Ru(PPh_3)_2(SH_2)]^+$: 7.0–7.5 (s, 30 H), 6.78 (m, 3 H), 4.67, 4.05 (d, 4 H), 3.47 (s, 2 H), 3.26 (t, J = 7 Hz, 2 H).

Reaction of $(ThiCp)Ru(PPh_3)_2SH$ with HOTf. To a solution of $(ThiCp)Ru(PPh_3)_2SH$ (7 mg, 0.02 mmol) in ca. 0.3 mL of $CDCl_3$ in a NMR tube was added HOTf (2 μL, 0.025 mmol). The ^1H NMR spectrum of this solution showed $[(ThiCp)Ru(PPh_3)_2]^+$ and $[(ThiCp)Ru(PPh_3)_2H_2]^+$, with the latter predominating; see Results.

Reaction of $[(ThiCp)Ru(PPh_3)_2]BF_4$ with H_2. A solution of $[(ThiCp)Ru(PPh_3)_2]BF_4$ (9 mg, 1.1 × 10^{-6} mmol) in ca. 0.3 mL of $CDCl_3$ was purged with H_2 and sealed under 1 atm of H_2. The ^1H NMR of this solution showed $[(ThiCp)Ru(PPh_3)_2H_2]^+$ together with dissolved H_2 (1.8 ppm, br). ^1H NMR ($CDCl_3$) for $[(ThiCp)Ru(PPh_3)_2H_2]^+$: 6.9–7.5 (m, 30 H), 6.2 (m, 3 H), 5.18, 4.41 (d, 4 H), 3.05 (s, 2 H), −7.28 (t, J_{PH} = 24 Hz, 2 H).

Crystallization of $[CpRu(PPh_3)_2(HSPr)](BF_4)$. Crystals of this material were unintentionally obtained according to the following method. Thiophene (Aldrich, 30 mL) was added to solid $CpRu(PPh_3)_2Cl$ (0.326 g) and $AgBF_4$ (0.1 g). After being stirred for 2 h, the reaction mixture was concentrated to half-volume, Schlenk filtered through Celite, and washed with 10 mL of CH_2Cl_2. The solution was layered with hexane; after 2 days yellow crystals were obtained that were characterized by single crystal X-ray diffraction.

X-ray Crystallography. The crystal and refinement data are presented in Table II. The ruthenium position was deduced from a Patterson map. A weighted Fourier synthesis gave positions for 34 of the remaining 55 non-hydrogen atoms and subsequent least-squares–difference Fourier calculations revealed the positions of the rest. Three fluorine atoms of the anion were rotationally disordered in two positions about the F1–B vector. The mercapto hydrogen atom was independently refined, but the remaining hydrogen atoms were included as fixed contributors in "idealized" positions. A group isotropic thermal parameter was varied for the disordered fluorine atoms. Phenyl carbon atoms were refined with isotropic thermal coefficients. The centric space group was supported by successful refinement of the proposed model. The final difference Fourier map had no significant features, and a final analysis of variance between observed and calculated structure factors showed no systematic errors. The atomic coordinates are contained in Table III. The scattering factors used are described in ref 67.

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(67) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101.

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Registry No. **1**, 110077-84-4; **2**$(OTf)_2$, 122070-54-6; **2**$(PF_6)_2$, 122070-55-7; **2**$(BF_4)_2$, 110077-73-1; **2**$(I)_2$, 122070-69-3; $CpRu(PPh_3)_2Cl$, 32993-05-8; $CpRu(PPh_3)_2H$, 34676-08-9; $[CpRu(PPh_3)]_2S_6$, 122070-48-8; $CpRu(PPh_3)(CO)(SH)$, 122070-50-2; $[CpRu(PPh_3)_2(SH_2)]OTf$, 122070-52-4; $CpRu(PPh_3)_2OTf$, 113322-93-3; $[CpRu(PPh_3)_2H_2]OTf$, 122070-53-5; $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2H_2)[PF_6]_2$, 122070-57-9; $CpRu(PPh_3)_2I$, 34692-10-9; $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[OTf]$, 122070-58-0; $[CpRu(PPh_3)_2(SC_2H_4)]OTf$, 113322-95-5; $[CpRu(PPh_3)_2]_2(\mu\text{-}SH)[OTf]$, 122070-60-4; $[CpRu(PPh_3)_2(CH_3SH)]OTf$, 122070-62-6; $[(ThiCp)Ru(PPh_3)_2]OTf$, 122070-63-7; $(ThiCp)Ru(PPh_3)_2Cl$, 98217-94-8; $(ThiCp)Ru(PPh_3)_2SH$, 122092-65-3; $(ThiCp)Ru(PPh_3)_2H$, 122092-66-4; $[(ThiCp)Ru(PPh_3)_2]BF_4$, 98217-96-0; H_2S, 7783-06-4; $[(ThiCp)Ru(PPh_3)_2(SH_2)]BF_4$, 122070-65-9; $[(ThiCp)Ru(PPh_3)_2H_2]OTf$, 122092-68-6; $[(ThiCp)Ru(PPh_3)_2H_2]BF_4$, 122170-09-6; $[CpRu(PPh_3)_2(HSPr)]BF_4$, 122070-67-1; $[CpRu(PPh_3)_2(HSPr)]BF_4 \cdot CH_2Cl_2$, 122070-68-2; $[CpRu(PPh_3)]_2S_4$, 122070-49-9; thiirane, 420-12-2; thiophene, 110-02-1.

