Reactions of Dithiolate Ligands in Mononuclear Complexes of Rhenium(V)

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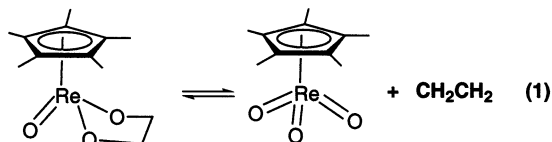
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Abstract: The thermal reactions of the Re(V) dithiolate complex Cp′ReCl$_2$(SCH$_2$CH$_2$S), **1** (where Cp′ = EtMe$_4$C$_5$), and related derivatives have been studied. When **1** is heated in toluene in a sealed evacuated tube at 100 °C, a dehydrogenation reaction occurs to form a new rhenium complex with a dithiolene ligand, Cp′ReCl$_2$(SCHCHS), **6**, in ca. 40% yield. The structure of **6** has been confirmed by an X-ray diffraction study. Under the thermal conditions studied, **1** also undergoes an olefin extrusion reaction. Free ethene is detected in the NMR spectrum of the products, and insoluble rhenium products are also formed. When **1** is reacted with excess ethene under mild conditions, a new organic product, 1,4-dithiane, is formed. Complex **1** is also found to react with oxidants, such as O$_2$ and S$_8$, under mild conditions to form the dehydrogenation product **6**. Kinetic studies of the thermal reaction of **1** and related derivatives have been completed, and possible mechanisms for the thermally induced dehydrogenation reaction are discussed.

Introduction

Metal dithiolate and metal sulfide complexes are related in some systems by the reversible addition and elimination of alkenes at the sulfur sites. For example, thermodynamic data have been reported for the reversible reactions of olefins with the sulfido ligands in ReS$_4^-$,[1] and kinetic and thermodynamic studies of alkene addition and elimination have been reported for a series of dinuclear molybdenum complexes with μ-sulfur ligands.[2] Alkene interactions with nickel dithiolene complexes have been known for many years,[3] and reversible olefin binding as a function of redox state has been examined recently.[4,5]

The addition of olefins to the terminal oxo ligands of a metal complex and the reverse alkene elimination from metal diolate complexes have also been observed for a number of high-valent metal complexes[6−13] and studied mechanistically in some cases,

e.g., eq 1.[6] These reactions are related to the asymmetric cis-

dihydroxylation of olefins catalyzed by derivatives of osmium tetroxide,[14] which has been extensively studied in both experimental and theoretical approaches.[15,16]

In this paper we report the syntheses and characterizations of new mononuclear Re(V) derivatives with 1,2-dithiolate ligands and a study of their thermal reactivity. Complexes of the formula Cp′ReCl$_2$(dithiolate) are found to undergo reversible alkene eliminations; but rather unexpectedly, a novel C−H activation process within the dithiolate ligand is also observed, and dehydrogenated complexes of the formula Cp′ReCl$_2$-(dithiolene) have been isolated and characterized. In addition, **1** reacts with alkenes and alkynes to undergo dithiolate ligand displacement forming uncoordinated cyclic bis(thioether) derivatives.

Results and Discussion

Syntheses and Characterization of 1,2-Alkanedithiolate Derivatives of Re(V). The reaction of Cp′ReCl$_4$ with 1 equiv

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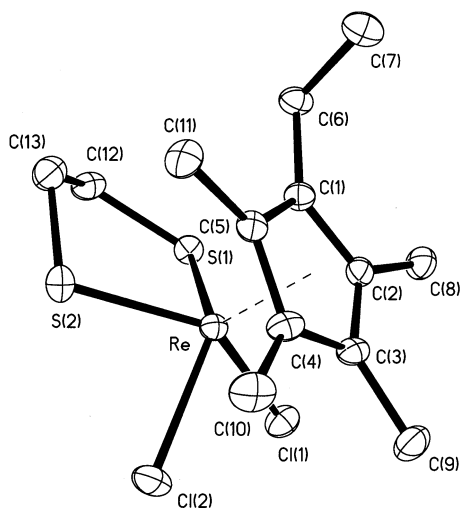
Figure 1. Perspective drawing and numbering scheme for Cp′ReCl₂(SCH₂-CH₂S), **1**. Thermal ellipsoids are shown at the 50% probability level.

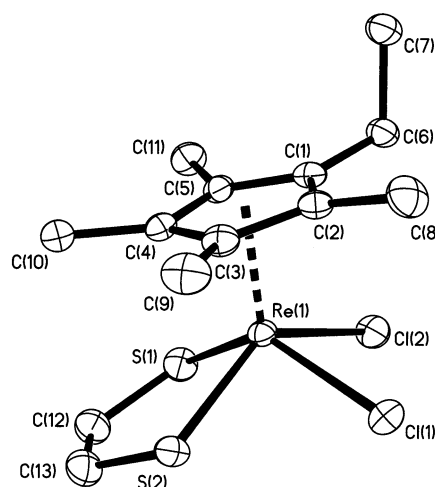**Figure 2.** Perspective drawing and numbering scheme for Cp′ReCl₂-(SCHCHS), **6**. Thermal ellipsoids are shown at the 50% probability level.

of ethanedithiol in THF proceeded cleanly to form the deep green product Cp′ReCl₂(η^2-SC₂H₄S), **1**, eq 2. In the ^{1}H spectrum

$$+ \; 2 \; HCl \quad (2)$$

1: R = R' = H

2: R = H, R' = Et

3: R = R' = Me
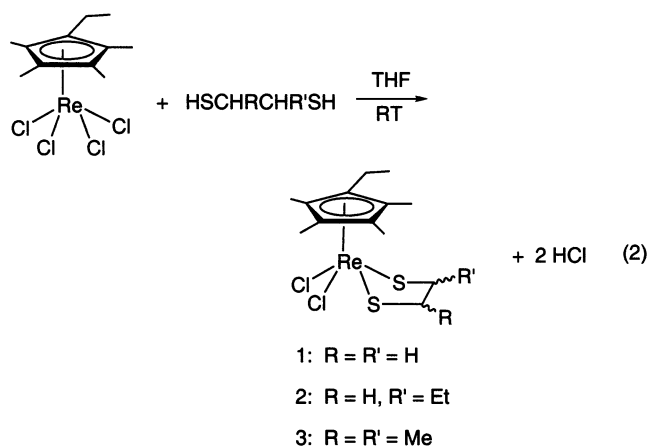
of **1** an AA′BB′ pattern for the ethanedithiolate protons was centered at 4.01 ppm (relative intensity 4), and in the ^{13}C spectrum the carbons of the chelated ligand were found to be equivalent with a single resonance at 48.7 ppm. The FAB mass spectrum showed peaks at m/z 498 and 463, which were assigned to P$^+$ and P$^+$ − Cl. However in the EI mass spectrum of analytically pure samples of **1**, peaks with m/z ratios that corresponded to dinuclear formulations, such as [Cp′ReS₂]₂, were observed. To confirm the structure of **1**, an X-ray diffraction study was carried out.

The structural study confirms that **1** is a mononuclear piano stool complex containing a single chelated ethanedithiolate ligand as well as two chloride ligands. The dinuclear species observed in the EI mass spectrum therefore appear to be formed during the mass spectroscopy experiment via ethylene loss and dimerization of the resulting fragment. A perspective drawing of **1** is shown in Figure 2, and selected bond distances and angles are given in Table 2. The dithiolate ligand is bound asymmetrically with Re−S1 = 2.2697(17) Å and Re−S2 = 3.3102(19) Å. The shorter distance suggests some π-donor properties for S1, since many reported Re−S distances for Re(V) thiolate

Table 1. Bond Distances (Å) and Angles (deg) for (EtMe₄C₅)ReCl₂(η^2-SCH₂CH₂S), **1**

Re−S(1)	2.2697 (17)	Re−S(2)	2.3102 (19)
Re−Cl(1)	2.4192 (18)	Re−Cl(2)	2.4022 (17)
S(1)−C(12)	1.835 (8)	S(2)−C(13)	1.835 (8)
Re−C(1)	2.309 (7)	Re−C(2)	2.252 (7)
Re−C(3)	2.278 (7)	Re−C(4)	2.371 (7)
Re−C(5)	2.385 (7)	C(1)−C(2)	1.443 (9)
C(2)−C(3)	1.442 (10)	C(3)−C(4)	1.432 (10)
C(4)−C(5)	1.426 (10)	C(5)−C(1)	1.448 (9)
S(1)−Re−Cl(1)	80.24 (7)	S(2)−Re-Cl(2)	80.39 (7)
S(1)−Re−S(2)	84.24 (7)	Cl(1)−Re−Cl(2)	80.27 (7)
Re−S(1)−C(12)	109.7 (3)	Re−S(2)−C(13)	104.6 (3)

