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Reactions of Thiiranes and a Thietane with a High Valent Metal Chloride

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Summary: Ethylene sulfide and propylene sulfide react with the high valent metal complex Cp′ReCl$_4$ (Cp′ = EtMe$_4$C$_5$) in THF solution to form a product with a chloroalkyl disulfide ligand of the formula Cp′Re(Cl)$_3$−S−S−CH(R)CH$_2$Cl (R = H or Me). In contrast, the thietane S(CH$_2$)$_3$ reacts with Cp′ReCl$_4$ to form a simple adduct, and no ring-opening reaction has been identified.

Introduction

The reactions of thiiranes with metal complexes have been explored in many different systems. A few examples of complexes containing the intact episulfide as a sulfur-donor ligand have been isolated and characterized.[1−3] However, in most reactions with low valent metals the reagent undergoes olefin elimination and serves as a sulfur source in the syntheses of mononuclear[4−8] or di- and polynuclear[9−12] metal sulfido complexes. Other metal complexes have been found to promote the ring opening of thiiranes without complete olefin elimination, and in these cases product complexes with thiolate or dithiolate ligands have been isolated.[12−14] Certain low valent metal carbonyl complexes have been found to catalyze the oligomerization of ring-opened thiiranes to produce cyclic disulfides.[3,15] However, we have not found previous reports on studies of the reactivity of thiiranes with high valent metal halide derivatives. During the course of our investigations into the syntheses of new rhenium complexes with thiolate and/or sulfido ligands,[16] we examined the reactions of Cp′ReCl$_4$ with thiiranes. We have identified a new type of thiirane-derived product which results from a combination of chloride-assisted ring opening and sulfur insertion reactions.

Results and Discussion

Reaction of Cp′ReCl$_4$ with Thiiranes. The reaction of the Re(V) derivative with excess ethylene sulfide in THF proceeded at room temperature to give a rapid color change from red to intense purple. The resulting product, **1**, was isolated and characterized by spectroscopic data, which confirmed that the thiirane was transformed in some way and coordinated to the rhenium ion. In the ^{1}H spectrum, in addition to resonances for the Cp′ ligand, two complex methylene multiplets were observed at 4.10 and 3.79 ppm (relative intensity 2 each), and the ^{13}C NMR spectrum of **1** shows two resonances at 43.9 and 42.6 ppm for inequivalent methylene carbons. The elemental analyses for **1** are consistent with a formulation that includes Cp′ReCl$_4$, C$_2$H$_4$S, and one additional sulfur atom. In the infrared spectrum a strong absorbance near 500 cm^{-1} that could be assigned to a Re═S stretch was not observed,[17] but a weak band was present at 507 cm^{-1}.

The reaction of Cp′ReCl$_4$ with propylene sulfide proceeded in an analogous manner to also form a deep purple product, **2**. The product appears to be a single regioisomer. In the ^{1}H NMR spectrum a single methyl doublet for the coordinated thiirane was observed at 1.6 ppm, and three multiplets assigned to methylene protons of this ligand were observed between 3.6 and 4.2 ppm. A single crystal of **2** was isolated from a dichloromethane/pentane solution, and the structure of the product was determined by an X-ray diffraction study.

A perspective drawing for **2** and selected bond distances and angles are given in Figure 1. The product is a monomeric piano stool derivative of Re(V) with an η^5-Cp′ ligand, three chlorides, and a monodentate chloroalkyl disulfide ligand of the formulation S−S−CH(Me)-CH$_2$Cl, eq 1. The alkyl disulfide ligand was disordered, and both enantiomeric forms of the ligand were modeled in the structure solution with relative occupancies of 64:36. Only one of the enantiomers is shown in Figure 1. The Re−S1 distance (2.221(2) Å) is significantly shorter than values observed for a single Re−S bond in

