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Syntheses of a Cp′Re═S Derivative and More Complex Products

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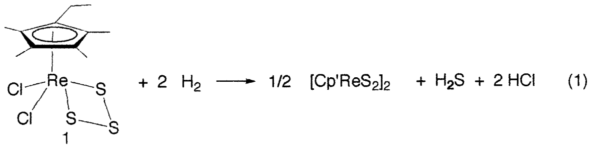
The reaction of Cp′$ReCl_2S_3$ (Cp′ = Me_4EtC_5) with slightly less than 2 equiv of a phosphine reagent results in the formation of [Cp′Re$(Cl)_2(\mu$-S)]$_2$, **2**, which has been characterized by an X-ray diffraction study. Reactions of **2** with nucleophiles did not lead to monomeric derivatives of the type Cp′ReS$(Cl)_2$(Nuc). The reaction of Cp′$ReCl_2(SC_2H_4S)$ with $(Me_3Si)_2S$ resulted in the formation of three new products: Cp′ReS(SC_2H_4S), **4**; Cp′Re$(S_3)(SC_2H_4S)$, **5**; and a tetranuclear derivative, [(Cp′Re)$_2(\mu$-S)$(\mu,\eta^2$-$SC_2H_4S)(\mu,\eta^1$-$SC_2H_4S]_2Cl_2$, **6**. Complexes **4** and **6** have been characterized by X-ray diffraction studies. The electrochemical properties of the mononuclear Re═S derivative, **4**, are compared with those of Re═O and Re═NR analogues.

Introduction

Many examples of metal complexes with di- or polysulfide ligands are known,[1,2] and their reactions with nucleophiles, such as phosphines, often provide a route to new metal sulfido derivatives through the elimination of one or more equivalents of phosphine sulfide.[1,3−7] The formation of complexes with terminal sulfido ligands is of particular interest because of the potential for comparisons in reactivity and electronic structures with a range of multiply bonded terminal ligands from groups 14 through 16.[8,9] We have recently reported the synthesis of a mononuclear trisulfide complex of Re(V), Cp′Re$(\eta^2$-$S_3)Cl_2$, **1**, and have studied its reaction with hydrogen which proceeds to remove one sulfur atom from the trisulfide ligand, as well as the chloride ligands, as shown in eq 1.[10]



In this paper we report a survey of reactions designed to produce Cp′Re derivatives with terminal sufido ligands. These include the characterization of the sulfur abstraction reactions of **1** with triphenylphosphine. In addition, **1** and other Cp′Re−dichloro derivatives have the potential to form terminal sulfido complexes by chloride ligand exchange reactions with sulfido reagents, and studies of these reactions are also reported here. Although several examples of Re═S derivatives are known,[11−17] to our knowledge, terminal sulfido ligands have not been characterized for cyclopentadienyl rhenium complexes. Previous studies of reactions of Cp*Re derivatives (where Cp* = C_5Me_5) with various sulfur reagents have led to the characterization of a number of Cp*Re−polysulfide complexes.[18] The absence of Cp*Re═S derivatives is notable in view of the extensive development of Cp*Re complexes with terminal oxo and imido

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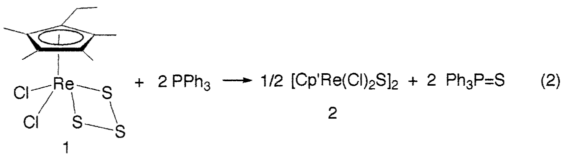
ligands.[19,20] Rhenium complexes with the Cp′ ligand have been reported to be more soluble in organic solvents than the Cp* analogues,[19b] and we have therefore used the Cp′ ligand in our synthetic studies.

Results and Discussion

Reactions of Cp′ReCl$_2$(S$_3$), 1, with PPh$_3$. The reaction of **1** with 1 equiv of triphenylphosphine was initially studied in an attempt to prepare the product with an η^2-disulfide ligand Cp′ReCl$_2$(S$_2$). However, when this reaction was monitored by NMR spectroscopy, it was apparent that only half of the rhenium starting material was consumed and that phosphine abstraction of two sulfur atoms from the trisulfide ligand was rapid. On the other hand, when more than 2 equiv of phosphine reagent were used, the reaction proceeded rapidly to form the previously reported sulfur-free complex, [Cp′ReCl$_2$]$_2$,[21] which was identified by NMR and mass spectral data. We found that optimum conditions for formation of a sulfur-containing product involved the reaction of **1** with 1.8 equiv of PPh$_3$, which proceeded to form [Cp′ReCl$_2$S]$_2$, **2**, isolated after recrystallization in ca. 30% yield as a green air-sensitive powder, eq 2. When reaction 2 was carried out at room temperature, the NMR spectrum showed the disappearance of **1** and a mixture of species that were not identified, but when reactions were heated overnight at 55−60 °C, quite clean formation of **2** was observed.



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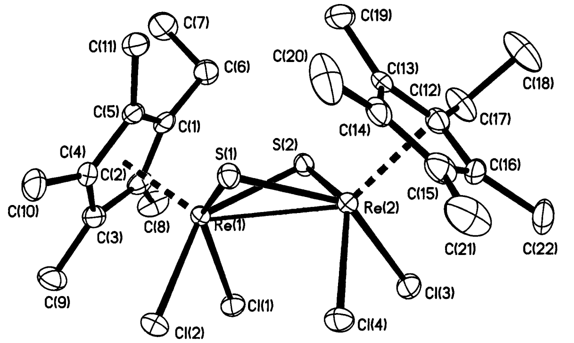


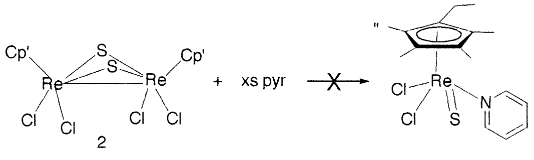
Figure 1. Perspective drawing and numbering scheme for [Cp′ReCl$_2$(μ-S)]$_2$, **2**. Thermal ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [(EtMe$_4$C$_5$)ReCl$_2$(μ-S)]$_2$·2CHCl$_3$, **2**

Re(1)−S(1)	2.2686(12)	Re(1)−S(2)	2.2815(12)
Re(2)−S(1)	2.2835(12)	Re(2)−S(2)	2.2706(12)
Re(1)−Cl(1)	2.4196(11)	Re(1)−Cl(2)	2.4389(11)
Re(2)−Cl(3)	2.4374(12)	Re(2)−Cl(4)	2.4195(12)
Re(1)−Re(2)	3.0606(3)	S(1)···S(2)	3.033
Re(1)−S(1)−Re(2)	84.50(4)	Re(1)−S(2)−Re(2)	84.50(4)
S(1)−Re(1)−S(2)	83.60(4)	S(1)−Re(2)−S(2)	83.51(4)
Cl(1)−Re(1)−Cl(2)	77.94(4)	Cl3(1)−Re(2)−Cl(4)	79.33(4)