Table 2. Bond Distances (Å) and Angles (deg) for (EtMe₄C₅)ReCl₂(η^2-SCH=CHS), **6**

Re−S(1)	2.2884 (9)	Re−S(2)	2.2888 (9)
Re−Cl(1)	2.4186 (9)	Re−Cl(2)	2.4111 (9)
S(1)−C(12)	1.711 (4)	S(2)−C(13)	1.720 (4)
Re−C(1)	2.408 (3)	Re−C(2)	2.401 (3)
Re−C(3)	2.255 (3)	Re−C(4)	2.202 (3)
Re−C(5)	2.272 (3)	C(1)−C(2)	1.414 (4)
C(2)−C(3)	1.439 (5)	C(3)−C(4)	1.447 (4)
C(4)−C(5)	1.448 (5)	C(5)−C(1)	1.445 (5)
S(1)−Re−Cl(2)	80.97 (3)	S(2)−Re−Cl(1)	80.16 (3)
S(1)−Re−S(2)	82.59 (4)	Cl(1)−Re−Cl(2)	81.88 (3)
Re−S(1)−C(12)	107.90 (15)	Re−S(2)−C(13)	108.05 (15)

complexes fall in the range 2.30−2.40 Å.[17−19] The S1−Re−S2 angle is 84.24°, and the other three angles in the piano stool base are all near 80°. The S−C−C−S dihedral angle in the dithiolate ligand is 39.9°. In the cyclopentadienyl ring the carbons trans to S1 show the longest Re−C distances, Re−C4 = 2.371(7) Å and Re−C5 = 2.385(7) Å, while the other three carbons have Re−C distances ranging from 2.25 to 2.28 Å. The C−C distances within the Cp ligand are equivalent within experimental error. Asymmetric η^3,η^2 coordination of Cp* rings has been observed previously in Re(V) derivatives containing a strong π donor, such as a terminal oxo or imido ligand.[20,21]

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In these cases the C−C distances within the ring were also inequivalent. The longer Re−C distances to the η^2-portion of the ring have been attributed to the trans effect of the multiply bonded oxo or imido group.[20] The π-donor thiolate sulfur in **1** appears to exert a similar, but weaker trans effect than oxo or imido ligands.

The reactions of Cp′ReCl₄ with 1,2-butanedithiol and with 2,3-butanedithiol were carried out under similar conditions to form the corresponding complexes with alkyl-substituted alkanedithiolate ligands, Cp′ReCl₂(η^2-SCH₂CH(Et)S), **2**, and Cp′ReCl₂(η^2-SCH(Me)CH(Me)S), **3**. Two diastereomers of **2** (in a 70:30 ratio) are observed in the ¹H NMR spectrum, each showing four inequivalent Cp methyl resonances. The major isomer is assumed to be that with the ethyl substituent directed away from the Cp′ ligand. In the ¹H NMR spectrum of **3**, two isomers in a 70:30 ratio are also observed, and the major isomer is assigned to a cis-Me derivative on the basis of the NMR data for the dithiolate hydrogens. Again the exo isomer is assumed to be favored. The spectrum of the second isomer shows inequivalent methyls and hydrogens in the dithiolate ligand and is therefore assigned as the trans isomer. Other spectroscopic data for **2** and **3**, detailed in the Experimental Section, are consistent with their simple mononuclear formulations.

In a previous report, the reaction of 2 equiv of Li₂-ethanedithiolate with Cp*WCl₄ at 0 °C produced [Cp*W(S)₃]⁻ in 82% yield.[22] In contrast, we found that 2 equiv of ethanedithiol reacted with Cp′ReCl₄ in THF at room temperature to form Cp′Re(SC₂H₄S)₂, **4**, which was isolated as a deep purple solid and characterized by spectroscopic data. In the ¹H NMR spectrum for **4** the multiplets for the ethanedithiolate protons centered at 3.22 ppm show a significant upfield shift relative to those of **1**. A related structure Cp*Re(SCR=CRS)₂, where R = CO₂Me, was synthesized previously by the addition of dimethylacetylene dicarboxylate to a Cp*Re-polysulfide derivative.[17b] For comparative purposes, Cp′ReO(η^2-SC₂H₄S), **5**, was also prepared. It was synthesized by the reaction of Cp′ReOCl₂[20] with ethanedithiol in dichloromethane. The Cp* analogue of this derivative has been reported previously.[7]

Thermal Reactions of Re(V) 1,2-Dithiolate Complexes. When **1** was heated to 100−108 °C in dry toluene-d_8 under vacuum in a sealed tube, the deep green color changed to brown, and a single new rhenium complex, **6**, was observed in the NMR spectrum in yields that ranged from 30 to 50%. In addition, a singlet at 5.26 ppm was confirmed as the resonance of ethene, and some insoluble material was observed in the tube. The ¹H NMR spectrum of **6** showed resonances for the Cp′ ligand, but the multiplets of the ethanedithiolate ligand were absent and a new singlet (relative intensity = 2) was observed at 8.4 ppm. In the ¹³C NMR spectrum of **6** a new resonance was observed at 165 ppm in CDCl₃. The data suggested the presence of an ethenedithiolate ligand, and **6** was formulated as Cp′ReCl₂(η^2-SC₂H₂S). The formulation was supported by the mass spectrum of the complex and confirmed by an X-ray diffraction study (see below). The thermal reaction of **1** therefore appears to involve the dehydrogenation of the alkanedithiolate ligand as

well as a competing elimination of olefin from the ligand, as summarized in eq 3 below. The rhenium product proposed to

6: R = R′ = H   ethene

7: R = H, R′ = Et   1-butene

8: R = R′ = Me   cis, trans 2-butene
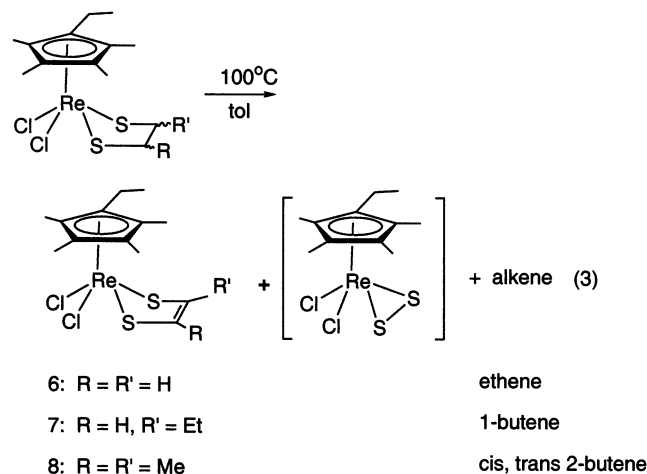
result from olefin elimination was not detected in the spectrum. It either decomposes or reacts in some way to form the observed insoluble material. Neither molecular hydrogen nor ethane was observed in the sealed tube reactions.

Similar dehydrogenation and olefin elimination reactions were observed for the alkanedithiolate derivatives, **2** and **3**, when these were heated in toluene at 100−110 °C. The products, Cp′ReCl₂-(η^2-SCH=C(Et)S), **7**, and CpReCl₂(η^2-SCMe=C(Me)S), **8**, were isolated and characterized by spectroscopic techniques. For example, in the ¹H NMR spectrum of **7**, a singlet at 8.9 ppm in CDCl₃ (relative intensity, 1 H) is assigned to the ethenedithiolate proton, while in the spectrum of **8**, the alkenedithiolate methyl groups appear as a singlet at 3.01 ppm. Additional data for these products are included in the Experimental Section. In addition the presence of 1-butene and *cis*- and *trans*-2-butene were observed in the NMR spectra of **7** and **8**, respectively, and some insoluble material was formed.

Although the Cp* analogue of **5** has been reported to lose ethene when heated to 200 °C,[7] in our studies no reactions were observed for Cp′ReO(η^2-SC₂H₄S), **5**, or for Cp′Re(η^2-SC₂H₄S)₂, **4**, in toluene under thermal conditions similar to those reported above. Similarly, in a recent report, no ethylene extrusion was observed for the related complex Tp′ReO(η^2-SC₂H₄S).[23] In compounds **1**−**3**, the electron-withdrawing character of the chloride ligands appears to be important for the dehydrogenation and elimination reactions to occur under these relatively mild conditions. The electronic differences between the dichloro complex **1** and its oxo analogue, **5**, are reflected in the electrochemical data for these two derivatives. Complex **5** undergoes an irreversible oxidation at a carbon electrode at 0.68 V vs Fc in acetonitrile solution and a reversible reduction at −2.14 V. The high negative reduction potential reflects the π-donating character of the oxo ligand. In contrast, the cyclic voltammogram of **1** shows an irreversible reduction at a much lower potential, −0.82 V, and additional waves are observed at more negative potentials.

