

Synthesis of a Rhenium(V) Polysulfide Complex and a Study of Its Reactivity with Hydrogen

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The reaction of $\text{Cp}'\text{ReCl}_4$ ($\text{Cp}' = \text{EtMe}_4\text{C}_5$) with 2–3 equiv of bis(trimethylsilyl)sulfide in chloroform in the presence of an oxidant results in the formation of $\text{Cp}'\text{Re}(\eta^2\text{-S}_3)\text{Cl}_2$, **2**. Complex **2** has been characterized by spectroscopic methods, and its structure has been confirmed by an X-ray diffraction study. Complex **2** reacts with hydrogen under mild conditions to form H_2S , HCl , and a rhenium product tentatively identified as $(\text{Cp}'\text{Re})_2\text{S}_4$, **3**. Complex **3** reacted with benzyl bromide to form $[(\text{Cp}'\text{Re})_2(\mu\text{-S}_2)(\mu\text{-SCH}_2\text{Ph})_2]\text{Br}_2$, **4**, which has been completely characterized by spectroscopic studies and an X-ray crystal structure. The structures and reactions of the $\text{Cp}'\text{Re}$ derivatives with sulfur ligands are compared to those of the related tetrasulfur-bridged CpMo derivatives.

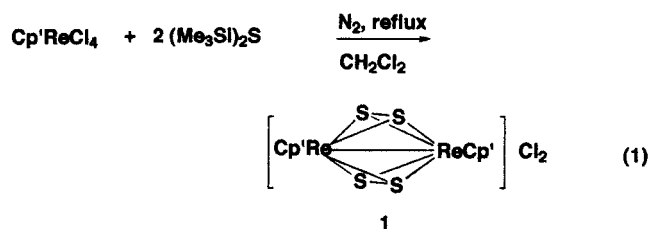
Introduction

Heterogeneous rhenium sulfides are active catalysts for a number of reactions including hydrogenations, dehydrogenations, and hydrotreating processes.^{1,2} Comparisons of hydrodesulfurization activity of the rhenium systems with that of the more economic commercial molybdenum sulfide catalysts have shown that the rhenium surfaces display significantly higher catalytic activity.^{3,4} The lower ΔH_f value for ReS_2 (42.7 ± 3 kcal/mol) compared to MoS_2 (65.8 ± 1 kcal/mol)⁵ and the weaker Re-S bond strength relative to Mo-S have been suggested to be important factors in the higher activity observed for ReS_2 . It has been proposed that weaker Re-S bond strengths allow facile hydrogenolysis of the Re-sulfide moiety to generate more sulfur vacancies, which correlate with higher catalytic activity.⁶ Discrete rhenium sulfide or polysulfide complexes provide the opportunity to better understand and model the reactivity and potential catalytic activity of sulfide-supported metal centers, but few relevant reactivity studies of rhenium sulfide derivatives with hydrogen and/or organic reagents have been carried out.^{7–11}

In previous work we have found that dinuclear cyclopentadienyl molybdenum complexes containing sulfido ligands show exceptional reactivity at the sulfur sites. For example, certain of the complexes react with hydrogen under mild conditions to form products with S-H ligands, and these S-H groups undergo further addition reactions with unsaturated organic substrates to ultimately give reduced products.^{12,13} Recently we have begun a study of related molecular rhenium sulfide derivatives in order to compare reactivity with that of the molybdenum derivatives. The systems also provide potential models for the respective metal sulfide surfaces. In this paper we report the synthesis of a mononuclear rhenium complex containing a polysulfide ligand and a study of its reaction with hydrogen. Observed differences between cyclopentadienylrhenium sulfide and molybdenum sulfide reactivity are discussed.

