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Synthesis, Structure, and Properties of $[CpRu(PR_3)_2]_2(\mu\text{-}S_2)^{2+}$. Effects of Strong π-Donation in a Disulfur Complex

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Compounds of the type $[CpRu(PR_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ were prepared via the unusual reaction of $CpRu(PR_3)_2Cl$, S_8, and silver salts. Another route to these dimers includes the displacement of dihydrothiophene from $[CpRu(PPh_3)_2(SC_4H_6)]^+$ with elemental sulfur. Optical and Raman spectroscopic studies of the dications indicate that their green colors ($\lambda_{max} = 718$ nm) arise from transitions within the Ru_2S_2 core. Cyclic voltammetric measurements indicate that the dication can be oxidized (for the PMe_3 derivative) and, in two well-separated steps, reduced. Salts of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$ were prepared via reduction of the dication with Et_3N, benzyl alcohol, or thiophenol. The EPR spectrum of the monocation shows a five-line pattern indicating the equivalency of the four phosphorus centers. The structure of $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[BF_4]_2\cdot 2C_6H_5NO_2$ was determined by X-ray diffraction. The compound crystallized in the monoclinic space group $P2_1/c$ with $a = 8.424$ (2) Å, $b = 18.117$ (5) Å, $c = 17.424$ (3) Å, and $\beta = 92.13$ (2)°. The structure was refined to a final $R = 0.053$ ($R_w = 0.062$). The dication is centrosymmetric with short Ru–S (2.208 (3) Å) and S–S (1.962 (4) Å) distances. The structure, electrochemistry, and stoichiometry of the dication indicate a delocalized, multiply bonded $\mathrm{Ru}\overset{\cdots}{-}\mathrm{S}\overset{\cdots}{-}\mathrm{S}\overset{\cdots}{-}\mathrm{Ru}$ core.

Introduction

Despite the elusiveness of the disulfur molecule,[1] transition-metal disulfides are fairly common.[2] For example, S_2 subunits are contained in several important minerals, including the iron disulfide isomers pyrite and marcasite.[3] Isostructural with pyrite is RuS_2, which occurs in nature as the mineral laurite.[4] Recent work at Exxon has identified RuS_2 as an extremely active catalyst for the hydrodesulfurization of dibenzothiophene.[5] The electrocatalytic properties of RuS_2 have also attracted considerable recent attention.[6] These results induced us to investigate the chemical properties of molecular ruthenium sulfides. Our previous reports described studies of thiophene complexation[7] and coordinative unsaturation[8] as they relate to catalysis by ruthenium sulfides. This paper focuses on the properties of the $Ru_2(\mu\text{-}S_2)$ functionality.

The history of molecular ruthenium disulfides begins with Taube's $[Ru(NH_3)_5]_2(\mu\text{-}S_2)^{4+}$.[9] The decaammine disulfide differs from most diamagnetic ruthenium ammines in that it is electron-deficient with regards to the σ-electron count: it is a 34e dimer. The unusual nature of this disulfide can perhaps best be appreciated if the species $Ru(NH_3)_5SH^+$ [10] is recognized as an electron-precise analogue of an organic thiol. Whereas a typical organic thiol undergoes two-electron oxidation to give a disulfide, i.e., R_2S_2, the ruthenium ammine thiol undergoes a *four*-electron oxidation to the disulfide. The structure of $[Ru(NH_3)_5]_2(\mu\text{-}S_2)Cl_4\cdot 2H_2O$ reveals short Ru–S distances indicative of multiple bonding.[11]

The properties of the ruthenium ammine sulfides are intriguing, particularly in view of a possible connection to the behavior of RuS_2 itself. The $CpRu(PPh_3)_2^+$ moiety ($Cp = \eta^5\text{-}C_5H_5$) represents an alternative to $Ru(NH_3)_5^{2+}$ because these two fragments display similar ligand affinities. Derivatives of the organoruthenium species exhibit good solubility characteristics and excellent kinetic stability. These properties have allowed us to characterize $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$ and its derivatives. This class of binuclear ruthenium disulfides have unusual and distinctive spectroscopic, structural, and electrochemical properties. On the basis of our measurements, we conclude that the $\mu\text{-}S_2$ ligand is an extremely powerful π-donor toward ruthenium.[12]

Results

Synthesis of $[(RCp)Ru(PR_3)_2]_2(\mu\text{-}S_2)^{2+}$. Addition of $AgBF_4$ to CH_2Cl_2 solutions containing $CpRu(PPh_3)_2Cl$ and elemental sulfur results in the rapid formation of the green $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ (**1**$[BF_4]_2$). The yields are high and the product is robust. Compound **1** is easily obtained as dark green, air-stable crystals. Compound **1** can also be obtained in good yield with methanol as solvent without recourse to the silver reagent although the conversion is much slower. Yield optimization experiments showed that these syntheses work well when the sulfur is used in exactly the stoichiometric quantities (eq 1). Compound

$$2CpRu(PPh_3)_2Cl + {}^1/_4S_8 + 2Ag^+ \rightarrow [CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+} + 2AgCl \quad (1)$$