X-ray Diffraction Study of Cp′ReCl₂(η^2-SC₂H₂S), 6. Single crystals of the dehydrogenation product, **6**, were obtained by diffusion of hexane into a toluene solution. A perspective

(20) Hermann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

(21) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489−496.

(22) Kawaguchi, H.; Yamada, K.; Yang, J. P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346−10358.

(23) Tp′ = tris(3,5-dimethylpyrazolyl)hydridoborate: Gable, K. P.; Chuawong, P.; Yokochi, A. F. T. *Organometallics* **2002**, *21*, 929−933.

Table 3. Kinetic Data for Thermal Reactions of Cp′ReCl₂(SCHRCHR′S)

complex	T (K)	solvent	k (s⁻¹)
1	353	toluene-d_8	4.89×10^{-7}
	358		9.94×10^{-7}
	363		1.58×10^{-6}
	368		1.88×10^{-6}
	373		4.36×10^{-6}
	377		6.23×10^{-6}
	381		1.37×10^{-5}
2	381		1.27×10^{-5}
3	381		1.98×10^{-5}
1	381	CD₃CN	3.71×10^{-6}

drawing of **6** is shown in Figure 2, and selected bond distances and angles are given in Table 2. The complex is a simple mononuclear piano stool structure with a chelating ethenedithiolate ligand. The C−C distance in the dithiolene ligand of 1.343 Å is significantly shorter than the corresponding C−C distance in **1** (1.46 Å) and is consistent with double-bond character. In addition, the S−C bond distances within the dithiolene ligand (av = 1.715(4) Å) are much shorter than those in the dithiolate complex (1.835(8) Å), suggesting that a contribution from a dithioglyoxal resonance form B is an important component of **6**. This description is consistent with the downfield chemical
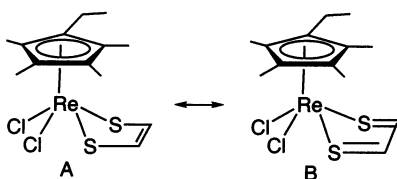
shift (8.4 ppm) observed for the dithiolene protons in the ¹H NMR spectrum.[24] Unlike the dithiolate bonding for **1**, the Re−S distances of the ethenedithiolate ligand are equivalent at 2.29 Å. An unsymmetrical coordination of the Cp′ ligand is again observed with long (2.40 Å) Re−C1 and Re−C2 distances, which are opposite the dithiolate sulfurs, while the other Re−C$_{Cp}$ distances average 2.243(3) Å.

Kinetic Studies. Kinetic data for the thermal reactions of **1**, **2**, and **3** in toluene-d_8 in evacuated sealed tubes were determined by NMR spectroscopy by monitoring the disappearance of the Cp′ resonances for the reactants over a period of several days. The thermal reaction of **1**, followed through 3 half-lives, was found to be first-order in **1**. Rate constants were determined over a temperature range of 80−108 °C, and rate constants were found to vary from 5×10^{-7} to 1×10^{-5} s⁻¹, Table 3. An Eyring plot, Figure 3, provided the following activation parameters: $\Delta H^{\ddagger} = 121 \pm 5$ kJ/mol and $\Delta S^{\ddagger} = -24 \pm 12$ J/mol K. Perhaps coincidentally, these activation parameters are very similar to those determined for ethene extrusion from Cp*ReO(OCH₂CH₂O).[6] The rates of disappearance of the major isomers of **2** and **3** were monitored at 108 °C in toluene-d_8. The first-order rate constants (Table 3) were found to be quite comparable to those of the parent complex, but increasing alkyl substitution appears to promote the rate of olefin elimination slightly.

The thermal reaction of **1** was also monitored in a polar solvent, acetonitrile-d_3, at 108 °C, and the rate in this solvent was found to be significantly slower than that in toluene (Table

(24) King, R. B.; Eggers, C. A. *Inorg. Chem.* **1968**, *7*, 340.

Table 4. Crystal Data for (EtMe₄C₅)ReCl₂(SCH₂CH₂S), **1**, and (EtMe₄C₅)ReCl₂(SCHCHS), **6**

	1	**6**
formula	C₁₃H₂₁Cl₂ReS₂	C₁₃H₁₉Cl₂ReS₂
fw (amu)	498.52	496.50
cryst syst	orthorhombic	orthorhombic
unit cell dimens		
a (Å)	8.4218(5)	13.5694(15)
b (Å)	13.4234(7)	14.764(2)
c (Å)	13.7910(8)	15.469(2)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
volume, Å³	1559.06(15)	3099.0(7)
space group	$P2_12_12_1$	$Pbca$
Z	4	8
density, calcd (mg/m⁻³)	2.124	2.128
λ(Mo Kα) (Å)	0.71073	0.71073
temp (K)	143(2)	143(2)
scan type	ω-scans	ω-scans
θ range	$2.12 < \theta < 30.93$	$2.43 < \theta < 31.48$
no. of ind reflns	4643 (R(int) = 0.0567)	4926 (R(int) = 0.0680)
no. of reflns obsd	4552	4258
abs coeff (mm⁻¹)	semiempirical from equivalents	semiempirical from equivalents
R^a	0.0448	0.0395
$R_w{}^b$	0.1269	0.1110
GOF^c	1.114	1.033
largest peak in final diff map (e⁻/Å³)	2.118 and −3.651	2.573 and −4.982

$^a R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. ^{c} GOF $= S = [\sum[w(F_o{}^2 - F_c{}^2)^2]/(M - N)]^{1/2}$ where M is the number of reflections and N is the number of parameters refined.
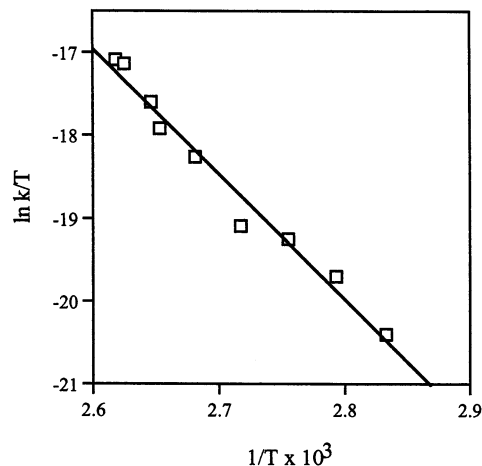
Figure 3. Eyring plot for the disappearance of **1** in the absence of air over the temperature range 80−108 °C.

3). The reaction proceeded in a similar way to form **6** (ca. 30%), ethene, and some insoluble material. In addition a new soluble rhenium complex was observed in the NMR spectrum (ca. 30% yield). Spectroscopic data are provided in the Experimental Section, but an X-ray diffraction study will be necessary before a structural identification can be confirmed.[25]

The disappearance of the dithiolate complex may be described by two competing first-order processes (Scheme 1). In this scheme the dehydrogenation reaction is independent of olefin extrusion, but relative yields suggest that the rate constants are comparable. The dehydrogenation might proceed through an

(25) Preliminary X-ray data from our lab suggest that "Cp′ReCl₂S₂" fragments may react with **1** or **6** to form dinuclear products with (μ-S) and either μ-dithiolate or dithiolene ligands.