Complex **2** has been synthesized previously in our laboratory by an alternate route, and spectroscopic data have been reported.[22] However, structural details were unknown. Single crystals of **2** were obtained by slow diffusion of ether into a chloroform solution, and an X-ray diffraction study was carried out. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are given in Table 1. The dinuclear structure contains two μ-sulfur ligands with two terminal *cis*-chloride ligands coordinated to each rhenium center. The S···S distance in **2** of 3.033 Å is significantly longer than a typical S−S single bond distance expected for a η^2-disulfide ligand (2.02−2.08 Å), and therefore **2** is best described as a Re(V) dimer with two μ-sulfido ligands. The oxo analogue of **2** has been synthesized,[19] and X-ray data for related syn structures have been reported previously, e.g., for Cp*ReO(μ-O)$_2$Re(Cl)$_2$Cp*,[19] **3a**, and for the Re(IV) derivative [Cp′Re(μ-Cl)Cl$_2$]$_2$, **3b**.[21] The Re−Re distance of 3.0606(3) Å in **2** is similar to that observed for the chloride bridged dimer, **3b** (3.074 Å), and significantly longer than that in **3a** (2.691 Å). The Re−S distances in **2** are all similar with an average value of 2.2770(4) Å; they are somewhat shorter than the Re−(μ-Cl) distances in **3b**, while **3a** shows inequivalent Re(1)−(μ-O) and Re(2)−(μ-O) distances. The Re−S−Re angles in **2** average 84.50(4)°, and the dihedral angle between the Re1−S1−S2 and Re(2)−S(1)−S(2) planes is 51.3°. The anti isomers of **2**, **3a**, or **3b** have not been observed to our knowledge. In related compounds of the type [LRe(O)(μ-S)]$_2$, the syn orientation of terminal ligands has been found to be thermodynamically more stable.[23]

In some previously studied systems, the addition of a donor ligand to early-metal μ-sulfido complexes has been found to favor the formation of mononuclear derivatives with terminal sulfido ligands.[4,8,24] However, evidence for the dissociation of **2** in this way was not observed. For example the addition of 2 equiv of pyridine to a solution of **2** did not produce new products containing a pyridine ligand, eq 3.



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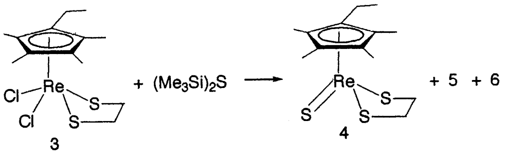
Although the structure of **2** appears to be well-suited for chloride metathesis by chelating ligands, the reaction of **2** with ethanedithiol or the deprotonated form of the dithiol did not form the expected product, $[Cp'Re(SC_2H_4S)S]_n$, where $n = 1$ or 2. In the ^1H NMR spectra of the products from these attempts, resonances for the Cp-methyl groups were observed near 2.2 ppm, but the dithiolate resonances were not consistent with the expected product (see Experimental Section). On the basis of later work, we concluded that the product is identical, or very similar, to one characterized below (**6**) in which redox chemistry between sulfur ligands and rhenium ions has occurred.

Reactions of $Cp'ReCl_2(SC_2H_4S)$ with Sulfide Reagents. To explore the formation of Re−sulfido derivatives with other coligands, we have investigated the chloride substitution reactions of $Cp'ReCl_2(SC_2H_4S)$.[25] The reaction of this complex with bis(trimethylsilyl)sulfide in various ratios (see below) resulted in the formation of three new products, **4**−**6**. These were separated by column chromatography and characterized. Extraction of the product mixture with toluene and elution on silica gel with the same solvent yielded a brown fraction which was isolated in about 30% yield by solvent evaporation and recrystallization. The spectroscopic data suggested that the complex was a monomeric species of the formulation $Cp'Re(S)(SC_2H_4S)$, **4**, eq 4. The ^1H NMR spectrum showed singlets for the Cp′Me groups at 2.00 and 2.05 ppm (6 H each), and multiplets for the dithiolate protons at 2.75 and 2.66 ppm (2 H each). The mass spectrum of **4** showed a parent ion at the expected mass of 460, and in the IR spectrum a strong absorption was observed at 486 cm^{-1}, assigned to a Re═S stretch. Single crystals of **4** were formed by cooling a concentrated pentane/ether solution, and the proposed formulation was confirmed by an X-ray diffraction study on an isolated crystal.



(4)

The structural study confirms that **4** is a mononuclear piano-stool derivative of Re(V) with a chelating dithiolate and a terminal sulfido ligand. A perspective drawing of **4** is shown in Figure 2, and selected bond distances and angles are given in Table 2. The Re−S(1) distance of 2.14 Å is longer than those observed previously for complexes with a single Re═S bond, which are generally in the range of 2.05−2.11 Å.[8] For the structures of ReS_4^- and derivatives with two adjacent Re═S bonds, distances of 2.12−2.13 Å have been reported.[12a,15] The Re−S(2) and Re−S(3) distances for the dithiolate ligand are similar with an average value of 2.270(2) Å. This contrasts with the structure of $Cp'ReCl_2(SC_2H_4S)$ in which the two Re−S distances have significantly different values of 2.25 and 2.30 Å.[25] The structural data suggest that the terminal sulfido ligand in **4** is a weaker π donor than in other examples of Re═S derivatives, perhaps because the thiolate sulfur atoms also contribute some π electron density to the rhenium ion.

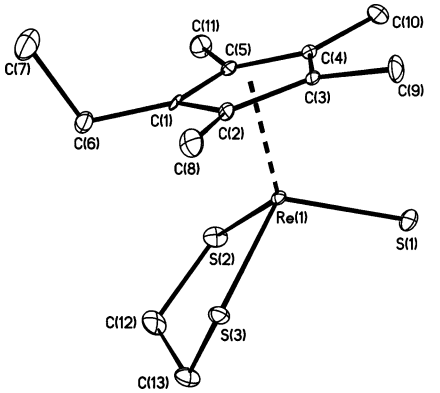


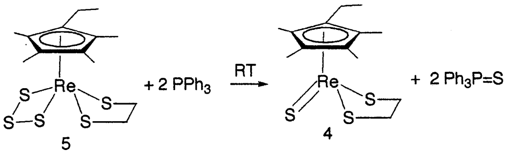
Figure 2. Perspective drawing and numbering scheme for $Cp'ReS(SC_2H_4S)$, **4**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $(EtMe_4C_5)ReS(\eta^2\text{-}SCH_2CH_2S)$, **4**

Re(1)−S(1)	2.1426(13)	Re(1)−S(2)	2.2785(12)
Re(1)−S(3)	2.2625(12)	S(3)−C(13)	1.838(6)
S(2)−C(12)	1.843(6)	Re(1)−C(1)	2.295(5)
Re(1)−C(2)	2.289(5)	Re(1)−C(3)	2.357(4)
Re(1)−C(4)	2.390(5)	Re(1)−C(5)	2.329(5)