1 also forms when $(MeCp)_2TiS_5$ is used as the sulfur source; here we observed the formation of a transient brown species. Compound **1** was characterized by elemental analysis and spectroscopic studies; furthermore, the PMe_3 analogue of **1** was examined by single-crystal x-ray diffraction. The ^1H NMR spectrum of **1** shows a single Cp resonance as well as a phenyl multiplet. The ^{31}P NMR spectrum consists of a single line at 38.5 ppm downfield of the 85% H_3PO_4 standard. The visible spectrum of **1** is dominated by an absorption at 718 nm ($\epsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}) (Figure 1). This absorption resembles that for $[Ru(NH_3)_5]_2(\mu\text{-}S_2)^{4+}$ in terms of both its wavelength and its intensity.[13] These bands are therefore assigned to transitions involving the Ru_2S_2 core. Consistent with this view, the intensity of the 414-cm^{-1} band in its Raman spectrum is very strong when the excitation wavelength is 647 nm (Figure 2). We assign this absorption as symmetric $\nu_{Ru\text{-}S}$. Also observed in the Raman spectrum is an absorption at 530 cm^{-1}, which is assigned to $\nu_{S\text{-}S}$. For comparison, $\nu_{Ru\text{-}S}$ and $\nu_{S\text{-}S}$ in $[Ru(NH_3)_5]_2(\mu\text{-}S_2)^{4+}$ are observed at 415 and 519 cm^{-1}.[13]

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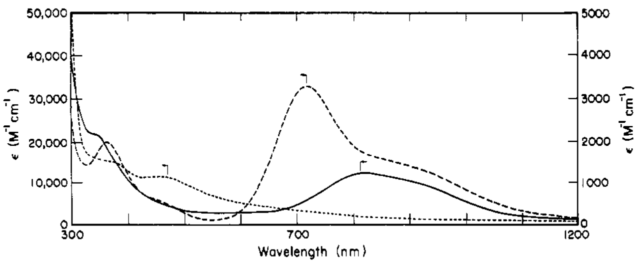


Figure 1. Visible absorption spectra of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$ (– –), $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]$ (—), and $CpRu(PPh_3)_2Cl$ (-----) in CH_2Cl_2 solution.

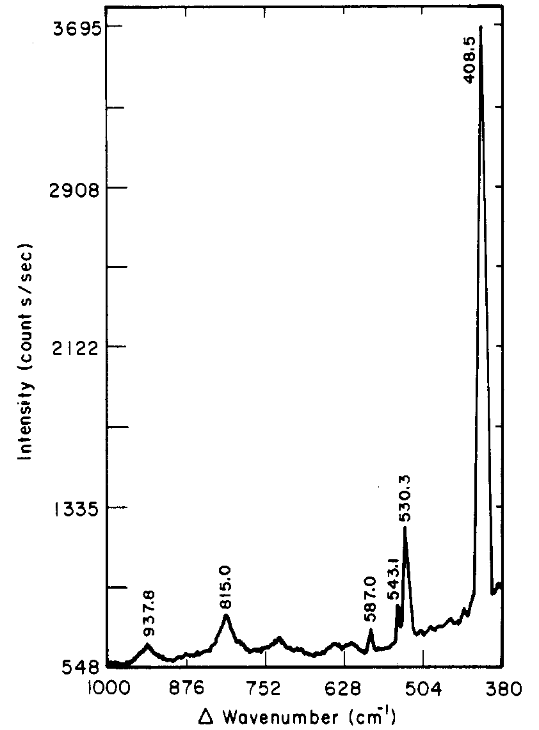
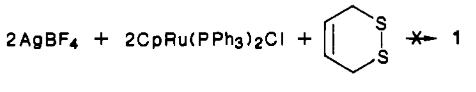


Figure 2. Raman spectrum of solid $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ with laser excitation at 647.1 nm.

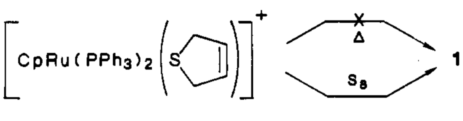
Analogues of **1** can be prepared in a straightforward manner, including $[(MeCp)Ru(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}$, $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)^{2+}$, and $[CpRu(Ph_2PC_2H_4PPh_2)]_2(\mu\text{-}S_2)^{2+}$. In terms of their spectroscopic and physical properties, these derivatives are similar to **1**. Aspects of the synthesis of the PMe_3 derivative of **1** were briefly examined. We found that addition of $AgBF_4$ to CH_2Cl_2 solutions of **1** in the absence of elemental sulfur resulted in the formation of the known[14] $[CpRu(PMe_3)_2Cl_2]BF_4$ in about 40% yield. This material was unreactive toward elemental sulfur under mild conditions.