Results and Discussion

Reactions of $\text{Cp}'\text{ReCl}_4$ with $(\text{Me}_3\text{Si})_2\text{S}$. In previous studies we found that the reaction of $\text{Cp}'\text{ReCl}_4$ with 2 equiv of $(\text{Me}_3\text{Si})_2\text{S}$ under nitrogen at room temperature led to a mixture of products, but after the reaction was refluxed briefly in dichloromethane, **1** was formed in good yield, as shown in eq 1.¹⁰ This synthesis was



repeated several times in our laboratory with yields in the range of 70–80%, but we found that the yield was

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shifts of the methyl singlets are significantly upfield from those observed at 2.44 and 2.43 ppm for the dicationic dimer **1**.¹⁰ The EI mass spectrum of **2** showed a weak pattern at m/z 502 that corresponded to the parent ion and the base fragmentation pattern at m/z 438 that resulted from the loss of two sulfur atoms. In the cyclic voltammogram of **2** a wide window of redox stability was observed; an irreversible reduction wave was present with $E_p = -0.975$ V vs Fc, and an irreversible oxidation occurred with $E_p = 1.032$ V.

Reactivity Studies of 2. Complex **2** is formally a 16-electron complex of Re(V). The rhenium sulfide distances in **2** are similar to those observed for single Re–S bonds in rhenium(V) thiolate derivatives^{11,22,23} and do not indicate significant π donation from a sulfur donor. Nevertheless **2** appears to be quite a stable complex. No further reaction was observed between **2** and 2 equiv of $(\text{Me}_3\text{Si})_2\text{S}$, either at room temperature or in refluxing acetonitrile. Unlike the Cp* analogue, which was reported to be hydrolyzed in moist solvents to form Re-oxo derivatives,¹⁵ no reaction of **2** with 2 equiv of water in CDCl_3 was observed over a period of several days. Although polysulfide ligands often undergo insertion reactions with acetylenes,²⁴ no reactions were observed between **2** and phenyl acetylene or dimethylacetylene dicarboxylate.

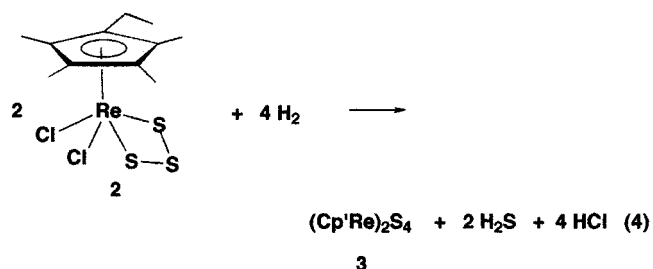
Despite the redox stability of **2**, the complex was found to react with 1–2 atm H_2 under mild conditions. When the reaction was carried out in CDCl_3 in a sealed NMR tube at room temperature, the red color of the solution changed to brown over a period of several days and a single new Cp'Re product was observed with the two Cp'-methyl singlets at 2.28 and 2.26 ppm. A singlet at 0.79 ppm was attributed to the formation of hydrogen sulfide, and the integration of this resonance suggested that approximately 1 equiv of H_2S was formed per Cp'Re unit. An additional broad resonance was observed near 7 ppm, and this was tentatively assigned to free HCl. No intermediate species were detected during the course of this reaction at room temperature.

Hydrogen additions to other metal sulfide complexes have been reported. A titanocene derivative with a terminal sulfido ligand, $\text{Cp}^*_2\text{Ti}(\text{py})(\text{S})$, was found to add hydrogen at room temperature to form $\text{Cp}^*_2\text{Ti}(\text{SH})(\text{H})$.²⁵ The reaction was proposed to occur via pyridine dissociation and formation of a four-centered transition state, and a Ti-dihydrogen adduct was proposed as a likely intermediate. The titanocene disulfide complex $\text{Cp}^*_2\text{Ti}(\eta^2\text{-S}_2)$ reacted with H_2 at 70 °C to form $\text{Cp}^*_2\text{Ti}(\text{SH})_2$, and in this case initial addition of hydrogen across a Ti–S bond was suggested as the likely pathway.²⁵ The reaction of the rhenium-trisulfide complex **2** with hydrogen differs from the above examples in that free hydrogen sulfide is eliminated as a product. The