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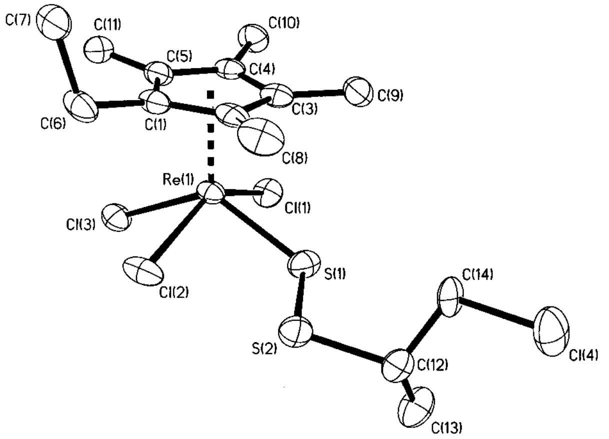
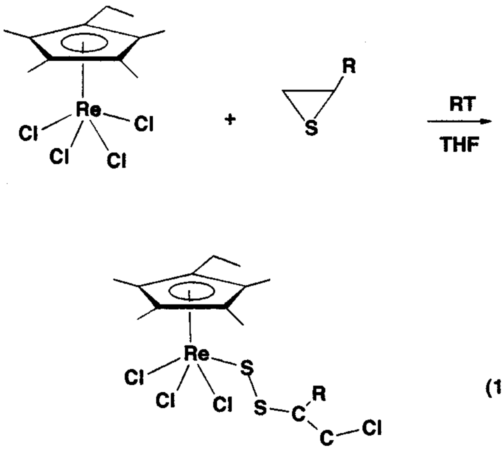


Figure 1. Perspective drawing of $(EtMe_4C_5)ReCl_3(S_2CH(CH_3)CH_2Cl)$, **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Re−S(1), 2.221(2); Re−Cl(1), 2.414(2); Re−Cl(2), 2.385(2); Re−Cl(3), 2.370(2); S(1)−S(2), 2.116(4); S(1)−Re−Cl(1), 77.22(7); S(1)−Re−Cl(2), 85.74(8); Re−S(1)−S(2), 110.97(16).

most Re(V) thiolate complexes (generally in the range 2.30−2.40 Å).[18−20] This suggests that the Re−S−S bond in **2** includes a ligand(p) → metal(d) π component.



1: R = H
2: R = Me

(1)

The mass spectra of **1** and **2** were interpreted only after the structure of **2** was completed. In the MALDI and FAB^+ mass spectra of **1**, no parent ion was observed, but a fragment at *m*/*z* 533 corresponded to the P−Cl ion. In addition evidence for higher molecular weight species was observed. For example, in the FAB spectrum peaks at *m*/*z* 593 and 653 correspond to 533 + 1 C_2H_4S and 533 + 2 C_2H_4S, respectively. In the MALDI spectrum *m*/*z* 620, corresponding to a formulation of P + 2 C_2H_4S, was also observed. Evidence for products with oligomerized thiiranes was not observed in the NMR spectra of isolated samples of **1** or **2**, and such products either are present only in trace amounts or are formed under the conditions of the mass spectrometry experiments. However, when reactions of $Cp'ReCl_4$ with excess thiiranes were carried out in benzene or toluene solutions, **1** and **2** were observed to undergo further reactions over a period of several hours. Spectroscopic data (see Supporting Information) suggest that the new products are mixtures of rhenium complexes with oligomeric ligands.

Studies of the Reaction Pathway. Complexes **1** and **2** appear to form by a chloride-assisted ring opening of a S-coordinated thiirane and an insertion of an additional sulfur atom to give the Re−S−S−R linkage, but the sequence of these steps is unknown. The reaction of $Cp'ReCl_4$ with 1 equiv of propylene sulfide in THF did not form an intermediate species. Instead **2** was observed in the product NMR spectrum as well as $Cp'ReOCl_2$,[21] in an approximate 1:1 ratio. In further attempts to determine the sequence of the reaction steps in the formation of **2**, $Cp'ReCl_4$ was reacted with excess ethylene sulfide in a nonpolar solvent (benzene-d_6 or toluene-d_8), and the reaction was monitored by NMR spectroscopy both at room temperature and at low temperature. Under these conditions, a single red intermediate was observed prior to the formation of **1**. The ^1H and ^{13}C NMR spectra of the intermediate at −45 °C, in particular the single carbon resonance for the coordinated ligand, indicate that this species does not contain a ring-opened thiirane (see Experimental Section for complete NMR data). The intermediate complex is assigned as a simple adduct of the intact thiirane, $CpReCl_4(SC_2H_4)$. A sulfur insertion product, $CpReCl_4(SSC_2H_4)$, seems unlikely, since only a trace amount of ethylene (<4%) was detected in the NMR spectra at low temperatures. When the solution is monitored at low temperature for longer periods or slowly warmed, the thiirane adduct converts to **1** with no further intermediates detected.