The stability of **1** led us to attempt other synthetic approaches. Compound **1** was not formed when 1,2-dithiin was used as a potential source of the disulfur molecule (eq 2). We prepared



(2)

and characterized the 2,5-dihydrothiophene complex $CpRu(PPh_3)_2(2,5\text{-}SC_4H_6)^+$, but this complex did not undergo elimination of 1,3-butadiene under mild conditions. The dihydrothiophene complex gave **1** upon treatment with elemental sulfur (eq 3).



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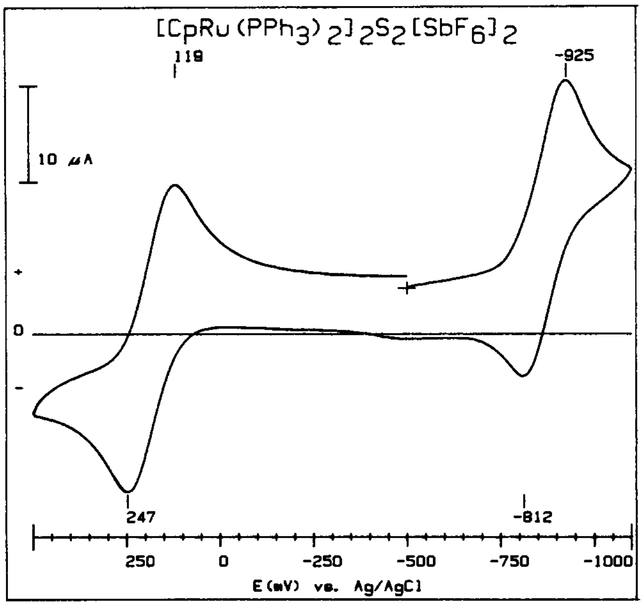

Figure 3. Cyclic voltammogram of an acetonitrile solution of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$ (10^{-3} M) with 10^{-1} M Bu_4NPF_6 electrolyte. The sweep rate was 100 mV/s.

Compound **1** is unreactive toward olefins, dienes, unactivated acetylenes, and carbon monoxide, at least under mild conditions. We have recently shown that **1** reacts with $(NBu_4)_2S_6$ to give *cyclo*-$[CpRu(PPh_3)]_2S_x$ ($x = 4, 6$).[15] Solutions of **1** are stable to quartz-filtered ultraviolet radiation. Boiling dichloroethane solutions of **1** decompose to give Ph_3PS and paramagnetic products, which are not investigated.

Synthesis and Characterization of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+$ (1r). Initial ^1H NMR studies of **1** were plagued by irreproducibly broad signals, which we now attribute to minor impurities of the monocation (**1r**), which apparently undergoes rapid electron exchange with **1**. San Filippo et al.[13] also observed residual paramagnetism in samples of $[Ru(NH_3)_5]_2(\mu\text{-}S_2)Br_4$, which they attributed to impurities. Compound **1** undergoes smooth reduction to **1r** by triethylamine. This reduction is accelerated by the addition of benzyl alcohol or thiophenol. Gas chromatographic measurements confirm the stoichiometry shown in eq 4 and 5. Compound **1r**

$$\underset{\mathbf{1}}{2[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^{2+}} + PhCH_2OH \xrightarrow[-2Et_3NH^+]{+2Et_3N} \underset{\mathbf{1r}}{2[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^+} + PhCHO \quad (4)$$

$$\mathbf{1} + PhSH \xrightarrow[-Et_3NH^+]{+Et_3N} \mathbf{1r} + {}^1/_2Ph_2S_2 \quad (5)$$

can be cleanly reoxidized; hence, these findings may provide the basis for electrocatalytic oxidation reactions. Further work on these reactions is planned.

Compound **1r** forms blue-green crystals (Figure 1). No absorptions are observed in the range 1100–1500 nm. The isotropic electron spin resonance spectrum of **1r** shows a five-line pattern centered at $g = 2.05$ with $A = 7.2$ G. This coupling pattern indicates delocalization of the unpaired spin over the bimetallic unit.