Scheme 1

$$Cp'ReCl_2(SCH_2CH_2S) \rightarrow H_2C=CH_2 + "Cp'ReCl_2S_2"$$

$$Cp'ReCl_2(SCH_2CH_2S) \rightarrow Cp'ReCl_2(SCH=CHS) + "H_2"$$

Scheme 2

$$CpReCl_2(SCH_2CH_2S) \rightarrow H_2C=CH_2 + "Cp'ReCl_2S_2"$$

$$"Cp'ReCl_2S_2" + CpReCl_2(SCH_2CH_2S) \rightarrow$$

$$"Cp'ReCl_2(SH)_2" + Cp'ReCl_2(SCH=CHS)$$

$$\downarrow$$

precipitate
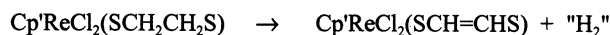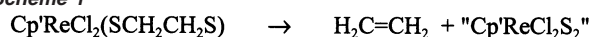
initial β-hydrogen elimination, although this type of reaction is not very favored for a five-membered chelate ring.[26] In addition, neither H_2 nor HCl has been detected as a product in the sealed tube reactions. A thermal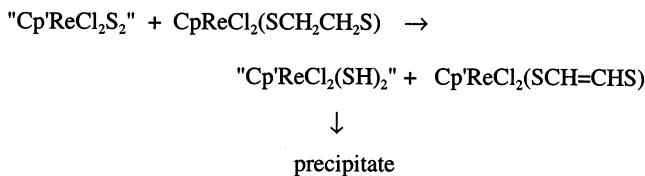ly induced β-hydrogen elimination reaction has been characterized for the 1,3-propanedithiolate analogue of **1**, $Cp'ReCl_2(SCH_2CH_2CH_2S)$. The rhenium product contains a chelated thioaldehyde ligand, $Cp'ReCl(\eta^1,\eta^2\text{-}SCH_2\text{-}CH_2CH=S)$, and in this case HCl is also formed.[27]

A second possibility is that the two processes may be sequential, as shown in Scheme 2. In this scheme, the olefin extrusion reaction is proposed to produce a reactive Re-disulfide or Re-bis(sulfido) intermediate, which serves as an oxidant for the dithiolate complex. This scheme seems more consistent with the observation that in the thermal reactions the formation of the dithiolene complex, **6**, is always accompanied by formation of some ethene, and the yield of **6** is always less than 50%. The reaction of **1** with $Cp'Re(SC_2H_4S)_2$, **4**, in toluene-d_8 at 105 °C in a sealed NMR tube also provides support for the formation of a reactive rhenium sulfide intermediate. As we reported above, **4** does not react when heated in toluene at 105 °C for several days. Control experiments also indicate that dithiolate/dithiolene ligand exchange reactions do not occur under these conditions. However when the mixture of **1** and **4** is heated for 1 day, we observe the formation of not only the dithiolene derivative $CpReCl_2(SC_2H_2S)$, **6**, but also a dehydrogenated product of **4**, $CpRe(SC_2H_4S)(SC_2H_2S)$, **9**, eq 4. The latter
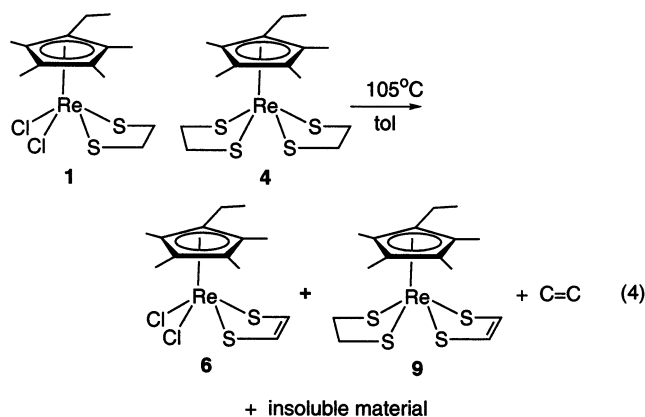
product is readily identified by its NMR spectrum, which includes a new singlet at 8.3 ppm, characteristic of the dithiolene

protons in these products. Additional yield and chemical shift data are given in the Experimental Section.

The reactive intermediate "$Cp'ReCl_2S_2$" is proposed to be a soluble discrete complex on the basis of the following experiment. The insoluble material generated during the course of the dehydrogenation of **1** was washed with toluene and then combined with a solution of **4**. When this reaction mixture was heated at 105 °C for 24 h, dehydrogenation of the dithiolate ligands of **4** was not observed. It therefore appears that "$Cp'ReCl_2S_2$" is a soluble species that reacts with **4** as the former is generated in solution.

Unfortunately, the sulfido and hydrosulfido complexes postulated in Scheme 2 are not observed by NMR spectroscopy after the high reaction temperatures required for olefin extrusion. However precedents for the role of metal sulfides in C−H cleavage reactions have been reported. In homogeneous systems, quite extensive C−H activation reactivity has been characterized for the conjugated Ru−S−S−Ru core in complexes of the type $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}S_2)]OTf$ and related derivatives.[28] For example the allylic C−H bond in many alkenes adds across the disulfide ligand to form new C−S and S−H bonds under mild conditions. In a second example the complex $[(CpMo\mu\text{-}S)_2(S_2CH_2)]_2^{2+}$ served as an oxidant for the conversion of benzylamine to benzylimine (hydrolyzed to benzaldehyde) and of benzyl alcohol to benzaldehyde.[29] In addition, heterogeneous rhenium and other metal sulfides function as dehydrogenation (and hydrogenation) catalysts.[30] Olefin hydrogenation mechanisms that involve S−H groups have been proposed for these surface reactions.[31] Sulfide sites with activity toward C−H activation should therefore also be considered in the mechanisms of the reverse dehydrogenation pathways. Additional studies were carried out to try to learn more about the formation of the reactive rhenium disulfide intermediate.

Reactions of 1 with Alkenes and Alkynes. The thermal reaction of **1** in toluene-d_8 was carried out in the presence of excess dry ethene in a sealed NMR tube in an effort to suppress the olefin elimination. We hoped to determine whether the dehydrogenation reaction occurred when competing olefin loss was inhibited. However under these conditions a new reaction was observed to compete with the dehydrogenation. After the tube was heated at 105 °C for several hours, the NMR spectrum showed the formation of a small amount (ca. 12%) of the dehydrogenation product, **6**. In addition, a new organic product that displayed a singlet at 2.41 ppm was identified as 1,4-dithiane by spectroscopic comparisons with an authentic sample. The reaction with excess ethene was found to proceed even at very mild temperatures, eq 5, and under these conditions no dehydrogenation product was observed.

No other rhenium products were observed in the NMR spectra for eq 5 provided that the ethene was thoroughly dried and degassed. A brown precipitate that formed during the course

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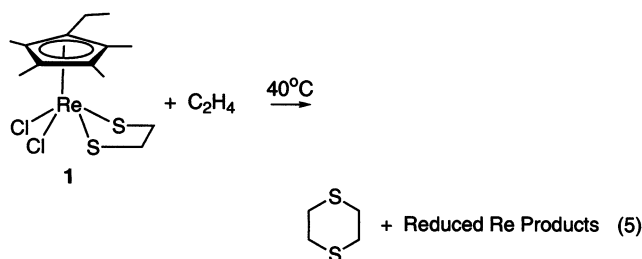
of this reaction in toluene-d_8 was redissolved in CDCl$_3$. The NMR spectrum showed very broad resonances in the Cp′ region over a temperature range of 25 to -50 °C, consistent with one or more reduced paramagnetic rhenium species. Although [Cp′ReCl$_2$]$_2$ is a known diamagnetic derivative,[32] this product was not detected in reaction 5, which was carried out in the presence of a large excess of ethene. Rather, the EI mass spectrum of the precipitate showed patterns at $m/z = 463$ and 435, consistent with the formulation Cp′ReCl$_2$(C$_2$H$_4$)$_n$, where $n = 1, 2$. When the paramagnetic material was exposed to air, the formation of Cp′ReOCl$_2$ was observed by NMR spectroscopy.

Complex **1** was also reacted with excess phenylacetylene at 60 °C. As shown in eq 6, the main rhenium-containing product was the 1-phenylethenedithiolate complex, **10**, which was isolated by column chromatography in 46% yield. A new organic product was also isolated and identified as 2,3-dihydro-5-phenyldithiin on the basis of its NMR spectrum and by comparing its mass spectrum with that of a standard sample. A second rhenium product that was isolated from the reaction mixture by chromatograpy was identified as [Cp′ReCl(PhCCH)$_2$]-Cl by NMR and mass spectroscopy. Related Re(III) bis-alkyne adducts have been reported previously.[32a]
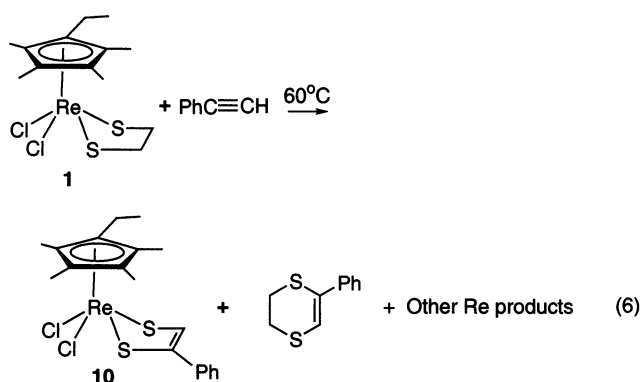
The rates of the reactions of **1** with 2 and 10 equiv of phenylacetylene were qualitatively compared by NMR spectroscopy, and the rates of formation of **10** and of the dithiin product were both found to increase as the concentration of the acetylene was increased. This suggests that both products are formed by an associative process. However no evidence for an intermediate in which the acetylene interacted with the sulfur sites or with the metal ion was detected in the NMR spectra. To our knowledge the formation of cyclic bis-thioethers by the reactions of an alkene or alkyne with a discrete dithiolate metal

complex has not been reported previously. However, a similar product has been trapped by the addition of an alkyne to the reaction of a tungsten carbonyl derivative with thiirane.[33] In a somewhat related system, the sequential reactions of Cp*ReO$_3$ with phosphine and an alkyne and then an oxidant were found to form free furan rings.[34]

