and 6.08 g (160 mmol) of MeOLi in 50 mL of methanol was added. The resulting mixture was stirred for 30 min. The solvent was evaporated and the solid residue taken up with pentane. The salts were filtered, and then the solvent was evaporated. The residue was distilled and yielded 3.9 g of n-Bu_3SiOMe (87%): bp 110–120 °C (19.9 hPa) [lit.[55] bp 239 °C (10^5 Pa)].

Silane. Complex **1a** (0.447 g, 1.12 mmol) in 2 mL of n-Bu_2O was treated with 14.6 mmol of a solution of $LiAlH_4$ in n-Bu_2O. A gas evolved and was collected in a measuring glass tube initially filled with inert oil. Gas (25 mL, 100%) was collected and identified as silane by IR spectroscopy;[56] IR (CCl_4) ν_{Si-H} 2180 cm^{-1}. Caution! SiH_4 is an air-flamable gas.

General Procedure To Recover Catechol. After acidic hydrolysis of the reaction mixture, the organosilane was extracted with ether. The combined extracts were washed with water and then with a 2 M solution of NaOH. These basic waters were then acidified and extracted three times with ether. Ether was evaporated, and crude catechol was obtained quantitatively in every case.

Registry No. 1a, 101519-12-4; HO-o-C_6H_4–OH, 120-80-9; $Si(OMe)_4$, 681-84-5; Et_3SiO-o-C_6H_4–OH, 101541-79-1; n-Bu_3SiO-o-C_6H_4–OH, 101541-83-7; $(CH_2{=}CHCH_2)_3Sio$-o-C_6H_4–OH, 106702-38-9; (i-Pr)$_3$SiH, 64885-79-6; $(CH_2{=}CHCH_2)_4Si$, 1112-66-9; Ph_3SiLi, 791-30-0; (i-Bu)$_3$SiH, 64885-81-0; $(PhCH_2)_3SiH$, 1747-92-8; (n-$C_{12}H_{25})_3SiH$, 18817-82-8; Et_3SiH, 617-86-7; n-Bu_3SiH, 998-41-4; Me_4Si, 75-76-3; n-Bu_3SiOH, 56889-90-8; n-Bu_4Si, 994-79-6; n-Hex_3SiOH, 60782-58-3; n-Hex_4Si, 3429-81-0; $(CH_2{=}CH)_4Si$, 1112-55-6; $(CH_3C{\equiv}C)_4si$, 20143-21-9; (n-BuC$\equiv$C)$_4$Si, 106702-39-0; $(PhC{\equiv}C)_4Si$, 18769-86-3; $(Me_3SiC{\equiv}C)_4Si$, 13888-92-1; Ph_4Si, 1048-08-4; Et_3SiCl, 994-30-9; n-Bu_3SiCl, 995-45-9; n-Bu_3SiBr, 2116-80-5; Et_3SiPh, 2987-77-1; n-Bu_3SiMe, 995-43-7; $Et_3Si(C{\equiv}CBu)$, 21693-13-0; $Et_3Si(C{\equiv}CPh)$, 4131-43-5; $Et_3Si(CH_2CH{=}CH_2)$, 17898-21-4; $Et_3SiGePh_3$, 18771-58-9; Ph_3GeLi, 3839-32-5; n-Bu_3SiOMe, 15811-64-0; SiH_4, 7803-62-5; Pentane-1,5-dimagnesium dichloride, 106702-37-8; butane-1,4-dimagnesium dichloride, 22758-42-5; 5-silaspiro[4.4]nonane, 176-51-2; 6-silaspiro[5.5]undecane, 181-09-9.

---

[56] Finholt, A. E.; Bond, A. C., Jr.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692.

Activation and Desulfurization of Thiophene and Benzothiophene by Iron Carbonyls

Ann E. Ogilvy, M. Draganjac, Thomas B. Rauchfuss,* and Scott R. Wilson

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received October 29, 1987

The synthesis, reactivity, and structure of thiaferroles $Fe_2(R_2C_4H_2S)(CO)_6$ and benzothiaferroles $Fe_2(C_8H_6S)(CO)_6$ (**1**) are surveyed. These compounds are prepared by the reaction of $Fe_3(CO)_{12}$ with thiophenes and benzothiophenes. The benzothiaferrole **1** undergoes oxidative demetalation to give the cyclic thioester thiocoumarin C_9H_6OS. Solutions of **1** are stable at 185 °C under N_2; at 160 °C, high pressures of CO convert **1** into $Fe(CO)_5$ and benzothiophene, i.e. reductive elimination. Solutions of **1** react with H_2 to give primarily ethylbenzene together with 2-ethylbenzenethiol and bis(2-ethylphenyl) sulfide. Compound **1** survives flash vacuum pyrolysis up to ~280 °C whereupon it eliminates benzothiophene. In contrast to the considerable thermal stability of thiabenzoferrole, solutions of the thiaferroles decompose at ~80 °C to give the ferroles regiospecifically and in high yield. The structure of the PPh_3 derivative of **1** was studied in the solid state. $Fe_2(C_8H_6S)(CO)_5(PPh_3)$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 12.498$ (2) Å, $b = 13.138$ (2) Å, $c = 10.618$ (2) Å, $\alpha = 113.00$ (1)°, $\beta = 111.22$ (1)°, and $\gamma = 100.37$ (1)°. Refinement of 3389 reflections converged to a final R of 0.030 ($R_w = 0.031$). The structure of this benzothiaferrole consists of a $Fe_2(CO)_5(PPh_3)$ core bridged by a C_8H_6S fragment involving both mercaptide and σ,π-vinyl bridging groups. One Fe center is six-coordinate, and the other Fe center is seven-coordinate. The low-temperature ^{13}C NMR spectrum of **1** shows six CO signals. Two dynamic processes are observed at higher temperatures: one involves turnstile rotation at one of the $Fe(CO)_3$ groups and the other, which equivalences all six CO groups, involves flip-flop of the organic ligand.

