First Examples of Homogeneous Hydrogenolysis of Thiophene to 1-Butanethiolate and Ethylthioketene Ligands: Synthesis and Reactivity of $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$

Glen P. Rosini and William D. Jones*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received June 29, 1992*

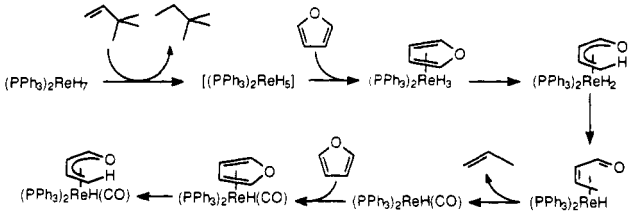
Abstract: The reaction of $ReH_7(PPh_3)_2$ with excess thiophene in the presence of the hydrogen acceptor 3,3-dimethyl-1-butene results in the formation of a new organometallic complex which has been identified as the thioallyl complex $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ (**1**). The thermolysis of a solution of **1** at 60 °C with excess trimethylphosphine results in the formation of free tetrahydrothiophene and the new cyclometalated organometallic complex $Re(PMe_3)_4(PPh_2C_6H_4)$ (**2**). Photolysis of a solution of **1** with excess trimethylphosphine proceeds differently, yielding a mixture of four new organometallic complexes, all of which contain a C–S-cleaved 1-butene-1-thiolate ligand. Two of the complexes contain an S-bound ethenethiolate ligand and exist as cis and trans isomers of $Re(SCH{=}CHEt)(PMe_3)_5$ (**3a,b**), while the other two complexes contain an η^3-allyl-bound ethenethiolate ligand and exist as cis and trans isomers of $Re(\eta^3\text{-}SCH{=}CHEt)(PMe_3)_4$ (**4a,b**). In both complexes the cis is the more thermodynamically stable isomer. The cis complex **3a** is seen to isomerize to the trans **3b** photochemically (cis:trans = 1.6:1), while thermally the trans isomerizes almost totally to the cis (cis:trans = 10:1 after several days). In the presence of a large excess of PMe_3, only complexes **3a,b** are seen, whereas removal of the free phosphine from solution gives only complexes **4a,b**. This interconversion has been shown to be reversible for several cycles of PMe_3 addition. It is shown that **4a** thermally rearranges to the single new complex containing an η^2 C=S-bound ethylthioketene ligand $ReH(S{=}C{=}CHEt)(PMe_3)_4$ (**5**). The reaction of a mixture of **4** and **5** with H_2 at room temperature results in the formation of the corresponding cis and trans dihydrido 1-butene-1-thiolate complexes $ReH_2(SCH{=}CHEt)(PMe_3)_4$ (**7a,b**). Upon being heated with H_2, **7** forms the analogous 1-butanethiolate complex $ReH_2(n\text{-}BuS)(PMe_3)_4$ (**8**). The mechanisms for the formation of all of these complexes are discussed, as are their relevance to the hydrodesulfurization of thiophene. Complex **1** crystallizes in the monoclinic space group *Pn* with $a = 10.300$ (2) Å, $b = 13.584$ (4) Å, $c = 13.913$ (2) Å, $\beta = 92.32$ (1)°, $V = 1945$ (1) Å^3, and $Z = 2$. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.868$ (6) Å, $b = 17.542$ (5) Å, $c = 17.564$ (3) Å, $\beta = 100.67$ (3)°, $V = 3291$ (4) Å^3, and $Z = 4$.

Introduction

The hydroprocessing of crude oil to remove heteroatoms (such as sulfur- and nitrogen-containing organic compounds) is a very large scale commercial process. The removal of sulfur from crude oil is known as hydrodesulfurization (HDS), and many studies have been done in an attempt to understand the mechanisms of the industrial processes.[1] In practice, petroleum is treated with H_2 at 400 °C over a catalyst which is generally described as a (Co–Mo) sulfide/γ-Al_2O_3.[2] The common sulfur impurities that are removed from crude oil are mercaptans, disubstituted sulfides, and thiophenes. The majority of the studies done to investigate the mechanisms of HDS have been done on thiophenes, as they are the most difficult of the sulfur-containing residues to desulfurize.[3]

The main questions that have been addressed in these studies are those of the binding modes of the thiophene[4] that are relevant to HDS (Figure 1)[5,6] and whether the bound thiophene is hydrogenated (partially or totally) prior to or after C–S insertion.

Scheme I. Mechanism for Furan Ring-Opening Proposed by Felkin



There are examples of complexes that have C–S inserted both with and without partial hydrogenation of the thiophene, and there are also cases in which the thiophene has been partially hydrogenated without C–S bond cleavage (Figure 2).[7,8]

The reactions of metal hydride complexes with thiophene, therefore, might serve as possible models for the interaction of thiophene with surface metal hydrides, which are probably present on the catalyst surface from the adsorption of H_2. Also of interest is the determination of the initial coordination mode of thiophene to an electron-rich metal hydride complex in which ligands are already present that can assist in C–S bond cleavage and thiophene hydrogenation steps analogous to those thought to occur during HDS.

(1) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. Mitchell, P. C. H. *The Chemistry of Some Hydrodesulphurization Catalysts Containing Molybdenum*; Climax Molybdenum Co. Ltd.: London, 1967.

(2) Weisser, O.; Landa, S. *Sulfide Catalysts. Their Properties and Applications*; Pergamon: Oxford, 1973.

(3) Zdrazil, M. *Appl. Catal.* **1982**, *4*, 107.

(4) (a) Rauchfuss, T. B. The Coordination Chemistry of Thiophenes. *Prog. Inorg. Chem.* **1991**, *39*, 259. (b) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

(5) For the importance of π-bonded species, see: (a) Richardson, N. V.; Campuzano, J. C. *Vacuum* **1981**, *31*, 449. (b) Stohr, J.; Gland, J. L.; Kollin, E. B.; Koestner, R. J.; Johnson, A. L.; Muetterties, E. L.; Sette, F. *Phys. Rev. Lett.* **1984**, *53*, 2161. (c) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313. (d) Preston, R. E.; Benziger, J. B. *J. Phys. Chem.* **1985**, *89*, 5010. (e) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (f) Gellman, A. J.; Farias, M. H.; Somorjai, G. A. *J. Catal.* **1984**, *88*, 546. (g) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484.

(6) For the importance of S-bonded species, see: (a) Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179. (b) Harris, S.; Chianelli, R. R. *J. Catal.* **1980**, *61*, 128. (c) Kolboe, S. *Can. J. Chem.* **1969**, *47*, 352.

(7) For C–S cleavage prior to hydrogenation, see: (a) Gellman, A. J.; Neiman, D.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 92. (b) Gellman, A. J.; Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 103. (c) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559. (d) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 879. (e) Kaesz, H. D.; King, R. B.; Manuel, T. A.; Nichols, L. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 4749. (f) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171. (g) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698.

(8) For hydrogenation prior to or without C–S cleavage, see: (a) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (b) Satterfield, C. N.; Modell, M.; Wilkens, J. A. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 154. (c) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (d) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.

0002-7863/92/1514-10767$03.00/0

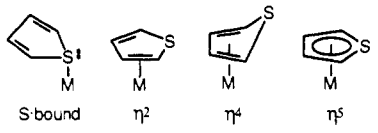


Figure 1. Possible modes of adsorption of thiophene.

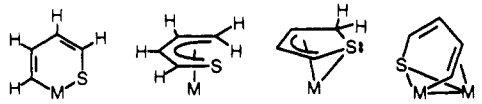
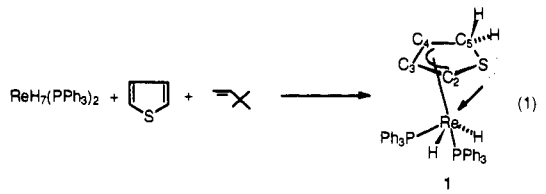


Figure 2. Various examples of C–S insertion/thiophene hydrogenation.

It has been previously seen that $ReH_7(PPh_3)_2$ reacts with furan to cleave the C–O bond in the presence of 3,3-dimethyl-1-butene to yield the ring-opened 1-oxapentadienyl complex $(\eta^5\text{-}C_4H_5O)Re(PPh_3)_2(CO)$.[9] The mechanism proposed for this unusual transformation is shown in Scheme I. We were interested in knowing whether thiophene would react with $ReH_7(PPh_3)_2$ in a manner similar to that of furan. Since rhenium has been shown to be a relatively good catalyst for HDS, we thought that this reaction might prove useful in modeling some key steps of HDS.[10] In this paper, we report the results of the reaction of thiophene with $ReH_7(PPh_3)_2$ in the presence of 3,3-dimethyl-1-butene and discuss the characterization and reactivity of the single complex formed. Mechanisms are proposed for the formation of the observed products, and their relevance to the hydrodesulfurization of thiophene is discussed.

