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Reactions of Dithiolate Ligands in Mononuclear Complexes of Rhenium(V). 2. $Cp''ReCl_2(\eta^2\text{-}SC_3H_6S)$ and Related Derivatives[†]

J. A. Kanney, B. R. Jagirdar, B. C. Noll, and M. Rakowski DuBois*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

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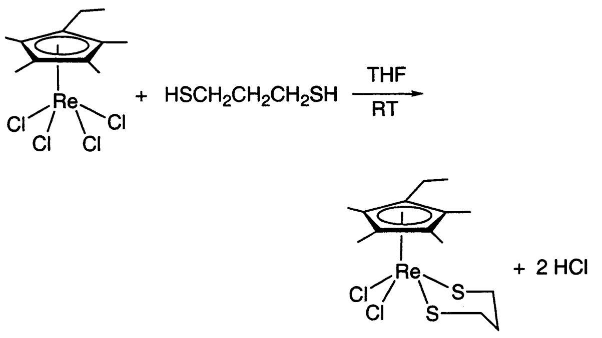
The syntheses and characterizations of $Cp''ReCl_2(SC_3H_6S)$, **1**, $Cp''ReCl_3(SCHMe_2)$, **2**, and $Cp''ReCl_2(SCHMe_2)_2$, **3**, are reported ($Cp'' = C_5Me_4Et$). Complex **2** has been characterized by an X-ray diffraction study, which confirms its mononuclear structure. Reactions of **1**, **2**, and **3** have been studied and compared with those characterized previously for $Cp''ReCl_2(SC_2H_4S)$. For example, the thermal reaction of **1** in toluene at 100 °C, results in the elimination of HCl and formation of a complex with a chelated thiolate/thialdehyde ligand, $Cp''ReCl(SCH_2CH_2CH{=}S)$, **5**. Complex **5** can also be synthesized at a lower temperature by the reaction of **1** with excess triethylamine. Spectroscopic characteristics and reactivity of **5** are reported.

Introduction

Metal thiolate complexes have been extensively studied,[1] and one area of focus has been the thermal reactions of the thiolate ligands to produce metal sulfido derivatives. In addition to the utility of this type of reaction in synthetic applications,[2−7] certain thermally induced reactions may have relevance to the industrial process of hydrodesulfurization.[8] However there are relatively few examples of reactions of coordinated thiolates that involve the retention and well-defined transformation of the hydrocarbon portion of the ligand.[9−12] We have recently reported that 1,2-alkanedithiolate complexes of rhenium of the formula $Cp''ReCl_2$(dithiolate) undergo a variety of reactions when heated in toluene, including dithiolate dehydrogenation (C−H cleavage) to form the corresponding $Cp''ReCl_2$(dithiolene) derivatives.[13] Alkene elimination (C−S cleavage) and alkanedithiolate coupling with alkenes and alkynes (Re−S cleavage) were also identified in this system. In this paper we report the syntheses and characterizations of related $Cp''Re$ complexes containing the 1,3-propanedithiolate ligand or monothiolate ligands. Studies of their thermal reactions reveal significant differences compared to those of the 1,2-dithiolate complexes.

Results and Discussions

Syntheses of Thiolate Complexes. The dithiolate complex $Cp''ReCl_2(SC_3H_6S)$, **1**, was synthesized by the reaction of $Cp''ReCl_4$ with 1 equiv of 1,3 propanedithiol in THF at room temperature, eq 1. The reaction solution changed color from purple to green, and the resulting product was isolated by THF/hexane crystallization. The ^1H NMR spectrum of **1** shows four multiplets for the dithiolate protons at 4.6 (2 H), 3.8 (1 H), 3.3 (2 H), and 2.4 (1 H), as expected for two exo and two endo



(1)

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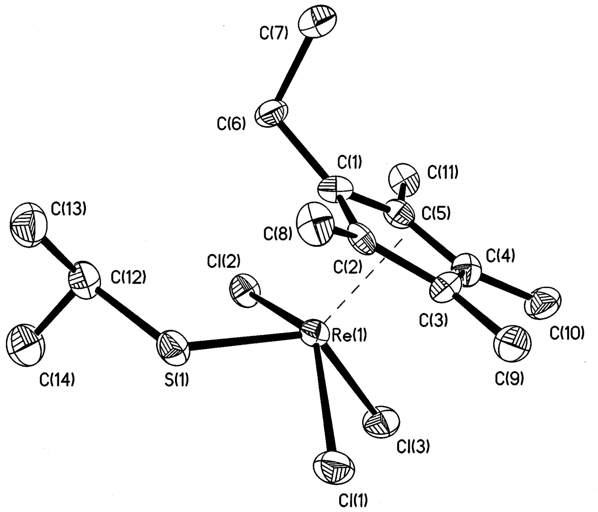


Figure 1. Perspective drawing and numbering scheme for Cp″ReCl$_3$(SCHMe$_2$), **2**. Thermal ellipsoids are shown at the 50% probability level.

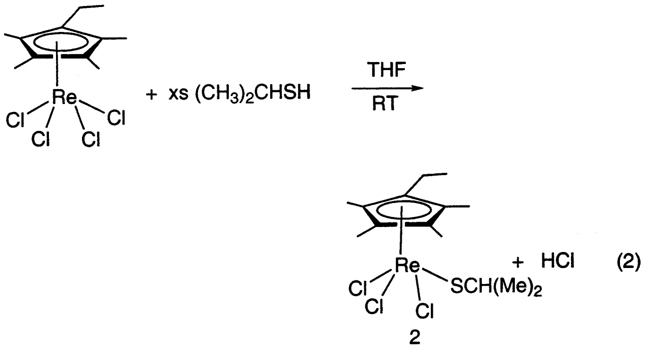
α-hydrogens and the inequivalent exo and endo β-hydrogens in the ligand. Other spectroscopic data are consistent with the proposed formulation of **1** and are presented in the Experimental Section. The cyclic voltammogram of **1** in acetonitrile shows an irreversible reduction with $E_{pc} = -0.867$ V vs Fc, as well as additional irreversible reductions at more negative potentials. The data are very similar to that observed for the related 1,2-ethanedithiolate complex Cp″ReCl$_2$(SC$_2$H$_4$S),[13] and **1** is assigned a similar mononuclear piano stool structure.