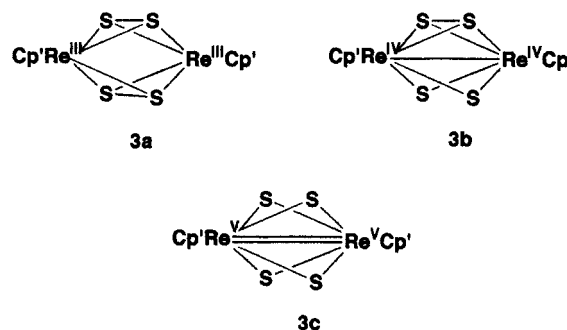
reaction of **2** with H_2 could involve a sequence of steps that includes both hydrogen addition across a Re–S bond and the formation of a dihydrogen adduct, since vacant rhenium coordination sites are generated during the reaction by the eliminations of H_2S and HCl.

Dinuclear cyclopentadienyl molybdenum complexes with sulfide and disulfido ligands have also been found to react with hydrogen under similar mild conditions.¹² In these systems, products with $\mu\text{-SH}$ ligands were formed and evidence for H_2S elimination was generally not observed.²⁶ This difference in reactivity between the molecular CpMo- and Cp'Re-sulfides parallels the differences in reactivity proposed for the heterogeneous molybdenum and rhenium sulfide surfaces.

Synthesis and Characterization of $(\text{Cp}'\text{Re})_2\text{S}_4$, **3, and Derivatives.** To obtain more information about the products of this hydrogen activation process, the reaction of **2** with hydrogen was repeated on a preparative scale at 40 °C using toluene as the solvent. In this case, the solution changed from red to green-brown within hours, and a green product, **3**, was isolated after removal of the solvent and recrystallization from $\text{CH}_2\text{-Cl}_2/\text{hexanes}$. The NMR spectrum of **3** showed a single product with Cp'-methyl singlets at 2.26 and 2.24 ppm. In the EI mass spectrum a strong pattern centered at m/z 798 is observed, and the isotope pattern closely matches that calculated for the formulation $(\text{Cp}'\text{Re})_2\text{S}_4$. The infrared spectrum of **3** does not show a strong absorption in the region 400–550 cm^{-1} that can be assigned to a Re=S stretch,^{11,27} and no NMR or IR spectroscopic evidence for the formation of S–H ligands was observed for the rhenium product. The structure is therefore tentatively assigned as a dimer with four sulfur bridges, eq 4. It is not possible to unambiguously



assign oxidation states to the sulfur ligands and the metal ions on the basis of the spectroscopic characterization, and possibilities that are related by intramolecular electron transfer are shown below. Attempts to obtain single crystals of **3** have been unsuccessful.



The complex is quite air sensitive and also appears to be unstable in solution over a period of time even when

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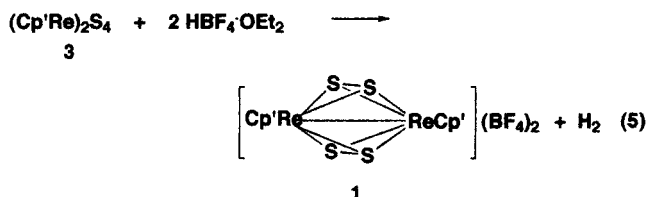
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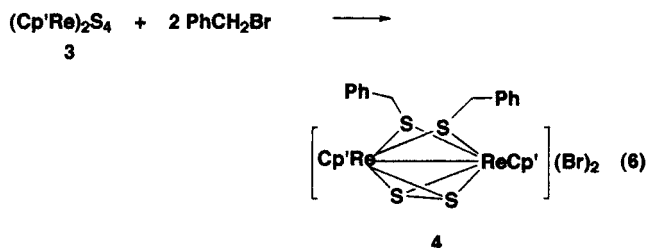
(25) Sweeney, Z. K.; Polse, J. L.; Bergman, R. B.; Andersen, R. A. *Organometallics* **1999**, *18*, 5502.