Results and Discussion

Synthesis and Characterization of $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ (1). The reaction of $ReH_7(PPh_3)_2$ with excess thiophene in the presence of 3,3-dimethyl-1-butene (there is no reaction in the absence of the hydrogen acceptor) results in the formation of a new organometallic complex, which has been spectroscopically and structurally characterized as being $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ (**1**) (eq 1). The ^1H NMR spectrum of **1** consists of two inequivalent



hydride resonances at δ −0.80 and −10.98 and five resonances between δ 5.13 and 1.87, with the low-field resonance and both hydrides showing coupling to two phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of two inequivalent phosphorus atoms. A ^{13}C DEPT NMR experiment indicated the presence of one methylene carbon atom in the molecule, and the J_{C-H} of 143.8 Hz for the methylene carbon atom is consistent with an sp^3-hybridized carbon.[11] ^{13}C–^1H HETCOR and ^1H–^1H COSY spectra allowed the total and unequivocal assignment of all ^1H and ^{13}C resonances for **1** as labeled in eq 1 (see Experimental Section).

In order to confirm the assignments of the exo and endo ^1H NMR resonances, the reaction was repeated using 2-deuteriothiophene in place of thiophene. The deuterium label was found to be scrambled over sites H^2 and H^{5exo} (the intensities of these two resonances were found to be one-half the intensity of the remaining three thiophene resonances), thus indicating an endo

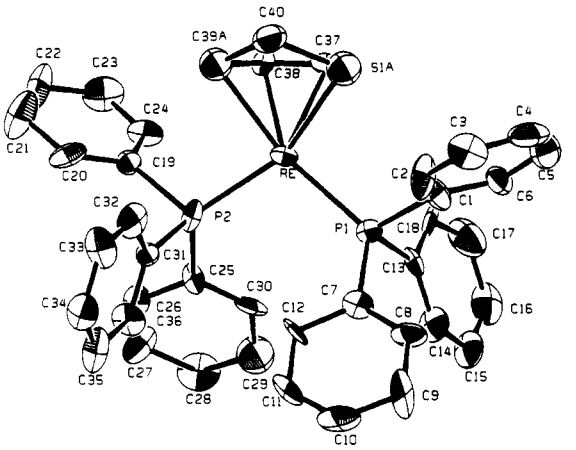
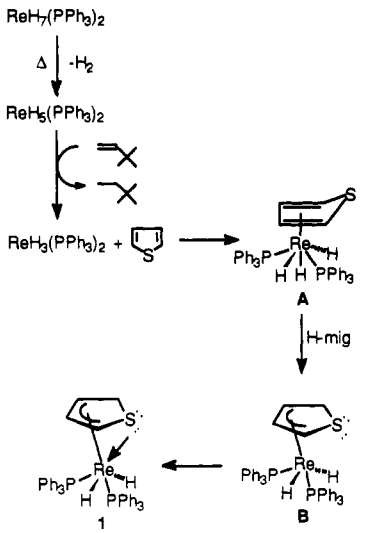


Figure 3. ORTEP diagram of **1** with the thermal ellipsoids shown at 50% probability. The hydride ligands were not located.

Table I. Selected Bond Distances (Å) and Angles (deg) for **1**

		Distances			
Re–S1A	2.42 (1)	Re–C38	2.20 (3)	C37–C38	1.41 (4)
Re–P1	2.359 (7)	Re–C39A	2.40 (1)	C38–C39A	1.63 (3)
Re–P2	2.346 (7)	S1A–C37	1.67 (3)	C39A–C40	1.69 (3)
Re–C37	2.20 (2)	S1A–C40	1.72 (3)		
		Angles			
P1–Re–P2	107.3 (2)			C37–C38–C39A	113 (2)
C37–S1A–C40	97 (1)			C38–C39A–C40	99 (1)
S1A–C37–C38	113 (2)			S1A–C40–C39A	105 (2)

Scheme II. Proposed Mechanism for the Formation of **1**



migration of a hydride ligand from the metal. This observation confirmed that the downfield resonance is, in fact, the exo proton and that it is the exo proton that exhibits coupling to the two phosphorus atoms.

The solid-state structure of **1** obtained by single-crystal X-ray diffraction (Figure 3) is in agreement with the NMR structural assignment. Selected bond lengths and angles for **1** are listed in Table I. The sulfur and the three carbon atoms of the allyl group are planar to within 0.023 Å, and the methylene carbon atom lies 0.59 Å above this plane. The methylene group is bent out-of-plane away from the Re atom by 35.8°. The methylene group lies in a plane bisecting the P1–Re–P2 angle (the dihedral angle between the plane formed by P1, Re, P2 and that formed by Re, C40, H33, H34 is 93.47°), consistent with the S/CH disorder observed in the positions α to the methylene group. The disorder was successfully modeled by varying the occupancy of the α position with sulfur or CH and obtaining multiplicity values of 0.61 for S1A and 0.39 for S1B.

(9) Baudry, D.; Daran, J.-C.; Dromzee, Y.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1983**, 813.
(10) (a) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400. (b) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430. (c) Bussell, M. E.; Somorjai, G. A. *Catal. Lett.* **1989**, *3*, 1. (d) Bussell, M. E.; Gellman, A. J.; Somorjai, G. A. *J. Catal.* **1988**, *110*, 423. (e) Burdett, J. K.; Chung, J. T. *Surf. Sci. Lett.* **1990**, *236*, L353. (f) Vissers, J. P. R.; Groot, C. K.; van Oers, E. M.; de Beer, V. H. J.; Prins, R. *Bull. Soc. Chim. Belg.* **1984**, *93*, 813. (g) Ledoux, M. J.; Michaux, O.; Agostini, G.; Pannissod, P. *J. Catal.* **1986**, *102*, 275.
(11) (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (b) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359.

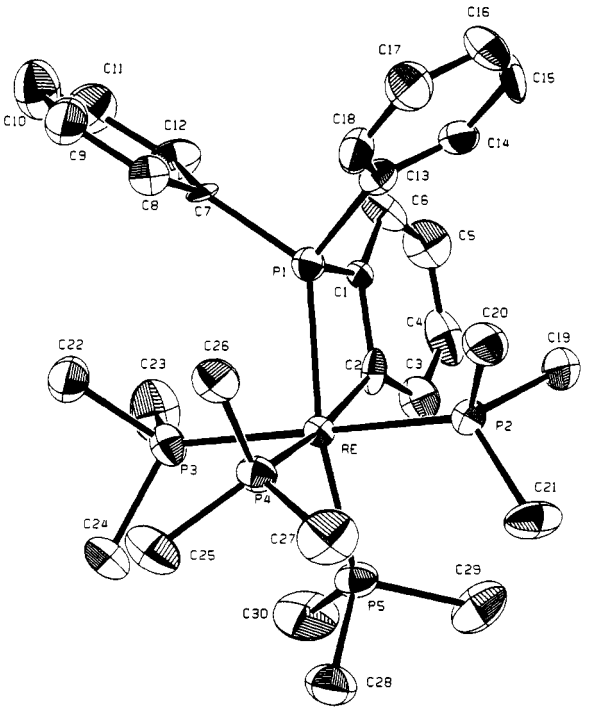
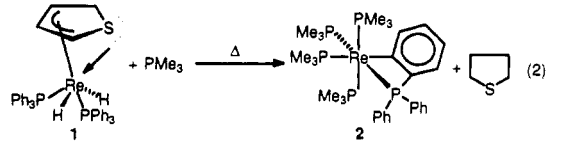


Figure 4. ORTEP diagram of **2** with the thermal ellipsoids shown at 50% probability.

A plausible mechanism for the reaction of $ReH_7(PPh_3)_2$ with thiophene leading to the formation of **1** is proposed in Scheme II. The heptahydride first loses H_2 forming the 16-electron species $ReH_5(PPh_3)_2$, which then goes on to hydrogenate 3,3-dimethyl-1-butene to form the highly reactive 14-electron intermediate $ReH_3(PPh_3)_2$.[12] This species can then react directly with thiophene to form the η^4-diene complex **A**. The thiophene is then intramolecularly hydrogenated to form the 16-electron η^3-bound allyl intermediate **B**. The Re atom can now bind to the endo lone electron pair of the sulfur atom to form **1**. The intramolecular migration of a hydride to the α position of the η^4-bound thiophene must be very rapid since **A** is not seen during the reaction, whereas in the analogous reaction of $ReH_7(PPh_3)_2$ with cyclopentadiene, the η^4-bound diene is stable and isolable at room temperature.[13]

Thermal Reactivity of $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ (1). When a solution of **1** in benzene is treated with excess trimethylphosphine and the reaction mixture is heated to 60 °C, the solution undergoes a color change from yellow to orange. The ^1H NMR spectrum of the reaction mixture indicates the presence of free triphenylphosphine and free tetrahydrothiophene (also confirmed by GC/MS), and several resonances are attributable to a single new organometallic complex (eq 2). The $^{31}P\{^1H\}$ NMR spectrum



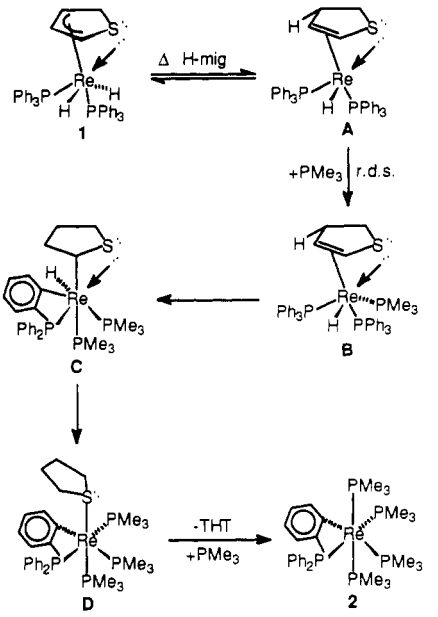
shows four multiplet resonances between δ −42 and −67 in a 1:2:1:1 ratio. These spectra allowed the formulation of the complex as the cyclometalated $Re(PMe_3)_4(PPh_2C_6H_4)$ (**2**).