Introduction

The interaction of thiophenes with transition metals is of technological importance and scientific interest for three reasons. First, the poisoning of metal catalysts by organic sulfur compounds, commonly thiophenes, is a major problem in the petroleum industry.[1] Second, the desulfurization of thiophenes and sulfides is the objective of catalytic hydrodesulfurization (HDS), one of the largest industrial applications of transition-metal catalysis.[2] Third, transition metal reagents, e.g. Raney nickel, are often used to stoichiometrically abstract sulfur from thiophenes as well as organosulfur compounds.[3]

Several recent studies have provided definitive information on the interaction of thiophenes with the surfaces of metals and metal sulfides. Temperature-programmed desorption studies and vibrational spectroscopy under ultrahigh vacuum (10^{-10} Torr) have shown that thiophene binds to Mo(100) surfaces in both η^1,S- and η^5-modes.[4] At higher temperatures the coordinated thiophene is observed to undergo stepwise dehydrogenation. Thiophene also binds to Pt(111) in both an η^1,S- and an η^5-manner.[5,6] On Pt(111) the coordinated thiophene rearranges to metallacycles and sulfide at higher temperatures.[5,6] The initial coordination events on Ni(111) and Ni(100) appear to be

---

[1] Oudar, J. In *Catalyst Deactivation*; Petersen, E. E., Bell, A. T., Eds.; Marcel Dekker: New York, 1987. Hegedus, L. L.; McCabe, R. W. *Catalyst Poisoning*, Marcel Dekker: New York, 1984.

[2] Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. In *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.

[3] Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Org. Chem.* **1983**, *48*, 2963; *J. Am. Chem. Soc.* **1986**, *108*, 7763.

[4] Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75.

[5] Stöhr, J.; Gland, J. L.; Kollin, E. B.; Koestner, R. J.; Johnson, A. L.; Muetterties, E. L.; Sette, F. *Phys. Rev. Lett.* **1984**, *53*, 2161.

[6] Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44.

0276-7333/88/2307-1171$01.50/0

similar to Pt(111).[7,8] The distribution of C_4 hydrocarbons resulting from thiophene HDS is very similar for both Mo(100) and MoS_2 catalyst,[9] indicating that the thiophene interacts *directly* with the Mo centers in both of these catalysts. The desulfurization of thiophene adsorbed on molybdenum catalysts does not appear to involve hydrogen or surface sulfide.[10,11]

Solution studies on the interactions of thiophenes with transition metals have been reported sporadically for the past 30 years. Thiophene is known to bind to metals in both an η^1- and η^5-manner,[12-22] and indications are that these binding modes are interrelated in the same way as the corresponding forms of the $C_5H_5^-$ ligand.[14] Cationic complexes of η^5-thiophenes undergo addition reactions similar to those for cationic arene complexes,[20] and very recent work has demonstrated this process labilizes the C–S bonds in compounds of the type $[CpRu(\eta^5\text{-}RC_4H_4S)]$.[21]

The cleavage of the C–S bond in thiophenes is of great interest since this is the means by which metals abstract sulfur from the hydrocarbon. We therefore developed an interest in the early work of Stone and co-workers, who discovered that thiophenes and $Fe_3(CO)_{12}$ react to give both ferroles and thiaferroles (eq 1).[23,24] In this report we

$$C_4H_4S \xrightarrow{Fe_3(CO)_{12}} Fe_2(C_4H_4)(CO)_6 + Fe_2(C_4H_4S)(CO)_6 \qquad (1)$$

show that the thiaferroles are precursors to ferroles, thereby establishing a plausible sequence of events for thiophene activation and desulfurization by metals.

It is generally accepted that the sulfur heterocycles are the most refractory forms of sulfur in fossil fuels. The recent surge of interest in coordination chemistry of thiophenes is due to the growing recognition of this situation. Of the thiophenes found in fossil fuels, benzo-, and dibenzothiophene derivatives are *much* more prevalent than alkylthiophenes.[25] This point is important since, as we show in this paper, the organometallic chemistries of benzothiophene and thiophene are very different.

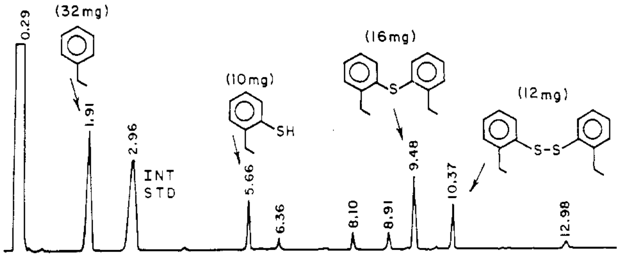
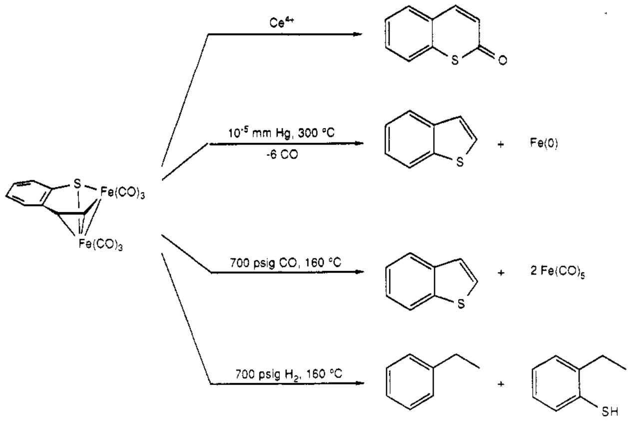


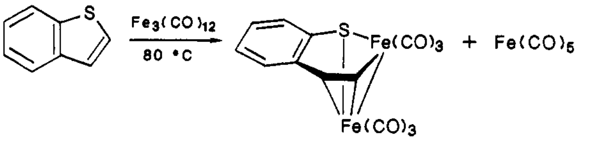
Figure 1. Gas chromatography trace of the volatiles formed in the hydrogenation of $Fe_2(C_8H_6S)(CO)_6$.

