One Step Closer to Structural Models for HDS Catalysts: Thienyl–Oxo Complexes of Re(V)

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The present investigation focuses on thiophene derivatives of oxometal centers with low d-electron counts. Treatment of a THF slurry of $ReOCl_3(PPh_3)_2$ with thienyllithium reagents afforded $Li(THF)_nReO(thienyl)_4$ where thienyl is $2\text{-}C_4H_3S$, $2\text{-}MeC_4H_2$, $2\text{-}C_8H_5S$ (benzothienyl), and $2\text{-}C_{12}H_7S$ (dibenzothienyl). In contrast to the previously reported low-valent derivatives these species are reactive toward protic and oxidizing reagents. Electrochemical studies demonstrate that these Re^V complexes undergo oxidation at mild potentials. Crystallographic analyses of $Li(THF)_3ReO(C_4H_3S)_4$ and $Li(THF)_4ReO(C_8H_5S)_4$ indicate a square pyramidal Re center with the four thienyl ligands tilted in a pinwheel arrangement. Studies on $Re(2\text{-}C_4H_3S)(CO)_5$ reveal that it is stable toward hydrolysis.

Introduction

Hydrodesulfurization (HDS) entails the hydrogenolysis of carbon–sulfur bonds to give H_2S and a sulfur-free hydrocarbon.[1] This process is employed on a massive scale industrially to purify petroleum feedstocks.[1] Because of its economic implications, the mechanism of the process has been heavily studied, focusing primarily on the interaction of thiophenic substrates with heterogeneous catalysts. Recent years have witnessed a number of soluble model complexes that simulate structural and mechanistic features of the catalytic system.

One obvious deficiency with current model systems is that the spectator ligands (arenes, cyclopentadienyls) are not representative of the pool of ligands available to the industrial catalysts, which consist of partially sulfided metal oxides.[1] These considerations led us to undertake the preparation of thiophene derivatives of oxometal centers with low d-electron counts. We chose rhenium complexes since the oxo–organorhenium chemistry is well developed[3] and since Re compounds are of proven activity in HDS catalysis.[4] The present efforts are of further interest as previous work on soluble metal–thiophene ensembles has focused almost exclusively on thiophene derivatives of metals with d^6 or d^8 configurations.[2] It is unlikely that such electron configurations are relevant to functioning industrial catalysts.

A second motivation derives from our interest in developing the chemistry of complexes with multiple thienyl ligands. The rich chemistry of polyalkyl and polyaryl metal complexes suggests that study of polythienyl complexes might be fruitful. By comparison with benzene, thiophene is more reactive toward electrophiles and more acidic, as indicated by its ready deprotonation with amides.[5] These characteristics suggest that polythienyl compounds should display novel reactivity. Known compounds with more than one thienyl ligand include $Zn(C_4H_3S)_2(dioxane)$[6] and the metallocene complexes $(C_5H_5)_2M(C_4H_3S)_2$ (M = Ti, Zr, Hf, Nb, W).[7] Metal thienyl complexes

Scheme 1
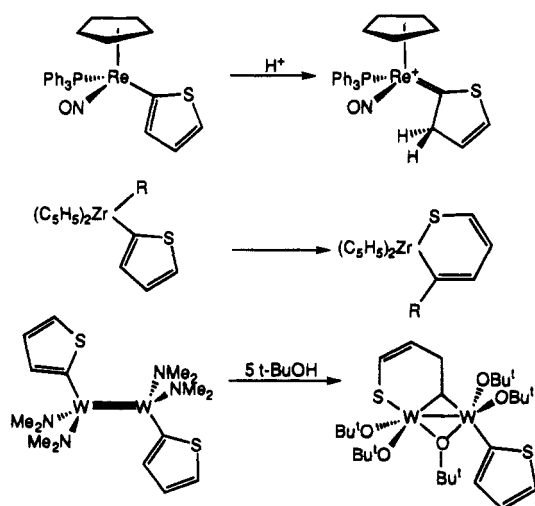
have been of recent interest,[8] representative reactions are summarized in Scheme 1.[9–11]

Results

Synthesis. Treatment of THF solutions of $ReOCl_3(PPh_3)_2$ with thienyllithium afforded red solutions which upon dilution with hexane produced purple microcrystals. ^1H and ^{13}C NMR characterization of this material revealed the presence of the thienyl group and THF. The ^1H NMR data show that the thienyl ligands are chemically equivalent and are attached through the 2-carbon centers. The diamagnetism of the compound is consistent with the low-spin d^2 configuration (Scheme 2). Complex **1** is stable at room temperature although it decomposes in refluxing toluene with formation of thiophene, bithienyl, and terthienyl along with other undetermined organic products. The

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Scheme 2
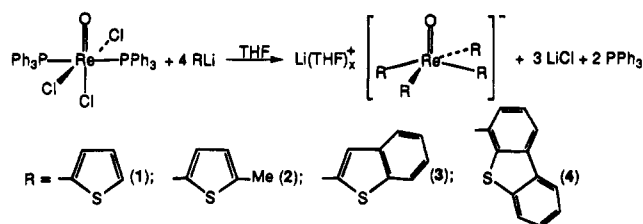
coupled oligothiophene products were assayed by gas chromatography and were identified by GC/MS analysis and by comparisons with authentic samples.