Electrochemistry of 1. Cyclic voltammetric studies on CH_2Cl_2 solutions of **1** show that it undergoes two one-electron reductions, reversibly at 180 mV and quasi-reversibly at −875 mV vs. Ag/AgCl (Figure 3). The nature of the first couple was confirmed by coulometry at −50 mV. The cyclic voltammogram of the PMe_3 analogue of **1** showed three waves, which we assign to the 3+/2+, 2+/1+, and 1+/0 couples. The effect of replacing PPh_3 by PMe_3 on the $E_{1/2}$ values is 325 mV for the 2+/1+ couple and 84 mV for the 1+/0 couple.[16]

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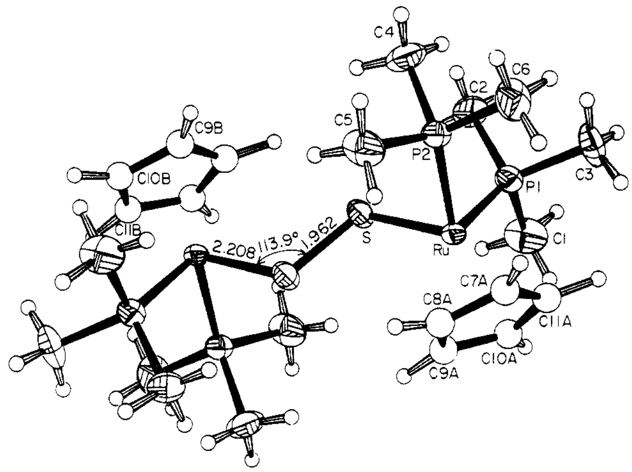

Figure 4. Molecular structure of the non-hydrogen atoms of the centrosymmetric $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)$ dication.

Table I. Selected Bond Distances and Angles for the Cation in $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2 \cdot 2C_6H_5NO_2$

		Distances (Å)			
Ru-S	2.208 (3)	S-S[a]	1.962 (4)	Ru-P1	2.300 (3)
Ru-P2	2.309 (3)	P1-C1	1.81 (1)	P1-C2	1.80 (1)
P1-C3	1.82 (1)	P2-C4	1.79 (1)	P2-C5	1.83 (1)
P2-C6	1.83 (1)	Ru-Cp	1.91 (2)		
		Angles (deg)			
S-Ru-P1	88.3 (1)	S-Ru-P2	89.7 (1)	S-Ru-Cp	130.5 (5)
P1-Ru-P2	94.9 (1)	P1-Ru-Cp	122.4 (6)	P2-Ru-Cp	120.9 (4)
Ru-S-S[a]	113.9 (2)	Ru-P1-C1	111.5 (5)	Ru-P1-C2	121.0 (5)
Ru-P1-C3	115.3 (5)	C1-P1-C2	100.3 (7)	C1-P1-C3	103.0 (6)
C2-P1-C3	103.4 (7)	Ru-P2-C4	121.3 (5)	Ru-P2-C5	110.4 (5)
Ru-P2-C6	115.3 (5)	C4-P2-C5	99.8 (7)	C4-P2-C6	102.0 (7)
C5-P2-C6	106.1 (6)				

[a] Equivalent positions at $1 - x$, $1 - y$, $1 - z$.

Crystallographic Studies. Crystals of $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2 \cdot 2C_6H_5NO_2$ were grown by slowly cooling a saturated nitrobenzene solution of **1**. The cation is well-behaved in the lattice and, consistent with the NMR results, possesses inversion symmetry (Figure 4). Each ruthenium atom is coordinated to the Cp ring, two trimethylphosphine groups, and to one end of a μ-S_2 unit giving pseudooctahedral coordination. Bond distances and angles are listed in Table I.

The sulfur-sulfur distance of 1.962 (4) Å lies between the S-S distances observed for free S_2 (1.89 Å)[1] and H_2S_2 (2.055 Å).[17,18] The majority of disulfido complexes feature S-S distances in the 2.01-2.05-Å range.[2] Appreciable double-bond character is therefore indicated for the μ-S_2 unit in $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$. Ruthenium-sulfur bond distances of 2.208 (3) Å are also very short compared to innocent Ru-S distances as found in $[CpRu(PPh_3)_2(n\text{-}PrSH)]BF_4$ (2.37 Å)[19] and the S-bound thiophene complex $[(2\text{-}(SC_4H_3)CH_2C_5H_4)Ru(PPh_3)_2]BF_4$[7] (2.408 Å). Short Ru-S bonds were also observed in $Ru(S\text{-}2,3,5,6\text{-}C_6Me_4H)_4CO$[20] (2.210 (3) Å) and $(C_5Me_4Et)_2Ru_2S_4$[8] (2.195 Å). π-Donation from sulfur to ruthenium was invoked to explain the short Ru-S distances in these electron-deficient complexes. The Ru-S distances in our compound are comparable to the Ru-S distances in $[(NH_3)_5Ru]_2(\mu\text{-}S_2)Cl_4 \cdot 2H_2O$ (2.191 (1) and 2.195 (1) Å).[11] The S-S distance in **1** is shorter than that in the ammine (2.014 (1) Å).[10] The Ru_2S_2 core of ruthenium ammine dimers lies on a crystallographically imposed mirror plane.