S(1)−Re(1)−S(2)	109.88(5)	S(1)−Re(1)−S(3)	107.35(5)
S(2)−Re−S(3)	85.64(5)	Re(1)−S(2)−C(12)	108.21(19)
Re(1)−S(3)−C(13)	107.72(19)	S(2)−C(12)−C(13)	111.0(4)
S(3)−C(13)−C(12)	109.4(4)		

A second neutral product from the reaction of $Cp'ReCl_2(SC_2H_4S)$ with $(Me_3Si)_2S$ was also eluted with toluene on a silica gel column as a deep green band. Removal of the solvent gave a complex formulated as $Cp'Re(SC_2H_4S)(\eta^2\text{-}S_3)$, **5**, in about 15% yield. ^1H NMR data for **5**, reported in the Experimental Section, are similar to that for **4**, but chemical shifts for **4** and **5** are easily distinguished. The EI mass spectrum for **5** shows a weak pattern for the expected parent ion at $m/z = 524$, and comparison of observed and calculated isotope patterns shows excellent agreement. Elemental analyses also support the formulation. The reaction of **5** with 2 equiv of PPh_3 results in a rapid reaction to form **4** and Ph_3P═S, identified by ^1H and ^{31}P NMR spectroscopy, respectively, eq 5. Addition of excess triphenylphosphine to this reaction did not cause any further change at room temperature, indicating that the terminal sulfido ligand in **4** is not readily removed by phosphine treatment. It is not clear how the S_3 ligand of **5** is formed, but the reaction of $(Me_3Si)_2S$ with a Re−chloro derivative to form a trisulfido ligand has been observed previously in the synthesis of **1**.[10]



(5)

In the reactions of $Cp'ReCl_2(SC_2H_4S)$ with $(Me_3Si)_2S$, in addition to **4** and **5**, a third complex, **6**, was formed as the

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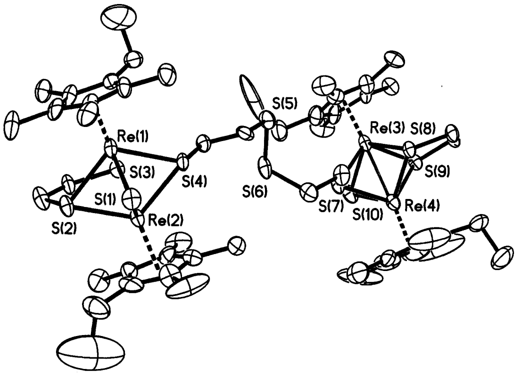

Figure 3. Perspective drawing and numbering scheme for the dication of **6**, $[(Cp'Re)_2(\mu\text{-}S)(\mu,\eta^2\text{-}SC_2H_4S)(\mu,\eta^1\text{-}SC_2H_4S)]_2^{2+}$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $\{[(EtMe_4C_5)Re]_2(\mu\text{-}S)(\mu,\eta^2\text{-}SCH_2CH_2S)(\mu,\eta^1\text{-}SC_2H_4S)\}_2(Cl)_2\cdot(CHCl_3)_2\cdot(Et_2O)_3$, **6**

Re(1)−S(1)	2.420(3)	Re(1)−S(2)	2.382(3)
Re(1)−S(3)	2.401(2)	Re(1)−S(4)	2.407(2)
Re(2)−S(1)	2.421(2)	Re(2)−S(2)	2.386(3)
Re(2)−S(3)	2.400(3)	Re(2)−S(4)	2.406(2)
Re(1)−Re(2)	2.5570(6)	S(5)−S(6)	2.029(4)
Re(1)−S(1)−Re(2)	63.76(6)	Re(1)−S(2)−Re(2)	64.88(6)
Re(1)−S(3)−Re(2)	64.36(6)	Re(1)−S(4)−Re(2)	64.19(6)
S(1)−Re(1)−S(2)	71.45(9)	S(2)−Re(1)−S(3)	75.48(8)
S(1)−Re(1)−S(4)	71.00(9)	S(3)−Re(1)−S(4)	76.26(8)

major product. This brown fraction was insoluble in toluene and was only eluted from a small silica gel column with methanol, suggesting an ionic formulation for the product. In the ^{1}H NMR spectrum of the crude product, the resonance of the Cp−Me groups occurred near 2.2 ppm. This chemical shift is similar to those observed for other dinuclear Cp′Re′ derivatives. The resonances for the dithiolate protons were not completely identified because of overlap with other products. After **6** was eluted from a silica gel column, a sharp NMR spectrum was observed that appeared to indicate a single product. Two singlets at 2.16 and 2.15 ppm (6 H each) were assigned to the Cp−Me groups, while four multiplets were observed for the dithiolate protons at 2.86, 2.21, 1.90, and 1.69 ppm (1 H each). In the ^{13}C NMR spectrum of **6**, in addition to the expected resonances for the Cp′ ligands, four resonances were observed in the region of 32−44 ppm for inequivalent dithiolate carbons. The electrospray mass spectrum of the complex provided evidence for a high-mass formulation with a pattern at $m/z = 1810$. We were unable to assign a structure on the basis of these spectroscopic data.

Single crystals of **6** were obtained from slow diffusion of hexanes into a chloroform solution. The complex crystallized in the centrosymmetric space group $P2_1/c$ with four molecules per unit cell. Several solvent molecules were also identified in the unit cell, but these were not within close contacts with the rhenium derivative. The X-ray diffraction study indicated that **6** was a tetranuclear derivative of the formula $[(Cp'Re)_2(\mu\text{-}S)(\mu,\eta^2\text{-}SC_2H_4S)(\mu,\eta^1\text{-}SC_2H_4S]_2Cl_2$. The product is consistent with the observed envelope in the mass spectrum at 1810, which corresponds to the parent dication plus one chloride. A perspective drawing of the dication is shown in Figure 3, and selected bond distances and angles are given in Table 3. Each dimer in the dication consists of two $Cp'Re^{IV}$ units bridged by four sulfur donors, including a sulfido ligand, an η^2-dithiolate, and an η^1-dithiolate, as indicated in the above formula. The two dimers are linked by a disulfide ligand resulting from the oxidation of two μ,η^1-ethanedithiolate ligands. The disulfide bond length, S(5)−S(6) is 2.030 (4) Å. The structural features within the dimers are very similar to each other. For example, the Re−Re distances are 2.5560(6) and 2.5578(6) Å, the Re−S distances range from 2.38 to 2.43 Å, and the Re−S−Re angles have values from 63.8 to 64.9°. These values are close to those reported for other, previously characterized dinuclear Re(IV) derivatives with four bridging sulfurs, such as $[(Cp'Re)_2(\mu\text{-}S_2)_2]Cl_2$[22] and for $[(Cp'Re)_2(\mu\text{-}S_2)(\mu\text{-}SCH_2Ph)_2]Br_2$.[10]