The IR spectrum of this product displays a strong band at 976 cm⁻¹ assigned to ν_{ReO}. This may be compared with a value of 992 cm⁻¹ for ReO(mesityl)₄.[12]

While **1** recrystallizes well, it is apparent from the ¹H NMR integrations that the amount of THF depends on the sample history. The variability in the number of THF ligands was also reflected in the microanalytical data as well, although we did succeed in obtaining analytically pure samples. On the basis of their high solubility, the THF is considered to be bound to Li⁺, which in turn may be coordinated to the oxo ligand. This pattern has been observed by Wilkinson and co-workers for the related compounds [(mesityl)₂ReO₂]Mg(THF)₄.[12] We also prepared the corresponding complex derived from 2-methylthienyl, Li(THF)ₙReO(2-C₄H₂S-5-Me)₄.

Recognizing that condensed thiophenes are important substrates for industrial hydrodesulfurization, we investigated Re^V O derivatives of benzothiophene and dibenzothiophene. The methods used to prepare **1** and **2** were also applied to these heterocycles. Starting from 2-lithiobenzothiophene we prepared Li(THF)₄ReO(C₈H₅S)₄ (**3**). The corresponding 8-lithiodibenzothiophene gave Li(THF)₄ReO(C₁₂H₇S)₄ (**4**). As for the simpler thienyl derivatives these species were obtained as dark red microcrystals and could be readily characterized by ¹H and ¹³C NMR spectroscopy (Figure 3). No evidence was obtained indicating that these compounds suffer from restricted rotation about the Re−C axes. Due to the lability of the Li-bound THF, we experienced great difficulty in obtaining analytically pure samples of **2−4**. Compensating for this deficiency, we have conducted crystallographic analyses for two of the four new compounds. These structural studies (see below) confirm the variability of THF stoichiometry; in **1** three THF molecules are bound to Li, while in **3** four THF molecules are complexed.

The alkylation of ReOCl₃(PPh₃)₂ appears quite versatile and was also used for the synthesis of the *o*-tolyl complex ReO(*o*-MeC₆H₄)₄⁻ which was oxidized in situ to give ReO(*o*-MeC₆H₄)₄. Wilkinson had originally prepared this compound by a less efficient route starting with (Me₃NH)ReO₄.[12]

Crystallographic Studies. The crystallographic analysis shows that **1** consists of a square pyramidal Re center. The four thienyl ligands are situated in the equatorial plane at C−Re−C angles of 81−85° and C−Re−O angles of 108−112°. Selected structural data are presented in Table 2. The thienyl groups are disordered such that the sulfur atoms are either oriented up, toward the oxo or down away from the oxo ligand. Also observed in the structure is the terminal oxo ligand which is bound to the lithium ion, which is bound to three molecules of THF, defining tetrahedral coordination about the alkali metal.

The benzothienyl complex was also examined by single crystal X-ray diffraction. The results are very similar to that for the thienyl case, including disordered thienyl ligands. In
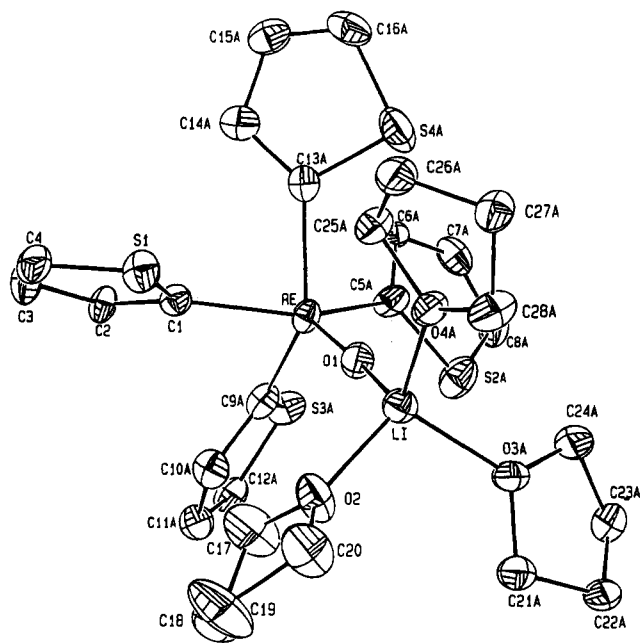