Scheme I



Results and Discussion

The Chemistry of Iron Carbonyl Derivatives of Benzothiophene. The reaction of benzothiophene with $Fe_3(CO)_{12}$ in refluxing benzene gives the benzothiaferrole $Fe_2(C_8H_6S)(CO)_6$ (**1**).[24] This reaction is quite clean, and the workup primarily involves the separation of **1** from elemental iron and the residual benzothiophene which is used in excess. $Fe(CO)_5$ was also observed as a byproduct (eq 2). On the basis of the stoichiometry of eq 2, the optimized yield of **1** was 49%. Chromatography revealed no other products. An X-ray structure of the monophosphine derivative of **1** (vide infra) confirms the hexacarbonyl formulation assigned to **1** as opposed to the pentacarbonyl structure proposed earlier.[24] Other iron reagents were tested for their reactivity toward benzothiophene. Neither $Fe(CO)_5$, $Fe_2(CO)_9$, nor $CpCo(CO)_2$ reacted with benzothiophene. The benzylideneacetone complex $Fe(C_{10}H_9O)(CO)_3$ is often employed as a reactive source of $Fe(CO)_3$,[26] but it failed to react with benzothiophene. We did however find that $Ru_3(CO)_{12}$ and benzothiophene react in refluxing octane to give a compound spectroscopically very similar to **1**. We were unable to induce a reaction between $Fe_3(CO)_{12}$ and dibenzothiophene or tetrahydrothiophene.



(2)

The cyclic voltammetry of **1** shows two reversible reductions at −1.03 V and −1.44 V vs. Ag/AgCl which agrees

---

(7) Zaera, F.; Kollin, E. B.; Gland, J. L. *Langmuir* **1987**, *3*, 555.

(8) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313.

(9) Gellman, A. J.; Neiman, D.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 92.

(10) Gellman, A. J.; Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 103.

(11) Friend, C. M.; Roberts, J. T. *Surf. Sci.* **1987**, *186*, 201.

(12) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. C. *J. Am. Chem. Soc.* **1984**, *106*, 5379.

(13) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55. Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

(14) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

(15) Other probable examples of S-bound thiophene complexes are described in the following: Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689. Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1983**, *248*, C9.

(16) Braitsch, D. M.; Kumarappan, R. *J. Organomet. Chem.* **1975**, *84*, C37. Guerchais, V.; Astruc, D. *J. Organomet. Chem.* **1986**, *316*, 335. Bachmann, P.; Singer, H. *Z. Naturforsch., B.: Anorg. Chem. Org. Chem.* **1976**, *31B*, 525.

(17) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.

(18) Lee, C. C.; Ibqual, M.; Gill, U. S.; Sutherland, R. G. *J. Organomet. Chem.* **1985**, *288*, 89.

(19) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5570.

(20) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.

(21) Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.

(22) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

(23) Kaesz, H. D.; King, R. B.; Manuel, T. A.; Nichols, L. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 4749.

(24) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600. King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *82*, 4557.

(25) Galpern, G. D. In *Thiophene and its Derivatives*; Gronowitz, S., Ed.; Wiley: New York, 1985; Part I.

(26) Brookhart, M.; Nelson, G. O. *J. Organomet. Chem.* **1979**, *164*, 193.

with the results of Dessy and Pohl.[27] Chemical reduction of 1 by Na(Hg) gave intractable materials. Oxidizing agents such as ferric ion convert 1 to the carbonylated heterocycle thiocoumarin.[28] The best reagent for this conversion was found to be ceric ammonium nitrate which gave thiocoumarin in ca. 35% yield (Scheme I). This synthesis of thiocoumarins from benzothiophene has not been explored previously[29,30] but has some synthetic potential. The sulfur atom in 1 is demonstrably nonnucleophilic since it resists oxygenation by *m*-chloroperoxybenzoic acid. This oxo transfer agent has been recently employed to oxygenate sulfur ligands in $Fe_3S_2(CO)_9$, $Fe_2(C_2H_4S_2)(CO)_6$, and $Fe(C_3H_4S)(CO)_3$.[31,32]

Compound 1 is a thermally robust material. Under nitrogen, solutions of 1 are stable at 180 °C. Carbonylation of solutions of 1 at 160 °C gave a homogeneous solution of $Fe(CO)_5$ and benzothiophene. Hydrogenation of a solution of 1 at 175 °C gave an insoluble iron-containing solid and a series of ethylbenzene derivatives identified by GC/MS. The major organic product was ethylbenzene (41.8%). Other important products are the 2-substituted ethylbenzenes: 2-ethylbenzenethiol (10.0%), bis(2-ethylphenyl) sulfide (18.3%), and bis(2-ethylphenyl) disulfide (12.1%) (Figure 1). The identities of the thiol and its disulfide were confirmed by comparisons with independently synthesized samples. Since solutions of 1 are stable at 180 °C under N_2, the H_2 obviously induces the decomposition of 1 leading to C–S hydrogenolysis. Solutions of benzothiophene itself were found to be stable under these reaction conditions.

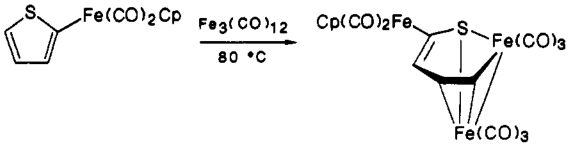
The results of the hydrogenolysis and oxidation of 1 led us to examine the thermal properties of 1 in the gas phase. Compound 1 is stable in the gas phase at temperatures ≤ 250 °C. Flash vacuum pyrolysis of 1 at 280 °C gave benzothiophene together with a trace of thiocoumarin. In these experiments, unidentified iron-containing compounds are deposited in the hot zone. Thiocoumarin survives flash vacuum pyrolysis at 280 °C; hence it is not an intermediate in this conversion. These results are summarized in Scheme I.

Compound 1 readily undergoes sequential substitution of two carbonyls by triphenylphosphine. Both the mono- and disubstituted derivatives were obtained in analytically pure form after silica gel chromatography.

The Chemistry of Iron Carbonyl Derivatives of Thiophenes. The reaction of $Fe_3(CO)_{12}$ with thiophene was found to proceed as described previously[23] to give low yields of both the thiaferrole $Fe_2(C_4H_4S)(CO)_6$ and the ferrole $Fe_2(C_4H_4)(CO)_6$.