The formation of **6** from the starting reagents involves a net two electron reduction because, although two thiolates undergo a two electron oxidation to form the disulfide linkage, all four rhenium atoms are reduced from Re(V) to Re(IV). The complication of rhenium sulfide chemistry by both intramolecular and intermolecular redox chemistry is well-documented.[26] When the reaction in CD_3CN was followed by NMR spectroscopy, the three major products appeared to be formed quickly; an immediate color change to brown was observed, and the NMR spectrum within 45 min showed the final products. No further change in product ratios was observed over 48 h. We have varied reaction conditions in attempts to maximize the formation of the mononuclear products **4** and **5**. For example, the amount of sulfide reagent was increased, or the reaction was carried out at high dilution, or the rhenium reagent was added to $(Me_3Si)_2S$ instead of vice versa, or the temperature was changed. In all cases a similar mixture of the three products was obtained, with **6** as the major product.

A survey of the reactions of $Cp'ReCl_2(SC_2H_4S)$ with alternate sulfide donors was also carried out. The stoichiometry of reactions of Na_2S in acetonitrile is difficult to control because of the low solubility of this reagent. The addition of 15-crown-5 to Na_2S in acetonitrile has been shown to improve product yields and purity in reactions with metal complexes.[27] The reaction of 1 equiv of Na_2S/15-crown-5 with $Cp'ReCl_2(SC_2H_4S)$ in acetonitrile at 60 °C proceeded to form primarily **6**, identified by NMR and mass spectroscopy, but smaller amounts of **4** and **5** were also detected. The reaction of $Cp'ReCl_2(SC_2H_4S)$ with NaSH/15-crown-5 yielded **4** in roughly 50% yield with a mixture of other unidentified products. The reaction presumably proceeds through the formation of $Cp'Re(SH)_2(SC_2H_4S)$ and subsequent elimination of H_2S, but evidence for the proposed intermediate rhenium derivative was not observed in the crude product mixture. Potential chloride exchange reactions of **1** were also studied. The reaction of **1** with $(Me_3Si)_2S$ and with ethanedithiol, both in the presence and absence of

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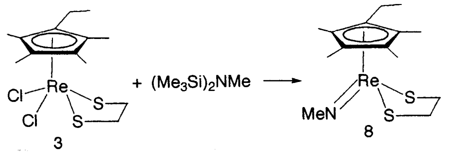
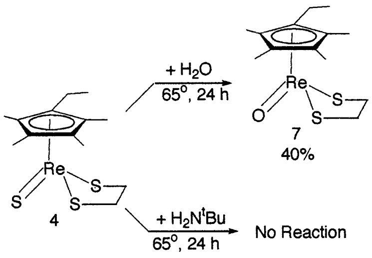
triethylamine, were explored, but the simple metathesis products, such as Cp′Re(S)(S_3) or **5** respectively, were not observed in these reactions.

Comparisons of Re=S, Re=O, and Re=NR Derivatives. Although attempted metathesis reactions of Cp′Re−chloro derivatives with sulfido reagents have proven to be complex, we are able to isolate the terminal sulfido complex **4** as a clean product for further studies. In this paper we include comparisons of relative reactivities and the electrochemical behavior of **4** with the previously prepared oxo analogue, Cp′Re(O)(SC_2H_4S),[25] **7**, and with an imido analogue, Cp′Re(NMe)(SC_2H_4S), **8**. Complex **8** has been synthesized in 80−90% yield by the reaction of Cp′ReCl_2(SC_2H_4S) with $(Me_3Si)_2NMe$, eq 6. Spectroscopic and analytical data, reported in the Experimental Section, are consistent with the proposed formulation. The Cp* analogue of **8** has been reported previously.[28]

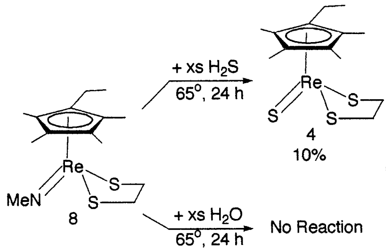


(6)

Cp′Re(S)(SC_2H_4S) is an air-stable compound, and it reacts only slowly with water. For example, when **4** was reacted with 5−6 equiv of water in toluene-d_8 at 60 °C for 24 h, ca. 45% of **4** was unreacted, 40% of the material was converted to the oxo derivative, **7,** and about 15% of **5** was formed. Conversion of **4** to an imido derivative under similar thermal conditions was unsuccessful. For example, no reaction of **4** with 2 equiv of $^tBuNH_2$ was observed when the mixture was heated in toluene-d_8 at 65° for 24 h, eq 7. However, when H_2S was bubbled into a toluene-d_8 solution of Cp′Re(NMe)(SC_2H_4S) and the solution was heated for 24 h, 5−10% of the complex was converted to **4**, eq 8.



(7)



(8)

The cyclic voltammograms of the oxo and sulfido derivatives **7** and **4**, respectively, are shown in Figure 4. Both the oxo and sulfido complexes show a reversible reduction wave and an irreversible oxidation. The sulfido complex is both easier to reduce ($E_{1/2} = -1.65$ V vs Fc) and easier to oxidize ($E_{pa} = +0.31$ V) compared to the oxo derivative (−2.14 and +0.68 V, respectively). Less negative reduction potentials have been observed for other sulfido complexes compared to their oxo analogues, and this trend is related to the poorer back-bonding ability of sulfido vs oxo ligands.[12c,13] The CV of **5** (not shown) includes a reversible reduction and an irreversible oxidation with potentials that are almost identical to those of **4**. An additional irreversible wave is observed for **5** at −1.35 V. Since this wave is not present in **4**, it is associated with the reduction of the η^2-S_3 ligand. The electron rich character of the Re(V) ion in Cp′Re(NMe)(SC_2H_4S) is reflected in the cyclic voltammogram which shows a reversible oxidation wave at +0.203 V vs Fc. No reduction waves were observed in the range of −2.2 V vs Fc. Further studies of the oxidized and reduced derivatives of these complexes are planned.

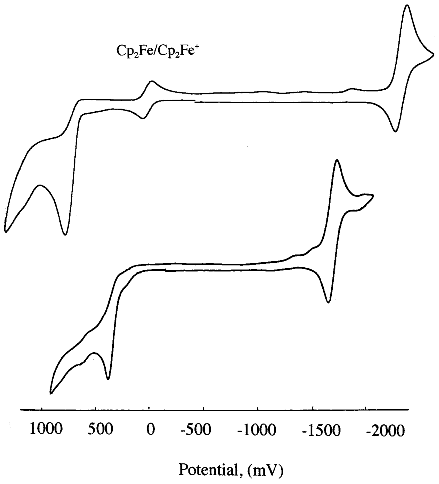


Figure 4. Cyclic voltammograms of Cp′ReO(SC_2H_4S), **7** (top), and Cp′ReS(SC_2H_4S), **4** (bottom), recorded in acetonitrile solutions with 0.3 M Bu_4NBF_4 at scan rates of 100 mV/s. Potentials are shown relative to the ferrocene/ferrocenium couple shown in the top scan.