Figure 1. Structure of the non-hydrogen atoms in Li(THF)₃[ReO(2-C₄H₃S)₄] (**1**).
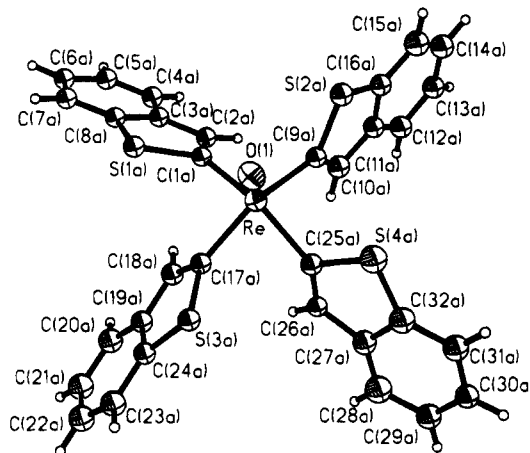
Figure 2. Structure of the non-hydrogen atoms in Li(THF)₄[ReO(2-C₈H₅S)₄] (**3**).

this case, the lithium center is bound to four molecules of THF, and there is no interaction between the lithium and the oxo ligand.

Preparation of Re(2-C₄H₃S)(CO)₅. For comparison with the corresponding Re(V) thienyl compounds, we prepared Re-(2-C₄H₃S)(CO)₅. This material was obtained from the reaction of the chlorozinc derivative 2-ClZnC₄H₃S[13] with ReBr(CO)₅. The reaction of 2-LiC₄H₃S with ReBr(CO)₅ gave the acyl Re-(C(O)C₄H₃S)(CO)₄(THF),[14] thus necessitating use of the milder organozinc reagent. The spectroscopic properties of Re(2-C₄H₃S)(CO)₅ were straightforward.

Oxidation and Hydrolysis of 1. The d¹ complexes ReO-(Ar)₄ have been prepared via the aerobic oxidation of reaction solutions that probably consist of Mg(THF)₄[ReO(Ar)₄]₂ (Ar = 2,4,6-Me₃C₆H₂, 2-MeC₆H₄).[12] In some cases these oxidations even employ hydrogen peroxide. This precedent led us to investigate the oxidation of **1−4**. To our surprise the thienyl complexes proved to be quite reactive toward both air and water. With oxygen we obtained a modest yield of 2,2′-bithienyl as

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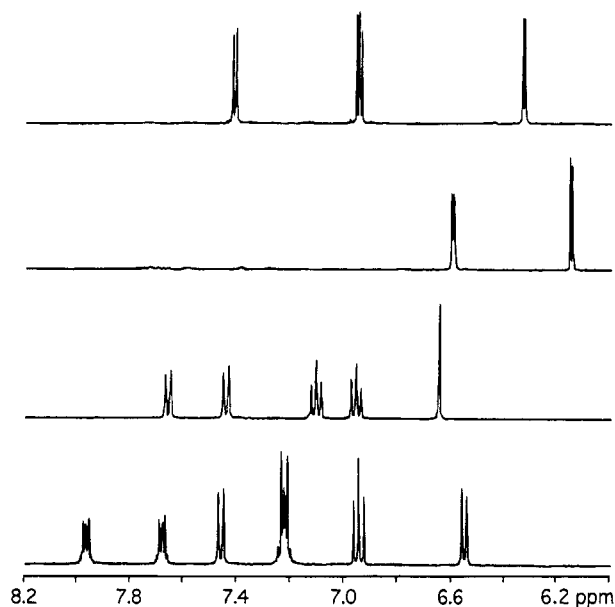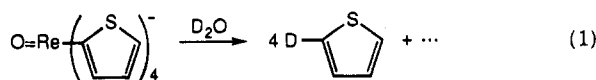(14) Stafford, P. R. Unpublished results.

Figure 3. 400 MHz ^{1}H NMR spectra for compounds **1**−**4**.

the major soluble product. These complexes also react rapidly with water to give the free thiophene. Treatment of **1** with D_2O gave 2-deuterothiophene in 70% yield (eq 1). THF solutions

of **1** are unreactive toward hydrogen (1 atm, 24 h). Attempts to O-silylate or O-stannylate **1** were unsuccessful; treatment of Li(THF)$_x$ReO(C$_4$H$_3$S)$_4$ with 1 equiv of Me$_3$SiCl and Bu$_3$SnCl afforded Me$_3$SiC$_4$H$_3$S[15] and Bu$_3$SnC$_4$H$_3$S,[16] respectively.

In contrast to the high reactivity of the Re(V) thienyl compounds, Re(2-C$_4$H$_3$S)(CO)$_5$ was completely stable to air and water.