Methyl substitution of the thiophene gave improved yields of the corresponding thiaferroles and ferroles but did not dramatically alter the product distribution. The characterization of the chemistry of the ferroles, thiaferroles, and their methyl-substituted derivatives (vide infra) was facilitated by their well-behaved chromatographic properties. The thiaferroles are characteristically red and migrate more slowly on silica gel than do the corresponding ferroles that are yellow. Thus both 2-methylthiophene and 2,5-dimethylthiophene reacted smoothly with $Fe_3(CO)_{12}$ to form the corresponding ferroles and thiaferroles. The ^1H NMR characteristics of the thiaferrole derived from 2-methylthiophene matched the data reported by Weiss, who also demonstrated that the iron inserted between sulfur and the unsubstituted ring carbon.[33a] This reaction appears to be regiospecific. The ^1H NMR spectrum of the thiaferrole derived from 2,5-dimethylthiophene showed two separate methyl resonances as well as an AB quartet. The fact that 2,5-dimethylthiophene behaves like the other thiophenes shows that the presence of an α-proton is not essential to the ring-opening process.

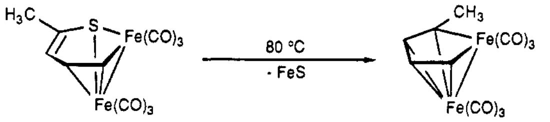
Russian workers have described the preparation of the compound $CpFe(CO)_2(C_4H_3S)$ that contains a 2-thienyl ligand σ-bonded to the iron center.[34] We prepared this compound and studied its reaction with $Fe_3(CO)_{12}$. The expected thiaferrole was obtained as shown in eq 3. This trimetallic complex was purified by using silica gel chromatography and was characterized spectroscopically. Its ^1H NMR spectrum indicates a single isomer, and the C_4H_3 resonances closely resemble those for $Fe_2(2\text{-}MeC_6H_3S)(CO)_6$ whose structure has been established.[33a] This reaction represents an unusual synthetic route to multimetallic compounds. Also isolated from this reaction are two products previously obtained from the reaction of α,α'-dithienyl and $Fe_3(CO)_{12}$ (eq 4).[35] These products arise from α,α'-dithienyl which forms when $CpFe(CO)_2(2\text{-}C_4H_3S)$ undergoes thermal decomposition.



(3)

$$\alpha,\alpha'\text{-}C_4H_3SC_4H_3S + Fe_3(CO)_{12} \rightarrow Fe_2(2,2'\text{-}C_4H_3SC_4H_3)(CO)_6 + Fe_2(2,2'\text{-}C_4H_3SC_4H_3S)(CO)_6 \quad (4)$$

The fact that 1 is so thermally stable sparked our interest in the properties of the corresponding thiaferroles. Both $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$ and $Fe_2(2,5\text{-}Me_2C_4H_2S)(CO)_6$ gave the corresponding ferrole complexes when heated in refluxing benzene. The facility of these conversions demonstrates that α-protons are uninvolved in the desulfurization event. The yields were high assuming that 2 equiv of the thiaferrole are required to form the ferrole concomitant with the elimination of iron sulfide (eq 5). An insoluble black byproduct is formed in this conversion; it contains both iron and sulfur. We suggest that this thiaferrole to ferrole conversion occurs via the elimination of FeS from the thiaferrole which would leave a metallacyclopentadiene of the formula $Fe(C_4R_4)(CO)_x$. Compounds of the type $CpCoL(C_4R_4)$[36] are known; therefore,



(5)

---

(27) Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 1995.

(28) The migration of vinyl groups to CO is known to be promoted by oxidizing agents: Reger, D.; Mintz, E. *Organometallics* **1984**, *3*, 1759. See also ref 30a.

(29) Meth-Cohn, O.; Tarnowski, B. *Synthesis* **1978**, 56. Meth-Cohn, O.; Tarnowski, B. *Adv. Heterocycl. Chem.* **1980**, *26*, 115.

(30) (a) Dennis, T. A. M. S. Thesis, Bowling Green State University, 1984. This unpublished report describes the synthesis of thiapyrones by the oxidation of thiaferroles. (b) Alper, H.; Chan, A. S. K. *J. Am. Chem. Soc.* **1973**, *95*, 4905.

(31) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3124. Messelhäuser, J.; Gutensohn, K. U.; Lorenz, I.-P.; Hiller, W. *J. Organomet. Chem.* **1987**, *321*, 377.

(32) Lorenz, I.-P.; Messelhäuser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 121. See also ref 42.

(33) (a) Hübener, P.; Weiss, E. *J. Organomet. Chem.* **1977**, *129*, 105. (b) Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213.

(34) Nesmeyanov, A. N.; Kolobova, N. E.; Goncharenko, L. V.; Anisimov, K. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1976**, 142. Ol'dekop, Yu. A.; Knizhnikov, V. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1982**, *52*, 1387.

(35) Manuel, T. A.; Meyer, T. J. *Inorg. Chem.* **1964**, *3*, 1049.

(36) See: Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1985**, *2*, 726.

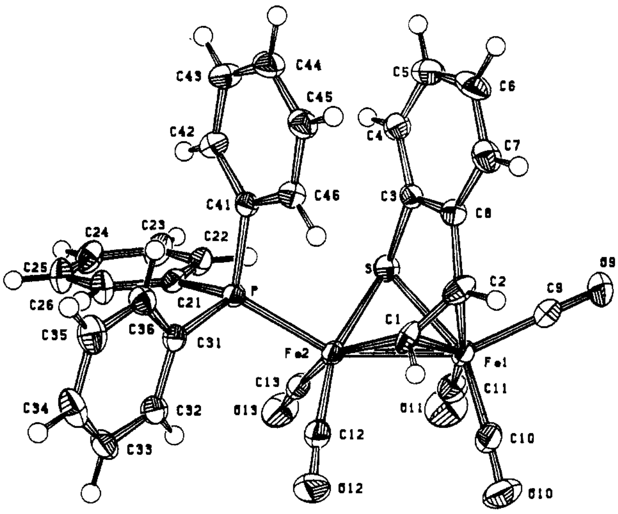


Figure 2. The structure of $Fe_2(C_8H_6S)(CO)_5(PPh_3)$ with thermal ellipsoids drawn at the 35% level.

it seems reasonable that the metallacycle $Fe(CO)_3(C_4R_4)L$ (L = CO, solvent) could have a transient existence. The rate and yield of the 2-methylthiaferrole to 2-methylferrole conversion are not qualitatively influenced by the addition of fresh $Fe_3(CO)_{12}$ during the reaction. Furthermore, control experiments show that the ferroles are stable toward $Fe_3(CO)_{12}$ (and its thermal decomposition products). Therefore the low yields of the ferroles in the reaction of $Fe_3(CO)_{12}$ and thiophenes are attributed to the inefficiency of the initial interaction of thiophene and $Fe_3(CO)_{12}$. The thiaferrole to ferrole conversion is a clean one.[46]

Our results on the thiaferrole to ferrole conversion are not consistent with the intermediacy of cyclobutadiene complexes $(C_4H_3R)Fe(CO)_3$ although such species are stoichiometrically logical. If the conversion of 2-methylthiaferrole to the methylferrole proceeded via cyclobutadiene intermediates, we would expect to obtain both 2- and 3-methylferroles,[33a] but the reaction is regiospecific (eq 5).