Reaction of $Cp'ReCl_4$ with Thietane. Nucleophile-assisted ring-opening reactions have been observed previously for metal complexes of thietane ligands.[22,23] To compare reactivity with that of the thiiranes, the reaction of $Cp'ReCl_4$ with trimethylene sulfide was studied. Addition of excess sulfur reagent to a THF solution of the rhenium complex resulted in a rapid color change at room temperature from red to orange. The resulting orange product, **3**, was isolated after several hours and characterized by both spectroscopic and X-ray diffraction techniques.

The molecular structure of **3** is shown in Figure 2 with selected bond distances and angles. The structure confirms that the intact thietane is weakly coordinated to $Cp'ReCl_4$ through a long Re−S bond of 2.5892(14) Å. The structure of **3** is similar to that reported for a trimethylphosphine adduct of Cp^*ReCl_4, which had a long Re−P bond distance of 2.607(3) Å.[24] The Re−Cl bond distances in **3** are all similar, with an average

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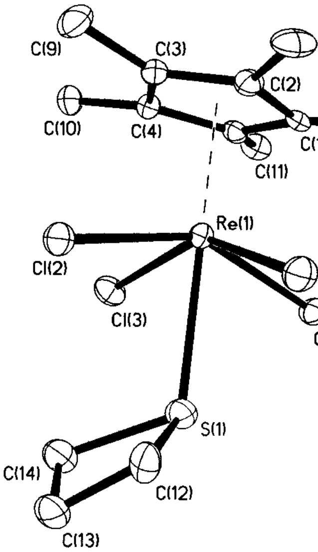

Figure 2. Perspective drawing of $(EtMe_4C_5)ReCl_4(S(CH_2)_3)$, **3.** Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Re−S(1), 2.5892(14); Re−Cl(1), 2.3876(13); Re−Cl(2), 2.4061(14); Re−Cl(3), 2.4045(13); Re(1)−Cl(4), 2.4167(13); S(1)−Re−Cl(1), 72.80(5); S(1)−Re−Cl(2), 77.42(5); S(1)−Re−Cl(3), 73.83(5); S(1)−Re−Cl(4), 73.01(5); Re−S(1)−C(12), 116.2(2); Re−S(1)−C(14), 114.4(2).

value of 2.404 Å. However, the chloride ligand that lies above the thietane (Cl(2)) is displaced upward relative to the other chlorides. The S−Re−Cl(2) angle is 77.42 (5)°, while the other S−Re−Cl angles average 73.21(5)°.

The ^1H NMR spectrum of **3** included four multiplets between 2 and 4.5 ppm that could be assigned to methylene protons of the coordinated ligand. The resonances were extremely broad at room temperature, but the spectrum sharpened and coupling was resolved at −35 °C. The coupling pattern observed at low temperature was simulated, and proton assignments are given in the Experimental Section. When 1 equiv of the thietane was added to **3** in $CDCl_3$, no change in chemical shifts was observed, but the NMR signals of both the free and coordinated rings were broadened. The broadened signal and loss of coupling for the free thietane suggest that an exchange process between free and coordinated ligand is occurring. The fluxional process responsible for the broad room-temperature resonances in **3** in the absence of excess ligand is attributed to an inversion at the sulfur center. The experiments with free thietane show that the inversion may occur through dissociation of the ligand from the metal ion.

Attempts were made to prepare a complex containing a ring-opened thietane ligand. We reasoned that in a more polar solvent chloride dissociation from **3** might promote the ring-opening reaction. However, when **3** was stirred in dried acetonitrile solution under nitrogen under various conditions, we observed gradual decomposition of **3** and eventual formation of $Cp'ReOCl_2$. A similar slow decomposition of solutions of $Cp'ReCl_4$ through reaction with trace water is also observed, even in dried distilled solvents. The addition of LiCl to a solution of **3** resulted in a rapid reaction, but clean formation of discrete Cp′Re products was not observed.