Electrochemical Studies. The high reactivity of the thienyl complexes toward electrophiles (H$^+$, O$_2$) led us to examine the electrochemical properties of the complexes, affording an opportunity to directly gauge the donor properties of the various thienyl ligands. Cyclic voltammetry studies showed that each of the complexes undergoes a one electron oxidation (eq 2).

$$ReO(C_4H_3S)_4^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} ReO(C_4H_3S)_4 \qquad (2)$$

The oxidations are reversible based on the fact that the ratio anodic and cathodic currents are close to unity. The order of ease of oxidation is as follows: 2-methylthienyl (170 mV) > thienyl (350 mV) > dibenzothienyl (530 mV) > benzothienyl (600 mV) Table 3). For comparison, a sample of ReO(o-tolyl)$_4$ was found to have an $E_{1/2}$ of 115 mV. Attempts to isolate the oxidized 2-methylthienyl complex using Fe(C$_5$H$_5$)$_2^+$ did not afford a stable Re(VI) derivative. Instead we obtained good yield of 5,5′-dimethyl-2,2′-bithienyl, resulting from oxidative coupling of thienyl ligands.

Discussion

Early attempts to treat aryllithium reagents with ReOCl$_3$-(PPh$_3$)$_2$ lead to reduced rhenium(II) or rhenium(III) compounds of the type [ReR$_2$(PPh$_3$)$_2$]$_n$ and ReR$_3$(PPh$_3$)$_2$, respectively.[17]

Wilkinson and co-workers found that stable organorhenium-(V,VI) derivatives could be prepared from Re$_2$O$_7$ and ReO$_4^-$ using organolithium and organomagnesium reagents as arylating agents.[18,19] It was proposed that these preparations proceed via the anionic d^2-intermediate ReO(Ar)$_4^-$.[19] In contrast to Wilkinson's results, the derivatives of the type ReO(Th)$_4^-$ are stable, and they can be prepared via rational stoichiometries starting with ReOCl$_3$(PPh$_3$)$_2$ and thienyllithium reagents.[5]

The novelty of the ReO(thienyl)$_4^-$ compounds lies in the coexistence of oxo and thienyl on the same metal center. In contrast to the stability observed for ReOAr$_4$, the species **1**−**4** could not be converted to stable Re^{VI} derivatives. Electrochemical measurements suggest that the thienyl complexes can be reversibly oxidized, but preparative scale oxidation of more electron rich species **1** and **2** generated only coupling products such as 2,2′-bithienyl. The redox potentials of the new thienyl compounds span 430 mV. At the top of this range, being most difficult to oxidize, was the benzothienyl complex **4**. The extended aromatic system presumably enhances the acceptor character of this substituent relative to the bi- and monocyclic substituents. At the other end of the scale, the 2-methylthienyl derivative is most easily oxidized of the four thiophene complexes. This species is still 55 mV less reducing than the corresponding o-tolyl complex ReO(o-MeC$_6$H$_4$)$_4^-$ and this difference may explain the instability of Re^{VI} thienyl compounds.

The protonation of Li(THF)$_x$ReO(2-C$_4$H$_3$S)$_4$ produces free thiophene and unidentified inorganic products. The sensitivity of this species to protonolysis contrasts with the observation that low valent thienyl compounds, e.g., Re(C$_4$H$_3$S)(CO)$_5$, are typically stable to weak acids. Clearly the Re^{V}O unit confers nucleophilic character to the heterocycles. These results suggest that the reactivity observed with low-valent thienyl complexes may not accurately simulate the behavior of complexes at higher oxidation states, which are presumed to exist under catalytic conditions. The detailed mechanism of the protonation was not elucidated although the initial site of protonation could be either the ipso carbon of the thienyl ligand or the oxide ligand. The fact that Li$^+$ coordinates to the oxide demonstrates the feasibility of the latter pathway.

Deuterolysis of **1** produces 2-deuterothiophene. Recent work has shown that low-valent 2-thienyl complexes can protonate at C3 to give carbenes.[9] This pathway does not apply to the present case since we observe no deuterium incorporation at C3.

Experimental Section

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Table 1. Spectroscopic Data for Compounds **1−4**

compd	^{1}H NMR^a	^{13}C{^{1}H} NMR^b	ν_{ReO} (cm^{-1})^c
1	7.42 (d, 1H), 695 (dd, 1H), 6.33 (d, 1H)	176.5, 138.6, 131.9, 126.5	976
2	6.59 (d, 1H), 6.14 (d, 1H), 2.49 (d, 3H)	174.7, 143.9, 137.1, 125.0, 15.5	983
3	7.66 (d, 1H), 7.45 (d, 1H), 7.11 (dd, 1H), 6.96 (dd, 1H), 6.65 (s, 1H)	179.4, 146.3, 141.3, 129.6, 122.1, 121.3, 120.9, 120.3	1000
4	7.98 (m, 1H), 7.68 (m, 1H), 7.47 (d, 1H), 7.23 (m, 2H), 6.95 (dd, 1H), 6.56 (d, 1H)	180.2, 147.9, 141.5, 138.6, 132.2, 130.2, 125.7, 123.8, 123.2, 1226, 121.9, 116.9	999