Structural Studies on the Benzothiaferroles. Because of the contrasting properties of 1 and the thiaferroles, the structure of 1 came into question. We were unable to obtain X-ray quality crystals of 1, but its triphenylphosphine-substituted derivative crystallized well. The compound consists of a normal metal–metal bonded $Fe_2(CO)_5PPh_3$ subunit spanned unsymmetrically by what may be viewed as a derivative of 2-mercaptostyrene (Figure 2, Table I). The vinyl group serves as an η^2-ligand to one of the iron centers and as an η^1-ligand to the other.[37] The iron center that is π-bonded to the vinyl group is seven-coordinate: it is directly bound to three carbonyls, two olefinic carbon atoms, sulfur, and the other iron. The benzo group leans toward the former iron atom. The Fe–Fe distance of 2.550 (2) Å is unexceptional as are the angles and distances in the carbonyls. The bond distances and angles in the 2-methylthiaferrole core[33a] resemble those in the benzothiaferrole core. Notable however is that the "olefinic" C(1)–C(2) linkage has an unusually short distance of 1.299 (5) Å. There is no evidence for a "semibridging" carbonyl group as seen in the ferroles $Fe_2(RC_4H_3)(CO)_6$.[33b]

The solution structure of 1 was studied by variable-temperature ^{13}C NMR spectroscopy (Figure 3). Two dynamic processes are observed. At very low temperature we observed six signals for the carbonyls, consistent with a static chiral structure. As the temperature is raised three of these signals coalesce into one peak which is coincident with one of the other three signals. The first process is attributed to the interchange of three carbonyls on one iron. DNMR studies on $Fe_3S_2(CO)_9$ have shown that seven-coordinate iron is considerably less stereochemically rigid than the two six-coordinate iron centers.[38] The seven-coordinate iron center in 1 is therefore considered as the less rigid $Fe(CO)_3$ site. At higher temperatures only one carbonyl resonance is observed.[39] This requires both the interchange of the three carbonyls at the second iron

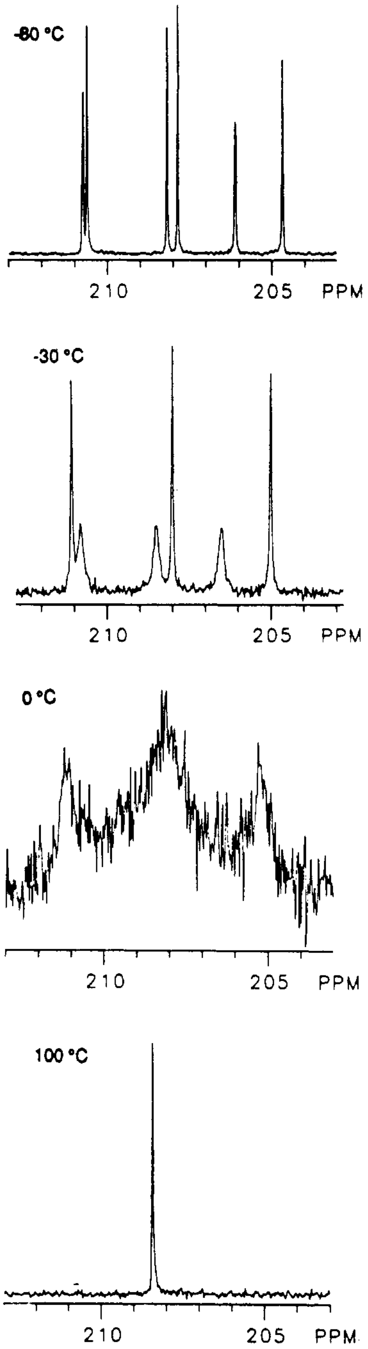


Figure 3. The 125-MHz ^{13}C NMR spectrum of the carbonyl region of 1 at various temperatures.

---

(37) A review of metal-containing heterocycles: Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Kaganovich, V. S. *J. Organomet. Chem.* **1973**, *47*, 1.

(38) Aime, S.; Milone, L.; Rossi, R.; Stanghellini, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 46.

(39) The ^{13}C NMR spectrum of the related ferrole derived from thiomalic anhydride shows two resonances at room temperature: Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *128*, 225.