Discussion

The synthesis of **1** and its analogues by metathetical replacement of Cl^- by S is highly unusual. We speculate that this process involves initial coordination of S_8. The fact that this method is useful for the preparation of thioether complexes (e.g., dihydrothiophene) supports this view. The finding that **1** can be prepared by using the exact stoichiometry, i.e., 2 Ru + $^1/_4$ S_8, does not preclude the possibility that the reactions occur via initial complexation of S_8 since the sulfur allotropes equilibrate rapidly in ionic media.[21] The η^1-S_8 species would be a 2e ligand, similar to a thioether ligand, as in $[CpRu(PPh_3)_2(dht)]^+$ (dht = dihydrothiophene). The putative $[CpRu(PPh_3)_2(\eta^1\text{-}S_8)]^+$ may be a precursor to $[CpRu(PPh_3)_2S]^+$, which dimerizes, but recent work fails to support this view.[22]

The structural and electrochemical properties of **1** are conveniently discussed within the framework of a qualitative molecular orbital model wherein the frontier orbitals of the Ru_2S_2 core are treated as a *trans*-butadiene-like π-network. For this analysis we view the 16e $CpRu(PPh_3)_2^+$ fragment as carrying a $(t_{2g})^6$ complement; one of the t_{2g} orbitals on *each* Ru center is of the appropriate symmetry and orientation for π-interaction with the disulfur ligand. The disulfur ligand contributes two electrons to this π-system. In this way the Ru_2S_2 π-network possesses six electrons and therefore resembles the dianion of butadiene. This model conforms with the planarity of the Ru_2S_2 core and the short Ru-S and S-S bonds. Delocalized π-bonding is also indicated by the fact that the EPR spectrum of the monocation **1r** shows hyperfine coupling of the valence electron to four equivalent phosphines.

The most striking aspect of the $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)^z$ series is the strong reducing power of the neutral member. Replacement of Cl^- in $CpRu(PPh_3)_2Cl$ by $^1/_2$ S_2^{2-} results in a cathodic shift of about 1450 mV! This unusually large substituent effect is attributed to the presence of four cumulated π-donors, viz. $Ru^{II}\text{-}S^{-II}\text{-}S^{-II}\text{-}Ru^{II}$.

Gladysz has recently ascribed the enhanced basicity of $CpRe(PPh_3)(NO)(PPh_2)$ to the stereoelectronic interference of lone pairs of electrons on the rhenium and phosphorus (phosphido) atoms.[23] This type of situation is well-recognized in main-group and organic chemistry, where it is referred to as the α or anomeric effect.[24] In the present case, this effect is manifested in the destabilization of the neutral diruthenium(II) disulfide as reflected by its extremely potent reducing properties.

The S-S bond length in $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ is the shortest known for a disulfur complex. We attach considerable importance to the S-S bond length since, in contrast to the case for the majority of disulfur complexes, the S-S distance is not constrained by other bridging ligands or chelation. The shortness of the S-S bond is particularly striking given that previous studies have clearly shown that S-S bonds tend to be longest when the X_2S_2 dihedral angles are 0 and 180°.[25,26] For dihedral angles of 0° (and 180°), the equilibrium S-S bond length in organic disulfides is predicted to be 2.10 Å. From Hordvik's scale,[26] the S-S π-bond order in **1** is ca. 0.8. In apparent contrast with this conclusion the value assigned to ν_{S-S} differs little from ν_{S-S} values in organic disulfides where there is little S-S double-bond character. However, both the Ru-S distances and the value of ν_{Ru-S} indicate significant multiple bonding.

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(16) $E_{1/2}$ values (sweep rate 200 mV s^{-1}; CH_2Cl_2 solution; vs Ag/AgCl) for the +1/0 couples of $CpRu(PR_3)_2Cl$, where R = Ph and Me, are 594 and 377 mV, respectively.

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Other bimetallic complexes are electronically similar to **1**, including $[Cp^*Mn(CO)_2]_2(\mu\text{-}S_2)$[27] and $[Ru(NH_3)_5]_2(\mu\text{-}S_2)^{4+}$.[9,11,13] Also relevant are the bimetallic cage compounds of the type $Cp_2M_2(\mu\text{-}S_2)_2$.[8,28] All are deeply colored dimers featuring M_2S_2 dihedral angles of 0 or 180° and relatively short M–S and S–S distances. Furthermore, each of these 34e dimers lacks direct metal–metal bonds. Our results indicate that the formal electron deficiency of this class of compounds is a consequence of the potent π-donor properties of the μ-S_2 ligand.

Experimental Section

Materials. All reactions were performed under an atmosphere of purified nitrogen, but workups were done aerobically. Hexanes and dichloromethane were redistilled under N_2 from sodium and P_4O_{10}, respectively. 3,6-Dihydro-1,2-dithiin,[29] $CpRu(PPh_3)_2Cl$,[30] $(MeCp)Ru(PPh_3)_2Cl$,[30] $CpRu(PMe_3)_2Cl$,[31] CpRu(dppe)Cl[31] (dppe = 1,2-bis(diphenylphosphino)ethane), and $(MeCp)_2TiS_5$[32] were prepared according to the literature methods. 2,5-Dihydrothiophene was prepared according to the literature method[29] by using commercial Li_2S (Aldrich) instead of Na_2S. Triethylamine was redistilled from KOH. Tetrabutylammonium hexafluorophosphate was prepared from NH_4PF_6 and tetrabutylammonium iodide and recrystallized from water. Other reagents were purchased from Aldrich.