The reaction of Cp″ReCl$_4$ with 1 equiv of 2-propanethiol proceeds cleanly in THF solution to form the red-orange monodentate thiolate complex Cp″ReCl$_3$(SCHMe$_2$), **2**. This is the only major product formed even when the reaction is carried out with excess thiol reagent. Complete spectroscopic data are summarized in the Experimental Section. In the room-temperature ^{13}C NMR spectrum the resonances for the isopropyl methyl groups were found to be significantly broadened and inequivalent. In the variable-temperature 400 MHz ^{1}H NMR spectrum of **2**, the single doublet observed for the isopropyl methyls at room temperature is split into two doublets below the coalescence temperature of −25 °C, providing evidence for restricted rotation about the Re−S bond. The $\Delta G^{\ddagger}$ for this rotation is calculated to be 54 kJ/mol.[14] In the FAB mass spectrum of **2**, a pattern at $m/z = 516$ expected for the parent ion was observed. However the data also showed higher mass peaks centered at $m/z = 1032$ consistent with a dimer [Cp″ReCl$_3$(SCHMe$_2$)]$_2$. An X-ray diffraction study of **2** was carried out to definitely establish the nuclearity.

Single crystals of **2** were obtained by recrystallization from CH$_2$Cl$_2$/pentane. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are given in Table 1. The structure confirmed that **2** is a monomeric piano stool type complex. The dinuclear product, mentioned above, appears to be formed under the conditions of the mass spectroscopy experiment. The Re−S bond length of 2.2525(18) Å is quite short compared to those of other Re(V) thiolates (often 2.30−2.40 Å)[15] and is consistent with assignment of π-donating character to the thiolate sulfur. The relatively strong donor properties of the thiolate ligand are also reflected in the unsymmetrical coordination of the Cp″ ligand. Re−C bond lengths are 2.393(7) and 2.462(7) Å for C3 and C4 in positions opposite the thiolate ligand, while the other Re−C distances for the ligand range from 2.190(7) to 2.298(6) Å. Similar unsymmetrical Cp coordinations have been observed for other rhenium complexes containing π-donor ligands.[13,16]

Table 1. Bond Distances (Å) and Angles (deg) for (EtMe$_4$C$_5$)ReCl$_3$(SCH(CH$_3$)$_2$), 2

Bond Distances			
Re−S	2.2525(18)	Re−Cl(1)	2.3971(17)
Re−Cl(2)	2.3883(15)	Re−Cl(3)	2.3606(17)
S−C(12)	1.843(8)	C(12)−C(13)	1.514(12)
Re−C(1)	2.190(7)	Re−C(2)	2.215(6)
Re−C(3)	2.393(7)	Re−C(4)	2.462(7)
Re−C(5)	2.298(6)	C(1)−C(2)	1.464(8)
C(2)−C(3)	1.422(9)	C(3)−C(4)	1.414(9)
C(4)−C(5)	1.438(9)	C(5)−C(1)	1.441(9)
Bond Angles			
S−Re−Cl(1)	77.64(6)	S−Re−Cl(2)	86.17(6)
Cl(1)−Re−Cl(3)	83.18(7)	Cl(2)−Re−Cl(3)	80.88(6)
Re−S−C(12)	118.9(2)		



The intense purple complex Cp″ReCl$_2$(SCHMe$_2$)$_2$, **3**, was synthesized by the addition of 2 equiv of 2-propanethiol and 2 equiv of triethylamine to Cp″ReCl$_4$ in THF with strict exclusion of air and moisture, eq 3. Characterization data for **3** are consistent with the

$$\mathrm{Cp'ReCl_4} + 2\,\mathrm{(CH_3)_2CHSH} \xrightarrow[\mathrm{THF/RT}]{\mathrm{2\,NEt_3}} \mathrm{Cp'ReCl_2(SCHMe_2)_2} + 2\,\mathrm{HNEt_3Cl} \qquad (3)$$

proposed formulation and are included in the Experimental Section. Although cis and trans isomers might

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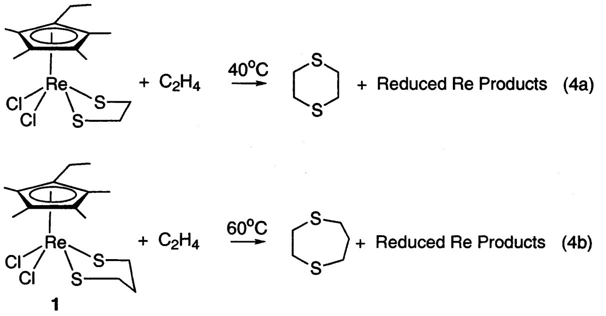
be expected, in the ^1H and ^{13}C NMR spectra of **3** at room temperature, resonances for only one isomer are resolved.

Reaction of $Cp''ReCl_2(SC_3H_6S)$, 1, with Ethene. In previous work we reported that the reaction of $Cp''ReCl_2(SC_2H_4S)$ with excess dry ethene proceeded at 60 °C in d_8-toluene to form the cyclic dithioether 1,4-dithiane and primarily reduced paramagnetic Re derivative(s), eq 4a.[13] The reaction of **1** with ethene was found to proceed in a similar way, again forming reduced rhenium compounds and a new cyclic dithioether, which was identified by NMR and mass spectral data, eq 4b. Although we are not aware of other reports of the displacement of a dithiolate ligand through coupling with an alkene or alkyne,[13] these displacement reactions appear to be fairly general for the $Cp''ReCl_2$(dithiolate) derivatives.