The solid-state structure of **2** obtained by single-crystal X-ray diffraction confirmed this assignment (Figure 4). Selected bond lengths and angles for **2** are listed in Table II. The molecule is octahedral, containing two equivalent trans trimethylphosphine ligands. The axis that contains the cyclometalated phosphorus atom deviates substantially from linearity (P1–Re–P5 is 154.0°). The P1–Re–C2 bond angle of only 65.1° reflects the strain associated with the four-membered metallacycle. There is also a large upfield shift in the ^{31}P resonance of the cyclometalated phosphorus atom of **2**, which is at δ −42.16 compared to the resonances of **1** at δ 39.79 and 33.86.

Table II. Selected Bond Lengths (Å) and Angles (deg) for **2**

		Distances			
Re–P1	2.435 (3)	Re–P3	2.389 (4)	Re–P5	2.356 (3)
Re–P2	2.382 (3)	Re–P4	2.355 (3)	Re–C2	2.17 (1)
		Angles			
P1–Re–P2	89.9 (1)	P2–Re–P5	91.5 (1)	P5–Re–C2	89.0 (3)
P1–Re–P3	89.8 (1)	P2–Re–C2	90.2 (3)	Re–P1–C1	106.7 (6)
P1–Re–P4	106.4 (1)	P3–Re–P4	89.7 (1)	Re–P1–C7	106.0 (5)
P1–Re–P5	154.0 (1)	P3–Re–P5	89.4 (1)	Re–P1–C13	96.5 (5)
P1–Re–C2	65.1 (3)	P3–Re–C2	90.7 (3)	P1–C1–C2	100.6 (8)
P2–Re–P3	178.8 (1)	P4–Re–P5	99.5 (1)	P1–C1–C6	134 (1)
P2–Re–P4	89.3 (1)	P4–Re–C2	171.5 (3)	Re–C2–C1	107.7 (8)

Scheme III. Proposed Mechanism for the Formation of **2**



A plausible mechanism for the observed thermal chemistry of **1** is proposed in Scheme III. During the thermolysis of **1**, the thiophene ligand is intramolecularly hydrogenated, and the cyclometalation of a PPh_3 ligand produces the final hydrogen needed for the production of tetrahydrothiophene. The first step is presumed to be the reversible migration of one of the hydrides[14] to the carbon adjacent to the methylene group in **1**, forming intermediate **A**. This is then followed by the rate-determining step, the coordination of a PMe_3 ligand to form **B**. In order to test whether the coordination of PMe_3 was, in fact, rate determining, a concentration study was undertaken to determine whether there was a dependence of the reaction rate on $[PMe_3]$ as predicted in Scheme III. The study showed that the rate is, indeed, dependent on $[PMe_3]$ (see Experimental Section) and therefore supports the initial steps of the thermolysis of **1** as shown in Scheme III.

Although it is not possible to determine the order of the subsequent steps from **B** to **C** (phosphine exchange, cyclometalation, and a hydride migration), the most probable final steps in the mechanism are shown in Scheme III. The stepwise hydrogenation of the thiophene ligand in **1** produces an S-bound tetrahydrothiophene ligand (**D**) which is then exchanged for PMe_3, leading to the formation of **2** and free tetrahydrothiophene. Transformations analogous to those proposed in Scheme III from intermediate **C** to **2** have also been proposed in the reactions of some

(12) (a) Green, M. A.; Huffman, J. C.; Caulton, K. G.; Kybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39. (b) Baudry, D.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1981**, *220*, C7.

(13) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301.

(14) A similar reversible migration is seen in $(\eta^4\text{-}C_4H_6)ReH_3(PPh_3)_2$, see: Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1728.

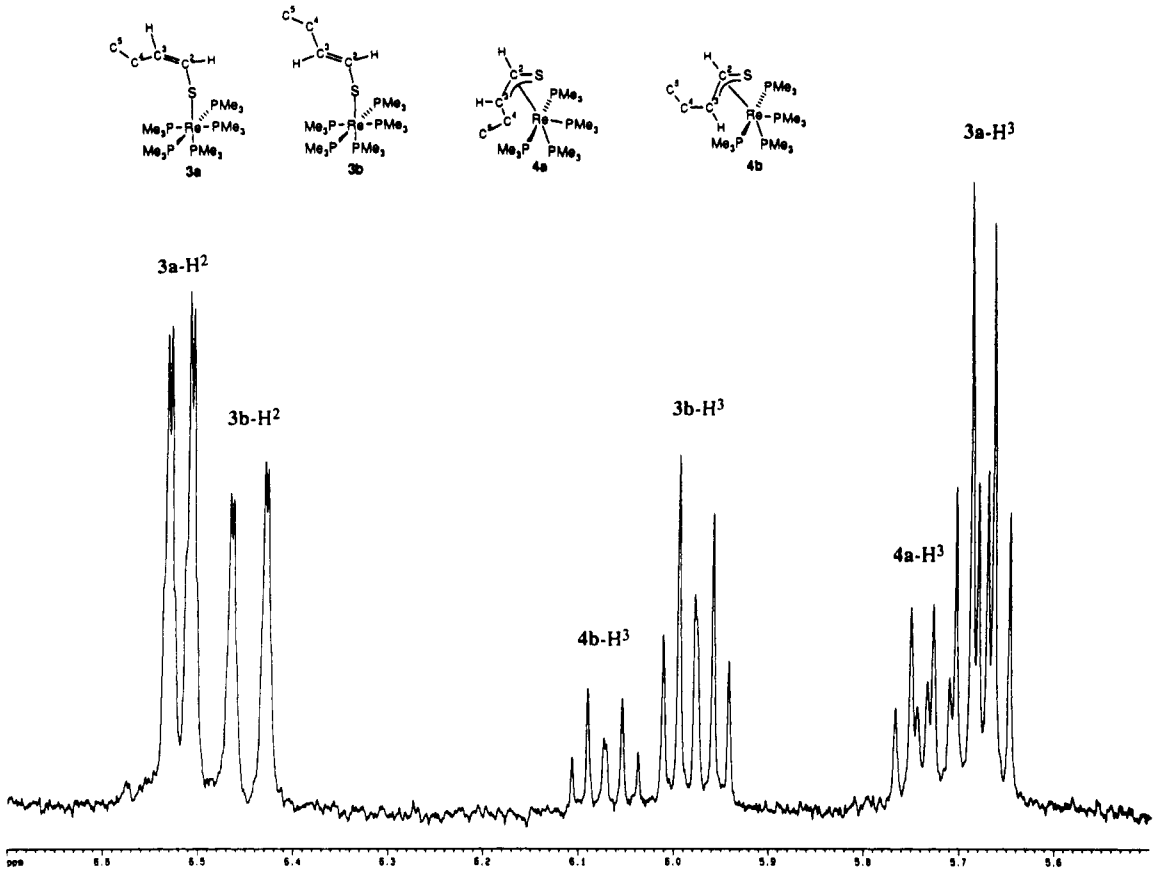


Figure 5. ^{1}H NMR spectrum of a mixture of **3** and **4** showing only the olefinic region.

Pd, W, and Os complexes with 2,3-dihydrothiophene,[15] therefore supporting the final steps of Scheme III as the steps leading to the production of tetrahydrothiophene from the thermolysis of **1**.

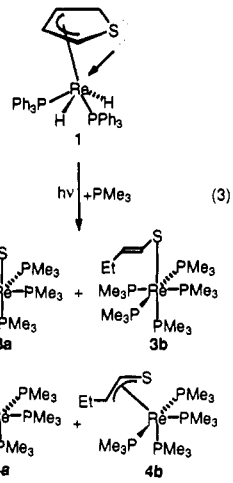
Attempted Catalytic Hydrogenation of Thiophene. We were interested in knowing whether **1** could act as a thermal catalyst for the hydrogenation of thiophene. A sample of **1** in C_6D_6 (0.01 M) with 50 equiv of thiophene was placed under 1 atm of H_2 and then heated at 60 °C overnight. The reaction was monitored by ^{1}H NMR spectroscopy and showed the formation of only 1 equiv of tetrahydrothiophene and the formation of $ReH_7(PPh_3)_2$. Several additional samples were than made, varying the amount of H_2 from 1 to 0.25 atm, and one sample was also made with 1 atm of H_2 with excess 3,3-dimethyl-1-butene added. Similar results were seen in these samples, with decomposition increasing with decreasing H_2 pressures. Apparently the hydrogen reacts with any intermediates much more rapidly than does thiophene, thereby inhibiting the formation of any additional **1** and rendering the hydrogenation reaction only stoichiometric instead of catalytic.