^{a} 400 MHz, acetone-d_6. ^{b} 100 MHz, acetone-d_6. ^{c} KBr pellet.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Li(THF)$_3$[ReO(2-C$_4$H$_3$S)$_4$] (**1**) and Li(THF)$_4$[ReO(2-C$_8$H$_5$S)$_4$] (**3**)

Compound 1		Compound 3	
Re−O(1)	1.660(5)	Re−O(1)	1.687(4)
Re−C(1A)	2.106(8)	Re−C(1)	2.081(5)
Re−C(9A)	2.095(12)	Re−C(5A)	2.080(10)
Re−C(17A)	2.075(9)	Re−C(9A)	2.036(9)
Re−C(25A)	2.045(13)	Re−C(13A)	2.084(8)
Li−O(2)	1.930(14)	O(1)−Li	1.969(9)
Li−O(3)	1.897(14)	O(2)−Li	1.898(10)
Li−O(4)	1.915(14)	O(3A)−Li	1.97(2)
Li−O(5)	1.91(2)	O(4A)−Li	1.914(14)
O(1)−Re−C(1A)	109.0(6)	O(1)−Re−C(1)	110.1(2)
O(1)−Re−C(9A)	108.7(5)	O(1)−Re−C(5A)	109.1(7)
O(1)−Re−C(17A)	112.0(5)	O(1)−Re−C(9A)	113.4(9)
O(1)−Rej−C(25A)	108.5(6)	O(1)−Re−C(13A)	110.7(4)
C(9A)−Re−C(1A)	85.0(10)	C(1)−Re−C(13A)	81.0(3)
C(17A)−Re−C(1A)	83.1(7)	C(5A)−Re−C(13A)	87.8(6)
C(25A)−Re−C(17A)	81.5(8)	C(9A)−Re−C(1)	82.7(9)
C(25A)−Re−C(9A)	84.9(11)	C(9A)−Re−C(5A)	79.6(10)

Table 3. Electrochemical Data for ReOR$_4$$^{-/0}$

R	$E_{1/2}{}^a$, V	R	$E_{1/2}{}^a$, V
2-MeC$_6$H$_4$	115	2-C$_8$H$_5$S	600
2-(5-Me)C$_4$H$_2$S	170	2-C$_{12}$H$_7$S	530
2-C$_4$H$_3$S	350		

^{a} Potentials vs Ag/AgCl.

spectrometer. Cyclic voltamograms were collected using a BAS-100 electrochemical analyzer on THF solutions which were 10^{-3} M in analyte and 0.3 M in [Bu$_4$N][PF$_6$]. Gas chromatography data were obtained on a Hewlett-Packard 5890A gas chromatograph with a fused methyl silicate capillary column. The negative ion FAB mass spectrum was recorded on a VG ZAB-SE instrument by the School of Chemical Sciences Mass Spectrometry Laboratory using a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Note that since these species crystallize with variable amounts of THF, it was difficult to obtain reproducible microanalytical data (this was done for **1**).

Li(THF)$_3$[ReO(C$_4$H$_3$S)$_4$]. A 50 mL Schlenk flask was charged with 10 mL of Et$_2$O and 740 μL of C$_4$H$_4$S (9.2 mmol). This was followed by the addition of 5.2 mL of 1.6 M BuLi in hexanes (8.3 mmol) resulting in a faint yellow solution. In a separate flask, 1.54 g of ReOCl$_3$(PPh$_3$)$_2$ (1.85 mmol) was slurried in 50 mL of THF and cooled to −78 °C (dry ice/acetone). After this was stirred at room temperature for 1 h, the LiC$_4$H$_3$S solution was added to the slurry. This mixture was allowed to warm to room temperature during which the slurry dissolved, resulting in a red solution. The solution was stirred at room temperature for 2 h before the solvent was evaporated. The dark red residue was extracted with 3 × 10 mL of toluene to give a red solution and filtered through Celite. This solution was concentrated to approximately 10 mL, and 50 mL of hexane was added, resulting in the formation of a red precipitate. The mixture was filtered and the brown filtrate was discarded. The red precipitate was recrystallized from toluene/hexane, washed with 3 × 10 mL of hexane, and dried under vacuum. Yield: 0.94 g (67%, based on ReOCl$_3$(PPh$_3$)$_2$). Anal. Calcd (found) for C$_{28}$H$_{36}$LiO$_4$ReS$_4$: C, 44.37 (44.08); H, 4.79 (4.74); Re, 24.57 (24.96); S, 16.92 (16.61). FAB-MS: 535 (M-H)$^-$.