Table I. Bond Distances (Å) and Angles (deg) for $Fe_2(C_8H_6S)(CO)_5(PPh_3)$

Fe1–Fe2	2.550 (2)	Fe1–S	2.297 (2)
Fe2–S	2.254 (2)	Fe2–P	2.235 (2)
Fe1–C1	2.127 (4)	Fe2–C1	1.981 (3)
Fe1–C2	2.197 (4)	C1–C2	1.299 (5)
S–C3	1.779 (3)	C2–C8	1.490 (4)
C3–C8	1.398 (4)	Fe1–C9	1.805 (4)
Fe1–C10	1.787 (4)	Fe1–C11	1.788 (4)
Fe2–C12	1.763 (4)	Fe2–C13	1.789 (4)
Fe2–Fe1–S	55.11 (7)	Fe2–Fe1–C1	49.08 (9)
Fe2–Fe1–C2	78.03 (10)	Fe2–Fe1–C9	154.6 (1)
Fe2–Fe1–C10	100.9 (1)	Fe2–Fe1–C11	94.6 (1)
S–Fe1–C1	80.17 (10)	S–Fe1–C2	80.72 (9)
S–Fe1–C9	104.7 (1)	S–Fe1–C10	155.5 (1)
S–Fe1–C11	86.7 (1)	C1–Fe1–C2	34.9 (1)
C1–Fe1–C9	117.9 (1)	C1–Fe1–C10	87.0 (2)
C1–Fe1–C11	142.2 (2)	C2–Fe1–C9	83.8 (2)
C2–Fe1–C10	100.5 (2)	C2–Fe1–C11	167.4 (2)
C9–Fe1–C10	99.8 (2)	C9–Fe1–C11	99.7 (2)
C10–Fe1–C11	90.9 (2)	Fe1–Fe2–S	56.72 (7)
Fe1–Fe2–P	150.03 (7)	Fe1–Fe2–C1	54.2 (1)
Fe1–Fe2–C12	104.1 (1)	Fe1–Fe2–C13	102.8 (1)
S–Fe2–P	99.96 (7)	S–Fe2–C1	84.4 (1)
S–Fe2–C12	160.7 (1)	S–Fe2–C13	90.4 (1)
P–Fe2–C1	109.8 (1)	P–Fe2–C12	98.9 (1)
P–Fe2–C13	95.2 (1)	C1–Fe2–C12	85.2 (2)
C1–Fe2–C13	155.0 (2)	C12–Fe2–C13	92.1 (2)
Fe1–S–Fe2	68.17 (7)	Fe1–S–C3	100.9 (1)
Fe2–S–C3	111.1 (1)	Fe1–C1–Fe2	76.7 (1)
Fe1–C1–C2	75.5 (2)	Fe2–C1–C2	131.3 (3)
Fe1–C2–C1	69.6 (2)	Fe1–C2–C8	108.4 (2)
C1–C2–C8	126.1 (3)	S–C3–C8	115.4 (2)
C2–C8–C3	118.6 (3)		

as well as the equivalencing of the two iron centers via the "flip-flop" of the organic ligand.

Conclusions

The activation of thiophenes by $Fe_3(CO)_{12}$ is proposed to occur via the binding of the heterocycle to an iron center. The C–S cleavage event that follows the coordination of the thiophene may be viewed as a specific example of the general reaction involving vinyl sulfide cleavage by $Fe_3(CO)_{12}$.[24] The observed reactivity of thiophenes with $Fe_3(CO)_{12}$ increases in the order dibenzothiophene (no reaction) < thiophene (~5% yield) < benzothiophene (~49% yield). In contrast, the nucleophilicity of these compounds increases in the order thiophene < benzothiophene < dibenzothiophene as shown by their dipole moments and their ability to form sulfones.[40] Apparently the nucleophilicity of the heterocycle is not the determining factor at work in these reactions.

The oxidative addition of C–S bonds is unusual but has been unambiguously demonstrated in the case of nickel complexes.[41,42] Also relevant is the formation of (η^4-thioacrolein)$Fe(CO)_3$ from the reaction of thiacyclobutene and $Fe_2(CO)_9$.[43]

Following are the key results of this research project:

1. Benzothiophene and thiophene have very different rates of reaction with $Fe_3(CO)_{12}$ in that the benzothiaferrole derivative is more readily formed than the thiaferrole from the respective heterocycles.

2. The thiaferroles and the benzothiaferrole have very different thermal stabilities. The thiaferroles are easily converted to the ferroles while the benzothiaferrole does not convert to a benzoferrole, although the latter is known to be stable.[44]

3. The desulfurization of the thiaferroles does not proceed via cyclobutadiene intermediates. Rather metallacyclopentadiene intermediates are invoked.

4. The presence of α-protons on the thiophene is irrelevant to formation and desulfurization of thiaferroles.

5. At temperatures where the benzothiaferrole 1 is stable under an N_2 atmosphere, it is reactive toward CO and H_2 resulting in reductive elimination of benzothiophene and hydrogenation/C–S hydrogenolysis, respectively.

6. The benzothiaferrole adopts a structure very similar to the thiaferroles,[33a] differences in their reactivity notwithstanding. The bridging C_8H_6S ligand is stereochemically nonrigid.

Our results highlight the differences between thiophenes and benzothiophenes. Despite these differences, the insertion of an iron atom into a C–S bond clearly activates these heterocycles toward desulfurization. A recent surface science study of thiophene HDS on partially sulfided molybdenum indicates that the rate-limiting step in desulfurization of this heterocycle occurs via C–S cleavage and is zero order in H_2.[10] The formation of thiaferrole-like heterocycles is a plausible activation mechanism.

Experimental

Materials and Methods. Syntheses were performed under an inert atmosphere by using prepurified nitrogen. Workups were handled aerobically unless otherwise specified. All solvents were of reagent grade. Solvents were distilled from the following: Na/K (hexane), P_4O_{10} (CH_2Cl_2), and CaH_2 followed by Na/K (THF). Benzene and heptane were dried over 4-Å molecular sieves and degassed with nitrogen prior to use. Triiron dodecacarbonyl was purchased from Pressure Chemical or was prepared as described in the literature.[45] Trimethylamine *N*-oxide dihydrate (Aldrich) was sublimed in vacuo. All other reagents were purchased from Aldrich and used as obtained.

GC analyses were carried out on a Hewlett-Packard 5890 gas chromatograph with a 3390A integrator using a silicone gum column (5 m × 530 μm × 2.65 μm). A Parr 4712 screw cap autoclave (45 mL) with a 4316 gauge block assembly was used for the hydrogenation experiment. Spectroscopic instruments include a Perkin-Elmer 1750 infrared Fourier transform IR spectrometer with a 7700 Professional computer and Model PP-1 plotter printer. NMR spectra were collected on General Electric GN 500 (500 MHz) and QE 300 (300 MHz) instruments. Woelm silica gel (32–63 μm) was used for flash chromatography on 15 × 1.3 in. or 10 × 2.5 in. columns. TLC analysis was done on Kodak 13181 silica gel with fluorescent indicator. Preparative TLC plates (fluorescent silica gel, 8 × 8 in.) were obtained from Analtech Uniplate. LREI (low-resolution electron-impact) mass spectral analyses were measured on a Finnegan-MAT CH5 mass spectrometer, FD (field desorption) mass spectra on a Finnegan-MAT instrument, and GC/LREI mass spectral analyses on a VG 70 SE mass spectrometer attached to a Hewlett-Packard 5890 gas chromatograph at the University of Illinois Mass Spectrometry Laboratory. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

$Fe_2(C_8H_6S)(CO)_6$ (1). Triiron dodecacarbonyl (11.1 g, 22.0 mmol) and benzothiophene (10.2 g, 76.0 mmol) were refluxed in 300 mL of benzene for 18 h during which time the color changed from green to orange-red. Solids formed were removed by fil-

---

(40) Hartough, H. D.; Meisel, S. L. In *Compounds with Condensed Thiophene Rings*, Weissberger, A., Ed.; Interscience: New York, 1954.