Further work has been carried out, primarily with reaction 4a, to identify the rhenium-containing products. As reported previously, mass spectral data on the paramagnetic product(s) showed *m*/*z* peaks consistent with the formulation of $Cp''ReCl_2(C_2H_4)_n$, $n = 1$ and 2.[13] Related diamagnetic Re(III) derivatives with one or two coordinated alkynes have been characterized previously.[17] In the electrospray mass spectrum of the toluene-insoluble solid from reaction 4a, peaks were also observed for dinuclear formulations such as $(Cp''ReCl)_2(SC_2H_4S)$, *m*/*z* 834, although resonances consistent with a diamagnetic product of this formulation were not observed in the NMR spectra in $CDCl_3$.

Chromatographic isolation of products was not successful, but recrystallization of the rhenium products from reaction 4a yielded brown crystals in low yield. An X-ray diffraction study on an isolated crystal indicated that it is a dinuclear Re(III) product of the formula $(Cp''Re)_2(\mu\text{-}Cl)_2(\mu\text{-}\eta^2\text{-}SC_2H_4S)$, **4**, as suggested by the mass spectrum. A perspective drawing of the centrosymmetric dimer is shown in Figure 2, and selected bond distances and angles are given in Table 2. An 18-electron count is observed for each rhenium ion in **4** with no metal−metal bond, but the four bridging atoms result in a short Re−Re distance. We have not found previous reports of structural data for neutral CpRe(III) dimers with four bridging ligands, but examples of dicationic Re(IV) dimers with four μ-sulfur ligands have been reported.[18] The Re−Re distance in **4** of 2.537(1) Å is shorter than those in $[(Cp''Re)_2(\mu\text{-}S_2)_2]^{2+}$ (2.61 Å) and in $[(Cp''Re)_2(\mu\text{-}S_2)(\mu\text{-}SR)_2]^{2+}$ (2.58 Å). The Re−S and Re−Cl distances (see Table 2) are typical for these ligands in bridging positions, and the values for the Re1−S−Re1A angle, 63.84(6)°, and the Re1−Cl−Re1A angle, 62.61(5)°, are similar.

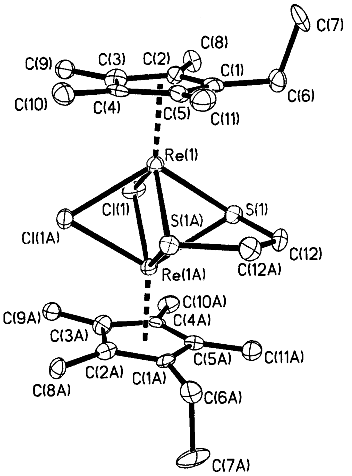
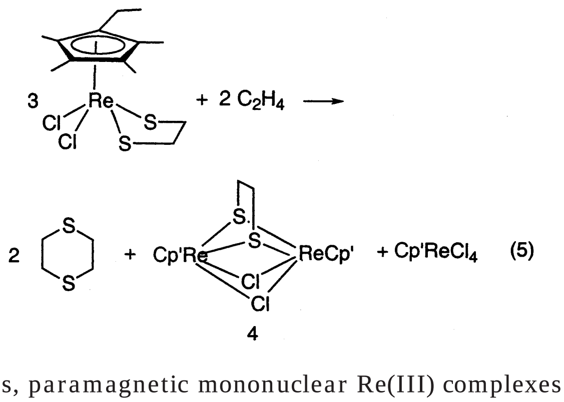


Figure 2. Perspective drawing and numbering scheme for $[Cp''Re(\mu\text{-}Cl)]_2(\mu\text{-}SC_2H_4S)$, **4**. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(EtMe_4C_5)ReCl]_2(\mu,\eta^2\text{-}SCH_2CH_2S)$, 4

	Bond Distances		
Re(1)−S(1)	2.406(2)	Re(1)−S(1A)	2.391(2)
Re(1)−Cl(1)	2.441(2)	Re(1)−Cl(1A)	2.441(2)
S(1)−C(12)	1.815(9)	C(12)−C(12A)	1.494(17)
Re(1)−C(1)	2.318(8)	Re(1)−C(2)	2.257(9)
Re(1)−C(3)	2.202(10)	Re(1)−C(4)	2.265(8)
Re(1)−C(5)	2.350(9)	Re(1)−Re(1A)	2.5367(7)
	Bond Angles		
S(1)−Re(1)−S(1A)	76.23(10)	S(1)−Re(1)−Cl(1)	72.53(8)
Cl(1)−Re−Cl(1A)	74.62(10)	Re(1)−S(1)−Re(1A)	63.84(6)
Re(1)−Cl(1)−Re(1A)	62.61(5)	S(1)−C(12)−C(12A)	113.5(3)

Complex **4** cocrystallizes with a molecule of $Cp''ReCl_4$ (not shown), and a balanced reaction of $Cp''ReCl_2(SC_2H_4S)$ with ethene can be written for these products, eq 5. However on the basis of spectroscopic characteristics, paramagnetic mononuclear Re(III) complexes of the formula $Cp''ReCl_2(\text{alkene})_{1\text{ or }2}$, formed under conditions of excess alkene, appear to be the predominant products formed in both reactions 4a and 4b.