Li(THF)$_3$[ReO(C$_4$H$_2$-5-MeS)$_4$] (2). The synthesis is similar to that for **1**. Starting with 2.08 g of ReOCl$_3$(PPh$_3$)$_2$ (2.50 mmol), the yield of Li(THF)$_3$-[ReO(C$_4$H$_2$(CH$_3$)S)$_4$] was 1.53 g (74%, based on ReOCl$_3$-(PPh$_3$)$_2$).

Li(THF)$_3$[ReO(C$_8$H$_5$S)$_4$] (3). The synthesis is similar to that for **1**. Starting with 2.06 g of ReOCl$_3$(PPh$_3$)$_2$ (2.48 mmol), the yield of Li(THF)$_3$[ReO(C$_8$H$_5$S)$_4$] was 1.25 g (53%, based on ReOCl$_3$(PPh$_3$)$_2$).

Li(THF)$_3$[ReO(C$_{12}$H$_7$S)$_4$] (4). A 100 mL Schlenk flask was charged with 3.16 g of dibenzothiophene and 50 mL of Et$_2$O. This was followed by the addition 10.2 mL of 1.6 M BuLi in hexanes. The solution was

heated at reflux for 24 h during which the color changed from colorless to yellow. The solution was allowed to cool to room temperature. In a separate flask, 2.00 g of ReOCl$_3$(PPh$_3$)$_2$ (2.41 mmol) was slurried in 100 mL of THF and cooled to −78 °C. The LiC$_{12}$H$_7$S solution was added to the slurry and the mixture was allowed to warm to room temperature resulting in a red solution. The solvent was evaporated and the red residue was redissolved in 10 mL of THF. The product was isolated by loading on a column of Bio-Beads SX-8 (38 × 2.5 cm) and eluting with THF. The product was recrystallized from THF and hexane. Yield: 2.05 g (74%, based on ReOCl$_3$(PPh$_3$)$_2$).

Hydrolysis of 1. A calibration curve for gas chromatographic analysis of thiophene in a 25 mM solution of naphthalene (internal standard) in toluene was prepared. A 100 mL Schlenk flask was charged with 0.12 g of Li(THF)$_3$[ReO(C$_4$H$_3$S)$_4$] and 25 mL of the naphthalene solution, followed by 100 μL of degassed H$_2$O. The H$_2$O resulted in the formation of a precipitate and a brown solution. The mixture was stirred overnight, after which 3 × 1 mL aliquots were removed, filtered, and analyzed by gas chromatography.

Oxidation of 1. A calibration curve for thiophene and 2,2′-bithienyl in a 3.1 mM solution of naphthalene in toluene was prepared. A 100 mL Schlenk flask was charged with 0.13 g of Li(THF)$_3$[ReO(C$_4$H$_3$S)$_4$] and 25 mL of the naphthalene solution. Oxygen, dried over P$_4$O$_{10}$, was bubbled through the solution for 5 min. The solution was stirred overnight during which a precipitate formed, 3 × 1 mL aliquots were removed, filtered, and analyzed by gas chromatography.

ReO(o-MeC$_6$H$_4$)$_4$. This compound was prepared by an adaptation of Wilkinson's method.[11] A THF solution of 2-MeC$_6$H$_4$MgBr (12 mmol) was prepared by the reaction of 1.45 mL of 2-MeC$_6$H$_4$Br and 0.6346 g of Mg turnings (26 mmol). This solution was added to a suspension of 2.0012 g of ReOCl$_3$(PPh$_3$)$_2$ (2.4 mmol) in THF cooled to −78 °C. The mixture was allowed to warm to room temperature, and the solvent was removed in vacuo. The residue was extracted with 3 × 20 mL CH$_2$Cl$_2$. Evaporation of the CH$_2$Cl$_2$ solution led to an orange solid which was recrystallized from 10 mL THF by the addition of 30 mL of ether. After washing with additional ether, the orange solid was dissolved in 30 mL of THF. O$_2$ was bubbled through the THF. After 30 min the solution began to turn green. After 12 h, the solvent was evaporated and the residue was extracted into CH$_2$Cl$_2$ and filtered through Celite. Evaporation of the filtrate gave 0.376 g of green microcrystals of ReO(o-MeC$_6$H$_4$)$_4$ (64% yield, based on ReOCl$_3$-(PPh$_3$)$_2$).