Summary and Conclusions

The reaction of Cp′ReCl_2S_3 with triphenylphosphine is very sensitive to both stoichiometry and reaction conditions, but under appropriate conditions the dinuclear complex [Cp′ReCl_2(μ-S)]$_2$, **2**, has been isolated as the major product. Our efforts to cleave dimer **2** with nucleophiles to form mononuclear derivatives with terminal sulfido ligands have so far been unsuccessful. In contrast, a Cp′Re complex with a terminal sulfido ligand, Cp′ReS(SC_2H_4S), **4**, has been isolated from the reaction of Cp′ReCl_2(SC_2H_4S) with $(Me_3Si)_2S$. In addition to **4**, two additional unexpected products are consistently formed in the above reaction. One of these contains a trisulfide ligand, Cp′ReS_3(SC_2H_4S), **5**, while the second is a tetranuclear product, **6**, that also results from electron transfer between rhenium ions and sulfur ligands. The nature of the products illustrates how anticipated simple metathesis reactions between sulfur reagents and Re(V) chloride derivatives can actually be quite complicated. Cp′ReS(SC_2H_4S) is stable to air and reacts only slowly with

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(28) Hermann, W. A.; Herdtweck, E.; Marz, D. W. *J. Organomet. Chem.* **1990**, *394*, 285.

Table 4. Crystal Data for Compounds **2**, **4**, and **6**

	2	**4**	**6**
formula	$C_{24}H_{36}Cl_{10}Re_2S_2$	$C_{13}H_{21}ReS_3$	$C_{66}H_{116}Cl_8O_3Re_4S_{10}$
FW (amu)	1115.55	459.68	2306.59
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
unit cell dimens			
a (Å)	17.9740(6)	9.1831(8)	14.9069(7)
b (Å)	8.1844(3)	9.6456(9)	38.048(2)
c (Å)	23.6931(8)	9.6471(9)	16.0079(7)
α (deg)	90	77.748(2)	90
β (deg)	93.0980(10)	74.050(2)	116.079(2)
γ (deg)	90	69.677(2)	90
vol, Å^3	3480.3(2)	763.98(12)	8154.9(7)
Z	4	2	4
density, calcd (g/cm^3)	2.129	1.998	1.879
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
temp (K)	137(2)	142(2)	143(2)
scan type	ω scans	ω scans	ω scans
θ range (deg)	1.72−31.52	2.21−31.53	1.52−26.37
unique reflns	11 523 (R(int) = 0.0646)	4458 (R(int) = 0.0343)	16 681 (R(int) = 0.111)
reflns obsd	10 296	4342	11 067
abs correction	semiempirical from equiv[d]	semiempirical from equiv[d]	semiempirical from equiv[d]
R_1[a]	0.0429	0.0503	0.0550
R_{w2}[b]	0.1100	0.1323	0.1325
GOF[c]	1.084	1.115	1.036
largest peak in final diff map (e/Å^3)	2.583 and −2.749	3.631 and −5.887	2.041 and −1.575

[a] $R = R_1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$. [b] $R_{w2} = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $\mathrm{GOF} = S = [\Sigma[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined. [d] Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *A51*, 33.

water. Cyclic voltammetry of Cp′ReS(SC_2H_4S) indicates that the complex undergoes a reversible one-electron reduction at a modest potential, and further reactivity studies of this electron rich derivative are in progress.

Experimental Section

Materials. Ethyltetramethylcyclopentadiene, *tert*-butylamine, 15-crown-5, 1,2-ethanedithiol, triphenylphosphine, iodomethane, sodium sulfide, and heptamethyldisilazane were purchased from Aldrich, dimethylphenylphosphine and sodium hydrogen sulfide were purchased from Strem, and bis(trimethylsilyl)sulfide was purchased from Strem, Aldrich, or Fluka and used without purification. Hydrogen sulfide was purchased from Scott Gas. Cp′$ReCl_4$ was synthesized from $Re_2(CO)_{10}$ (Strem) by a published procedure.[18b] Cp′ReS_3Cl_2 [10] and Cp′$ReCl_2$(SC_2H_4S) [25] were prepared according to literature procedures. 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 CaH_2 prior to use. Tetrahedrofuran, toluene, and diethyl ether were distilled from sodium/benzophenone. Column chromatography was carried out using Fischer Scientific silica gel 60−200 mesh (75−250 μm). Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-300 or Varian Inova 500 MHz instruments. Chemical shifts are reported in parts per million relative to tetramethylsilane (^{1}H) or an external standard of phosphoric acid (^{31}P). 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 or on a Nicolet Impact 410 spectrometer. Visible spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammetry experiments were carried out under nitrogen on acetonitrile solutions containing 0.3 M Bu_4NBF_4 with a Cypress Systems electrolysis system. The working electrode was a glassy carbon disk (2 mm diameter). The counter electrode was a glassy carbon rod. An Ag/AgCl reference electrode was used to fix the potential. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

Synthesis of [Cp′$ReCl_2$(μ-S)]$_2$, 2. Cp′Re(η^2-S_3)Cl_2, **1** (0.050 g, 0.10 mmol), was dissolved in 5 mL of freeze−pump−thaw degassed MeCN, and dry PPh_3 (0.048 g, 0.184 mmol) was dissolved in 5 mL of freeze−pump−thaw degassed MeCN. The two solutions were combined in a reaction tube, and it was sealed with a Teflon vacuum stopcock. The solution was stirred at room temperature for 24 h and then at 55 °C for 24 h. The brown solution was dried in vacuo, and then degassed toluene was used to extract the unreacted red reagent **1**, leaving a green solid. Yield: ca. 35%. The green solid was recrystallized from CH_2Cl_2/Et_2O. ^{1}H NMR ($CDCl_3$): δ 2.31 (q, 4 H, $CpCH_2$); 2.20, 2.15 (2 s, each 12 H, CpMe); 1.13 (t, 6 H, $CpCH_2CH_3$).[22] Mass Spectrum (ESI): (m/z) 841 (P $^-$ Cl).