Thermal Reaction of 1. When $Cp''ReCl_2(SC_2H_4S)$ is heated in d_8-toluene under vacuum at 100 °C, the alkenedithiolate complex $Cp''ReCl_2(SC_2H_2S)$ is formed in 35−45% yield, and free ethene is also observed in the NMR spectrum, eq 6.[13] A similar thermal reaction was carried out with **1** in order to compare products. The

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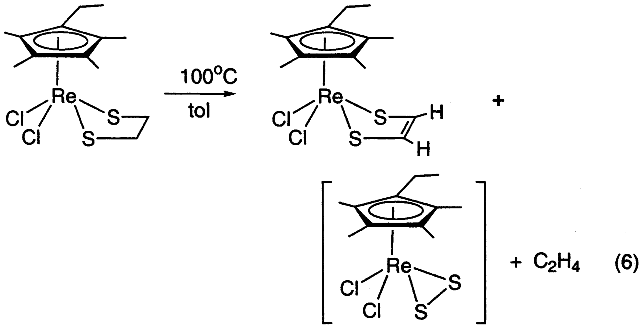
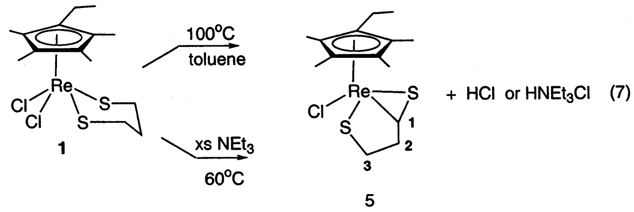
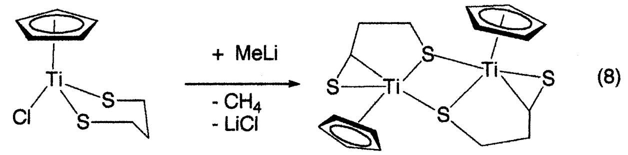


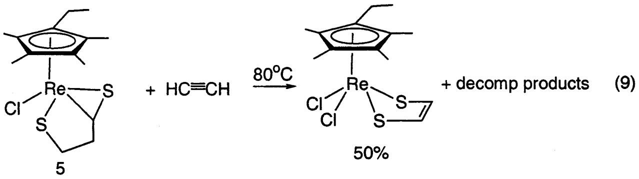
reaction proceeded to form a mixture, but a major product was identified, as shown in eq 7, as a complex with a chelated thiolate/thioaldehyde ligand, Cp″ReCl(SC_3H_5S), **5**. Complex **5** was isolated as a single diastereomer in ca. 30% yield by column chromatography. Since the thermal reaction proceeded with the elimination of HCl, the reactions of **1** with various bases were explored as an alternate route to **5**. The reactions of **1** with strong bases, such as MeLi or LiN($SiMe_3$)$_2$, produced small amounts of **5**, but were not very clean. However, the reaction of **1** with excess (ca. 5 equiv) NEt_3 in THF at 60 °C led to the formation of **5** in 80% isolated yield, eq 7.



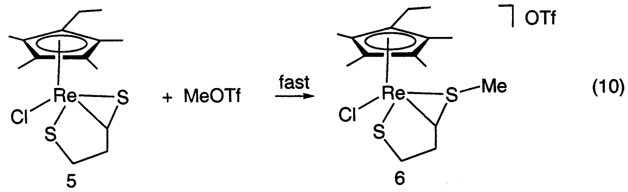
The ^1H NMR spectrum of **5** in $CDCl_3$ confirmed that the product is one of low symmetry. Four singlets assigned to inequivalent Cp-Me's are observed between 1.8 and 1.9 ppm. We have found that these upfield chemical shifts are quite characteristic of mononuclear Cp′Re complexes with sulfur donor ligands. The nature of the chelating sulfur ligand in **5** could be established unambiguously by a combination of ^1H and ^{13}C NMR and 2D-heteronuclear correlation experiments. Five multiplets are observed in the ^1H NMR spectrum, each corresponding to one hydrogen of the chelating sulfur ligand. DEPT experiments established that the multiplet at 6.12 ppm can be assigned to a methine proton, while four multiplets between 3.3 and 2.0 ppm are assigned to methylene hydrogens. The ^{13}C and HETCOR experiments establish that a carbon resonance at 67.15 ppm can be assigned to the methine carbon (C1, see eq 7), a resonance at 40.5 (C3) correlates with proton resonances at 3.28 and 2.10 ppm, and a carbon resonance at 24.6 ppm (C2) correlates with proton multiplets at 2.6 and 2.2 ppm. Other spectroscopic and analytical data for **5** support the proposed formulation and are included in the Experimental Section.

A similar type of transformation has been reported previously for a titanium 1,3-propanedithiolate derivative.[11] CpTiCl(SC_3H_6S) was treated with MeLi to form the dimeric η^2-thioaldehyde as shown in eq 8. This dimer reacted with a range of unsaturated organic substrates, including ketones, imines, and nitriles, by insertion into the thioaldehyde carbon−metal bond. Similar insertions were not observed for the rhenium thioaldehyde complex, **5**. For example, no evidence for reaction of **5** with benzophenone was observed over a period of 2 days at RT and 55 °C. Similarly no reaction was observed between **5** and excess acetylene at room temperature for 2 days. When this reaction was heated, the formation of Cp″$ReCl_2(SC_2H_2S)$[13] (ca. 50% yield) was observed in the NMR spectrum as the only major product, eq 9.





Sulfur Alkylation Reactions. A number of metal complexes containing the η^2-thioaldehyde or related ligands have been synthesized previously by various routes.[19] The nucleophilic character of the sulfur site in η^2-thioaldehyde complexes has been quite well established. Several examples of the alkylation of the sulfur atom in these types of derivatives have been reported previously,[19a,c−e] although an example of nucleophilic attack on the sulfur site of the ligand in [CpReNO(PPh_3)(η^2-$H_2C{=}S$)]$^+$ has also been reported.[19f] When **5** was reacted with an equivalent of methyl triflate, an instant color change from red to brown was observed, and a single product was isolated and identified as the sulfur-methylated complex [Cp″ReCl(SC_3H_5-SMe)]OTf, **6**, eq 10.



Once again ^1H and ^{13}C NMR along with heteronuclear correlation experiments establish the nature of the ligand. The S−Me resonance is assigned to a singlet at 2.24 ppm. The resonances assigned to the methine and methylene protons and corresponding carbon atoms in **6** are also assigned by 2D NMR experiments. The IR spectrum of **6** shows a strong absorption at 1270 cm^{-1}, consistent with a noncoordinating triflate counterion.[20] We expect that the methylated sulfur ligand remains coordinated to the rhenium as shown in eq 10 to give an 18-electron count at the metal ion.