Photochemical Reactivity of $(\eta^4$-$C_4H_5S)ReH_2(PPh_3)_2$ (1). When a solution of **1** in benzene or toluene is treated with excess trimethylphosphine and irradiated for several hours, the ^{1}H NMR spectrum of the reaction mixture indicates the presence of free triphenylphosphine and resonances attributable to four new organometallic complexes (along with the formation of small amounts of **2**). When the reaction is run with a large excess of PMe_3, only two of the complexes are present by ^{1}H NMR spectroscopy, and when the free PMe_3 is removed from solution, only the other two complexes are present. The interconversion of these pairs of products by addition or removal of PMe_3 is reversible and has been taken through several cycles with no apparent decomposition of any of the species. This observation suggests that there are two pairs of isomeric complexes that differ only in their number of PMe_3 ligands. Each of the complexes has four ^{1}H NMR resonances for the thiophene-derived ligand, and the corresponding resonances for each compound all have very similar chemical shifts and coupling patterns. The ^{1}H NMR resonances for the PMe_3 ligands of these complexes appear in two similar sets and indicate that two of the complexes have four PMe_3 ligands, while the other two complexes have five PMe_3 ligands.

The sulfur ligand resonances for each of the four complexes are in a 1:1:2:3 ratio, and their couplings are consistent with the presence of two olefinic protons, one methylene group, and one methyl group (the presence of the methylene and methyl groups were confirmed by ^{13}C DEPT, ^{1}H-^{1}H COSY, and ^{13}C-^{1}H HETCOR NMR experiments, but only for **4** since the free phosphine was removed prior to NMR data collection, facilitating the conversion of **3** to **4**). The presence of a methyl group suggests that the C–S bond has been cleaved, since this is the most probable way in which a methyl group could be formed. The observation that the methyl group is only coupled to the methylene group suggests that these complexes may have arisen from the hydrogenation of a C–S-inserted 2,3-dihydrothiophene ligand (the C–S insertion must have occurred on the aliphatic side of the 2,3-dihydrothiophene ligand in order to explain the formation of an ethyl group). These data support the structures proposed in eq 3. The α-olefinic protons are at δ 6.58 (major, **3a**), 7.09 (major, **4a**), 6.50 (minor, **3b**), and 7.03 (minor, **4b**), and the β-olefinic protons are at δ 5.74, 5.85, 6.06, and 6.21, respectively (the chemical shifts of the α-olefinic protons of **4** were obtained by a ^{1}H-^{1}H COSY NMR experiment because they were obscured). These downfield resonances are consistent with the presence of an olefinic group, and the 0.5-ppm downfield shift in the α resonances upon PMe_3 loss is consistent with the conversion to an allylic binding mode in which there is an increase in the C–S bond order. Figure 5 shows a ^{1}H NMR spectrum (in toluene-d_8) of the olefinic region confirming the coexistence of all four complexes.

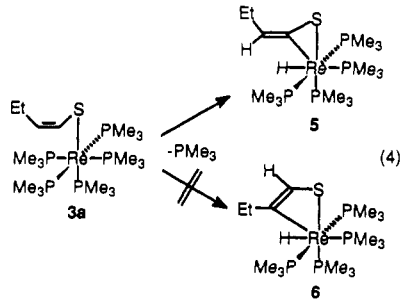
The coupling constants observed for the olefinic protons in these complexes are also indicative of a C–S-cleaved species, since they are much larger than those found for either free or S-bound 2,3-dihydrothiophene (J = 14.5 Hz for **3b**, **4b** and 9.2 Hz for **3a**,

(15) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1989**, *8*, 1856.



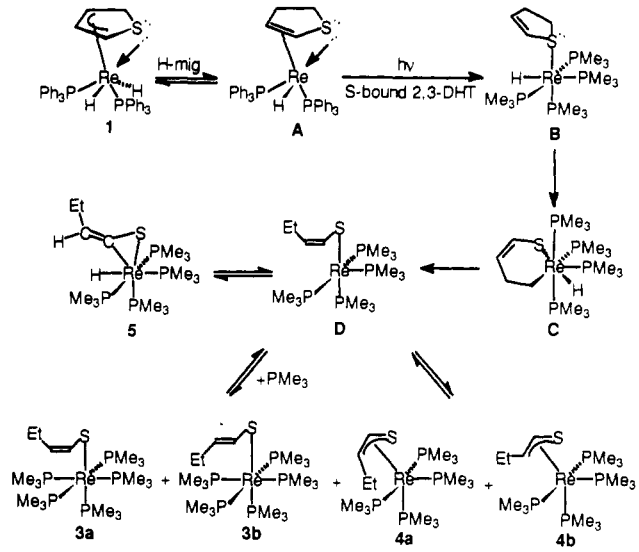
4a versus 5.9 Hz for free or S-bound 2,3-dihydrothiophene).[16] One would expect the coupling constant to increase if the five-membered ring has opened, since this would remove the strain from the olefinic bond by allowing the bond angles of the olefin to approach 120°. The magnitude of the coupling constant also allows the assignment of the isomers as trans (minor product, J = 14.5 Hz) and cis (major product, J = 9.2 Hz). This represents the first time that thiophene has been homogeneously transformed to a butenethiolate ligand, although the transformation to a butadienethiolate ligand has been previously observed in the reaction of (π-thiophene)RuCp$^+$ with nucleophiles.[11]

After the solvent and excess PMe_3 are removed in vacuo and fresh deuterated solvent is added, the ^1H NMR resonances of **3a** and **3b** are absent, leaving only those of **4a** and **4b** and other resonances attributable to a single new organometallic complex (Figure 6). These new resonances are also seen to begin growing in to a smaller extent upon irradiation when small amounts of PMe_3 are used in the reaction with **1**. This new product is apparently formed thermally, since irradiation is not required for the interconversion. The ^1H NMR spectrum of the new product shows the presence of four PMe_3 ligands and an upfield ^1H NMR resonance at δ −7.53 (ddt, J = 64.5, 61.4, 9.2 Hz) which integrates as one hydride. The $^{31}P\{^1H\}$ NMR spectrum shows three multiplet resonances between δ −36 and −48 in a 1:2:1 ratio and confirms the presence of four phosphine ligands. There are, however, only three olefinic resonances which are in a 1:2:3 ratio. The presence of both a methylene and methyl group was again confirmed by ^{13}C DEPT and ^{13}C-^1H HETCOR NMR experiments. Apparently one of the olefinic C–H bonds has oxidatively added to the metal center to form the metal hydride. The oxidative addition of the α-olefinic C–H bond would yield an η^2 C=S-bound thioketene, while the oxidative addition of the β C–H bond would yield a metallathiocyclobutene (eq 4). Several experimental observations



(discussed later) suggest that the structure of the new complex is, indeed, that of the thioketene $ReH(S{=}C{=}CHEt)(PMe_3)_4$ (**5**). There are numerous examples of transition-metal thioketene complexes,[17] but this is the first example of the transformation of a bound thiophene to a thioketene complex. Previously characterized transition-metal thioketene complexes were obtained either by ligand exchange with a stable thioketene or by the addition of elemental sulfur to a vinylidene complex.[17]

Scheme IV. Proposed Mechanism for the Formation of **3** and **4**



Proposed Mechanism for the Formation of 3, 4, and 5. The photochemical reactivity of **1** is shown in Scheme IV. The initial step is presumed to be the reversible migration of a hydride to the β position adjacent to the methylene group of **1**, as in the thermal reaction, in order to account for the formation of small amounts of **2** and tetrahydrothiophene during photolysis. The metal–olefin bond is then photochemically liberated, forming an S-bound 2,3-dihydrothiophene (**B**) and thus preventing the further hydrogenation of the olefin. The aliphatic carbon–sulfur bond is then cleaved, producing **C**. Reductive elimination then results in the formation of a 16-electron *cis*-ethenethiolate complex (**D**) which can either be trapped by excess PMe_3 to form **3** or, in the absence of a large excess of PMe_3, recoordinate the olefinic bond to form **4** (photochemical isomerization of the free olefinic bond in **D** and **3** can account for the observed formation of both cis and trans isomers, see below) or oxidatively add the α-olefinic C–H bond, resulting in the formation of **5**.

After a sample of **1** in C_6D_6 with excess PMe_3 has been irradiated for several hours, the removal of the free PMe_3 in vacuo yields a mixture of **4a**, **4b**, and **5**. Upon allowing the solution to stand at room temperature, the resonances of **4b** are seen to slowly diminish while those of **4a** are seen to increase (the resonances for **5** also increase but to a much lesser extent). After **4b** is completely gone, the resonances of **5** continue to slowly grow in, while those of **4a** concurrently diminish. This suggests that **5** is actually formed from **4a** (and **3a** after the loss of a PMe_3 ligand), not from **4b** (or **3b**). This also suggests that **4a** (cis) is the more thermodynamically stable isomer, since **4b** (trans) thermally rearranges to **4a** upon standing at room temperature.