Reaction of Cp′$ReCl_4$ with Na_2S. Cp′$ReCl_4$ (0.025 g, 0.052 mmol) and Na_2S (0.004 g, 0.052 mmol) were dissolved in freeze−pump−thaw degassed MeCN, and 11 μL 15-crown-5 (unpurged) was syringed into the solution. The reaction tube was sealed with a Teflon vacuum stopcock, and the solution was stirred at room temperature overnight to form a brown solution. The ^{1}H NMR spectrum showed evidence for a mixture of five products, including two unidentified complexes with CpMe peaks at 2.37, 2.36 and 2.07, 2.06 ppm, and Cp′Re(η^2-S_3)Cl_2, (ca. 15%), Cp′$ReOCl_2$, (ca. 25%), [Cp′$ReCl_2S$]$_2$, **2** (ca. 10%).

X-ray Diffraction Study of [Cp′$ReCl_2S$]$_2$, 2. Crystals of [Cp′$ReCl_2S$]$_2$ were obtained from a $CHCl_3/Et_2O$ solution and manipulated under a light hydrocarbon oil. Crystals formed in the space group $P2_1/c$. The asymmetric unit consists of one rhenium dimer, and two chloroform molecules. Chloroform C2s is disordered with two sites for each Cl; site occupancy was refined to 0.55 for the major group. Details on the crystal data, experimental conditions, solution, and refinement information are given in Table 4.

Reaction of [Cp′ReCl$_2$S]$_2$ with Pyridine. [Cp′ReCl$_2$S]$_2$ (0.010 g, 0.012 mmol) was dissolved in freeze−pump−thaw degassed CDCl$_3$ to form a green solution, and pyridine (3 μL, 0.037 mmol) was syringed into the NMR tube. The solution turned brown upon addition and was shaken at room temperature for 15 min. The ^{1}H NMR spectrum revealed two new sets of CpMe peaks at 2.14, 2.12 and 1.91, 1.88 ppm. No change was observed upon addition of more pyridine (3 μL, 0.037 mmol). The products were isolated by elution on a silica gel column. The ^{1}H NMR spectrum indicated that the same two (unidentified) products were present. No pyridine resonances were observed.

Reaction of [Cp′ReCl$_2$S]$_2$ with 1,2-Ethanedithiol. [Cp′ReCl$_2$S]$_2$ (0.010 g, 0.012 mmol) was dissolved in 20 mL of N$_2$-purged MeCN to form a green solution. A N$_2$-purged MeCN stock solution (0.5 mL) containing 0.05 M 1,2-ethanedithiol (0.025 mmol) and 0.1 M pyridine (0.05 mmol) was syringed into the Schlenk tube that was then sealed with a Teflon vacuum stopcock. The solution turned brown upon mixing and was stirred at room temperature for 30 min. The solvent was removed in vacuo to give a brown solid. The ^{1}H NMR spectrum revealed a product that appears to be [(Cp′Re)$_2$(μ-S)(μ,η^2-SC$_2$H$_4$S)(μ,η^1-SC$_2$H$_4$S)]$_2$Cl$_2$, **6**, although resonances are slightly shifted (see below for comparison). ^{1}H NMR (CDCl$_3$): δ 2.86, 2.26, 1.82, 1.63 (4 m, 4 H each, SCH$_2$CH$_2$S); 2.22, 2.21 (2 s, 48 H, CpMe); 2.18 (q, 8 H, Cp*CH$_2$*CH$_3$); 1.15 (t, 12 H, CpCH$_2$*CH$_3$*).

Synthesis of [Cp′ReCl$_2$]$_2$. Compound **1** (0.030 g, 0.059 mmol) was dissolved in 20 mL of MeCN and purged with N$_2$. Me$_2$PhP (25 μL, 0.177 mmol) was syringed into the reaction tube, which was sealed with a Teflon vacuum stopcock. The red solution turned olive green upon addition and then bright green. The solution was stirred at room temperature overnight. The solvent was removed in vacuo to give a green solid identified as [Cp′ReCl$_2$]$_2$.[21] The same product is formed when 3 equiv of Ph$_3$P are used as the sulfur-abstracting agent. Yield: ca. 95%. ^{1}H NMR (CDCl$_3$): δ 2.16, 2.07 (2 s, each 12 H, CpMe); 2.15 (q, 4 H, CpCH$_2$); 1.15 (t, 6 H, CpCH$_2$*CH$_3$*). Mass Spectrum (EI): (*m*/*z*) 812 (weak, P$^+$); 406 (P − Cp′ReCl$_2$). When exposed to air, the compound is rapidly converted to Cp′ReOCl$_2$.[19b]

Reaction of Cp′ReCl$_2$(SC$_2$H$_4$S) with (Me$_3$Si)$_2$S. Syntheses of 4−6. Cp′ReCl$_2$(SC$_2$H$_4$S) (0.080 g, 0.161 mmol) was dissolved in 10 mL of freeze−pump−thaw degassed MeCN in a Schlenk tube. (Me$_3$Si)$_2$S (50 μL, 0.241 mmol) was syringed into the solution, and the tube was sealed with a Teflon vacuum stopcock. The green solution was stirred at 65 °C for 90 min at which time the solution was brown. The solvent was removed in vacuo. The ^{1}H NMR spectrum of the crude reaction mixture reveals three new Cp′Re complexes. A small amount (ca. 5%) of Cp′Re(SC$_2$H$_4$S)$_2$[25] was also observed in the spectrum. The crude brown solid was extracted with toluene to give a brown solution and a brown residue. The brown toluene solution was purified by silica gel column chromatography. Eluted with toluene, the first fraction was brown and contained **4**. Yield: ca. 30%. ^{1}H NMR (CDCl$_3$): δ 2.75, 2.65 (2 m, 2 H each, SCH$_2$CH$_2$S); 2.21 (q, 2 H, Cp*CH$_2$*CH$_3$); 2.05, 2.00 (2 s, 12 H, CpMe); 1.05 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): δ11.84, 12.01 (CpMe); 14.78 (CpCH$_2$*CH$_3$*); 20.72 (Cp*CH$_2$*CH$_3$); 48.46 (SC$_2$H$_4$S); 104.99, 106.78, 109.34 (Cp). IR (KBr; cm^{-1}): 485 (s, $\nu_{\mathrm{Re=S}}$). Mass spectrum (EI): (*m*/*z*) 460 (P$^+$); 432 (P − C$_2$H$_4$). UV/Vis Spectrum (in MeCN, nm (ϵ in M^{-1} cm^{-1})): 416 (3700); 471 (sh). CV (CH$_3$CN, V vs Fc): −1.65 (ΔE_p = 59 mV); +0.31 (irr.). Compounds isolated from toluene showed by NMR spectroscopy a trace of this solvent even after drying under vacuum. The analyses reflect the presence of trace toluene. Anal. Calcd for C$_{13}$H$_{21}$S$_3$Re•1/7C$_7$H$_8$: C, 35.56; H, 4.69. Found: C, 35.53; H, 5.03.