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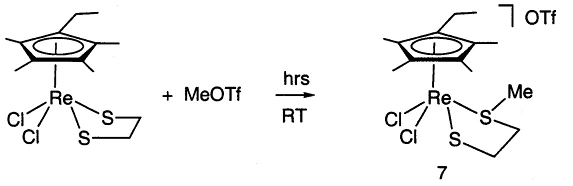
We wished to compare the relative nucleophilicity of the sulfur atom in the thioaldehyde complex **6** with that of the sulfur sites in the dithiolate complexes. The reaction of $Cp''ReCl_2(SC_2H_4S)$ with MeOTf proceeded gradually with a color change from green to red-orange over a period of 14 h to form the sulfur-alkylated product $[Cp''ReCl_2(SC_2H_4SMe)]OTf$, **7**, eq 11. The product was isolated and identified by spectroscopic data. ^1H and ^{13}C NMR data confirmed the low symmetry of the product. For example in the ^1H spectrum, four Cp−Me resonances and four multiplets for the ethanedithiolate protons were observed, as well as a singlet at 2.75 ppm for the SMe group. As described for the previous complexes, a 2D HMQC NMR experiment allowed correlations of the proton and carbon resonances. In addition, an HMBC NMR experiment showed that long-range coupling was observed between the SMe group and the ^{13}C resonance at 48.97 ppm, confirming the site of methylation and providing an assignment of the individual dithiolate carbons and protons, as indicated in the Experimental Section.



(11)

A slow reaction was also observed over a period of 12−15 h when methyl triflate was added to the propanedithiolate complex, **1**. ^1H NMR data on the crude product suggested that a similar sulfur-methylated product was formed. However, this product was significantly less stable than **7** and decomposed to multiple unidentified products over a period of a day or two, both in solution and in the solid state (under nitrogen). Our qualitative synthetic comparisons indicate that the thioaldehyde sulfur in **5** is considerably more nucleophilic than the dithiolate sulfurs in related Cp″Re derivatives.

Reactions of Monodentate Thiolate Derivatives. Examples of interesting thiolate reactivity have also been observed for certain monodentate thiolate metal complexes.[9−12] For example, methyl(alkylthiolate)zirconocene derivatives were converted to the corresponding thioaldehyde complexes under thermal conditions through the elimination of methane.[9] The thermal reactions of the rhenium complexes containing the isopropylthiolate ligand were studied to determine if transformations similar to those observed for **1** could be identified. When **2** was heated to 105 °C in d_8-toluene in a sealed NMR tube for 24 h, the ^1H NMR spectrum showed that ca. 50% of the starting material remained unchanged. Resonances were also observed for free isopropyl disulfide (35% yield), suggesting that some homolytic Re−S bond cleavage is promoted at elevated temperatures. Complex **2** reacted with triethylamine at 60 °C over a period of 36 h to give a complex mixture of decomposition products. An η^2- thioaldehyde complex could not be identified in this reaction.

The bis(isopropylthiolate) derivative, **3**, is proposed to be less acidic than the ligand in **2**, consistent with the replacement of an electron-withdrawing chloride by a more electron-donating thiolate ligand. No reaction of **3** was observed with triethylamine at 60 °C over a period of 24 h. However **3** showed lower thermal stability than **2**, and after heating in d_8-toluene at 105 °C for 24 h, only 5% of **3** remained. Isopropyl disulfide (∼20% yield) was the only product identified in the NMR spectrum. It seems clear that for the Cp″Re derivatives the kinetic stability of the chelating dithiolate ligands is a significant factor in permitting the clean transformations of these ligands at high temperatures.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using strandard Schlenk techniques. Solvents were distilled under nitrogen from the appropriate drying agents. Thiols were dried over anhydrous $MgSO_4$ and filtered before use, and triethylamine was distilled before use. $Cp''ReCl_4$, **1**, was prepared from $Cp''ReO_3$ according to the literature report.[15a] IR spectra were recorded as KBr pellets with a Nicolet Impact 410 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Varian Unity 300 and Varian Inova 500 spectrometers. Chemical shifts are relative to TMS. Heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple bond coupling (HMBC), field gradient heteronuclear single quantum coherence (gHSQC), and $^1H-^1H$ correlation spectroscopy (COSY) experiments were conducted on the Varian Inova instrument. 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 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 $Cp''ReCl_2(SC_3H_6S)$, 1. $Cp''ReCl_4$ (0.062 g, 0.129 mmol) was dissolved in ca. 15 mL of THF, and 1,3-propanedithiol (13 μL, 0.129 mmol) was added to the flask by syringe. The reaction was stirred at room temperature for 12 h, during which time the dark red solution turned brown, then finally intense green. The solvent was removed under vacuum, and the green solid was recrystallized with dichloromethane/hexanes. Yield: 0.054 g, 82%. ^1H NMR ($CDCl_3$): 4.64 (m, 2 H); 3.78 (m, 1 H); 3.33 (m 2 H); 2.41 (m, 1 H); 2.23 (q, 2 H, $Cp''CH_2$); 2.13 (s, 6 H, Cp″Me); 2.02 (s, 6 H, Cp″Me); 1.08 (t, 3 H, $Cp''CH_2CH_3$). ^{13}C NMR ($CDCl_3$): 109.3, 104.9, 102.8 (Cp); 35.48 ($SCH_2CH_2CH_2S$); 30.56 ($SCH_2CH_2CH_2S$); 21.52 ($Cp''CH_2$-CH_3); 14.36 ($Cp''CH_2CH_3$); 12.72, 12.60 (Cp″Me). Mass spectrum (EI) *m*/*z*: 512 (P^+, 5%); 476 (P−Cl), base). E_c (V vs Fc, 100 mV/s)): −0.87, −1.26 (irrev); −1.88, ($\Delta E = 155$ mv). Anal. Calcd for $C_{14}H_{23}Cl_2S_2Re$: C, 32.80; H, 4.53. Found: C, 33.35; H, 4.45.