solutions are maintained under nitrogen. A similar formulation, $[\text{Cp}^*\text{ReS}_2]_2$, has been mentioned briefly in previous work.²⁸

To obtain more information about the structure of **3**, further reactions were carried out in attempts to prepare a derivatized form of this complex. To obtain a product with a protonated or methylated sulfur ligand, the reaction of **3** with tetrafluoroboric acid or with methyl triflate was carried out. Each of these reactions led to the rapid oxidation of **3** and formation of **1**, which was identified by NMR spectroscopy, e.g., eq 5.



When **3** was reacted with benzyl bromide (2 equiv) in dichloromethane, some of the oxidized product **1** was formed (approximately 50%), but we also observed the formation of a new alkylated derivative, **4**, which was isolated by chromatography on a silica gel column and tentatively formulated as $[\text{Cp}'\text{Re}(\text{S})(\text{SCH}_2\text{Ph})]_2\text{Br}_2$, eq 6. The composition of the product was confirmed by the



FAB⁺ mass spectrum, which showed a weak peak at m/z 1060 for the cation with one bromide and several fragmentation patterns consistent with the formula. In the ¹H NMR spectrum of **4**, only one isomer was observed with one singlet for the benzylic hydrogens (relative intensity 4) at 4.2 ppm and the Cp-Me singlets at 2.34 and 2.38 ppm.

Further information on the oxidation states of the metal ions and the μ -sulfur ligands was obtained from an X-ray diffraction study. Single crystals of **4** were obtained from a CH_2Cl_2 /hexanes solution. The product was found to contain a dicationic dinuclear rhenium(IV) derivative with two bridging benzylthiolate ligands in equatorial configurations and a μ - η^2 -disulfido ligand. Two bromide counterions are also observed at nonbonding distances (>4.9 Å) from the metal ions. A perspective drawing of the dication is shown in Figure 2, and selected bond distances and angles are given in Table 2. The Re(1)–Re(2) distance of 2.5887(5) Å is similar to values in other Re(IV) dimers with multiple M–M bond character,^{9,29} but the metal–metal distances in dimers

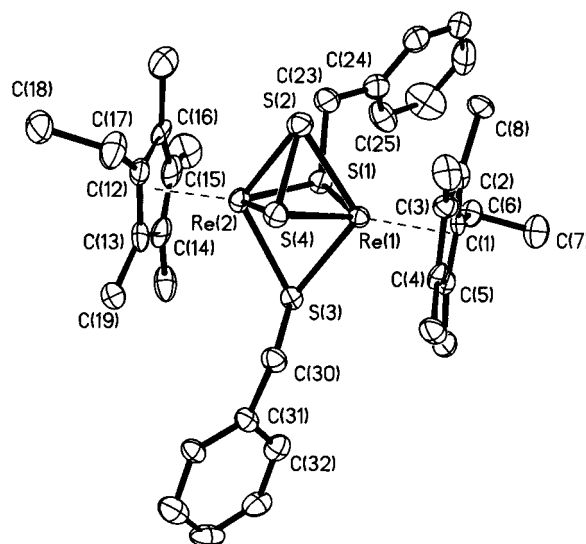


Figure 2. Perspective drawing and numbering scheme for $[(\text{Cp}'\text{Re})_2(\mu\text{-S}_2)(\mu\text{-SCH}_2\text{Ph})_2]\text{Br}_2$, **4**. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances and Angles for $[(\text{EtMe}_4\text{C}_5\text{Re})_2(\mu\text{-S}_2)(\mu\text{-SCH}_2\text{Ph})_2]\text{Br}_2$, **4**