Instrumentation. All standard ^1H NMR spectra were obtained on Varian XL-200 or Nicolet QE-300 instruments. $^{31}P\{^1H\}$ NMR spectra were obtained at 101.265 00 MHz on a modified spectrometer at ambient temperatures using an internal D_2O lock with 85% H_3PO_4 as an external reference (downfield shifts are positive). IR spectra were obtained with KBr pellets on a Nicolet MX-5 FTIR spectrometer. UV/vis spectra were taken with a Varian 2300 spectrometer. Fast atom bombardment mass spectra (FABMS) were run on a Varian 731 spectrometer at the University of Illinois Mass Spectrometry Laboratory. 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). Constant-potential electrolysis experiments were performed by using a two-compartment 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 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.

The microanalyses were performed by the School of Chemical Sciences microanalytical laboratory.

$[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$ ($1[SbF_6]_2$). Solid $AgSbF_6$ (0.5 g, 1.5 mmol) was added to a stirred slurry of S_8 (0.25 g, 1 mmol) and $CpRu(PPh_3)_2Cl$ (0.725 g, 1 mmol) in 20 mL of CH_2Cl_2. The solution quickly turned from orange to green. After 6 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated to about 5 mL and diluted with hexanes to give 0.73 g (0.38 mmol, 76%) of green crystals. Anal. Calcd for $C_{82}H_{70}P_4Ru_2S_2Sb_2F_{12}$: C, 51.36; H, 3.63. Found: C, 50.36; H, 3.90. ^1H NMR (acetone-d_6; ppm): 7.0–7.5 (m, 60 H), 5.12 (s, 10 H). $^{31}P\{^1H\}$ NMR (acetone-d_6; ppm): 38.5. UV/vis (CH_2Cl_2 solution; λ_{max}, nm (ϵ)): 820 sh, 718 (32 000), 445 sh, 362 (19 000). With use of similar procedures, the MeCp and diphos derivatives were prepared and isolated as green crystals. Tetrafluoroborate salts were prepared similarly by using $AgBF_4$ instead of $AgSbF_6$.

Table II. Crystal Data Collection and Refinement Parameters

formula	$C_{34}H_{56}F_6N_2O_4P_4Ru_2S_2Sb_2$
cryst syst	monoclinic
space group	$P2_1/c$
cell constants	
a, Å	8.424 (2)
b, Å	18.117 (5)
c, Å	17.424 (3)
β, deg	92.13 (2)
cell vol, V, Å^3	2657 (2)
formula units/cell, Z	2
calcd density, g cm^{-3}	1.773
abs coeff, cm^{-3}	18.29 (numerical cor)
transmission factors	0.614–0.579 (SHELX-76)
cryst dimens, mm	0.3 × 0.3 × 0.7
radiation	Mo Kα
scan technique	ω/θ
2θ scan range, deg	2–53
ω scan angle, deg	$1.5[1.00 + 0.35 \tan \theta]$
intensities measd ($-h,-k,\pm l$)	6123 ($R_i = 0.018$)
unique intensities	5497 (2617, $I > 2.58\sigma(I)$)
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.053
$R_w = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{1/2}$	0.062 ($p = 0.03$)
max shift/error	0.016

$[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$. Anal. Calcd for $C_{82}H_{70}P_4Ru_2S_2B_2F_8$: C, 60.80; H, 4.35. Found: C, 59.14; H, 4.53. FABMS (m/e): 1533 ($M^+ - BF_4$), 1444 ($M^+ - 2\ BF_4$), 1184 ($Cp_2Ru_2(PPh_3)_3S_2^+$), 724 ($CpRu(PPh_3)_2S^+$, 691 ($CpRu(PPh_3)_2^+$). $^{31}P\{^1H\}$ NMR ($CDCl_3$; ppm): 38.53.

$[(MeCp)Ru(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$. Anal. Calcd for $C_{84}H_{74}P_4Ru_2S_2B_2F_8$: C, 61.20; H, 4.17. Found: C, 59.26; H, 4.53. ^1H NMR ($CDCl_3$; ppm): 7.0–7.5 (m, 60 H), 4.52 (s, 4 H), 4.92 (s, 4 H), 1.20 (s, 6 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$; ppm): 43.84.