Synthesis of $Cp''ReCl_3(S^iPr)$, 2. To a solution of $Cp''ReCl_4$ (0.15 g, 0.31 mmol) in degassed THF was added 2-propanethiol (60 μL, 0.64 mmol). The solution was stirred at room temperature overnight, during which time the solution became orange-red. The solution was vacuum-dried, and the residue was extracted with 3 × 10 mL of toluene. The extractions were combined, filtered, and reduced to ca. 5 mL. This was layered with a large excess of hexanes and stored at 0 °C for several hours. The resulting dark orange precipitate was isolated, washed with cold pentane, and vacuum-dried. Yield: 0.15 g, 92%. ^1H NMR (300 MHz, $CDCl_3$): 5.68 (sept, 1H, $SCHMe_2$); 2.30 (s, 6 H, CpMe); 2.23 (q, 2 H, $CpCH_2$); 2.11 (s, 6 H, CpMe); 1.53 (d, 6 H, $SCHMe_2$); 1.11 (t, 3 H, $CpCH_2CH_3$). ^{13}C NMR ($CDCl_3$) (assignments were made on the basis of HSQC data): 12.90, 12.82 (CpMe); 15.24 ($CpCH_2CH_3$); 22.00 ($CpCH_2$); 22.46, 24.84 (br, ^{i}Pr-Me); 50.92 ($SCHMe_2$); 106.97 (2 C, Cp); 107.13

(2 C, Cp); 114.91 (1 C, Cp). Variable-temperature ^{1}H NMR studies were carried out on a 400 MHz instrument in CD$_2$Cl$_2$ solvent over a temperature range of +30 to −80 °C. MS (FAB): 516 (P, 32%); 481 (P−Cl, 100%); 441 (Cp″ReCl$_3$, 28%). Vis spec. λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 494 (3000); 430 and 386 (sh). E_c (V vs Fc): −0.64, (irrev); −1.05 (irrev). Anal. Calcd for C$_{14}$H$_{24}$ReCl$_3$S: C, 32.52; H, 4.69. Found: C, 32.90; H, 4.69.

Synthesis of Cp″ReCl$_2$(S^{i}Pr)$_2$, 3. Cp″ReCl$_4$ (0.115 g, 0.024 mmol) was dissolved in 10 mL of THF, and a THF solution of 2-propanethiol (47 μL, 0.051 mmol) was added. The solution was stirred for 24 h at room temperature and the color changed to deep red-orange, indicating formation of **2**. The solution was then treated with a THF solution of NEt$_3$ (0.12 mmol). An immediate color change to dark blue-green was observed, and this developed into a deep purple over a period of 30 min. After stirring for 24 h, the solvent was removed under vacuum, and the residue was extracted with 4 × 15 mL of hexanes and filtered. The filtrate was reduced in volume under vacuum to ca. 15 mL and cooled to −78 °C in a dry ice/acetone bath for 1 h. Solvent was removed via cannula from the deep purple precipitate, which was then dried under vacuum. Yield: 0.077 g (57%). ^{1}H NMR (CDCl$_3$): 4.77 (septet, 2 H, SCHMe$_2$); 2.28 (q, 2 H, CpCH$_2$); 2.15 (s, 6 H, CpMe); 2.07 (S, 6 H, CpMe); 1.38 (d, 12 H, SCHMe$_2$); 1.11 (t, 3 H, CpCH$_2$CH$_3$). ^{13}C (CDCl$_3$): 11.98 (CpMe); 12.22 (CpMe); 14.17 (CpCH$_2$*C*H$_3$); 20.51 (CpCH$_2$);105.12 (Cp); 107.22 (Cp). Resonances for thiolate carbons were not sharp, but were observed in a gHMQC experiment: 41.61 (*C*HMe$_2$); 25.70 (CH*Me*$_2$). MS (FAB$^+$) m/z: 556 (P); 521 (P − Cl). UV/vis spec. (λ_{max} in CH$_3$CN, nm (ϵ in M^{-1} cm^{-1})): 574 (7000); 428 (3800); 262 (6600); and 226 (15000). E_p (V vs Fc): 0.771 (irrev); −0.957 (irrev); −1.179 (irrev). Anal. Calcd for C$_{17}$H$_{31}$ReCl$_2$S$_2$: C, 36.67; H, 5.62. Found: C, 37.14; H, 5.52.

Synthesis of Cp″ReCl(η^1,η^2-SCH$_2$CH$_2$CH=S), 5. Complex **1** (0.035 g, 0.068 mmol) was dissolved in ca. 15 mL of toluene, and the flask was sealed and heated to 105 °C for ca. 30 min. The color changed from dark green to red-orange. The solvent was removed under vacuum, and the remaining solid was dissolved in dichloromethane and purified by column chromatography on silica gel. The first minor fraction eluted with dichloromethane was not characterized. The second fraction, eluted with 2:1 dichloromethane/acetonitrile, contained the product. Yield: 0.011 g, 33%. ^{1}H NMR (CDCl$_3$): 6.20 (m, 1 H, SCH); 3.28 (m, 1 H, S*CH*$_2$CH$_2$CH=S, couples with H resonance at 1.99 ppm); 2.64 (m, 1 H, SCH$_2$*CH*$_2$CH=S, couples with H at 2.06 ppm); 1.99 (m, 1 H); 2.07 (q, 2 H, CpEt); 2.06 (m, 1 H); 1.86, 1.85, 1.814, 1.812, (4 s, 3 H each, CpMe); 1.09 (t, 3H, CpEt). ^{13}C NMR (CDCl$_3$) (assignments based on DEPT and 2D COSY experiments): 103.8, 103.3, 102.3, 100.3, 99.6 (Cp′); 67.15 (SCH); 40.53 (SCH$_2$); 24.61 (SCH$_2$*C*H$_2$CHS). MS (EI) m/z: 476 (P$^+$). Anal. Calcd for C$_{14}$H$_{22}$ClS$_2$Re: C, 35.32; H, 4.67. Found: C, 35.26; H, 4.92.