If the mechanism proposed in Scheme IV is valid, then **D** should lead only to the formation of the cis complexes **3a** and **4a**, and the trans complexes should not be observed, since they are the thermodynamically less stable isomers. The fact that the trans complexes are seen (cis:trans = 1.6:1) suggests that the σ-ethenethiolate complexes may undergo photochemical olefin isom-

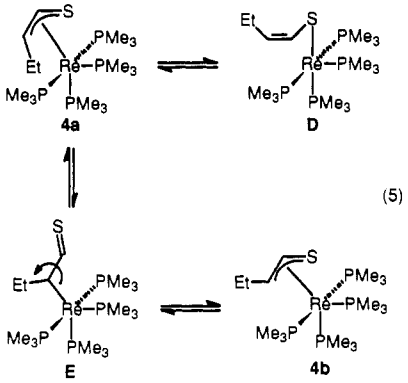
(16) For free 2,3-dihydrothiophene, see: Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 113. For S-bound 2,3-dihydrothiophene transition-metal complexes see: (a) Sauer, N. N.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 2160. (b) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1989**, *28*, 1751.

(17) (a) Weinand, R.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1145. (b) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988**, *340*, 161. (c) Werner, H.; Hofmann, L.; Wolf, J.; Müller, G. *J. Organomet. Chem.* **1985**, *280*, C55. (d) Werner, H.; Paul, W.; Knaup, W.; Wolf, J.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *358*, 95. (e) Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1985**, *118*, 873. (f) Wormsbächer, D.; Edelmann, F.; Behrens, U. *Chem. Ber.* **1982**, *115*, 1332. (g) Wormsbächer, D.; Edelmann, F.; Behrens, U. *Chem. Ber.* **1981**, *114*, 153. (h) Green, M.; Osborn, R. B. L.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 944.

erization to yield a nonthermodynamic ratio of the cis and trans isomers and that after photolysis the trans complexes then thermally rearrange to the cis complexes.

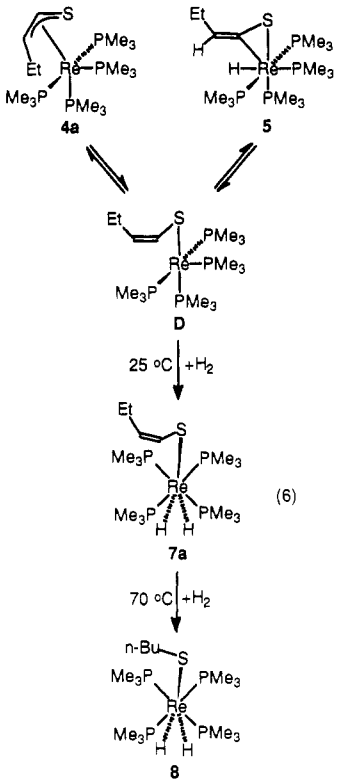
In order to test the reversibility of the oxidative addition of the σ-ethenethiolate intermediate **D**, excess PMe_3 was added to a sample that contained a 1:1 mixture of **5** and **4a**. The reaction was followed by ^1H NMR spectroscopy, showing the conversion of both **5** and **4a** to **3a** at the same rates. Upon removal of the free PMe_3 from solution, **5** and **4a** were regenerated at the same rate at which **3a** disappeared. This indicates that the formation of **5** is reversible and that **5** reductively eliminates to give exclusively the cis intermediate **D** since only cis **3a** is formed. These observations, therefore, support the formulation of **5** as the η^2 C=S-bound thioketene (which would give a cis complex upon reductive elimination) and not the metallathiocyclobutene complex **6** (which should give exclusively a trans complex after reductive elimination).

The preparation of a sample that consisted mostly of **3a** made it possible to test whether the cis complex **3a** can in fact photochemically isomerize to the trans complex **3b**. The sample of **3a** was prepared by allowing a mixture of **4a,b** and **5** to stand at room temperature for several days (thus facilitating the interconversion of **4b** to **4a**), followed by the addition of excess PMe_3, which converts both **4a** and **5** to **3a**. Upon allowing the solution to stand overnight at room temperature, only a small amount (4.5%) of **3b** remained by ^1H NMR spectroscopy. However, photolysis of the sample for only 0.5 h (samples of **1** with excess PMe_3 are typically irradiated for 5–10 h) resulted in the formation of a substantial amount of trans complexes (19% of **3b** and 4.8% of **4b**), indicating that photochemical isomerization of the free olefin of **3a** from cis to trans is indeed occurring. The slow thermal rearrangement of trans to cis can be explained by the formation of the σ-C-bound isomer of **E**, which can then interconvert the two isomers by rotation about the C–C bond (eq 5).[18]



(5)

Hydrogenation of Thiophene to Butanethiolate. The desulfurization of ethenethiolates has been previously seen under relatively mild conditions (70 °C, 1 atm H_2) on binuclear Mo complexes by Rakowski DuBois and co-workers.[23] Therefore, the reactivity of the 1-butene-1-thiolate complexes **3** and **4** with H_2 was of interest for determining whether similar results could be obtained. Since the removal of free PMe_3 from solution results in the transformation of **3** into a mixture of **4** and **5**, the reactions reported here were run with solutions that contained a mixture of **4a** and **5** (**4b** had almost completely isomerized to **4a** prior to H_2 addition). The addition of 1 atm of H_2 to a solution of **4a** and **5** in C_6D_6 resulted in the rapid quantitative conversion of both species into a single new organometallic complex at room temperature. Analysis of the ^1H NMR spectrum of the solution revealed the presence of a cis 1-butene-1-thiolate ligand, as in **3a** (similar chemical shifts and couplings), a single broad PMe_3 resonance, and an upfield quintet which integrated as two hydrides and showed the presence of four PMe_3 ligands. These data are consistent with the formulation of the new complex as $ReH_2(SCH{=}CHEt)(PMe_3)_4$ (**7a**) (eq 6), in which the unsaturated intermediate **D** is trapped by 1 equiv of H_2 (a small amount of a second complex was also formed and has been assigned as being the trans isomer **7b**, formed from the small amount of **4b** which was present at the start of the reaction).



(6)

Upon allowing the solution to stand at room temperature under 1 atm of H_2, new ^1H resonances are seen to begin growing in as those of **7** concurrently diminish. Heating of the solution of **7** (still under H_2) at 70 °C for 15 min showed the quantitative conversion of both **7a** and **7b** to a single new organometallic complex. Analysis of the ^1H NMR spectrum of this new complex shows that there are still two hydrides and four PMe_3 ligands, but the resonances attributed to the 1-butene-1-thiolate ligand have disappeared. In their place are four new upfield resonances in a 2:2:2:3 ratio, suggesting that hydrogenation of the thiolate ligand has occurred. A ^{13}C DEPT NMR experiment confirmed the presence of three methylene groups and allowed for the formulation of the new complex as the 1-butanethiolate complex $ReH_2(n\text{-}BuS)(PMe_3)_4$ (**8**) (eq 6), representing the first homogeneous hydrogenolysis of thiophene to a 1-butanethiolate ligand.

The formulation of **8** as a 1-butanethiolate complex was confirmed by the reaction of $HRe(PMe_3)_5$ with 1-butanethiol. The thermolysis (70 °C) or photolysis (through a 365 BP filter) of a solution of $HRe(PMe_3)_5$ and 1-butanethiolate in C_6H_6 gave **8** as determined by ^1H NMR spectroscopy, thus not only confirming the formulation of **8** but also giving credence to the reactions shown in eqs 3–6 as the steps leading to the production of **8** from **1**. The thermolysis reaction also showed substantial amounts of oligomerization (only a very small amount of oligomerization was observed to have occurred photochemically). Attempts to induce the reductive elimination of 1-butanethiol from **8** by thermolysis at 70 °C in the presence of excess PMe_3 also resulted in extensive decomposition of **8** along with the formation of H_2 (some HRe-

(18) Lumbroso, H.; Curé, J.; Mahatsekake, C.; Andrieu, C. G. *J. Mol. Struct.* **1990**, *216*, 315.
(19) Fan, M., Ph.D. Thesis, University of Rochester, 1989.
(20) Thioaldehydes are extremely unstable and oligimerize rapidly at room temperature. For example, see: (a) Duus, F. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1978; Vol. 3, p 373. (b) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1. (c) *Organic Compounds of Sulphur, Selenium and Tellurium*; Reid, D. H., Ed.; The Chemical Society: London; Volumes 1 to current.
(21) For the oligimerization of 1-butanethial, see: Brandsma, L. *Rec. Trav. Chim.* **1970**, *89*, 593.
(22) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11.
(23) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.