Further Studies of the Dehydrogenation Reactions. When the thermal reactions of **1** were carried out in sealed evacuated NMR tubes, the dithiolene product **6** was formed only at $T > 80$ °C. However in additional studies we have found that **1** reacts with various oxidants under milder conditions to form **6**. For example, the reaction of **1** with excess dry oxygen (ca. 0.5 atm) proceeded slowly in the dark at 40 °C to cleanly form **6** as shown in eq 7. No intermediates were detected. Hydrogen
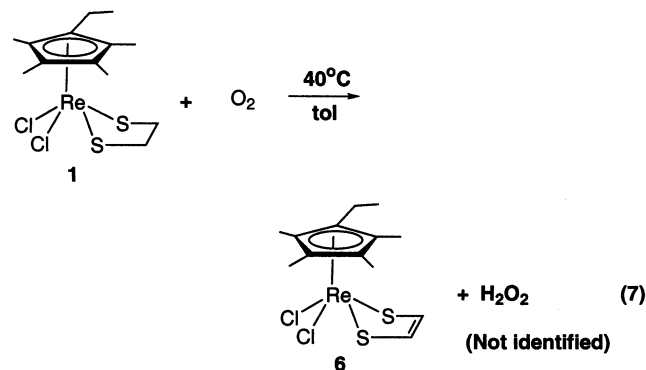
peroxide is proposed to be the second product, but it was not identified in the NMR spectrum of the sealed tube reaction. Although both the thermal dehydrogenation and the reaction with oxygen form **6**, the reactions appear to involve distinct pathways. To confirm that trace oxygen was not responsible for the thermal reactions, samples were subjected to extensive freeze−pump−thaw cycles (see Experimental Section), and kinetic studies at 108 °C were repeated. Kinetic data were found to be completely reproducible with previous runs, with $k = 1.4 \times 10^{-5}$/s.

In previous work, the reactions of certain Ni(II) and Pd(II) thiolate complexes with O$_2$ to form sulfonate and sulfoxide derivatives have been characterized.[35] The 1,2-diphenyldithiolate ligand in an electron-rich platinum(II) diimine complex was oxidized to the dithiolene complex under photochemical conditions using O$_2$ as the oxidant.[36] The reaction was proposed to proceed through singlet oxygen attack on the dithiolate sulfur ligand. However, reaction 7 was quite unexpected, since the cyclic voltammogram (see above) of the 16-electron Re(V) complex, **1**, suggests that the complex should be quite electrophilic and much less electron rich than the previously studied d^8 complexes. Further work will be necessary to explore the mechanistic features of reaction 7. The facile reaction with oxygen does seem to establish that the dithiolate ligand in **1** is

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quite susceptible to oxidation. This may be attributed in part to the stabilization resulting from the dithiolene/dithioglyoxal resonance forms.

Complex **1** also reacted with excess elemental sulfur in toluene-d_8 at 70 °C to form **6** and H_2S. A blank reaction of **1** heated under identical conditions in the absence of sulfur showed no change. However, unlike the reaction of **1** with O_2, the reaction with sulfur also formed other rhenium products, including $Cp'ReCl_2S_3$,[37] and the possible role of these products in the dehydrogenation process could complicate mechanistic interpretations of this reaction. The reaction of zinc polysulfide complexes with activated alkenes has been found to produce zinc dithiolene derivatives.[38] Initial formation of zinc alkanedithiolate complexes was proposed with subsequent ligand displacement and oxidation by sulfur.

Conclusions. The dithiolate ligands in the complexes $Cp'ReCl_2$-(dithiolate) show an unusual reactivity that includes both olefin extrusion and a dehydrogenation reaction at high temperatures. The dithiolate ligands can also be dehydrogenated at mild temperatures by reactions with certain oxidants. In addition the dithiolate complex undergoes an associative reaction with alkenes and alkynes under mild conditions to form free cyclic bis-thioethers. We have been particularly interested in the dehydrogenation reactions of the rhenium-dithiolates because we believe these transformations raise some intriguing mechanistic questions about the ease of C−H bond activation in dithiolate ligands and about the role of a rhenium disulfide (or bis-sulfido) complex in reactions with C−H bonds. Further work in our laboratory will address the problems of synthetic access to such derivatives and the scope of their reactions.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using strandard Schlenk techniques or a nitrogen-filled glovebox. Solvents were distilled under nitrogen from the appropriate drying agents. $Cp'ReCl_4$ was prepared from $Cp'ReO_3$ according to the literature report.[20] Dithiols and 1,4-dithiane were purchased from Aldrich and used without purification. Ethene was purified by a published procedure[39] by passage through a series of columns. The first column contained Drierite, the next two contained concentrated H_2SO_4, the fourth column contained KOH pellets, and the last contained activated carbon. The ethene was then condensed in a *n*-pentane−liquid nitrogen slush bath. When sufficient liquid ethene was collected, it was subjected to three freeze−pump−thaw cycles on a high-vacuum line by alternating the pentane slush bath during the thaw cycle with liquid nitrogen for the freeze cycle. After completion of these cycles, the ethene was carefully allowed to warm to generate the desired pressure needed for the NMR tube experiments and was transferred into the tube on the vacuum line. Extra dry oxygen was supplied by Airgas and passed through a dry ice/acetone trap immediately before use.

IR spectra were recorded on KBr pellets with a Nicolet Impact 410 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 spectrometer. Chemical shifts are reported relative to TMS. Mass spectra were obtained on a VG Autospec with EI/CI sources and liquid secondary ion MS capabilities or on a Hewlett-Packard 5989A electrospray ionization LC mass spectrometer. Visible spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammograms were obtained on acetonitrile solutions containing

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0.3 M Bu_4NBF_4 using a Cypress Systems potentiostat. A glassy carbon working electrode was used, and potentials are reported relative to the ferrocene couple, which was used as an internal standard. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Synthesis of $Cp'ReCl_2$(dithiolate) Derivatives. The dithiolate complexes were all synthesized by a similar procedure.

$Cp'ReCl_2(SCH_2CH_2S)$, 1. $Cp'ReCl_4$ (0.097 g, 0.20 mmol) was dissolved in ca. 20 mL of THF and treated with a THF solution containing 1,2-ethanedithiol (18 μL, 0.21 mmol). The solution was stirred for 20 h at room temperature, during which time it changed from deep red to brown and finally to dark green. The solvent was reduced to ca. 4 mL, a large excess of hexanes was layered on top, and the solution was stored at 0 °C for several hours. The resulting dark green precipitate was isolated from the solution and washed with 2 × 10 mL of cold hexanes. Yield: 0.063 g, 62%. ^1H NMR ($CDCl_3$): 4.01 (AA′BB′ pattern, 4 H, SCH_2CH_2S); 2.24 (q, 2 H, $CpCH_2$); 2.19 (s, 6 H, CpMe); 2.04 (s, 6 H, CpMe); 1.03 (t, 3 H, $CpCH_2CH_3$). ^1H NMR (500 MHz, tol-d_8): 3.39 (m, 4 H, SCH_2CH_2S); 1.90 (q, 2 H, $CpCH_2$); 1.79 (s, 6 H, CpMe); 1.61 (s, 6 H, CpMe); 0.62 (t, 3 H, $CpCH_2CH_3$). ^{13}C NMR ($CDCl_3$): 12.97, 13.14 (CpMe); 14.89 ($CpCH_2CH_3$); 22.27 ($CpCH_2$); 48.70 (SCH_2CH_2S); 102.86 (Cp); 105.19 (Cp); 112.58 (Cp). MS (FAB): 498 (P, 7%); 463 (P − Cl, 52%); 444 (base, $Cp'ReO(SC_2H_4S)$). UV/vis (λ_{max} in CH_3CN, nm (ϵ in M^{-1} cm^{-1})): 654 (2200); 470 (2000); and 338 (5400). $E_{1/2}$ or E_p (V vs Fc): +0.70 ($\Delta E = 158$ mV, $i_a/i_c = 1.4$); −0.83 (irrev); −1.52 ($\Delta E = 41$ mV); −2.13 ($\Delta E = 94$ mV). Anal. Calcd for $C_{13}H_{21}Cl_2S_2Re$: C, 31.31; H, 4.25. Found: C, 31.65; H, 4.13.