$[CpRu(dppe)]_2(\mu\text{-}S_2)[SbF_6]_2$. Anal. Calcd for $C_{62}H_{58}P_4Ru_2S_2Sb_2F_{12}$: C, 44.71; H, 3.49; S, 3.85. Found: C, 44.12; H, 3.25; S, 4.15. ^1H NMR (acetone-d_6; ppm): 7.7–7.1 (m, 40 H), 5.22 (s, 10 H), 2.83 (m, 4 H), 2.32 (m, 4 H). $^{31}P\{^1H\}$ (acetone-d_6; ppm): 80.05.

$[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ from $(MeCp)_2TiS_5$. To a solution of $(MeCp)_2TiS_5$ (0.146 g, 0.4 mmol) in 10 mL of CH_2Cl_2 was added a solution of $CpRu(PPh_3)_2Cl$ (0.29 g, 0.4 mmol) in 10 mL of CH_2Cl_2 and solid $AgBF_4$ (0.08 g, 0.5 mmol). Stirring for 24 h resulted in a color change from red-brown to dark green. The solution was filtered through a pad of Celite, rinsed with CH_2Cl_2, and concentrated to about 5 mL. Chromatography using Bio-Beads S-X8 (eluent CH_2Cl_2) gave a green band. Crystallization from CH_2Cl_2/hexanes gave $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$ (0.30 g, 0.18 mmol, 90%) of dark green crystals.

$[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$. Solid $AgSbF_6$ (0.50 g, 1.5 mmol) was added to a stirred slurry of S_8 (0.256 g, 1 mmol) and $CpRu(PMe_3)_2Cl$ (0.35 g, 1 mmol), in acetone (20 mL). The solution quickly turned from orange to brown and then blue-green within seconds. After it was stirred for 6 h, this solution was filtered through a pad of Celite, concentrated to ca. 10 mL, and diluted with 50 mL of CH_2Cl_2. After storage at −10 °C overnight, the blue-green needles of the product were collected, washed with CH_2Cl_2, and dried in vacuo overnight; yield 0.30 g (0.28 mmol, 56%). Anal. Calcd for $C_{22}H_{46}P_4Ru_2S_2Sb_2F_{12}$: C, 22.53; H, 3.92; S, 5.46. Found: C, 22.34; H, 3.77; S, 5.50. ^1H NMR (acetone-d_6; ppm): 5.72 (s, 10 H), 1.75 (t, 36 H). $^{31}P\{^1H\}$ (acetone-d_6; ppm): 7.14.

$[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]$ ($1r[SbF_6]$). Sequential addition of Et_3N (11 μL, 0.08 mmol) and PhSH (12 μL, 0.1 mmol) to a solution of $[CpRu(PPh_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$ (0.15 g, 0.08 mmol) in 15 mL of methanol gave a blue-green precipitate. The resultant slurry was stirred for 30 min and filtered. The solid product was washed with methanol and extracted with acetone, leaving a paramagnetic purple residue. The acetone extract was concentrated, diluted with methanol, and cooled overnight at −20 °C. The dark green microcrystals were collected, washed with methanol, and dried in vacuo; yield 0.07 g (0.04 mmol, 40.5%). Anal. Calcd for $C_{82}H_{70}P_4Ru_2S_2SbF_6$: C, 58.58; H, 4.17. Found: C, 58.38; H, 4.31. UV/vis (CH_2Cl_2 solution; λ_{max}, nm (ϵ)): 820 (1270), 350 (2120) sh. X-Band EPR (25 °C, CH_2Cl_2 solution): $g = 2.054$, $A(^{31}P) = 72$ G.

$[CpRu(PMe_3)_2Cl_2][BF_4]$. Solid $AgBF_4$ (0.2 g, 1 mmol) was added to a solution of $CpRu(PMe_3)_2Cl$ (0.30 g, 0.9 mmol) in 20 mL of CH_2Cl_2. A fine black precipitate formed immediately, and the orange solution darkened. After the mixture was stirred several minutes, a yellow-gray precipitate started to form. This solution was stirred for 16 h, and the precipitate was collected, washed with CH_2Cl_2, and extracted with 20 mL of acetone. The product was isolated in 40% yield (0.17 g, 0.36 mmol) as brown crystals from an acetone/CH_2Cl_2 solution. Anal. Calcd for $C_{11}H_{23}P_2RuCl_2BF_4$: C, 27.73; H, 4.83; Cl, 14.91. Found: C, 27.38; H, 4.92; Cl, 14.56. ^1H NMR ($C_6D_5NO_2$; ppm): 5.97 (s, 5 H), 2.05 (t, 6 H). $^{31}P\{^1H\}$ NMR (acetone-d_6; ppm): 24.46. IR (KBr; cm^{-1}): 1050 (broad, ν_{BF}).