Experimental Section

All syntheses and manipulations were carried out under an inert atmosphere of prepurified nitrogen using standard Schlenk techniques. Reagent grade THF, toluene, and diethyl ether were deoxygenated and dried by distillation over sodium benzophenone under nitrogen prior to use. ^1H and ^{13}C NMR spectra were recorded on Varian VXR300s and Varian Unity Inova-500 spectrometers, and the data are listed in ppm relative to TMS. Visible spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer. IR spectra were measured on a Perkin-Elmer Model 1600 FTIR spectrometer using KBr pellets. 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. $Cp'ReCl_4$ was synthesized as described previously.[21] Thiiranes and thietane were purchased from Aldrich and dried over anhydrous $MgSO_4$ prior to use. Elemental analyses were obtained from Desert Analytics, Tucson, AZ.

$Cp'ReCl_3(SSCH_2CH_2Cl)$ (1). $Cp'ReCl_4$ (110 mg, 0.23 mmol) was dissolved in ca. 30 mL of THF and treated with ethylene sulfide (35 μL, 0.59 mmol). The solution immediately went from red to very light green upon ethylene sulfide addition, then darkened to intense purple over a period of about 6 min. The solution was stirred for ca. 14 h at room temperature, then the solvent was removed in vacuo and the solid was recrystallized with dichloromethane/pentane to give a very dark purple powder. Yield: 75 mg, 57%. ^1H NMR (500 MHz, $CDCl_3$): δ 4.10 (m, 2H, CH_2), 3.79 (m, 2H, CH_2), 2.21 (s, 3H, CpMe), 2.14 (s, 3H, CpMe), 2.07 (s, 6H, CpMe), 1.12 (t, 3H, $CpCH_2\mathit{Me}$). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ 113.7 (Cp), 108.1 (Cp), 107.8 (Cp), 107.0 (Cp), 43.9, 42.6 (SCH_2 and CH_2Cl), 20.5 ($CpCH_2$), 14.5 (CpMe), 12.2 (CpMe), 12.1 (CpMe), 11.6 (CpMe). UV−visible (λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$), dichloromethane): 534 (4420), 420 (1345). MALDI mass spectrum: m/z 533 ($P^+ - Cl$), 518 ($P^+ - CH_2Cl$). (Higher mass peaks were also observed; see discussion in text.) IR (KBr): ν_{S-S} 507 cm^{-1}. Anal. Calcd for $C_{13}H_{21}ReS_2Cl_4$: C, 27.42; H, 3.72; S, 11.26. Found: C, 27.95; H, 3.58; S, 11.77.

$Cp'ReCl_3(SSCH(CH_3)CH_2Cl)$ (2). A procedure similar to that described for **1** was followed. Recrystallization from CH_2Cl_2/hexanes usually resulted in a dark purple oily solid. In most cases attempts to isolate the product as a powder were unsuccessful, but repeated chromatography on a silica gel column eluting with 6:1 CH_2Cl_2/CH_3CN and subsequent recrystallization from CH_2Cl_2/pentane produced a small amount of dry powder. ^1H NMR (500 MHz, $CDCl_3$): 4.15, 3.90, 3.75 (3 m, 3 H, $SCHCH_2$); 2.20 (s, 3H, CpMe); 2.13 (s, 3H, CpMe); 2.06 (s, 6H, CpMe); 1.57 (d, 3H, Me), 1.12 (t, 3H, $CpCH_2C\mathit{H}_3$). Visible spectrum (λ_{max} in CH_3CN): 537, 426, 360 (sh). MALDI mass spectra, m/z: 551 (P − S); 620 (P + 2 C_2H_4S). IR (KBr): ν_{S-S} 509 cm^{-1}. Anal. Calcd for $C_{14}H_{23}Cl_4S_2Re$: C, 28.82; H, 3.97; S, 10.99. Found: C, 29.19; H, 4.14; S, 12.05. The analyses are consistently slightly high, and this suggests that a small amount of oligomerized thiirane may be present in the isolated product (see discussion of MS data in text). For example, data calcd for **2** + $[C_3H_6S]_{1/4}$: C, 29.42; H, 4.10; S, 11.98.