Distances (Å)			
Re(1)–S(1)	2.393 (2)	Re(1)–S(2)	2.401 (2)
Re(1)–S(3)	2.397 (2)	Re(1)–S(4)	2.410 (2)
Re(1)–Re(2)	2.5887 (5)	Re(2)–S(1)	2.379 (2)
Re(2)–S(2)	2.421 (2)	Re(2)–S(3)	2.389 (2)
Re(2)–S(4)	2.396 (2)	S(2)–S(4)	2.074 (3)
S(1)–C(23)	1.829 (10)	S(3)–C(30)	1.839 (9)
Angles (deg)			
S(1)–Re(1)–S(3)	73.58 (8)	S(1)–Re(1)–S(2)	83.75 (8)
S(2)–Re(1)–S(3)	113.27 (8)	S(1)–Re(1)–S(4)	112.77 (8)
S(3)–Re(1)–S(4)	81.89 (8)	S(2)–Re(1)–S(4)	51.07 (8)
Re(1)–S(1)–Re(2)	65.70 (6)	Re(1)–S(2)–Re(2)	64.94 (6)
Re(1)–S(3)–Re(2)	65.48 (6)	Re(1)–S(4)–Re(2)	65.18 (6)
Re(1)–S(1)–C(23)	115.1 (4)	Re(2)–S(1)–C(23)	109.1 (3)

with four bridging sulfur ligands have been found to be quite insensitive to metal oxidation state and are not a good indicator of bond order.³⁰ Only a single Re–Re bond in **4** is necessary to reach an 18-electron count for each metal ion. The average of the four Re distances to the $\mu\text{-S}_2$ ligand is 2.407(2) Å, while the average Re–S(thiolate) distance is slightly shorter at 2.390(2) Å. The S(2)–S(4) distance is 2.074(3) Å. This value is quite typical for a single bond in a disulfide ligand and is significantly shorter than the unusually long S–S distance (2.228(10) Å) reported for the closely related dimer $[(\text{Cp}'\text{Re})_2(\mu\text{-S}_2)]_2(\text{Cl})_2$, **1**.¹⁰ Distances between the bromide counterions and the sulfur atoms of the $\mu\text{-S}_2$ ligand were in the range 3.336–3.604 Å. These distances are close to the sum of the van der Waals radii (3.65 Å) and indicate much weaker interactions between the halide and the disulfide ligand than those observed for **1**.¹⁰

The structural characterization of **4** suggests that the structure of **3** may be that shown above in structure **3b**, where two μ -sulfido ligands are susceptible to electrophilic attack by the alkylating agent. However, definite conclusions regarding the structure and oxidation states

(26) For an exception see: Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

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(29) Lente, G.; Shan, X.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **2000**, *39*, 3572.

(30) See for example: Miller, W. K.; Haltiwanger, R. C.; VanDerveer, M. C.; Rakowski DuBois, M. *Inorg. Chem.* **1983**, *22*, 2973. Kaul, B. B.; Noll, B. C.; Renshaw, S.; Rakowski DuBois, M. *Organometallics* **1997**, *16*, 1604.

Table 3. Crystal Data for (EtMe₄C₅)ReS₃Cl₂, **2, and for [(EtMe₄C₅Re)₂(μ-S₂)(μ-SCH₂Ph)₂]Br₂, **4****

	2	4
formula	2(C ₁₁ H ₁₇ Cl ₂ ReS ₃)	C ₃₆ H ₄₈ Br ₂ Re ₂ S ₄
fw (amu)	1005.05	1141.20
cryst syst	triclinic	monoclinic
unit cell dimens		
<i>a</i> (Å)	6.8496(2)	43.368(5)
<i>b</i> (Å)	16.1733(4)	9.3628(11)
<i>c</i> (Å)	16.3060(4)	20.084(2)
α (deg)	60.71	90
β (deg)	80.2160(10)	110.840(2)
γ (deg)	78.4330(10)	90
volume, Å ³	1538.02(7)	7621.7(15)
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>Z</i>	2	8
density, calcd, g/cm ³	2.170	1.989
λ (Mo K α) (Å)	0.71073	0.71073
temp (K)	154(2)	143(2)
scan type	ω scans	ω scans
θ range (deg)	1.46 to 31.05	1.00 to 27.50
no. of ind reflns	9027	8754
no. of reflns obsd	7618	6255
abs coeff, mm ⁻¹	8.632	8.688
<i>R</i> ^a	0.0487	0.0488
<i>R</i> _w ^b	0.1303	0.0992
GOF	1.036	1.013
largest peak in final diff map (e/Å ³)	3.962 and -3.379	2.138 and -2.147