$Cp'ReCl_2(SCH_2CH(Et)S)$, 2. Yield: 70%. ^1H NMR (tol-d_8): 3.60 (m 2 H, $SCH_2CH(Et)S$); 3.45 (m, 1 H, $SCH_2CH(Et)S$); 1.96 (q, 2 H, $CpCH_2$); 1.821, 1.817, 1.636, 1.634 (4s, 3 H each, CpMe's, major isomer, ca. 80%); 1.85, 1.80, 1.66, 1.63 (4s, 3 H each, CpMe's, minor isomer, ca. 20%); 1.72 (m, $SCHCH_2CH_3$); 0.93 (t, 3 H, $SCHCH_2CH_3$); 0.64 (t, 3 H, $CpCH_2CH_3$). ^1H NMR ($CDCl_3$): 4.25, 4.15, 3.95 (3 m, 3 H, $SCH_2CH(Et)S$); 2.38 (q, 2 H, Cp CH_2); 2.23, 2.228, 2.074, 2.070 (4s, 3 H each, CpMe's, major isomer, ca. 80%); 2.26, 2.23, 2.09, 2.07 (4s, 3 H each, CpMe's, minor isomer, ca. 20%); 2.1 (m, $SCHCH_2$-CH_3); 1.19 (t, 3 H, $SCHCH_2CH_3$); 1.08 (t, 3 H, $CpCH_2CH_3$). ^{13}C NMR ($CDCl_3$) major isomer (ca. 80%): 12.95, 13.13, 15.38, 14.90 (CpMe); 22.63 ($CpCH_2CH_3$); 27.23 ($CpCH_2CH_3$); 22.65 ($SCHCH_2CH_3$); 29.73 ($SCHCH_2CH_3$); 52.64, 63.56 ($SCH_2CH(Et)S$); 102.70, 102.78, 105.05, 112.50, 112.58 (Cp). MS (EI): 524 (P − 2H, 90%); 489 (P − 2H − Cl, base). UV/vis (λ_{max} in CH_3CN, nm (ϵ in M^{-1} cm^{-1})): 644 (2400); 472 (2300); and 340 (5400).

$Cp'ReCl_2(SCHMeCHMeS)$, 3. Yield: 66%. ^1H NMR ($CDCl_3$) exo-cis isomer (70%): 4.25 (m, 2 H SCH); 2.2 (q, 2 H, CpCH2); 2.18, 2.02 (2 s, MeCp); 1.56 (m, 6 H, SCMe); 1.03 (t, 3 H, $CpCH_2CH_3$). Trans isomer (30%): 3.9 and 3.2 (2m, 2 H, SCH); 2.22, 2.19, 2.05, 2.02 (4s, 12 H, CpMe); 2.25 (q, 2 H, $CpCH_2$); 1.88, 1.82 (2d, 6 H, SCMe); 1.04 (t, 3 H, $CpCH_2CH_3$). ^1H NMR (tol-d_8) exo-cis isomer (70%): 3.82 (m, 2 H, SCH); 1.96 (q, 2 H, $CpCH_2$); 1.82, 1.63 (2s, MeCp); 1.31 (m, 6 H, SCMe); 0.64 (t, 3 H, $CpCH_2CH_3$). Trans isomer (30%): 3.38 and 2.84 (2m, 2 H, SCH); 1.86, 1.81, 1.67, 1.57 (4s, 12 H, CpMe); 1.42, 1.56 (2d, 6 H, SCMe); 0.65 (t, 3 H, $CpCH_2CH_3$). ^{13}C NMR ($CDCl_3$) major isomer (ca. 70%): 12.96, 13.14 (CpMe); 14.83 ($CpCH_2CH_3$); 22.30 ($CpCH_2CH_3$); 58.54 (SCH*Me*); 102.5, 105.0, 112.8 (Cp). MS (EI) m/z: 526 (P^+, 20%); 470 (P − C_4H_8, base). UV/vis (λ_{max} in CH_3CN, nm (ϵ in M^{-1} cm^{-1})): 636 (2200); 476 (2100); and 340 (5100). Anal. Calcd for $C_{15}H_{25}Cl_2S_2Re$: C, 34.21; H, 4.79. Found: C, 34.60; H, 4.77.

$Cp'Re(SC_2H_4S)_2$, 4. The procedure described above for **1** was followed, except that $Cp'ReCl_4$ was reacted with 2 equiv of ethanedithiol. ^1H NMR ($CDCl_3$): 3.22 (2m, 8 H, SCH_2CH_2S); 2.29 (q, 2 H, $CpCH_2$); 2.08 (s, 6 H, CpMe); 2.01 (s, 6 H, CpMe); 0.95 (t, 3 H, $CpCH_2CH_3$). ^1H NMR (tol-d_8): 3.15, 2.90 (2m, 8 H, SCH_2CH_2S); 1.81 (s, 6 H, CpMe); 1.65 (s, 6 H, CpMe); 0.65 (t, 3 H, $CpCH_2CH_3$). ^{13}C NMR ($CDCl_3$): 12.16, 12.39 (CpMe); 14.07 ($CpCH_2CH_3$); 21.02

(CpCH$_2$); 41.53 (SCH$_2$CH$_2$S); 99.95 (Cp); 103.33 (Cp); 105.43 (Cp). MS (EI): 520 (P, 47%); 492 (P − C$_2$H$_4$, 55%); 464 (base, Cp′ReS$_4$). UV/vis (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): approximately 640 (sh); 538 (3650); 432 (1350); and 312 (3800). $E_{1/2}$ or E_p (V vs Fc): −1.41 V (ΔE = 130 mV); E_a = +0.41 (irrev). Anal. Calcd for **5** + 1/2THF (THF observed in NMR spectrum of dried sample), C$_{16}$H$_{27}$O$_{1/2}$S$_4$Re: C, 35.47; H, 4.99. Found: C, 35.38; H, 4.88.

Cp′ReO(SCH$_2$CH$_2$S), 5. Cp′ReCl$_4$ (0.080 g, 0.0.17 mmol) was dissolved in 15 mL of CH$_2$Cl$_2$ and treated with water (50 μL, 2.78 mmol). The solution was stirred for 12 h, then evaporated to dryness under vacuum. The green residue (Cp′ReOCl$_2$) was redissolved in 20 mL of CH$_2$Cl$_2$, then treated with 1,2-ethanedithiol (15 μL, 0.18 mmol) and stirred for 24 h. The resultant brown solution was reduced to ca. 3 mL, then loaded on a silica gel column and eluted with CH$_3$CN. Yield: 0.062 g (83%). ^{1}H NMR (CDCl$_3$): 2.56 (2m, 4 H, SCH$_2$CH$_2$S); 2.28 (q, 2 H, CpCH$_2$); 2.00 (s, 6 H, CpMe); 1.98 (s, 6 H, CpMe); 1.08 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): 110.91, 108.87, 108.08 (Cp); 43.96 (SCH$_2$CH$_2$S); 19.50 (Cp*C*H$_2$CH$_3$); 14.77 (CpCH$_2$*CH$_3$*); 11.11, 10.85 (CpMe). MS (EI): 444 (P$^+$, base). UV/vis (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 698 (170); 464 (430); 366 (2000). $E_{1/2}$ or E_p (V vs Fc): +0.68 (irrev); −2.14 (ΔE = 74 mV). Anal. Calcd for C$_{13}$H$_{21}$OS$_2$Re: C, 35.17; H, 4.77; S, 14.46. Found: C, 35.73; H, 4.74; S, 13.20.