Preparation of $Cp'ReCl_4(SC_3H_6)$ (3). $Cp'ReCl_4$ (115 mg, 0.24 mmol) was dissolved in ca. 25 mL of THF, then treated with 15 mL of a THF solution containing trimethylene sulfide (26 μL, 0.36 mmol, 1.5 equiv). The solution immediately changed from red to a light orange-red color. After about 14 h the solvent was removed in vacuo and the resulting solid was recrystallized with dichloromethane/pentane, yielding an orange-red powder, **3.** Yield: 0.094 g, 71%. ^1H NMR (500 MHz, $CDCl_3$): δ 4.3 (b, 2 H); 3.4 (b, 2 H); 2.6 (b 1 H); 2.3 (b, 1 H); 2.13 (s, 6H); 2.11 (q, 2H); 2.06 (s, 6H); 1.23 (t, 3H). ^1H NMR, toluene-d_8, −35 °C): 4.3 (app q, α endo H); 3.4 (app t, α exo H); 2.6 (app sex, β endo H); 2.0 (app q, β exo H). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ 118.1 (Cp), 115.9 (Cp), 113.1 (Cp), 38.7

Table 1. Crystal Data for $(EtMe_4C_5)ReCl_3(S_2CH(CH_3)CH_2Cl)$, 2, and $(EtMe_4C_5)ReCl_4S(CH_2)_3$, 3

	2	**3**
formula	$C_{14}H_{23}Cl_4ReS_2$	$C_{14}H_{23}Cl_4ReS$
fw (amu)	583.44	551.38
cryst syst	triclinic	monoclinic
unit cell dimens		
a (Å)	6.702(5)	14.291(2)
b (Å)	11.957(7)	8.532(2)
c (Å)	12.070(7)	14.787(3)
α (deg)	90.04 (2)	90
β (deg)	96.64(3)	105.297(12)
γ (deg)	98.03(3)	90
volume (Å^3)	951.2(11)	1739.1(6)
space group	$P\bar{1}$	$P2_1/c$
Z	2	4
density, calcd (mg/m^{-3})	2.037	2.106
λ(Mo Kα) (Å)	0.71073	0.71073
temp (K)	150(2)	141(2)
scan type	ω scans	ω scans
θ range	$1.70 < \theta < 29.00$	$1.48 < \theta < 31.22$
no. of ind reflns	4984 (R(int) = 0.0539)	5293 (R(int) = 0.059)
no. of reflns obsd	11 500	15 806
abs coeff (mm^{-1})	multiscan	7.710
R^a	0.0551	0.0542
$R_w{}^b$	0.1122	0.0960
GOF^c	1.036	1.012
largest peak in final diff map (e$^-$/Å^3)	2.003 and −2.934	2.442 and −2.371

[a] $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. [3] GOF $= S = [\sum[w(F_o{}^2 - F_c{}^2)^2]/(M - N)]^{1/2}$ where M is the number of elections and N is the number of parameters refined.

(SCH$_2$), 19.6, 18.5 (SCH$_2$*C*H$_2$, CpCH$_2$), 12.8 (CpMe), 12.2 (CpMe), 11.7 (CpMe). MS (EI): m/e 549 (M$^+$, very weak), 514 (M$^+$ − Cl, very weak), 440 (M$^+$ − [SC$_3$H$_6$] − Cl). UV−visible (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), dichloromethane): 504 (219), 700 (61). Anal. Calcd for $C_{14}H_{23}ReSCl_4$: C, 30.49; H, 4.18; S, 5.81. Found: C, 30.29; H, 4.18; S, 5.45.

X-ray Structures of 2 and 3. Crystals were mounted using a small amount of silicone grease to a thin glass fiber affixed to a tapered copper mounting pin. This assembly was placed into the cold stream of a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus.

For each structural determination, unit cell parameters were determined on indexing reflections harvested from three orthogonal sets of 20 0.3° ω scans. An arbitrary hemisphere of data was collected to 0.68 Å again with 0.3° ω scans, each exposed for 30 s using the correlated scan method. All data were corrected for Lorentz and polarization effects. For **2**, data were corrected for absorption using redundant reflections,[25] and for **3** an empirical correction based on multiple scans of equivalent reflections was employed.

Structure solutions via direct methods or the Patterson heavy atom method revealed the entire non-hydrogen structures. Hydrogen atoms were placed at a calculated geometry and allowed to ride on the parent atom during subsequent cycles of least-squares refinement. Non-hydrogen atoms were refined using anisotropic parameters for thermal motion. Selected details are given in Table 1, and complete descriptions of the structural studies are included in Supporting Information.

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Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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