(41) Osakada, K.; Maeda, M.; Nakamura, Y.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1986**, 442. Wenkert, E.; Shepard, M. E.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1390.

(42) For related chemistry of vinyl sulfides see: Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 637. Tiecco, M.; Testaferri, L.; Tingoli, M.; Wenkert, E. *Tetrahedron* **1983**, *39*, 2289.

(43) Parker, E. J.; Bodwell, J. R.; Sedergrau, T. C.; Dittmer, D. C. *Organometallics* **1982**, *1*, 517. Dittmer, D. C.; Takahashi, K.; Iwanami, M.; Tsai, A. I.; Chang, P. L.; Blidner, B. B.; Stamos, I. K. *J. Am. Chem. Soc.* **1976**, *98*, 2795.

(44) Davis, R. E.; Barnett, B. L.; Amiet, R. G.; Merk, W.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7108.

(45) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 193.

(46) The ferrole is also observed in the co-condensation of Fe atoms and thiophene in a carbon monoxide atmosphere: Chivers, T.; Timms, P. L. *Can. J. Chem.* **1977**, *55*, 3509.

tration through Celite, and the filtrate was concentrated to a red oil. The oil was sublimed (25–30 °C, 0.02 mmHg) to remove the excess benzothiophene. Further sublimation (80–90 °C, 0.02 mmHg) afforded 4.48 g (49% yield) of 1 as shiny red crystals: ^1H NMR ($CDCl_3$) δ 8.99 (d, 1 H), 7.18–6.80 (m, 4 H), 5.48 (d, 1 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 208.3, 173.5, 144.0, 131.1, 128.42, 128.38, 127.4, 127.2, 95.6; IR (hexane) ν_{CO} 2077, 2044, 2006, 1994, 1961 cm^{-1}. Anal. Calcd for $C_{14}H_6Fe_2O_6S$: C, 40.58; H, 1.45; Fe, 27.05; S, 7.73. Found: C, 40.65; H, 1.48; Fe, 26.86; S, 7.36.

$Fe_2(C_8H_6S)(CO)_5(PPh_3)$ (2). A solution of triphenylphosphine (315 mg, 1.2 mmol) and 1 (500 mg, 1.2 mmol) in THF (25 mL) was treated with trimethylamine *N*-oxide (147 mg, 1.3 mmol) in portions at 0 °C. After 0.5 h, the dark red solution was concentrated to dryness. Flash column chromatography eluting with 85:15 hexane/CH_2Cl_2 removed unreacted 1. Subsequent elution with 7:3 hexane/CH_2Cl_2 gave two dark red bands, the first and largest being 2 and the second being $Fe_2(C_8H_6S)(CO)_4(PPh_3)_2$. The fraction containing 2 was evaporated to dryness affording 394 mg (50% yield) of a fluffy red solid: IR (CH_2Cl_2) ν_{CO} 2051, 1996 (br), 1937 cm^{-1}. Anal. Calcd for $C_{31}H_{21}Fe_2O_5PS$: C, 57.39; H, 3.24. Found: C, 57.28; H, 3.24. Evaporation of the slower moving iron complex gave 176 mg of dark red solid (17%). Anal. Calcd for $C_{48}H_{36}Fe_2P_2O_4S$: C, 65.31; H, 4.11. Found: C, 65.40; H, 4.18.

Electrochemistry of 1. A BAS electrochemical analyzer was used for cyclic voltammetry measurements. A platinum working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode were used in all CV experiments. THF solutions of 1 were deaerated with N_2 for 20–30 min. Tetrabutylammonium hexafluorophosphate (TBAHP), the supporting electrolyte, was dried at 120 °C for 4 h.

Reaction of 1 with $(NH_4)_2Ce(NO_3)_6$. Ceric ammonium nitrate (193 mg, 0.35 mmol) was added over 5 min to a stirred solution of 1 (103 mg, 0.25 mmol) in 10 mL of acetone in air. Immediate gas evolution ensued and a fine precipitate appeared before addition of the cerium reagent was complete. After the solution was stirred for 2 h, no trace of 1 was visible by TLC (hexane). Filtration of the solution through Celite removed an orange-brown solid (36% Fe by analysis). The yellow filtrate was diluted with ether until no further precipitation occurred. The solution was again filtered through Celite and evaporated to dryness. The GLC response factors of the resulting off-white needles were assayed in acetone solution and compared to those of a known concentration of pure 1-thiocoumarin. The yields by GLC were 35.5% 1-thoucoumarin and 4.4% benzothiophene. Larger scale reactions were purified by prep TLC (1:1 v/v CH_2Cl_2/hexane) which gave off-white needles. Recrystallization was effected by dissolution in CH_2Cl_2, filtration, evaporation, redissolution in warm methanol, and storage at −20 °C for a few hours: GC/LREIMS, *m/e* 162; ^1H NMR ($CDCl_3$) δ 7.72 (d, 2 H), 7.62–7.42 (m, 4 H), 6.56 (d, 1 H); IR (CH_2Cl_2) ν_{CO} 1643 cm^{-1}. Anal. Calcd for C_9H_6OS: C, 66.62; H, 3.73. Found: C, 65.93; H, 3.79.

Attempted Oxygenation of 1 with mCPBA. A toluene solution (15 mL) of mCPBA (0.6 mmol) was added in small portions via cannula to 250 mg of 1 (0.6 mmol) in toluene (30 mL) at 0 °C. The red-orange solution was allowed to warm slowly to room temperature and then was stirred 2 h followed by heating at 80 °C for 15 h. Both TLC and IR (ν_{SO} region) indicated that no reaction had occurred.