Alternate Synthesis of 5. Complex **1** (0.070 g, 0.137 mmol) was dissolved in ca. 10 mL of THF, and a THF solution of triethylamine (1.05 M, 0.65 mL, 0.685 mmol) was added. The reaction was stirred overnight in an oil bath at 60 °C. The color changed from green to red-orange. The solvent was removed under vacuum, and the product was extracted with several 15 mL portions of benzene. The extract was filtered and dried to yield **5**. Yield: 0.055 g, 85%.

Cp″ReCl(SCH$_2$CH$_2$CH(SCH$_3$))](OTf), 6. Complex **5** (0.041 g, 0.086 mmol) was dissolved in ca. 10 mL of CH$_2$Cl$_2$, and methyl triflate (10 μL, 0.090 mmol) was added. The solution immediately turned brown. The reaction was stirred at RT overnight. No further color change was observed. The solution was reduced to ca. 2 mL, and a large excess of hexanes was layered on top. The flask was stored in a freezer for several hours. The solution was decanted from the resulting dark brown precipitate, and the solid was dried. Yield: 0.034 g, 62%. To confirm that the formation of **6** was rapid, the reaction was monitored in CDCl$_3$ by NMR spectroscopy. After addition of MeOTf, **5** disappeared and an immediate precipitate formed. This was dissolved in CD$_3$CN and confirmed to be the product by NMR spectroscopy. ^{1}H NMR (CD$_3$CN) (assignments based on 2D-g-COSY and gHMQC experiments): 6.67 (m, 1 H, SCH); 3.36, 2.04 (2 m, 1 H each, SCH$_2$C*H*$_2$CH(SCH$_3$)); 2.55, 2.37 (2m 1 H each, SC*H*$_2$CH$_2$CH(SCH$_3$)); 2.24 (s, 3 H SCH$_3$); 2.12 (q, 2 H, CpEt); 2.05, 2.02, 1.99, 1.98 (4 s, 3 H each, CpMe); 1.19 (t, 3 H, CpEt). ^{13}C NMR (CD$_3$CN) (assignments based on 2D-gHMQC and DEPT experiments): 111.6, 110.2, 108.1, 106.7 (Cp); 67.97 (SCH$_2$CH$_2$*C*H(SCH$_3$)); 37.74 (SCH$_2$*C*H$_2$CH(SCH$_3$)): 31.27 (S*C*H$_2$CH$_2$CHSCH$_3$)); 23.30 (SCH$_2$CH$_2$CH(S*C*H$_3$)); 19.50 (Cp*C*H$_2$CH$_3$); 13.40 (CpCH$_2$*C*H$_3$); 11.56, 11.38, 11.02, 11.00 (CpMe). MS (EI) m/z: 491 (P$^+$, base); 476 (P$^+$ − CH$_3$, 20%); 455 (P$^+$ − Cl, 30%). Anal. Calcd for C$_{16}$H$_{25}$ClS$_3$F$_3$O$_3$Re: C, 30.00; H, 3.94. Found: C, 29.45; H, 4.20. IR (KBr) (cm^{-1}): 1272 s, 1150, 2, 1027 s, 917 vs, 885 vs, 636.

[Cp″ReCl$_2$(SCH$_2$CH$_2$SCH$_3$)]OTf, 7. The 1,2-dithiolate complex Cp″ReCl$_2$(SC$_2$H$_4$S) (0.084 g, 0.017 mmol) was dissolved in 5 mL of dichloromethane, and methyl triflate (0.029 mL, 0.026 mmol) was added. The color gradually changed from green to red-orange over a period of about 16 h. The solvent was removed under vacuum, and the resulting product was isolated in >90% purity as indicated by NMR spectroscopy. However, attempts to recrystallize **7** from distilled and degassed solvents led to decomposition of the product, and elemental analyses were not obtained. ^{1}H NMR (CD$_3$CN) (assignments based on HMQC, HMBC, and 2D-COSY experiments): 4.76, 4.11 (2 m, 1 H each, SC*H*$_2$CH$_2$SCH$_3$); 3.52, 3.43 2 (m, 1 H each, SCH$_2$C*H*$_2$SCH$_3$); 2.75 (s, 3 H, SCH$_3$); 2.43, 2.39, 2.26, 2.21 (4 s, 3 H each, CpMe); 2.35 (m, 2H, CpCH$_2$CH$_3$); 1.12 (t, 3 H, CpCH$_2$CH$_3$). ^{13}C NMR (CD$_3$CN): 111.1, 110.6, 110.3 (Cp); 54.11 (S*C*H$_2$CH$_2$SCH$_3$); 48.97 (SCH$_2$*C*H$_2$SCH$_3$); 24.13 (SCH$_2$CH$_2$S*C*H$_3$); 22.23 (Cp*C*H$_2$CH$_3$); 14.83 (CpCH$_2$*C*H$_3$): 13.38 (2 C, CpMe: 12.98, 12.67 (CpMe). MS (LSIMS) m/z: 513 (P$^+$ of cation, 40%). (Higher mass peaks were also observed at 528, (P + Me), 563 and 865). IR (cm^{-1}): 1264 vs, OTf$^-$.

Reaction of 1 with MeOTf. Complex **1** (0.066 g, 0.013 mmol) was dissolved in ca. 5 mL of dichloromethane, and MeOTf (24 μL, 0.021 mmol) was added. The reaction was stirred at room temperature for 14 h, during which time the color gradually changed from dark green to red-orange. The solvent was removed under vacuum to leave a dark red-orange residue formulated as Cp″ReCl$_2$(SCH$_2$CH$_2$CH$_2$SCH$_3$))]OTf. Attempts to purify the product by recrystallization or by column chromatography led to decomposition. ^{1}H NMR of crude product (CDCl$_3$): 5.94 (m, 1 H); 4.93 (m, 1 H); 3.61 (m, 1 H); 3.35 (m, 2 H); 2.76 (s, 3 H, SCH$_3$);2.45, 2.44, 2.35, 2.32 (4 s, 3 H each, CpMe); 2.38 (m, 2 H, CpCH$_2$); 1.18 (t, 3 H, CpCH$_2$CH$_3$).