Cp′ReCl$_2$(dithiolene) Derivatives. Cp′ReCl$_2$(SCHCHS), 6. Complex **1** (0.090 g, 0.18 mmol) was dissolved in toluene, the solution was freeze−pump−thaw degassed three times, and the stopcock was closed. The reaction was heated in toluene for 24−48 h at 100−108 °C. The color changed from green to brown. The solvent was removed and the remaining product extracted with THF, then recrystallized from dichloromethane/hexanes. Analytically pure samples were obtained by silica gel chromatography with CH$_3$CN as the eluent. Yield: 0.034 g (38%). ^{1}H NMR (CDCl$_3$): 9.18 (s, 2 H, SCH); 1.84, 1.81 (2s, 12 H, CpMe); 1.78 (q, 2 H, CpCH$_2$); 0.96 (t, 3 H, CpCH$_2$*CH$_3$*). ^{1}H NMR (toluene-d_8): 8.42 (s, 2 H, SCH); 1.46 (q, 2 H, CpCH$_2$); 1.41, 1.40 (2s, 12 H, CpMe); 0.56 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): 165.01 (SCH); 109.80, 102.47, 101.38 (Cp); 20.01 (Cp*C*H$_2$CH$_3$); 14.23 (CpCH$_2$*CH$_3$*); 11.99, 11.31 (CpMe). MS (EI) *m/z*: 496 (P$^+$); 461 (P − Cl). UV/vis (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 478 (5100); 422 (2300); 346 (2400); 290 (3900); 226 (8900). E_p (V vs Fc): −1.15 (irrev). Anal. Calcd for C$_{13}$H$_{19}$Cl$_2$S$_2$Re: C, 31.44; H, 3.86; S, 12.91. Found: C, 31.56; H, 3.90; S, 12.00.

Cp′ReCl$_2$(SCHC(Et)S), 7. Yield: 22%. ^{1}H NMR (CDCl$_3$): 8.94 (s, 1 H, SCH); 3.50 (m, 2 H, SCCH$_2$); 1.80 (s, 6 H, CpMe); 1.78 (s, 6 H, CpMe); 1.75 (q, 2 H, CpCH$_2$); 1.43 (t, 3 H, SCCH$_2$*CH$_3$*); 0.97 (t, 3 H, CpCH$_2$*CH$_3$*). ^{1}H NMR (tol-d_8): 8.30 (s, 1 H, SCH); 3.02 (m, 2 H, SCCH$_2$); 1.448, 1.454, 1.462 (12 H, CpMe); 1.57 (m, 2 H, CpCH$_2$); 1.10 (t, 3 H, SCCH$_2$*CH$_3$*); 0.62 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$) (assignments based on DEPT experiments): 185.96 (S*C*Et); 159.70 (SCH); 109.27, 109.19, 102.35, 101.24, 101.16 (Cp); 29.84, 20.0 (CH$_2$); 17.29, 14.26 (Me); 11.90, 11.22 (CpMe). UV/vis (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 484 (3800); 420 (1400); 346 (1600); 292 (2900). MS (EI) *m/z*: 524 (P, 90%); 489 (P − Cl, base).

Cp′ReCl$_2$(SC(Me)C(Me)S), 8. Yield: 40%. ^{1}H NMR (CDCl$_3$): 3.01 (s, 6 H, SCMe); 1.78, 1.76 (2s, 12 H, CpMe); 1.71 (q, 2 H, CpCH$_2$); 0.96 (t, 3 H, CpCH$_2$*CH$_3$*). ^{1}H NMR (tol-d_8): 2.50 (s, 6 H, SCMe); 1.450, 1.449 (2s, 12 H, CpMe); 1.58 (q, 2 H, CpCH$_2$); 0.62 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$): 171.84 (S*C*Me); 109.19, 102.11, 100.86 (Cp); 22.93 (SC*C*H$_3$); 19.93 (Cp*C*H$_2$CH$_3$); 14.26, 11.84, 11.19 (CpMe). UV/vis (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 490 (1700); 402 (1100); 330 (2400); 232 (7100). MS (EI) *m/z*: 524 (P$^+$, 85%); 489 (P − Cl, base). Anal. Calcd for C$_{15}$H$_{23}$Cl$_2$S$_2$Re: C, 34.34; H, 4.43. Found: C, 34.17; H, 4.60.

Reaction of CpReCl$_2$(SC$_2$H$_4$S), 1, with Cp′Re(SC$_2$H$_4$S)$_2$, 4. Complexes **1** and **4** were dissolved in toluene-d_8 in a 2:1 ratio, and *p*-dimethoxybenzene (2−3 mg) was added as an internal standard. The NMR tube was freeze−pump−thaw degassed and sealed. The initial

NMR spectrum was recorded, and then the tube was heated at ca. 108 °C for 1 day. The NMR spectrum showed that all of **1** had reacted, but approximately 50% of **4** remained. Two rhenium products were observed in the spectrum: Cp′ReCl$_2$(SC$_2$H$_2$S), **6**, 24% based on initial **1**, and Cp′Re(SC$_2$H$_4$S)(SC$_2$H$_2$S), **9**, 30% based on initial **4**. A singlet for free ethene (5.26 ppm) was also observed. ^{1}H NMR for **9** (tol-d_8): 8.31 (s, 2 H, SC$_2$H$_2$S); 2.68, 2.38 (2m, 2 H each, SC$_2$H$_4$S); 1.515 (s, 6 H, CpMe); 1.504 (s, 6 H, CpMe); 0.60 (t, 3 H, CpCH$_2$CH$_3$).

In a second experiment, **1** (0.025 g) was dissolved in toluene, the solution was degassed three times, and the tube was sealed. The solution was heated at 100−105 °C for 1 day to form **6** and some insoluble material. The solution was removed, and the remaining precipitate was washed with toluene two times. A solution of **4** in toluene-d_8 was then added to the precipitate, and this solution was heated at 100−105 °C for 1 day. No significant reaction was observed for **4**. A small amount (<10%) of **6** was formed and only a trace (<5%) of **9**. These are attributed to the presence of a small amount (<10%) of **1** left in the precipitate after the washings.

Reaction of 1 with Ethene. In the glovebox a saturated solution of **1** in toluene-d_8 was gravity filtered through a fritted funnel to remove undissolved solids, then placed into a NMR tube equipped with a Schlenk adapter. The apparatus was closed, removed from the box, frozen with liquid N$_2$, then evacuated on a high-vacuum line. After thawing, the tube was charged with 0.6 atm of purified ethene. The tube was then frozen and flame sealed. The sample was heated to 67 °C in a constant-temperature bath, and reaction progress was periodically monitored by NMR. The reaction was complete after 20 h of heating, giving a pale solution and a brown precipitate. The only product observed in the ^{1}H NMR spectrum was *p*-dithiane. ^{1}H NMR (toluene-d_8): 2.42 (s). ^{13}C NMR (toluene-d_8): 29.26. MS (EI, *m/z*): 120, P$^+$. NMR data were compared to those of an authentic sample of *p*-dithiane: ^{1}H NMR 2.42; ^{13}C NMR 29.24. The solvent was removed from the brown precipitate, and this solid was dissolved in CDCl$_3$ under N$_2$. The NMR spectrum showed very broad resonances at 1.25, 1.6, 2.3, and 2.5 ppm. The resonances did not sharpen at lower temperatures (−50 °C). MS (ES): 463 (Cp′ReCl$_2$(C$_2$H$_4$)$_2$); 435 (Cp′ReCl$_2$(C$_2$H$_4$)). (Additional MS patterns were observed in the dimer region, e.g., 834 and 806.) Upon exposure to air, Cp′ReOCl$_2$ was rapidly formed and identified by NMR spectroscopy. ^{1}H NMR of Cp′ReOCl$_2$ (CDCl$_3$): 2.36 (q, 2 H, CpCH$_2$); 2.21 (s, 6 H, CpMe); 2.13 (s, 6 H, CpMe); 1.23 (t, 3 H, CpCH$_2$*CH$_3$*). MS (EI) *m/z*: 444 (P).

Reaction of 1 with Phenylacetylene. Phenylacetylene was dried by storage over molecular sieves prior to use. In a glovebox, **1** (0.060 g, 0.12 mmol) was dissolved in ca. 20 mL of dry THF in a Schlenk tube. Phenylacetylene (75 μL, 0.72 mmol) was added by syringe, and the tube was closed and removed from the box. The dark green solution was stirred for 5 days at 60 °C, during which time the color changed to deep red. The solution was reduced to ca. 5 mL and the product purified by silica gel chromatography. Fraction 1 was a yellow band eluted with toluene. The solvent was removed, and the solid was identified as 2,3-dihydro-5-phenyldithiin. Yield: 25−30%. ^{1}H NMR (CDCl$_3$): 7.64, 7.4, and 7.3 (m, Ph); 6.37 (s, 1 H, PhCC*H*); 3.26 (m, 4 H, SCH$_2$CH$_2$S). MS (EI) *m/z*: 194 (P, base); 166 (P − C$_2$H$_4$, 40%). Fraction 2 was a dark red band eluted with 5:1 toluene/acetonitrile. The solvent was removed, and the product was identified as Cp′ReCl$_2$-(SCHC(Ph)S, **10**. Yield: 0.033 g, 46%. ^{1}H NMR (CDCl$_3$): 9.44 (s, 1 H, SCH); 7.77 (m, 2 H, Ph); 7.46 (m, 2 H, Ph); 7.40 (m, 1 H, Ph); 1.86 (s, 6 H, CpMe); 1.85 (s, 3 H, CpMe); 1.84 (s, 3 H, CpMe); 1.8 (m, CpCH$_2$); 0.98 (t, 3 H, CpCH$_2$*CH$_3$*). ^{13}C NMR (CDCl$_3$) (assignments were made on the basis of DEPT experiments): 180.21 (SCH); 160.25 (S*C*Ph); 129.55, 128.57, 128.10 (Ph); 110.08, 109.79, 102.56, 101.57, 101.25 (Cp); 20.04 (Cp*C*H$_2$); 14.33 (CpCH$_2$*CH$_3$*); 12.04, 12.01, 11.41, 11.33 (CpMe). $E_{1/2}$ or E_p (V vs Fc): −1.12 (irrev); −1.37 (irrev); −2.2 (ΔE = 74 mV). MS (EI): 572 (P$^+$, 80%); 537 (P − Cl, base). Another red-orange Cp′Re-containing product was eluted from the column with acetonitrile and tentatively identified as [Cp′ReCl(PhCCH)$_2$]Cl. ^{1}H