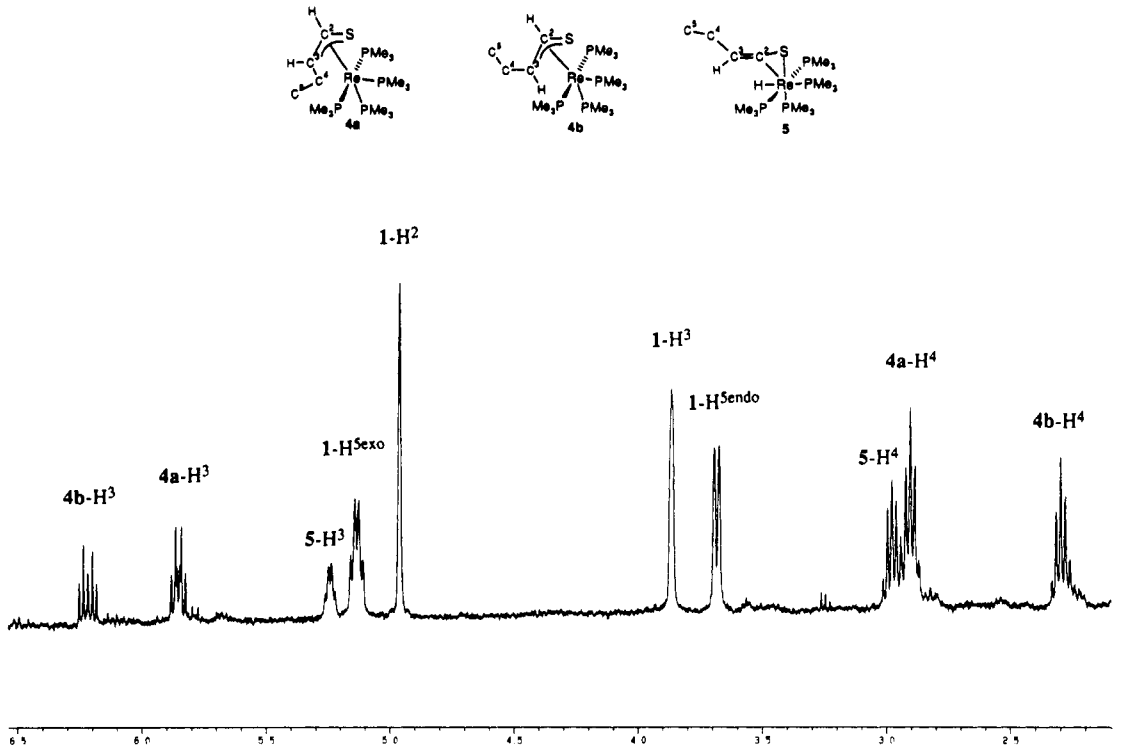


Figure 6. ^1H NMR spectrum of the same sample as in Figure 5 after removal of solvent and excess PMe_3, showing the disappearance of **3** and the appearance of **5**.

$(PMe_3)_5$ was also observed by ^1H NMR spectroscopy). No reaction was observed for the photolysis of **8** in the presence of excess PMe_3. These results suggest that **8** thermally loses H_2 (similar to what has been observed for $ReH_3(PMe_3)_4$)[19] and that the resulting intermediate can undergo an oxidative addition similar to that of **3a** in eq 4, yielding a 1-butanethial complex which thermally decomposes and oligomerizes upon decomplexation.[20,21]

Relevance to the Mechanism of the HDS of Thiophene. While the industrial HDS processes are heterogeneous and thermal in nature, it is still useful to study the thermal and photochemical reactivities of homogeneous metal complexes to gain insight into potential mechanistic details of HDS. The studies presented herein suggest that both π-bound and S-bound species are important during the reactions of thiophene with metal hydride complexes. It is apparent that thiophene is facilely hydrogenated when π-bound to a metal center in the presence of metal hydrides. However, C–S cleavage was not seen to occur thermally for **1**, but instead the weakly S-bound tetrahydrothiophene ligand was exchanged for PMe_3 at 60 °C.

The cleavage of the C–S bond seems to be highly dependent on the metal used, as can be seen in the comparison of the several metal–(thiophene·H) complexes that have been prepared. For Re and Mn,[8c] complexes are formed in which the C–S bonds are intact, but when Ru is used,[11] C–S bond cleavage is observed to have taken place. The Ru complex is proposed to partially hydrogenate the thiophene prior to C–S cleavage to obtain a complex that is analogous to the Re and Mn complexes. As presented herein, it is not until the thiophene is hydrogenated one step further, to 2,3-dihydrothiophene, that C–S bond cleavage is observed for Re. When tetrahydrothiophene is produced during the thermolysis of **1**, C–S insertion is not observed to occur. This is in agreement with the observation that 2,3-dihydrothiophene is much more reactive toward desulfurization (C–S bond cleavage) than either thiophene or tetrahydrothiophene.[22] However, the observed C–S bond cleavage in **1** might be due solely to the fact that the reaction was photochemical and not due to the enhanced reactivity of 2,3-dihydrothiophene versus tetrahydrothiophene. The formation of the ethenethiolate complexes **3** and **4** is very intriguing, as it has been shown that ethenethiolate complexes can be easily desulfurized at 70 °C under 1 atm of H_2.[23] It is also important to point out that the thiophene hydrogenation and hydrogenolysis reactions described here do not require external nucleophiles or electrophiles as in all previous examples but instead use hydrogen ligands already bound to the metal center.

Finally, we can compare and contrast the current chemistry of thiophene with that of furan. Felkin's proposal (Scheme I) showed the cleavage of the furan ring prior to hydrogenation.[9] Decarbonylation of the aldehyde led to the formation of a metal carbonyl product, which is apparently faster than hydrogenation to give a ketene ligand. In the present case, hydrogenation of one double bond was found to precede the ring cleavage reaction, and subsequent hydrogenation reactions to give the thioketene complex were found to be faster than formation of a thiocarbonyl ligand.

Conclusions

The thioallyl complex $(\eta^4\text{-}C_4H_5S)ReH_2(PPh_3)_2$ (**1**) has been found to undergo vastly different thermal reactions and photochemical reactions. Thermally, **1** has been shown to intramolecularly hydrogenate the bound thiophene·H ligand to give free tetrahydrothiophene. Photochemically, however, the thiophene·H ligand in **1** undergoes C–S bond cleavage, and products have been identified that contain an ethylthioketene ligand, a 1-butene-1-thiolate ligand, and a 1-butanethiolate ligand, representing the first such homogeneous hydrogenolysis transformations of thiophene. Mechanisms have been proposed that explain the formation of all of the complexes observed, and their relevance to the hydrodesulfurization of thiophene is discussed.

Experimental Section

General Procedures. Nearly all of the compounds that were used in this work are only slightly air sensitive in the solid state but are unstable in solution toward prolonged exposure to oxygen and moisture. All reactions were performed under vacuum or a nitrogen atmosphere in a Vacuum Atmospheres Dry-Lab glovebox. All reagents were obtained commercially and put through three freeze–pump–thaw cycles for degassing before use. All deuterated solvents were purchased from MSD Isotopes Merck Chemical Division, distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. All other solvents were dried similarly and stored in the glovebox. The syntheses of $ReH_7(PPh_3)_2$[13] and $HRe(PMe_3)_5$[14] were as previously reported. 2-Thienyllithium was purchased from Aldrich and used without further purification.

Proton, carbon, and phosphorus NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer. Resealable NMR tubes were

purchased from the Brunfeldt Company. ^1H NMR chemical shifts were measured in ppm (δ) relative to tetramethylsilane, using the residual ^1H resonances in the deuterated solvents as an internal reference: C_6D_6 (δ 7.15), toluene-d_8 (δ 2.09), and THF-d_8 (δ 3.58). ^{13}C NMR chemical shifts were measured in ppm relative to C_6D_6 (δ 128). ^{31}P NMR chemical shifts were measured relative to 30% H_3PO_4 (δ 0.0). GC/MS spectra were recorded using a Hewlett-Packard 5890 Series II gas chromatograph. Elemental analyses were carried out at Desert Analytics-Organic Microanalysis Laboratory. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination. Photolyses were carried out by using a high-pressure 200-W Hg focused beam Oriel lamp fitted with an infrared-absorbing water filter. Experiments involving more than one sample to be photolyzed under identical conditions were carried out in a merry-go-round apparatus.

Preparation of 2-Deuteriothiophene. A 50-mL sample of a 1 M solution (50 mmol) of 2-thienyllithium in THF was reduced in volume in vacuo to 10 mL. The solution was then quenched under N_2 at 0 °C with 1.5 mL (75 mmol) of D_2O, and the resulting solution was stirred for 2 h. The product was then vacuum transferred (along with the residual THF) and dried over CaH_2 for 4 h. The dried product solution was then vacuum transferred into an ampule for storage. ^1H NMR spectroscopy indicated >99.5% D in the α-site.

Preparation of (η^4-C_4H_5S)$ReH_2(PPh_3)_2$ (1). To a stirred solution of 80 mg (0.111 mmol) of $ReH_7(PPh_3)_2$ in 10 mL of THF was added 0.25 mL (2.09 mmol) of 3,3-dimethyl-1-butene followed by 0.5 mL (6 mmol) of thiophene. The reaction was stirred at 40 °C for 2 h as the solution gradually turned green. The solvent was evaporated in vacuo to give a yellowish-green solid, and the crude product was then dissolved in 2 mL of benzene. The solution was then allowed to stand overnight, giving the product as a yellow precipitate. Filtration of the mixture gave 66 mg (74%) of **1** as a yellow powder. Analysis of the mother liquor revealed that the reaction was incomplete, and 15 mg of $ReH_7(PPh_3)_2$ was recovered, giving **1** in 91% yield at 81% conversion. ^1H NMR (C_6D_6): δ 7.71 (t, J = 8.4 Hz, 12 H), 6.96 (m, 18 H), 5.13 (dt, J = 7.8, 6.1 Hz, 1 H, H^{5exo}), 4.96 (br s, 1 H, H^2), 3.86 (br s, 1 H, H^3), 3.68 (d, J = 7.8 Hz, 1 H, H^{5endo}), 1.87 (br s, 1 H, H^4), −0.80 (ddd, J = 36.9, 28.8, 9.8 Hz, 1 H), −10.98 (ddd, J = 47.0, 36.9, 9.8 Hz, 1 H). ^{13}C (C_6D_6): δ 134.42 (d, J_{C-P} = 10.2 Hz, C^{ortho}), 128.48 (s, C^{para}), 127.22 (d, J_{C-P} = 9.0 Hz, C^{meta}), 63.75 (d, J_{C-H} = 178.9 Hz, C^3), 59.41 (t, J_{C-H} = 143.8 Hz, C^5), 54.57 (d, J_{C-H} = 199.8 Hz, C^2), 30.80 (dd, J_{C-H} = 169.8 Hz, J_{C-P} = 11.3 Hz, C^4). $^{31}P\{^1H\}$ (C_6D_6): δ 39.79 (s), 33.86 (s). Anal. Calcd (found) for $C_{40}H_{37}P_2ReS$: C, 60.21 (60.96); H, 4.67 (4.73).