Reaction of 1 with Ethene. Complex **1** (0.013 g, 0.025 mmol) was dissolved in d_8-toluene, and the solution was degassed on a high-vacuum line in a freeze−pump−thaw cycle. Prepurified ethene[13] (0.7 atm) was added at room temperature. The tube was flame sealed and heated to 60 °C for 3 days. The ^{1}H NMR spectrum of the resulting light brown solution showed no sharp resonances for rhenium products, but broad resonances assigned to paramagnetic products were observed. Spectroscopic data for these have been reported previously.[13] Resonances for the cyclic bis-thioether compound C$_5$H$_{10}$S$_2$ were observed. ^{1}H NMR (d_8-toluene): 2.75 (t, 4 H, SC*H*$_2$CH$_2$C*H*$_2$S); 2.45 (s, 4 H, SCH$_2$CH$_2$S); 1.58 (m, 2 H, SCH$_2$C*H*$_2$CH$_2$S). MS (EI) m/z: 134 (P$^+$).

Thermal Reactions of Cp″ReCl$_3$(S^{i}Pr), 2, and Cp″ReCl$_2$(S^{i}Pr)$_2$, 3. Complex **2** (0.012 g, 0.0023 mmol) was dissolved in d_8-toluene in an NMR tube, which was sealed under vacuum. The tube was warmed to 105 °C in a constant-temperature bath for 24 h. The ^{1}H NMR spectrum showed that **2** was the main diamagnetic complex present. Yield: 50%. Resonances for ^{i}PrSS^{i}Pr were also present and identified by comparison with an authentic sample. Yield: 35%. ^{1}H NMR of disulfide (d_8-tol): 1.145 (d, SCH*Me*$_2$); 2.75 (m, SC*H*Me$_2$).

The same procedure was followed for **3**. After 24 h, less than 5% of **3** remained in solution. Significant resonances for other Cp″Re products were not observed, but ^{i}PrSS^{i}Pr was formed in ca. 20% yield.

X-ray Diffraction Study of Cp″ReCl$_3$(S^{i}Pr), 2. Crystals were examined under a light hydrocarbon oil. The 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 949 reflections chosen from 7589 with $K > 10\sigma(I)$ from the entire data set for **2**. 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 $Pna2_1$ revealed the non-hydrogen structure. 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 atom. The absolute structure was determined using the method described by Flack.[21] The Flack parameter refined to 0.008(11). No significant features were present in the final difference electron density map of **2**.

X-ray Diffraction Study of 4. Single crystals were obtained by slow solvent diffusion of toluene into an acetonitrile solution of the precipitate deposited from reaction 4a. Cell parameters were determined using reflections harvested from three orthogonal sets of 20 0.3° ω scans. Final cell parameters were refined using 6483 reflections with $I > 10\sigma(I)$ chosen from 36 848 reflections in the entire data set. A hemisphere of data was collected to 0.68 Å using 0.3° ω scans measured for 30 s in two correlated 30-s exposures. During later stages of refinement, these data were truncated to 0.75 Å resolution because of poor intensity at higher resolution. One hundred percent of the unique data was measured. All data were corrected for Lorentz and polarization effects, as well as for absorption.

Structure solution via direct methods in centrosymmetric space group $P2/c$ revealed the unique component of this structure. The asymmetric unit is comprised of 1/2 Re dimer, **4**, one Cp″ReCl$_4$, and one badly disordered molecule of toluene. 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 position of the parent atom. The toluene is badly disordered; no model provided a good fit to the data. This site was analyzed with SQUEEZE,[22] which gave good agreement for toluene, and contributions from this region to the overall electron density were removed from the observed data. Largest peaks in the final difference electron density map, 2.30 e$^-$/Å^3, were clustered unreasonably close to Re positions. Selected crystallographic details for **2** and **4** are given in Table 3.

Table 3. Crystal Data for (EtMe$_4$C$_5$)ReCl$_3$(S$_2$CH(CH$_3$)$_2$), 2, and [(EtMe$_4$C$_5$)ReCl]$_2$(μ-η^2-SCH$_2$CH$_2$S)(EtMe$_4$Cp)ReCl$_4$, 4

	2	**4**
formula	$C_{14}H_{24}Cl_3ReS$	$C_{30}H_{44}Cl_5Re_2S$
fw (amu)	516.94	986.36
cryst syst	orthorhombic	monoclinic
unit cell dimens		
a (Å)	12.0082(12)	16.167(2)
b (Å)	11.8010(12)	8.5472(10)
c (Å)	12.4398(13)	22.286(2)
α (deg)	90	90
β (deg)	90	100.446(2)
γ (deg)	90	90
volume (Å^3)	1762.8 (3)	3028.5(6)
space group	$Pna2_1$	$P2/c$
Z	4	4
density, calc (mg/m^{-3})	1.948	2.163
λ(Mo Kα) (Å)	0.71073	0.71073
temp (K)	142(2)	140(2)
scan type	ω scans	ω scans
θ range	$2.38 < \theta < 31.24$	$2.38 < \theta < 28.28$
no. of ind reflns	4705 (R(int) = 0.0561)	7539 (R(int) = 0.1133)
no. of reflns obsd	4084	5331
abs coeff (mm^{-1})	semiempirical from equivalents	8.518
R^a	0.0360	0.0503
$R_w{}^b$	0.0886	0.1074
GOF^c	1.117	1.013
largest peak in final diff map (e$^-$/Å^3)	1.757 and −1.902	2.297 and −1.394

[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.

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

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