The second fraction eluted with toluene from the silica gel column was green and contained **5**. Yield: ca. 15%. ^{1}H NMR (CDCl$_3$): δ 2.92, 2.49 (2 m, 2 H each, SCH$_2$CH$_2$S); 2.21 (q, 2 H, Cp*CH$_2$*CH$_3$); 1.96, 1.89 (2 s, 12 H, CpMe); 1.05 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): δ 10.98, 11.44 (CpMe); 13.96 (CpCH$_2$*CH$_3$*); 19.77 (Cp*CH$_2$*CH$_3$); 37.52 (SC$_2$H$_4$S); 101.34, 104.16, 105.61 (Cp). IR (KBr; cm^{-1}): 489 (med, $\nu_{\mathrm{s-s}}$). Mass spectrum (EI): (*m*/*z*) 524 (P$^+$); 496 (P − C$_2$H$_4$). UV/Vis Spectrum (in MeCN, nm (ϵ in M^{-1} cm^{-1})): 384 (3600); 452 (2200); 698 (3600). CV (CH$_3$CN, V vs Fc): −1.67 (ΔE_p = 73 mV); −1.35 (irr.); +0.34 (irr.). Anal. Calcd for C$_{13}$H$_{21}$S$_5$Re•1/7C$_7$H$_8$: C, 31.32; H, 4.13. Found: C, 31.64; H, 4.38.

The brown residue that was insoluble in toluene was dissolved in MeCN and purified on a silica gel pipet column. Complex **6** was eluted with MeOH as a red/brown band and recrystallized from CHCl$_3$/hexane. Yield: ca. 45%. ^{1}H NMR (CDCl$_3$): δ 2.85, 2.20, 1.89, 1.68 (4 m, 4 H each, SCH$_2$CH$_2$S); 2.16, 2.15 (2 s, 48 H, CpMe); 2.12 (q, 8 H, Cp*CH$_2$*CH$_3$); 1.14 (t, 12 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): δ 12.38, 12.44, 12.76, 12.78 (CpMe); 15.42 (CpCH$_2$*CH$_3$*); 21.07 (Cp*CH$_2$*CH$_3$); 32.66, 37.70, 38.90, 43.58 (SC$_2$H$_4$S); 99.77, 100.14, 102.30, 102.51, 104.29 (Cp). HMQC (CDCl$_3$): (^{1}H − ^{13}C) 2.85−38.90; 2.20−32.66; 1.89−43.58; 1.68−37.70. Mass spectrum (EI): (*m*/*z*) 948 (P − (Cp′Re)$_2$(μ-S$_2$)(μ-SC$_2$H$_4$S)). Mass spectrum (ES): (*m*/*z*) 1810 ([P]$^{2+}$Cl), 948 (P − (Cp′Re)$_2$(μ-S$_2$)(μ-SC$_2$H$_4$S)). CV (CH$_3$CN, V vs Fc): +0.080 (ΔE_p = 131 mV). Anal. Calcd for C$_{52}$H$_{84}$Cl$_2$S$_{10}$Re$_4$•CHCl$_3$: C, 32.39; H, 4.36. Found: C, 32.31; H, 4.61.

NMR Scale Reaction of Cp′ReCl$_2$(SC$_2$H$_4$S) with (Me$_3$Si)$_2$S. Cp′ReCl$_2$(SC$_2$H$_4$S) (0.010 g, 0.02 mmol) was dissolved in freeze−pump−thaw degassed CD$_3$CN in a NMR tube and (Me$_3$Si)$_2$S (6.5 μL, 0.031 mmol) was syringed into the solution. The solution turned from green to brown in less than 5 min. The ^{1}H NMR spectrum was taken after 45 min and showed the three products: **4** (ca. 30%), **5** (ca. 15%), and **6** (ca. 45%). After 3, 24, and 48 h, the ^{1}H NMR spectra were taken again and there was no change in the spectra over time.

Reaction of Cp′ReCl$_2$(SC$_2$H$_4$S) with Na$_2$S/15-Crown-5. Cp′ReCl$_2$(SC$_2$H$_4$S) (0.025 g, 0.05 mmol) was dissolved in 10 mL of freeze−pump−thaw degassed MeCN, and Na$_2$S (0.004 g, 0.05 mmol) was dissolved in 1 mL of 0.1 M 15-crown-5 stock solution in MeCN. The two solutions were combined in the reaction tube, and it was sealed with a Teflon vacuum stopcock. The green solution was stirred at 65 °C for 3 h. The solution turned brown, and the solvent was removed in vacuo to give a brown solid. The ^{1}H NMR spectrum showed evidence for the complexes **4** (ca. 20%) and **5** (ca. 10%), but the major product was **6** (ca. 60%). Full data are given above.

Reaction of Cp′ReCl$_2$(SC$_2$H$_4$S) with NaSH/15-Crown-5. Cp′ReCl$_2$(SC$_2$H$_4$S) (0.025 g, 0.05 mmol) was dissolved in 10 mL of freeze−pump−thaw degassed MeCN, and NaSH (0.006 g, 0.10 mmol) was dissolved in 1 mL of 0.1 M 15-crown-5 stock solution in MeCN. The two solutions were combined in the reaction tube, and it was sealed with a Teflon vacuum stopcock. The green solution was stirred at 65 °C for 3 h. The solution turned brown, and the solvent was removed in vacuo to give a brown solid. The ^{1}H NMR spectrum showed evidence for the two complexes: **4** (ca. 50%); **5** (ca. 5%); and two unidentified products with CpMe peaks at 2.17, 2.14 and 2.12, 2.08 ppm. Silica gel chromatography failed to fully remove the 15-crown-5 from the Cp′Re(S)(SC$_2$H$_4$S) containing fraction and afforded a generally impure product. When the same procedure was carried out in the absence of 15-crown-5, no reaction was observed.

X-ray Diffraction Study of Cp′Re(S)(SC_2H_4S), 4. Crystals of Cp′Re(S)(SC_2H_4S) were obtained from a cold pentanes/Et_2O solution and manipulated under a light hydrocarbon oil. Crystals formed in the space group $P\bar{1}$. Details on the crystal data, experimental conditions, and solution and refinement information are given in Table 4.

X-ray Diffraction Study of [(Cp′Re)$_2$(*μ*<rsf>-S)(*μ*<rsf>,*η*^{2}-SC_2H_4S)(*μ*<rsf>,*η*^{1}-SC_2H_4S)]$_2$$Cl_2$, 6. Crystals of [(Cp′Re)$_2$(μ-S)(μ,η^2-SC_2H_4S)(μ,η^1-SC_2H_4S)]$_2$$Cl_2$ were obtained from a $CHCl_3$/Et_2O solution and manipulated under a light hydrocarbon oil. Crystals formed in the space group $P2_1/c$. Least-squares refinement showed five sites for solvent. Modeling with SQUEEZE[29] indicated electron density consistent with two molecules of chloroform and three molecules of diethyl ether. Details on the crystal data, experimental conditions, and solution and refinement information are given in Table 4.