(CO)$_5$Re(C$_4$H$_3$S). A 100 mL Schlenk flask was charged with 50 mL of THF, 0.4 mL of C$_4$H$_4$S (5.0 mmol), and 3.1 mL of 1.6 M BuLi in hexanes (15.0 mmol). The resulting faint yellow solution was stirred at room temperature for 2 h and cooled to −78 °C. In a separate 50 mL Schlenk flask a solution of 0.6882 g of ZnCl$_2$ (5.1 mmol) in 10 mL of THF was cooled to −78 °C and then added to the thienyllithium solution. After stirring at room temperature for 4 h, the yellow (C$_4$H$_3$S)ZnCl solution was treated with 2.01 g of Re(CO)$_5$Br (4.95 mmol). After a further 12 h, the solution was cooled to 0 °C and the solvent was removed under vacuum. The resulting yellow paste was extracted with 3 × 20 mL of benzene. After evaporation of the solvent from the extract, (CO)$_5$Re(C$_4$H$_3$S) was collected as colorless crystals

by sublimation under a static vacuum at 40 °C, 0.25 mm Hg. Yield: 0.78 g (47%). Sublimation at 100 °C and 0.25 mm Hg gave 0.37 g of unreacted Re(CO)$_5$Br. Anal. Calcd (found) for C$_9$H$_3$O$_5$ReS: C, 26.40 (26.34); H, 0.74 (0.77); Re, 45.48 (45.25); S, 7.83 (7.76). EI-MS: 410. ^{1}H NMR (400 MHz acetone-d_6): 7.42 (d), 7.15 (d), 6.98 (dd) ppm. ^{13}C{^{1}H} (75.5 MHz, CD$_2$Cl$_2$): 181.9, 181.7, 139.8, 130.7, 129.2, 123.0 ppm. IR (KBr) ν_{CO} 2139, 2067, 2029, 2010 (sh), 1975 cm^{-1}.

Crystallographic Characterization of Li(THF)$_3$[ReO(C$_4$H$_3$S)$_4$]. The purple, columnar crystal was mounted using oil to a thin glass fiber with the (4$\bar{1}\bar{1}$) scattering planes roughly normal to the spindle axis. The data crystal was bound by the (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (100), and ($\bar{1}$00) faces. Distances from the crystal center to these facial boundries were 0.04, 0.04, 0.08, 0.08, 0.25, and 0.25 nm, respectively. Data were measured at 198 K on an Enraf-Nonius CAD4 diffractometer. Crystal and refinement data are available in the supplementary material. Systematic conditions suggested the ambiguous space group $P\bar{1}$; refinement confirmed the prescence of a symmetric center. Periodically monitored standard intensities showed a 2.7% decay; no decay correction was applied. Step-scanned intensity data were reduced by profile analysis[22] and corrected for Lorentz-polarization effects and for absorption.[23] Scattering factors and anomalous dispersion terms were taken from standard tables.[24]

The structure was solved by Patterson methods;[25] the correct Re atom position was deduced from a vector-map. Partial structure expansion gave positions for the remaining non-H atoms and revealed a complex disorder. Owing to high correlation coefficients, chemically similar 1,2- and 1,3-atom separations were restrained to equivalent values with an effective standard deviation of 0.03 Å. Rigid bond restraints (esd = 0.01) were applied to the anisotropic thermal displacement parameters. Disordered positions separated by less than 1.1 Å were restrained (esd = 0.02) to have the same U_{ij} coefficients. Despite these restraints, anisotropic thermal parameters for atoms C(6A,B) and C(13B) converged with non positive definite displacements and were, therefore, refined with isotropic thermal parameters. Independent site occupancy factors were refined for each disordered ligand. Major site occupancies converged at 0.52(1) for S2A = C4A, 0.670(7) for S3A > C12A, 0.724(7) for S4A > C16A, 0.501(8) for O3A > C23A, and 0.57(1) for O4A > C28A. Hydrogen atoms, included as fixed contributors in idealized positions, were assigned U's as 1.2 U_{eq} of attached C atoms. Successful convergence was indicated by the maximum shift/error for the final cycle of the full-matrix least-squares refinement on F^2.[26] Two of the highest eight peaks in the final difference Fourier map were located in the vicinity of atoms C(6A) and C(6B), the other six were in the vicinity of the Re; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed a dependence on amplitude and resolution. The details of the data collection and refinement are presented in Table 4.