Reaction of $ReH_7(PPh_3)_2$ with 2-Deuteriothiophene. $ReH_7(PPh_3)_2$ was reacted with 2-deuteriothiophene as in the above reaction with thiophene. The yellow product obtained was analyzed by ^1H NMR spectroscopy and found to be analogous to **1** except for the intensity of the ^1H resonances at δ 5.13 and 4.96, which were each $^1/_2$ the intensity of the remaining thiophene ^1H resonances.

Preparation of $Re(PMe_3)_4(PPh_2C_6H_4)$ (2). To a solution of 50 mg (0.063 mmol) of **1** in 5 mL of benzene was added 0.25 mL (2.46 mmol) of PMe_3. The yellow solution was then stirred at 60 °C for 12 h, giving an orange solution. The solvent was evaporated in vacuo to give an orange solid. The crude product was washed with 1 mL of hexane and then filtered to give 41 mg (87%) of **2** as an orange powder. ^1H NMR (C_6D_6): δ 8.13 (dt, J = 7.9, 1.9 Hz, 4 H), 7.72 (d, J = 7.0 Hz, 1 H), 6.99 (m, 9 H), 1.56 (d, J = 5.0 Hz, 9 H), 1.53 (d, J = 6.1 Hz, 9 H), 1.06 (pt, J = 2.4 Hz, 18 H). $^{31}P\{^1H\}$ (C_6D_6): δ −42.16 (dt, J = 143.9, 20.9 Hz, PPh_3), −43.67 (dt, J = 19.3, 15.8 Hz, trans PMe_3), −48.10 (dt, J = 18.8, 15.3 Hz), −67.3 (dq, J = 143.9, 17.8 Hz). Anal. Calcd (found) for $C_{30}H_{50}P_5Re$: C, 47.93 (47.56); H, 6.70 (6.63).

Phosphine Concentration Study for the Thermolysis of 1. To a stock solution of 5 mg (6.3×10^{-3} mmol) of **1** in 1 mL of C_6D_6 was added 8 μL of THF as an internal standard. Two NMR samples were then prepared from the stock solution. To each sample was then added PMe_3 (sample 1 received 1 μL (9.8×10^{-3} mmol) and sample 2 received 50 μL (0.49 mmol)), and the samples were then heated at 70 °C. A ^1H NMR spectrum of each of the samples was recorded after 25 min, and they showed that the rate of the reaction of **1** to **2** is dependent on the concentration of PMe_3 used, as sample 1 showed only a 40% conversion after 25 min while sample 2 showed greater than a 90% conversion after 25 min.

Thermolysis of 1 with Excess Thiophene and H_2. Saturated samples of **1** in C_6D_6 (0.5 mL, 0.01 M) were placed in resealable NMR tubes with 20 μL of thiophene (50 equiv, 0.5 M). Four samples were prepared as follows: (1) 1 atm of H_2, (2) 0.5 atm of H_2, (3) 0.25 atm of H_2, and (4) 1 atm of H_2 and 20 μL (0.5 M) of 3,3-dimethyl-1-butene. The samples were then thermolyzed at 60 °C overnight and monitored by ^1H NMR. Each showed the formation of only 1 equiv of tetrahydrothiophene and the formation of $ReH_7(PPh_3)_2$. As the amount of H_2 decreased in the samples, more decomposition was observed.

Preparation of $Re(\eta^1$-SCH=CHEt$)(PMe_3)_5$ (3a,b), $Re(\eta^3$-SCH=CHEt$)(PMe_3)_4$ (4a,b), and $ReH(\eta^2$-S=C=CHEt$)(PMe_3)_4$ (5). To a sample of 5 mg of **1** in C_6D_6 (0.011 M) in a resealable NMR tube were added 5 μL of PMe_3 (9 equiv, 0.11 M) and THF (0.88 mM) as an internal standard. The sample was then irradiated for 5 h. ^1H NMR spectroscopy showed the formation of **3a** (1.0 mM), **3b** (0.5 mM), **4a** (1.9 mM), **4b** (1.3 mM), and **5** (2.0 mM) along with remaining **1** (2.0 mM), giving a combined yield of 74% at 82% conversion. The instability of the complexes to chromatography, their similar solubilities, and the interconversion of the complexes (**4** to **3** in the presence of free PMe_3, **b** to **a**, and **3** to **5**) have made attempts to purify or crystallize the complexes unsuccessful. The samples generally also contain small amounts of **1** and **2**, making purification even more difficult, and are consequently characterized only by NMR spectroscopy. ^1H, ^{31}P, and ^{13}C NMR spectra are all recorded in C_6D_6 at room temperature. Due to the mixture of complexes and their concentrations, the complete assignment of ^{13}C NMR resonances could not be achieved. Only those resonances unequivocally determined by ^{13}C DEPT and ^{13}C–^1H HETCOR experiments are reported. All compounds are labeled with C^2 being α to S. Hydrogens are given the same number as the carbon to which they are attached. **3a**. ^1H NMR: δ 6.58 (dq, J_{2-3} = 9.2 Hz, J_{2-4} = 1.5 Hz, J_{2-P} = 1.5 Hz, 1 H, H^2), 5.74 (dt, J_{3-4} = 6.7 Hz, 1 H, H^3), 2.84 (ddq, J_{4-5} = 7.4 Hz, 2 H, H^4), 1.44 (br s, 36 H), 1.29 (t, 3 H, H^5), 1.28 (d, J = 5.8 Hz, 9 H). **3b**. ^1H NMR: δ 6.50 (dq, J_{2-3} = 14.5 Hz, J_{2-4} = 1.4 Hz, J_{2-P} = 1.5 Hz, 1 H, H^2), 6.06 (dt, J_{3-4} = 6.7 Hz, 1 H, H^3), 2.24 (ddq, J_{4-5} = 7.4 Hz, 2 H, H^4), 1.46 (br s, 36 H), 1.30 (d, J = 5.8 Hz, 9 H), 1.07 (t, 3 H, H^5). **4a**. ^1H NMR: δ 7.09 (obscured, 1 H, H^2), 5.85 (dt, J_{2-3} = 9.2 Hz, J_{3-4} = 6.7 Hz, 1 H, H^3), 2.90 (ddq, J_{2-4} = 1.5 Hz, J_{4-5} = 7.4 Hz, 2 H, H^4), 1.44 (pt, J = 3.0 Hz, 18 H), 1.27 (d, J = 6.7 Hz, 9 H), 1.29 (t, 3 H, H^5), 1.12 (d, J = 6.7 Hz, 9 H). $^{13}C\{^1H\}$ NMR: δ 34.60 (s, CH_2, C^4), 14.90 (s, CH_3, C^5). **4b**. ^1H NMR: 7.03 (obscured, 1 H, H^2), 6.21 (dt, J_{2-3} = 14.5 Hz, J_{3-4} = 6.7 Hz, 1 H, H^3), 2.30 (ddq, J_{2-4} = 1.4 Hz, J_{4-5} = 7.4 Hz, 2 H, H^4), 1.48 (pt, J = 3.0 Hz, 18 H), 1.27 (d, J = 6.7 Hz, 9 H), 1.11 (d, J = 6.7 Hz, 9 H), 1.07 (t, 3 H, H^5). $^{13}C\{^1H\}$ NMR: δ 27.40 (s, CH_2, C^4), 15.60 (s, CH_3, C^5). **5**. ^1H NMR: δ 5.24 (q, J_{3-4} = 6.0 Hz, J_{3-P} = 6.0 Hz, 1 H, H^3), 2.97 (dq, J_{4-5} = 7.4 Hz, 2 H, H^4), 1.49 (d, J = 8.1 Hz, 9 H), 1.46 (d, J = 7.5 Hz, 9 H), 1.40 (t, 3 H, H^5), 1.26 (pt, J = 2.6 Hz, 18 H), −7.53 (ddt, J = 64.5, 61.4, 9.2 Hz, 1 H). $^{13}C\{^1H\}$ NMR: δ 22.2 (s, CH_2, C^4), 15.63 (s, CH_3, C^5). $^{31}P\{^1H\}$ NMR: δ −37.16 (m), −37.61 (m), −47.05 (pt, J = 16.5 Hz).