NMR (CDCl$_3$): 1.76, 1.75 (2s, 12 H, Cp-Me's); 1.91 (q, 2 H, Cp-CH$_2$); 1.08 (t, 3 H, CpCH$_2$C*H$_3$*); 7.39, 7.23, 6.85 (3m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): 10.6, 10.8, 13.3 (Cp-Me); 19.2 (CH$_2$); 101.9, 103.7 (Cp); 127.0, 127.8, 130.0 (Ph). MS (ES): 610 (P, <5%); 575 (P − Cl, base).

Reaction of 1 with S$_8$. Two NMR scale solutions of **1** in toluene-d_8 were prepared in a glovebox as described above for the reaction with ethylene. A large excess of S$_8$ (ca. 25 mg) was added to one of the tubes, the second serving as a blank. The tubes were closed, removed from the box, freeze−pump−thaw degassed three times, and then sealed under vacuum. The tubes were heated to 70 °C in a constant-temperature bath, and reaction progress was monitored by ^{1}H NMR spectroscopy. Before heating, the NMR spectrum showed only the resonances for the starting material. After several days of heating, the blank showed no change, while the tube with S$_8$ showed resonances for three rhenium products: Cp′ReCl$_2$(S$_3$), 50%; CpReCl$_2$(SC$_2$H$_2$S), **6**, 30%; and an unidentified dithiolate complex Cp′Re(SC$_2$H$_4$S)(S$_x$), 20%. A singlet at 0.19 ppm was assigned to H$_2$S by comparison with an authentic sample. A second singlet at 2.71 was tentatively assigned to free dithiolate, but attempts to prepare a standard of this dianion in toluene-d_8 were unsuccessful. CpReCl$_2$(S$_3$): ^{1}H NMR (toluene-d_8): 1.99 (q, 2 H, CpCH$_2$); 1.56 (s, 6 H, CpMe); 1.42 (s, 6 H, CpMe); 0.67 (t, 3 H, CpCH$_2$C*H$_3$*). Cp′Re(SC$_2$H$_4$S)(S$_x$): ^{1}H NMR (toluene-d_8): 2.82, 2.30 (2m, 4 H, SCH$_2$CH$_2$S); 1.64 (s, 6 H, CpMe); 1.50 (s, 6 H, CpMe); 0.72 (t, 3 H, CpCH$_2$C*H$_3$*).

Reaction of 1 with O$_2$. Two NMR scale solutions of **1** in toluene-d_8 were prepared in a glovebox as described above. The tubes were closed, removed from the box, and then freeze−pump−thaw degassed three times on a high-vacuum line. To one of the tubes, 0.8 atm of dry O$_2$ was added, the other serving as a blank. The tubes were sealed and protected from light with aluminum foil. The samples were heated to 40 °C in a constant-temperature bath, periodically monitoring reaction progress with ^{1}H NMR. After several days of heating, no change was observed in the blank. The sample containing O$_2$ steadily produced Cp′ReCl$_2$(SC$_2$H$_2$S), **6**, over time. No other products were observed.

Kinetic Studies. All kinetic experiments were set up in a similar manner. In a glovebox, a solution of Cp′ReCl$_2$(dithiolate) in toluene-d_8 was placed in an NMR tube equipped with a Schlenk adapter. A small amount of *p*-dimethoxybenzene (ca. 2−3 mg) was added to this solution as an internal standard. The tube was closed, removed from the glovebox, frozen with liquid N$_2$, freeze−pump−thaw degassed one or two times, and flame sealed. An initial NMR spectrum was recorded; then the tube was heated in a constant-temperature bath. Reaction progress was monitored periodically by ^{1}H NMR spectroscopy by integrating the CpMe resonances of the starting complex. NMR integration values were referenced to the 4-H resonance of the p-DMB internal standard. Reactions at higher temperatures were followed through 3 half-lives, but for the slowest reactions at lower temperatures, initial rates were determined. Plots of ln A/A_{st} vs time were linear with correlation coefficients > 0.98; a sample plot is provided in the Supporting Information. First-order rate constants are given in Table 3. The color of the solution changed from green to brown, and a dark brown precipitate coated the sides of the NMR tube. Soluble products, which were identified by ^{1}H NMR spectroscopy, were Cp′ReCl$_2$-(dithiolene) (yields, ca. 40%) and free alkene. ^{1}H NMR data for the reactants and products in toluene-d_8 are included in the synthetic

descriptions above. To check for oxygen contamination, the procedure was repeated with more extensive degassing that included four freeze−pump−thaw cycles. Identical products and rate constants were observed.

Reaction of Cp′ReCl$_2$(SC$_2$H$_4$S) in CD$_3$CN. The same procedure was followed to determine the rate constant for thermal dehydrogenation at 108 °C. The color of the solution changed from green to brown, and a brown precipitate was observed. Soluble products were free ethene, Cp′ReCl$_2$(SC$_2$H$_2$S) (ca. 30%), and a new Re product (ca. 30%), not yet identified.[25] ^{1}H NMR of Cp′ReCl$_2$(SC$_2$H$_2$S) (CD$_3$CN): 9.24 (s, 2 H, SCH); 1.78 (s, 12 H, MeCp); 0.95 (t, 3 H, CpCH$_2$CH$_3$). ^{1}H NMR of unidentified product (CD$_3$CN): 2.29, 2.24 (2s, 12 H, CpMe); 1.16 (t, 3 H, CpCH$_2$CH$_3$). MS (ES): 854 (Cp′ReSC$_2$H$_2$S)$_2$; 826 (Cp′Re(S)-SC$_2$H$_4$S)$_2$; 800 (Cp′ReS$_2$)$_2$, base.

X-ray Diffraction Studies of Cp′ReCl$_2$(SCH$_2$CH$_2$S), 1, and Cp′ReCl$_2$(SCH=CHS), 6. Crystals were examined under a light hydrocarbon oil. Each selected crystal was mounted with silicone vacuum grease to a thin glass fiber affixed to a tapered copper mounting pin. This assembly was transferred to the goniometer of a Siemens SMART CCD diffractometer equipped with an LT-2A low-temperature apparatus operating at 142−143 K.

Cell parameters were determined using reflections harvested from three orthogonal sets of 20 0.3° ω-scans. Final cell parameters were refined using 6089 reflections chosen from 12 177 with $I > 10\sigma(I)$ from the entire data set for **1** and 7647 relections with $I > 10\sigma(I)$ chosen from 29 708 unmerged reflections in the entire data set of **6**. An arbitrary hemisphere of data was collected to 0.68 Å using 0.3° ω-scans exposed for 30 s in two correlated 15 s exposures. All data were corrected for Lorentz polarization and absorption.

Structure solution via direct methods in non-centrosymmetric space group $P2_12_12_1$ revealed the non-hydrogen structure of **1**, and structure solution via direct methods in centrosymmetric space group *Pbca* revealed the non-hydrogen structure of **6**. In each case, all non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the isotropic thermal parameter of the parent atoms of **1**. Absolute structures were determined using the method described by Flack.[40] The Flack parameter refined to 0.008(11). Hydrogen atoms of **6** were located via Fourier difference map and freely refined in subsequent cycles of least squares refinement. Significant features in the final difference electron density maps of **1** and **6** are clustered about the Re position and are likely to be absorption artifacts. Data are given in Table 4.

Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **1** and **6**, a sample first-order kinetic plot of ln [1]/[st] vs time, and control experiments to check for ligand exchange reactions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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