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Table III. Positional Parameters for $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2\cdot 2C_6H_5NO_2$

	x/a	y/b	z/c
Sb	0.0134(1)	0.16580(5)	0.22042(5)
Ru	0.62833(9)	0.38967(5)	0.41280(5)
S	0.4591(3)	0.4523(2)	0.4814(2)
P1	0.4896(4)	0.2842(2)	0.4403(2)
P2	0.4786(4)	0.4171(2)	0.3028(2)
F1	-0.086(2)	0.1667(7)	0.3080(7)
F2	-0.138(2)	0.2241(9)	0.183(1)
F3	0.117(2)	0.2483(7)	0.2458(9)
F4	0.109(2)	0.1635(9)	0.1337(7)
F5	0.162(2)	0.108(1)	0.2634(9)
F6	-0.089(2)	0.0847(7)	0.1919(10)
O1	0.360(2)	0.4285(8)	-0.002(1)
O2	0.343(2)	0.493(1)	0.0938(9)
N	0.311(2)	0.4794(9)	0.0285(9)
C1	0.556(2)	0.2451(8)	0.5315(8)
C2	0.279(1)	0.2867(8)	0.4526(8)
C3	0.514(2)	0.2078(7)	0.3735(8)
C4	0.267(1)	0.4141(8)	0.3014(8)
C5	0.508(2)	0.5136(7)	0.2750(8)
C6	0.523(2)	0.3617(9)	0.2184(7)
C7A	0.855(2)	0.392(1)	0.3487(6)
C8A	0.854	0.453	0.3991
C9A	0.854	0.426	0.4756
C10A	0.855	0.348	0.4725
C11A	0.856	0.326	0.3941
C7B	0.845(2)	0.4336(9)	0.3515(7)
C8B	0.853	0.4596	0.4284
C9B	0.863	0.3974	0.4780
C10B	0.861	0.3329	0.4317
C11B	0.850	0.3552	0.3535
C12	0.205(1)	0.5309(7)	-0.0120(8)
C13	0.141(2)	0.5854(8)	0.026(1)
C14	0.040(3)	0.633(1)	-0.014(2)
C15	0.013(3)	0.619(1)	-0.087(2)
C16	0.067(3)	0.564(2)	-0.126(1)
C17	0.174(2)	0.517(1)	-0.0879(9)

X-ray Crystallography. The details of the crystal data, data collection methods, and refinement procedures are presented in Table II. Data collection was performed at ambient temperatures by using an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å).

The opaque, dark blue, prismatic crystal of $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2\cdot 2C_6H_5NO_2$ used for data collection was grown by slowly cooling a saturated solution of $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$ in nitrobenzene. The crystal was immersed in epoxy and mounted in a 0.5-mm thin-walled tapered glass capillary with the (−1,0,0) scattering planes roughly normal to the spindle axis. The data were corrected for Lorentz and polarization effects, anomalous dispersion, and absorption;[33] no correction for extinction was applied.

The structure was solved by Patterson methods;[34] correct positions for the antimony and ruthenium atoms were deduced from a weighted Patterson map. Two consecutive weighted Fourier summations gave positions for the remaining non-hydrogen atoms. Subsequent least-squares/difference Fourier calculations revealed two discrete orientations for the five-membered ring. The geometry of the two disordered cyclopentadienyl rings was "idealized", and a site occupancy factor was refined (0.50 (2)). In the final cycle of least squares, all independent non-hydrogen atoms were refined with anisotropic thermal coefficients, independent isotropic thermal coefficients were refined for the disordered ring carbon atoms, and the group isotropic thermal parameter was varied for the hydrogen atoms. Fractional atomic coordinates are presented in Table III.

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Registry No. **1**$^{2+}$, 110077-71-9; **1**$[SbF_6]_2$, 110077-72-0; **1**$[BF_4]_2$, 110077-73-1; **1r**$^+$, 110077-80-0; **1r**$[SbF_6]$, 110077-81-1; $CpRu(PPh_3)_2Cl$, 32993-05-8; $[(MeCp)Ru(PPh_3)_2]_2(\mu\text{-}S_2)[BF_4]_2$, 110077-75-3; $[CpRu(dppe)]_2(\mu\text{-}S_2)[SbF_6]_2$, 110077-77-5; $(MeCp)Ru(PPh_3)_2Cl$, 55272-36-1; $CpRu(dppe)Cl$, 71397-10-9; $(MeCp)_2TiS_5$, 78614-86-5; $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2$, 110077-79-7; $CpRu(PMe_3)_2Cl$, 74558-74-0; $[CpRu(PMe_3)_2Cl_2][BF_4]$, 110095-12-0; $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2\cdot 2C_6H_5NO_2$, 110077-82-2; $[CpRu(PPh_3)_2(3,4\text{-}SC_4H_6)]^+$, 110077-83-3; $CpRu(PPh_3)_2SH$, 110077-84-4.

Supplementary Material Available: For $[CpRu(PMe_3)_2]_2(\mu\text{-}S_2)[SbF_6]_2\cdot 2C_6H_5NO_2$, listings of thermal parameters, calculated hydrogen atom positions, and bond lengths and angles for the anion and solvate molecule (5 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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