Preparation of $ReH_2(SCH{=}CHEt)(PMe_3)_4$ (7). A sample of a 1:1 mixture of **4a** and **5** in C_6D_6 (prepared as above) was placed under an atmosphere of H_2 and allowed to stand at room temperature for 2 h. ^1H NMR spectroscopy showed the conversion of both **4a** and **5** to **7a** (trace amounts of **7b** were also observed due to the presence of small amounts of **4b** in the sample due to incomplete conversion to **4a**). ^1H NMR resonances attributable to **8** are also seen to begin growing in upon allowing the solution to stand at room temperature, preventing the isolation of pure **7**. **7a**. ^1H NMR (C_6D_6): δ 6.60 (dt, J = 9.3, 1.5 Hz, 1 H, H^2), 5.69 (dt, J = 9.3, 6.7 Hz, 1 H, H^3), 2.83 (ddq, J = 7.5, 6.7, 1.5 Hz, 2 H, H^4), 1.47 (br s, 36 H), 1.24 (t, J = 7.5 Hz, 3 H, H^5), −9.16 (qn, J = 23.5 Hz, 2 H). **7b**. ^1H NMR (C_6D_6): δ 6.48 (dt, J = 14.4, 1.5 Hz, 1 H, H^2), 6.05 (dt, J = 14.4, 6.7 Hz, 1 H, H^3), 2.23 (ddq, J = 7.5, 6.7, 1.5 Hz, 2 H, H^4), 1.51 (br s, 36 H), 1.03 (t, J = 7.5 Hz, 3 H, H^5), −9.18 (qn, J = 23.5 Hz, 2 H).

Preparation of $ReH_2(n$-BuS$)(PMe_3)_4$ (8). The sample of **7** in C_6D_6 prepared above was heated at 70 °C under 1 atm of H_2 for 15 min. ^1H NMR spectroscopy showed the quantitative conversion of **7** to **8**. PPh_3 also remained from dissociation from **1**. ^1H NMR (C_6D_6): δ 2.49 (t, J = 7.5 Hz, 2 H, H^2), 1.97 (qn, J = 7.5 Hz, 2 H, H^3), 1.68 (sextet, J = 7.5 Hz, 2 H, H^4), 1.51 (br s, 36 H), 1.02 (t, J = 7.5 Hz, 3 H, H^5), −9.24 (qn, J = 24.4 Hz, 2 H). $^{13}C\{^1H\}$ (C_6D_6): δ 39.80 (s, CH_2), 38.88 (s, CH_2), 29.86 (d, J = 28.7 Hz, PCH_3), 23.61 (s, CH_2), 14.54 (s, CH_3). $^{31}P\{^1H\}$ NMR: δ −52.28 (br s).

Reaction of $HRe(PMe_3)_5$ with 1-Butanethiol. Two NMR samples were prepared containing $HRe(PMe_3)_5$ (15 mg, 0.05 M) and 1-butanethiol (30 μL, 0.56 M) in 0.5 mL of C_6D_6. One sample was heated at 70 °C for 5 h, and the other sample was irradiated through a 365 BP filter overnight. Analysis of the two reactions by ^1H NMR spectroscopy showed that **8** was formed in both samples. The thermal reaction showed extensive oligomerization, as evidenced by the formation of several large broad peaks in the ^1H NMR spectra (this occurred to a much lesser extent in the sample that was irradiated). The photochemical reaction afforded **8** as the major product. During photolysis, the solution darkens significantly, thus stopping the reaction at approximately 25% conversion. The separation of pure **8** from excess unreacted $HRe(PMe_3)_5$ has yet to be accomplished due to their similar solubilities.

Solution and Refinement of Crystal Structures. (η^4-C_4H_5S)$ReH_2(PPh_3)_2$ (1). A yellow crystal of **1** with approximate dimensions 0.08 ×

Table III. Summary of Crystallographic Data for 1 and 2

	1	2
empirical formula	$C_{40}H_{37}P_2ReS{\cdot}C_7H_8$	$C_{30}H_{50}P_5Re$
cryst syst	monoclinic	monoclinic
space group	Pn (No. 7)	$P2_1/n$ (No. 14)
Z	2	4
a, Å	10.300 (2)	10.868 (6)
b, Å	13.584 (4)	17.543 (5)
c, Å	13.913 (2)	17.564 (3)
β, deg	92.32 (1)	100.67 (3)
V, Å^3	1945 (1)	3291 (4)
d_{calcd}, g/cm^3	1.516	1.517
t, °C	-50	-20
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
$\lambda_{Mo K\alpha}$ (graphite monochr)	0.710 69	0.710 69
scan type	$2\theta/\omega$	$2\theta/\omega$
scan rate, deg/min	2-16.5	2-16.5
tot background time	scan time/2	scan time/2
take-off angle, deg	2.6	2.6
scan range, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	2-25	2-22
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collected	3577	4192
no. of unique data $>3\sigma$	2122	2436
no. of parameters varied	362	320
abs coeff, cm^{-1}	33.294	39.997
systematic absences	$h0l$, l odd	$0k0$, k odd $h0l$, l odd
abs correction	differential	differential
range of transm factors	0.97-1.01	0.94-1.11
equivalent data	$0kl$, $0k\bar{l}$	$0kl$, $0k\bar{l}$
agreement of equiv data (F_o)	0.103	0.065
R_1	0.052	0.037
R_2	0.051	0.037
goodness of fit	1.216	1.073
largest peak in final E map	1.090	0.643

0.15 × 0.19 mm^3 was mounted on a glass fiber and placed on the diffractometer under a stream of nitrogen at -50 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected in accord with the parameters in Table III. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal stability. The space group was assigned as Pn ($P2/n$ also possible), and the correctness of this choice was confirmed by the successful solution of the Patterson map, showing the Re atom. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure. The location of the sulfur atom could not be determined as the peak intensities of the positions α to the methylene group in the difference Fourier map were similar, suggesting S/CH disorder in the α position. The disorder was modeled by placing an individual sulfur atom at each position (S1A and S1B) and then constraining the coordinates of the carbon atoms (C39B and C39A, respectively) to those of the sulfur atoms. The B_{eq} values of the sulfur atoms were constrained together, as were those of the carbon atoms. The population was then varied to convergence, giving values of 0.61 and 0.39 for the population of the disordered molecules. Attempts to vary the coordinates of all four atoms independently led to divergence. A toluene solvent molecule of crystallization was also located in a difference Fourier map. The solvent molecule was refined isotropically as a group. An empirical absorption correction was applied after isotropic refinement of all non-hydrogen atoms by using the program DIFABS. Anisotropic refinement of all remaining non-hydrogen atoms allowed for the use of a difference Fourier map for the location of the hydrogen atoms. Four carbon atoms were refined isotropically, since anisotropic refinement led to nonpositive definite values. The hydrogens attached to the Re atom were not located. The coordinates of the remaining hydrogen atoms were subsequently idealized. The largest residual peaks in the final E-map were located in the vicinity of the solvent molecule. Selected bond distances and angles are given in Table I.

$\overline{Re(PMe_3)_4(PPh_2C_6H_4)}$ (2). An orange crystal of **2** with approximate dimensions 0.19 × 0.15 × 0.15 mm^3 was mounted on a glass fiber and placed on the diffractometer under a stream of nitrogen at -20 °C. Data collection was as for **1** with a monoclinic crystal system. Data were collected in accord with the parameters in Table III. The space group was uniquely assigned as $P2_1/n$, and the correctness of this choice was confirmed by the successful solution of the Patterson map, showing the Re atom. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure. An empirical absorption correction was applied after isotropic refinement of all non-hydrogen atoms by using the program DIFABS. After anisotropic refinement of all non-hydrogen atoms, the coordinates of the hydrogen atoms were idealized. Selected bond distances and angles are given in Table II.

Acknowledgment is made to the National Science Foundation, grant CHE9102318, for support of this work. W.D.J. also thanks NATO for a travel grant.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and bond distances and angles for complexes **1** and **2** (21 pages); calculated and observed structure factors for complexes **1** and **2** (32 pages). Ordering information is given on any current masthead page.

Six New Saddle-Shaped Hosts Based on Fused Dibenzofuran Units[1,2]

Elaine Benaksas Schwartz, Carolyn B. Knobler, and Donald J. Cram*

Contribution from the Department of Chemistry and Biochemistry of the University of California at Los Angeles, Los Angeles, California 90024. *Received June 29, 1992*

Abstract: The syntheses of six new host systems are reported whose semirigid, saddle-shaped structures are based on incorporation of three to four dibenzofuran units into a macroring (**4-9**). The two clefts in **4** have long axes mutually perpendicular to one another, each of which is structurally complementary to molecules such as dibenzofuran. The single clefts of **5-9** have a similar long axis. The width of their clefts varies with connecting groups A, which provide potential binding or catalytic sites on the floor of each cleft. Crystal structures are reported for **4**, **6**, and **8**. A survey of potential guests for binding **4** revealed weak binding to occur between **4** and 1,3-$(NC)_2C_6H_4$ and 1,3-$(O_2N)_2C_6H_4$ in $CDCl_3$. Host **8** was found to complex guanine in CD_3OD as solvent.

The dibenzofuran unit is attractive for use in assembling cavitands with large interiors. It possesses two large flat surfaces, undergoes metalation readily in its 4- and 6-positions, and undergoes electrophilic substitution in its 2- and 8-positions.[3] We

0002-7863/92/1514-10775$03.00/0