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad ^b wR2 = \frac{\{\sum [w(F_o^2 - F_c^2)]^2\}}{\{\sum [wF_o^2]^2\}}^{1/2}.$$

of **3** cannot be made on this basis because facile intramolecular electron transfers have been well characterized for various rhenium sulfide/disulfide derivatives.^{7,31}

Summary and Conclusions. The reaction of Cp'–ReCl₄ with (Me₃Si)₂S in air results in the unexpected, but clean formation of a complex with a η^2 -S₃ ligand, Cp'ReS₃Cl₂, **2**. Although **2** is stable to air and moisture, it reacts with hydrogen under mild conditions to generate H₂S and a product formulated as (Cp'Re)₂S₄, **3**. Further reaction of **3** with benzyl bromide generates the complex [(Cp'Re)₂(μ-S₂)(μ-SCH₂Ph)₂]Br₂, **4**. To our knowledge the reaction of **2** with hydrogen is the first example of the hydrogen-induced elimination of hydrogen sulfide from a mononuclear metal polysulfide complex. While dinuclear Cp-molybdenum sulfide complexes were found to react quite generally with hydrogen to form S–H ligands, examples of both dinuclear¹⁰ and now mononuclear Cp-rhenium sulfide complexes have been found to generate a vacant coordination site much more readily by H₂S elimination. This trend reflects the relative metal–sulfur bond strengths proposed for the heterogeneous molybdenum and rhenium sulfides. The new entry into Cp'₂Re₂S₄ derivatives reported here should permit us to make further comparisons with the chemistry of the reactive Cp₂Mo₂S₄ complexes.

Experimental Section

General Procedures and Materials. Except where noted, syntheses were carried out under nitrogen using Schlenk line and vacuum line techniques and a Vacuum Atmospheres glovebox. Dichloromethane and acetonitrile were distilled from CaH₂ prior to use. Tetrahydrofuran, toluene, and diethyl ether were distilled from sodium/benzophenone. ¹H and ¹³C NMR spectra were recorded on Varian VXR-300 or Varian Inova 500

MHz instruments. All chemical shifts are reported in ppm relative to tetramethylsilane. Mass spectra were obtained on a Hewlett-Packard 5989A electrospray ionization LC mass spectrometer, on a VG Autospec with EI/CI sources and liquid secondary ion MS capabilities, or on a Finnigan MATR LCQ ion trap mass spectrometer. Infrared spectra were obtained on KBr pellets using a Perkin-Elmer Model 1600 FTIR spectrometer. Cyclic voltammetry experiments were carried out under nitrogen on acetonitrile solutions containing 0.3 M Bu₄NBF₄ with a Cypress Systems electrolysis system. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ. Ethyltetramethylcyclopentadiene was purchased from Aldrich, and bis(trimethylsilyl)sulfide was purchased from Strem, Aldrich, or Fluka and used without purification. Cp'ReCl₄ was synthesized from Re₂(CO)₁₀ (Strem) by a published procedure.¹⁴