Reaction of Cp′Re(*μ*,*η*^{2}-S_3)(SC_2H_4S) with PPh_3 To Form Cp′Re(S)(SC_2H_4S). Compound **5** (0.006 g, 0.012 mmol) was dissolved in 10 mL of freeze−pump−thaw degassed MeCN in a Schlenk tube, and dry PPh_3 (0.005 g, 0.019 mmol) was added. The tube was sealed with a Teflon vacuum stopcock. The green solution was stirred at room temperature for 90 min at which time the solution was brown and the solvent was removed in vacuo. The ^1H NMR spectrum showed the presence of **4** (ca. 95%), and a small amount of unreacted Cp′Re(η^2-S_3)(SC_2H_4S) (ca. 5%). In the ^{31}P NMR spectrum only $Ph_3P{=}S$ was observed (s, 44 ppm). The reaction mixture was redissolved in 10 mL of freeze−pump−thaw degassed MeCN, and an additional 4 equiv of PPh_3 (0.013 g, 0.049 mmol) was added and stirred at room temperature for 24 h. Analysis of an aliquot by ^1H NMR revealed that only Cp′Re(S)(SC_2H_4S) was present. Upon heating the solution at 65 °C for 6 h, the solution turned yellow in color and the ^1H NMR spectrum revealed numerous unidentified decomposition products.

Reaction of Cp′Re(S)(SC_2H_4S) with H_2O. Cp′Re(S)(SC_2H_4S) (0.010 g, 0.022 mmol) was dissolved in ca. 2 mL of toluene-d_8 and water (5−6 equiv) was added. The brown solution was stirred at 60 °C for 24 h. The solution was transferred to an NMR tube, and the ^1H NMR spectrum showed both the starting complex, Cp′Re(S)(SC_2H_4S) (ca. 54%), and the new complex, Cp′Re(O)(SC_2H_4S) (ca. 46%). ^1H NMR for Cp′Re(S)(SC_2H_4S) (toluene-d_8): δ 2.62, 2.50 (2 m, 2 H each, SCH_2CH_2S); 2.04 (q, 2 H, Cp$CH_2$$CH_3$); 1.79, 1.69 (2 s, each 6 H, CpMe); 0.77 (t, 3 H, Cp$CH_2$$CH_3$). ^1H NMR for Cp′Re(O)(SC_2H_4S) (toluene-d_8): 2.38 (m, 4 H, SCH_2CH_2S); 2.11 (q, 2 H, CpCH_2CH_3); 1.72, 1.69 (2 s, each 6 H, CpMe); 0.84 (t, 3H, CpCH_2CH_3).

Attempted Reaction of Cp′Re(S)(SC_2H_4S) with H_2N^tBu. Compound **4** (0.010 g, 0.022 mmol) was dissolved in toluene-d_8 in an NMR tube, and H_2N^tBu (5 μL, 0.048 mmol) was syringed into the tube. The reaction was monitored at 50 °C for 24 h and then at 65 °C for 24 h with no color change and no change in the ^1H NMR spectrum.

Synthesis of Cp′Re(NMe)(SC_2H_4S), 7. Cp′ReCl_2(SC_2H_4S) (0.060 g, 0.121 mmol) was dissolved in 10 mL of freeze−pump−thaw degassed tetrahydrofuran (THF) in a Schlenk tube and $(TMS)_2NMe$ (105 μL, 0.482 mmol) was syringed into the tube which was sealed with a Teflon vacuum stopcock. The green solution was stirred at room temperature for 24 h. The resulting red/orange solution was dried in vacuo to give a red/orange solid. The ^1H NMR spectrum usually indicated a clean product. However, if necessary, further purification can be carried out by chromatography on silica gel eluting with 5:1 chloroform/acetonitrile. Yield: 87%. ^1H NMR ($CDCl_3$): δ 2.28 (q, 2 H, Cp$CH_2$$CH_3$); 2.21, 1.96 (2 m, 2 H each, SCH_2CH_2S); 2.16 (s, 3 H, NCH_3); 1.96, 1.88 (2 s, 12 H, CpMe); 1.08 (t, 3 H, Cp$CH_2$$CH_3$). ^1H NMR (toluene-d_8): δ 2.18 (q, 2 H, Cp$CH_2$$CH_3$); 2.45, 2.10 (2 m, 2 H each, SCH_2CH_2S); 1.71 (s, 3 H, NCH_3); 1.81, 1.73 (2 s, 12 H, CpMe); 0.93 (t, 3 H, Cp$CH_2$$CH_3$). ^{13}C NMR ($CDCl_3$): δ 105.6, 105.3, 103.1 (Cp); 52.44 (NCH_3); 38.92 (SCH_2CH_2S); 19.71 (Cp′CH_2CH_3); 15.44 (Cp′CH_2CH_3); 10.98 (Cp′Me). Mass spectrum (EI) *m/z*: 457 (P^+, base). CV (CH_3CN, V vs Fc): +0.203 ($\Delta E_p = 72$ mV). Anal. Calcd for $C_{14}H_{24}NS_2Re$: C, 36.81; H, 5.31. Found: C, 37.31; H, 5.53.

Attempted Reaction of Cp′Re(NMe)(SC_2H_4S) with *tert*-Butylamine. Cp′Re(NMe)(SC_2H_4S) (0.012 g, 0.024 mmol) was dissolved in ca. 2 mL of dry toluene-d_8. H_2N^tBu (5 μL, 0.048 mmol) was syringed into the Schlenk tube under nitrogen, and the vessel was sealed with a Teflon vacuum stopcock. The solution was stirred at 65 °C and monitored for a total of 3 days. There was no color change, and the ^1H NMR spectra contained only resonances for the starting reagents.

Attempted Reaction of Cp′Re(NMe)(SC_2H_4S) with H_2O. Cp′Re(NMe)(SC_2H_4S) (0.010 g, 0.02 mmol) was dissolved in ca. 10 mL of toluene, and a few drops of water were added. The red/orange solution was stirred at 65 °C for 24 h. There was no observable color change, and the ^1H NMR spectra contained only resonances for the starting reagents.

Reaction of Cp′Re(NMe)(SC_2H_4S) with H_2S. Cp′Re(NMe)(SC_2H_4S) (0.010 g, 0.02 mmol) was dissolved in ca. 10 mL of toluene in a Schlenk tube and bubbled with N_2, then bubbled with H_2S for 10 min, and sealed with a Teflon vacuum stopcock. The red/orange solution was stirred at 65 °C for 24 h. The solvent was removed in vacuo to give a red solid. The ^1H NMR spectrum showed resonances primarily for the starting reagent, Cp′Re(NMe)(SC_2H_4S) (ca. 90%) and for a small amount of Cp′Re(S)(SC_2H_4S) (ca. 10%).

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Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances and bond angles for **2**, **4**, and **6 (CIF)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) SQUEEZE is a routine included in: Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.