Supplementary Material Available: Tables of idealized hydrogen coordinates and thermal parameters (4 pages); a table of structure factors (18 pages). Ordering information is given on any current masthead page.

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Structural, Vibrational, and Solid-State NMR Studies of the Halogenocuprate(I) Complexes $[(PPh_3)_2CuI_2]^-$ and $[(PPh_3)CuI_3Cu(PPh_3)]^-$

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Single-crystal X-ray diffraction, vibrational spectroscopy, and solid state ^{31}P NMR spectroscopy have been used to characterize two new types of ionic copper(I) complexes. The anion in $[PPh_3Me]^+[(PPh_3)_2CuI_2]^-$ contains two PPh_3 ligands coordinated to the copper atom of a CuI_2 unit in a pseudotetrahedral arrangement, with Cu–P = 2.292 (2), 2.288 (2) Å, Cu–I = 2.692 (1), 2.702 (1) Å, P–Cu–P = 121.24 (9)°, and I–Cu–I = 108.62 (4)° (monoclinic, $P2_1/c$, a = 12.138 (5) Å, b = 14.776 (6) Å, c = 28.197 (14) Å, β = 103.76 (4)°, Z = 4, R = 0.040 for 4490 "observed" ($I > 3\sigma(I)$) reflections). The far-IR spectrum shows a strong band at 118 cm^{-1} that is assigned to the antisymmetric Cu–I stretching mode of the CuI_2 unit. The CPMAS ^{31}P NMR spectrum shows a strong singlet at 18.1 ppm (relative to 85% H_3PO_4) due to the cation and a weaker quartet centered at −16.7 ppm due to the coordinated PPh_3 in the anion, with line spacings due to Cu–P coupling of 1.08, 1.20, and 1.23 kHz. The anion in $[PPh_3Me]^+[(PPh_3)CuI_3Cu(PPh_3)]^-$ consists of an approximately D_{3h} Cu_2I_3 unit with three iodine atoms bridging the two copper atoms and with one PPh_3 molecule completing a pseudotetrahedral arrangement around each copper atom. The crystallographically imposed symmetry of the ion is C_{3v}, with the 3-fold axis passing through the P–Cu bonds. The core structural parameters are Cu–P = 2.215 (3), 2.202 (3) Å, Cu–I = 2.701 (2), 2.730 (2) Å, P–Cu–I = 116.83 (8), 118.05 (8)°, I–Cu–I = 101.21 (5), 99.70 (5)°, and Cu–I–Cu = 54.88 (4)° (cubic, $P2_13$, a = 17.744 (10) Å, Z = 4, R = 0.036 for 1390 "observed" reflections). This is the first reported example of a binuclear copper(I) complex with three bridging ligands and is an example of an unusual bonding situation in which two coordination tetrahedra are linked by sharing a common face. This has the effect of producing an unusually short Cu- - -Cu separation of 2.50 Å. The far-IR spectrum shows a band at 127 cm^{-1} that is assigned to the doubly degenerate perpendicular Cu–I stretching mode of the Cu_2I_3 unit. The CPMAS ^{31}P NMR spectrum shows a strong singlet at 20.1 ppm due to the cation and a broad quartet centered at −15.8 ppm due to the coordinated PPh_3 in the anion. The splitting pattern for this quartet does not conform to expectations for an AX spin system involving coupling between $I = {}^1/_2$ and $I = {}^3/_2$ nuclei. The assignments of the ν(Cu–I) IR bands in both complexes are supported by approximate normal-coordinate analyses, and the resulting Cu–I force constants are compared with the values obtained in similar analyses of related iodocopper(I) complexes.

Introduction

Copper(I) exhibits a remarkable diversity in its structural chemistry. This is demonstrated by the wide variety of structural types that are encountered in complexes of the copper(I) halides. Copper(I) halides form mononuclear or multinuclear complexes with neutral phosphine or amine ligands in which the copper coordination number ranges from 2 to 4.[2–4] Halogenocuprate(I) complexes, formed by the reaction of copper(I) halides with halide ion, likewise show a wide diversity of mononuclear and multinuclear structures, although there is a noticeable preference for lower coordination numbers; in such complexes the coordination number 4 is only found in oligomeric or infinite polymeric structures.[2,3,5,6]

Little work has been done to investigate the structures and properties of complexes that result from the reaction of the potentially coordinatively unsaturated halogenocuprates(I) (e.g. $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_4X_6]^{2-}$, etc.) with neutral ligands such as phosphines and amines. We have recently shown that the anionic bromocuprate(I) complex $[CuBr_2]^-$ reacts with 1 mol of triphenylphosphine, PPh_3, to yield the species $[(PPh_3)CuBr_2]^-$, in which the copper(I) ion has the unusual coordination number of

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