Synthesis of Cp'Re (η^2 -S₃) Cl₂, **2.** Cp'ReCl₄ (0.34 g, 0.70 mmol) was dissolved in chloroform in air, and (Me₃Si)₂S (0.44 mL, 2.10 mmol) was added. The solution was stirred in air for 2–3 days, until the color had changed to deep red. The solvent was evaporated, and the remaining solid was extracted with toluene and filtered. The filtrate was dried to give the desired product, which could be recrystallized from toluene/hexanes. Yield: ca. 60%. Additional product could be isolated by extraction of crude solid with THF and workup as described above. ¹H NMR (CDCl₃): 2.04, 1.92 (2 s, each 6 H, CpMe); 2.10 (q, 2 H, CpCH₂); 1.14 (t, 3 H, CpCH₂CH₃). ¹³C NMR (CDCl₃): 11.26, 11.85 (CpMe); 14.40 (CH₂CH₃); 19.97 (CpCH₂); 103.84, 105.47, 110.53 (Cp). IR (KBr): 417, 512 (med, ν_{S-S}). Mass spectrum (EI): *m/z* 502 (weak, P⁺); 438 (Base, P-2S); 402 (P-2S-Cl). Visible spectrum (CDCl₃): 512 nm (ϵ 3700 M⁻¹ cm⁻¹); 450 nm (sh). CV (CH₃CN, V vs Fc): -0.975 (irr); 1.032 (irr.). Anal. Calcd for C₁₁H₁₇Cl₂S₃Re: C, 26.26; H, 3.41; S, 19.14. Found: C, 26.40; H, 3.43; S, 19.43.

X-ray Diffraction Study of Cp'Re (η^2 -S₃) Cl₂, **2.** Red crystals were grown from diffusion of hexanes into a concentrated chloroform solution. Several crystals were examined under Exxon Paratone oil, and the specimen crystal was cut successively from a larger cluster. After mounting and optical alignment of the crystal on the Siemens SMART CCD diffractometer, a set of three series of 20 0.3° ω scans was collected and used for preliminary cell determination. An arbitrary sphere of data was collected to 0.69 Å resolution using 30 s 0.3° ω scans. Final cell dimensions were determined from 7928 reflections chosen with *I* > 10 σ (*I*).

The structure was solved by direct methods in centrosymmetric space group *P*1. There are two crystallographically independent molecules in the asymmetric unit. Hydrogens were placed at calculated geometries and allowed to ride on the position of the parent atom. All non-hydrogen atoms were refined with anisotropic parameters for thermal motion. Isotropic hydrogen thermal parameters for methyl hydrogens were set to 1.5 times the equivalent isotropic *U* value of the parent atom. Methylene hydrogens were 1.2 times the value for the parent atom. Residual electron density peaks were located near the rhenium atoms and were likely artifacts of absorption. See Table 3 for details of the structural studies.

Reaction of **2 with Hydrogen. NMR Scale Reaction.** Complex **2** (0.015 g, 0.03 mmol) was dissolved in CDCl₃ in an NMR tube, and the solution was degassed in two freeze–pump–thaw cycles on a vacuum line. Hydrogen (42 cm) was added at -196 °C, and the tube was flame sealed. The solution was warmed to room temperature, and the reaction was monitored by ¹H NMR spectroscopy over a period of several days. The resonances for **1** slowly decreased in intensity, and new resonances were observed for a single new product. A color change from red to brown was observed. ¹H NMR: 2.29, 2.28 (2 s, CpMe); 2.24 (q, CpCH₂); 1.16 (t, CpCH₂CH₃). In the sealed tube, a sharp singlet was also observed at 0.79 ppm (relative

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intensity, ca. 2 H, H₂S), and a broad resonance at 7.12 was assigned to HCl exchanging with water in the solvent.

Synthesis of (Cp'Re)₂(μ-S)₄, 3. CpReS₃Cl₂, **2** (0.050 g, 0.10 mmol), was dissolved in ca. 20 mL of toluene, and the solution was freeze–pump–thaw degassed two times. Excess hydrogen (40 cm) was added at –196 °C, the reaction tube was sealed with a Teflon vacuum stopcock, and the solution was heated at 45 °C overnight with stirring. The color changed to green-brown. The solvent was evaporated, and the remaining solid was recrystallized under nitrogen from toluene/hexane. The hexane-soluble fraction was evaporated to give pure **3**. Yield: ca. 50%. ¹H NMR (CDCl₃): 2.24, 2.26 (2 s, 12 H each); 2.32 (q, 4 H); 1.13 (t, 6 H). Mass spectrum (*m/z*): 800 (Cp'₂(¹⁸⁷Re)₂S₄); 768 (P – S); 736 (P – 2 S). UV vis (CH₃CN, nm (ε, M^{–1} cm^{–1})): 730 (616); 474 (530). Elemental analyses were obtained under nitrogen on independently prepared samples with identical NMR spectra, but reproducible values were not obtained.