Crystallographic Characterization of Li(THF)$_3$[ReO(C$_8$H$_5$S)$_4$]. The red, equidimensional crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber with the (100) scattering planes roughly normal to the spindle axis. The data crystal was excised from the center of a clump of amorphous material and was approximately bound by the (011), (0$\bar{1}\bar{1}$), (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (100), and ($\bar{1}$00) faces. Distances from the crystal center to the facial boundaries were 0.06, 0.06, 0.07, 0.07. 0.09, 0.09, 0.09, and 0.09 nm, respectively. Data were measured at 198 K on an Enraf-Nonius diffractometer. Crystal and refinement details are given in the supplementary material. Average values of the normalized structure factors and the absence of systematic conditions suggested the ambiguous space group $P\bar{1}$; however, refinement confirmed the presence of a symmetry center. Periodically monitored standard intensities showed no decay. Step-scanned intensity

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Table 4. Crystal Data and Structure Refinement Details for Li(THF)$_3$ReO(2-C$_4$H$_3$S)$_4$ (**1**)

empirical formula: C$_{28}$H$_{36}$LiO$_4$ReS$_4$
fw = 757.95
temp = 198(2) K
wavelength = 0.71073 Å
cryst syst: triclinic
space group: $P\bar{1}$
unit cell dimens: a = 9.704(4) Å, b = 10.489(2) Å, c = 15.879(3) Å, α = 90.150(1)°, β = 98.38(2)°, γ = 105.12(2)°
vol = 1542.2(8) Å^3
Z = 2
d(calcd) = 1.632 g/m^3
abs coeff: 4.241 mm^{-1}
F(000) = 756
cryst size: 0.50 × 0.16 × 0.08 mm
θ range for data collcn: 1.30–23.97°
Index ranges: $0 \leq h \leq 11$, $-11 \leq k \leq 11$, $-18 \leq l \leq 17$
no. of reflcns collcd: 5140
no. of indep reflcns: 4817 [R(int) = 0.0291]
abs cor: integration
max and min transm: 0.7076 and 0.5065
refinement method: full-matrix least-squares on F^2
data/restraints/params: 4817/661/553
goodness-of-fit on F^2: 1.090
final R indices [$I > 2\sigma(I)$]: R_1 = 0.0295, wR_2 = 0.0678
R indices (all data): R_1 = 0.0443, wR_2 = 0.0739
largest diff peak and hole: 0.835 and -1.001 e/Å^3

Table 5. Crystal Data and Structure Refinement Details for Li(THF)$_4$ReO(C$_8$H$_5$S)$_4$ (**3**)

empirical formula: C$_{48}$H$_{52}$LiO$_5$ReS$_4$
fw = 1030.28
temp = 198(2) K
wavelength = 0.71073 Å
cryst syst: triclinic
space group: $P\bar{1}$
unit cell dimens: a = 9.804(2) Å, b = 12.235(5) Å, c = 19.693(7) Å, α = 77.14(3)°, β = 88.35(2)°, γ = 84.46(3)°
vol = 2292.2(13) Å^3
Z = 2
d(calcd) = 1.493 g/m^3
abs coeff: 2.877 mm^{-1}
F(000) = 1044
cryst size: 0.18 × 0.18 × 0.12 mm
θ range for data collcn: 1.06–23.75°
index ranges: $0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$
no. of reflcns collcd: 7380
no. of indep reflcns: 6910 [R(int) = 0.0325]
abs cor: integration
max and min transm: 0.7841 and 0.6237
refinement method: full-matrix least-squares on F^2
data/restraints/params: 6909/935/546
goodness-of-fit on F^2: 1.057
final R indices [$I > 2\sigma(I)$]: R_1 = 0.0424, wR_2 = 0.0956
R indices (all data): R_1 = 0.0443, wR_2 = 0.1095
largest diff peak and hole: 0.955 and -0.803 e/Å^3

data were reduced by profile analysis[22] and corrected for Lorentz–polarization effects and for absorption.[23] Scattering factors and anomalous dispersion terms were taken from standard tables.[24]

The structure was solved by direct methods;[25] correct positions for the anion atoms were deduced from an E-map. Two cycles of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis gave positions for cation atoms and revealed disordered positions for both the anion and cation ligands. Hydrogen atoms were included as fixed contributors in idealized positions. Numerous constraints were required for successful least-squares convergence. Anion ligands were assigned to equivalent geometries with an effective standard deviation of 0.03 Å. THF ligands were also restrained to equivalent geometries. Rigid bond restraints (esd 0.01) were applied to all anisotropic thermal displacement parameters and disordered atoms separated by less than 1% Å^{-1} were restrained to have the same U_{ij} (esd 0.05). In the final cycle of full-matrix least-squares refinements on F^2,[26] disordered anion non-H atoms were refined with isotropic

thermal parameters and the remaining non-H atoms were refined with anisotropic thermal coefficients. Site "A" occupancy factors for disordered anion ligands 1−4 and the disordered THF ligand converged at 0.833(7), 0.53(3), 0.826(8), 0.541(8), and 0.40(2), respectively. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peak in the final difference Fourier map was located above the base plane of the metal complex roughly between atoms S(2B) and C(1B); the next highest peak (0.86 e Å^{-3}) was in vicinity of the Re atom. The final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.[25] Details are presented in Table 5.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond angles and distances (14 pages). Ordering information is given on any current masthead page.