Synthesis of [(Cp'Re)₂(μ-S₂)(μ-SCH₂Ph)₂]Br₂, 4. [Cp'-ReS₂]₂, **3** (0.050 g, 0.063 mmol), was dissolved in CH₂Cl₂, and benzyl bromide (15 μL, 0.13 mmol) was added. The solution was stirred overnight, and the resulting red or red brown solution was evaporated. The ¹H NMR spectrum of the crude product was somewhat broadened, but resonances for **1** were observed as well as those of another product in ca. 1:1 ratio. The mixture was eluted on a silica gel column with CH₃CN/MeOH. Complex **1** decomposed on the column to give several fractions, but **4** was eluted in a red band. This was evaporated to give the product in pure form. Yield: ca. 20%. ¹H NMR (CDCl₃): 2.34, 2.38 (2 s, CpMe); 1.10 (t, 6 H, CpCH₂CH₃); 2.35 (q, 4 H, CpCH₂); 4.19 (s, 4 H, SCH₂); 7.30, 7.60 (2 m, 10 H, Ph). ¹³C NMR (CDCl₃): 12.70, 12.95, (CpMe); 15.26 (CpCH₂CH₃); 21.15 (CpCH₂); 48.25 (SCH₂); 105.37, 107.58, 109.70 (Cp); 128.25, 128.58, 129.68, 137.18 (Ph). FAB mass spectrum, *m/z*: 1060 (very weak, P – Br); 982 (P – 2 Br); 889 (Cp'₂Re₂S₄-CH₂Ph); 798 ((Cp'₂Re₂S₄). Analysis of NMR sample isolated from CDCl₃, calcd for **4** + 1/2 CDCl₃: C_{36.5}H_{48.5}Re₂S₄Br₂Cl_{1.5}: C, 36.50; H, 4.07; S, 10.68. Found: C, 36.46; H, 4.18; S, 10.05.

X-ray Diffraction Study of 4. Crystals of **4** were obtained from a toluene/hexanes solution and manipulated under a light hydrocarbon oil. The datum crystal was affixed with a small amount of silicone stopcock grease to a thin glass fiber attached

to a tapered copper mounting-pin. This assembly was transferred to the goniometer of a Bruker SMART CCD diffractometer equipped with an LT-2a low-temperature apparatus operating at 143 K.

Cell parameters were determined using reflections harvested from a series of three orthogonal sets of 20 0.3 ω scans. Final cell parameters were refined using 8274 reflections with *I* > 10σ(*I*) chosen from the entire data set. All data were corrected for Lorentz and polarization effects, as well as for absorption. The anisotropy of the crystal created some absorption artifacts in the final structure.

Structure solution in centrosymmetric space group *C2/c* revealed the heavy atom positions. Carbon positions were located after four cycles of least-squares refinement followed with difference Fourier synthesis. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. All non-hydrogen atoms were refined with anisotropic parameters for thermal motion. Thermal parameters for hydrogen atoms were set to 1.2 times the equivalent isotropic *U* of the parent. Each bromine atom is present at multiple sites. Atom Br(1) is disordered across two sites, with site occupancies of 0.852(3) and 0.147(3). Atom Br(2) is disordered across three sites, the principle site, occupancy 0.889(4), and two minor sites, which are related by crystallographic symmetry. Site occupancy at each of these equivalent sites is 0.056(2). No other disorder is present. All peaks in the final difference map are reasonably close to heavy atom sites and are likely absorption artifacts.

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Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **2** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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