Flash Vacuum Pyrolysis (FVP) of 1. A straight Pyrex sample tube (10 × 1.7 cm) was connected via a clear glass joint to the hot zone (14.5 × 1 cm) connected to a cold trap at its other end. A vacuum of 10^{-5} Torr was applied to the apparatus after the sample tube was charged with 150 mg of 1. The temperature of the hot zone was controlled with a heating tape while a Kugelrohr oven warmed the sample tube. The tape temperature was monitored by a thermocouple fitted into a glass capillary next to the tube inside the tape. When the hot zone had stabilized (285–315 °C), the sample tube was warmed (80–85 °C) to maintain steady sublimation of 1 into the hot zone. After 2 h, the sample tube was empty, the neck of the cold trap contained unreacted 1, and an orange-white solid ringed the inner tube of the trap. The hot zone was coated by a black solid composed mainly of iron. The trap was rinsed with acetone and the amount of benzothiophene present analyzed by GC using a known amount of benzothiophene as an external standard. Under these conditions, 63% of 1 was converted to give benzothiophene containing less than 1% of thiocoumarin and other organic products. Approximately 36% of 1 had passed unaffected through the hot zone. Packing material, such as glass wool, raises the conversion rate moderately without altering the product distribution, yet it greatly increases the reaction time.

Reaction of 1 with H_2. An autoclave cup was loaded with 1 (300 mg, 0.72 mmol) and 5 mL of a 125:1 v/v hexane/anisole solution, assembled, and pressurized with hydrogen to 500 psig at 25 °C. The reactor was heated to 175 °C for 20 h (650 psig). After cooling and venting, the contents of the bomb were filtered to give 63 mg of black solid and a red-orange filtrate after being rinsed with hexane. Sulfur-containing aromatics in the filtrate were identified by GC-mass spectrometry (vide infra). The black solid was sometimes slightly pyrophoric when dry and was insoluble in common solvents. Analysis of this solid (four runs) indicated 62–71% Fe with small amounts (2–5%) of sulfur and hydrocarbon present. Residual starting material was quantified by comparing the intensities of ν_{CO} bands in the filtrate to those of 1 in a solution of known concentration. Under these conditions hydrogenation was 45% complete. Stirring of the solution during hydrogenation did not seem to affect the outcome of the reaction and was not used.

Reaction of 1 with CO. An autoclave cup was loaded with 1 (247 mg, 0.60 mmol) and 5 mL of hexane and pressurized to 500 psig of CO at 25 °C. The reactor was heated to 160 °C (700 psig) for 19 h. After being cooled to room temperature, the clear red solution was transferred to a Schlenk flask under N_2. Approximately 37 mg of benzothiophene was detected by GC (external standard), indicating a conversion of 50%. The presence of $Fe(CO)_5$ was confirmed by GC and IR.

2-Ethylbenzenethiol. A slurry of Mg powder (1.3 g, 53.5 mmol) in 45 mL of anhydrous ether was activated with dibromoethane (0.15 mL). Freshly distilled (73 °C, 9 mmHg) 1-bromo-2-ethylbenzene (9.1 g, 49.2 mmol) was added in 0.2-mL portions so as to maintain a fairly fast reflux rate. After being refluxed 12 h, the solution was cooled to −25 °C and sulfur (1.7 g, 54.1 mmol) added in one portion. The flask was warmed to room temperature and stirred 1.5 h. The reaction mixture was carefully acidified with 0.4 M H_2SO_4 (~15 mL). The layers were separated, and the ether layer was washed twice with 25 mL of H_2O followed by two washings with a saturated NaCl solution. The pale gray ether layer was dried over Na_2SO_4, filtered, and concentrated to an oil: yield 65–80%; ^1H NMR ($CDCl_3$) δ 7.28–7.06 (m, 4 H), 3.30 (s, 1 H), 2.69 (q, 3 H), 1.25 (t, 2 H); GC/LREIMS, *m/e* 138.

Bis(2-ethylphenyl) Disulfide. In air, 2-ethylbenzenethiol (0.035 mL) was added dropwise to a clear blue solution of $Cu_2(OOCCH_3)_4(H_2O)_2$ (26 mg, 0.13 mmol of Cu^{2+}) in 5 mL of absolute methanol. The yellow precipitate was removed by filtration. The filtrate was evaporated in vacuo and the solid extracted with 3 mL of hexane. Concentration of the hexane solution afforded viscous yellow bis(2-ethylphenyl) disulfide in quantitative yield which was pure by GC: ^1H NMR ($CDCl_3$) δ 7.54 (d, 2 H), 7.15 (m, 6 H), 2.82 (q, 4 H), 1.24 (t, 6 H).

$Fe_2(2\text{-}MeC_4H_3S)(CO)_6$. A benzene solution (350 mL) of $Fe_3(CO)_{12}$ (6.6 g, 13.1 mmol) and 2-MeC_4H_3S (3.0 mL, 31.0 mmol) was refluxed for 18 h during which time an Fe mirror formed and the color changed from green to red. The solution was filtered and evaporated at room temperature. Flash column chromatography eluting with hexanes gave two bands. The first orange-red band was evaporated to dryness giving 470 mg (9.5%) of dark red crystals of $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$: ^1H NMR ($CDCl_3$) δ 8.99 (d, 1 H), 5.92 (q, 1 H), 4.93 (q, 1 H), 1.67 (s, 3 H); IR ν_{CO} (hexane) 2078, 2044, 2007, 1990 cm^{-1}. The second bright yellow band yielded, after evaporation, 269.3 mg (5.8%) of $Fe_2(2\text{-}MeC_4H_3)(CO)_6$ as a dull yellow powder: ^1H NMR ($CDCl_3$) δ 6.67 (q, 1 H), 6.20 (q, 1 H), 5.95 (d, 1 H), 2.42 (s, 3 H).

$Fe_2(2,5\text{-}Me_2C_4H_2S)(CO)_6$. The 2,5-dimethylthiaferrole and 2,5-dimethylferrole were synthesized by the same method used for the 2-methyl derivatives beginning with 6.6 g of $Fe_3(CO)_{12}$ (13.1 mmol) and 4.0 mL of 2,5-$Me_2C_4H_2S$ (35.1 mmol). Following flash column chromatography, 102.8 mg of dark red $Fe_2(2,5\text{-}Me_2C_4H_2)(CO)_6$ (2.0%) and 119.3 mg of yellow $Fe_2(2,5\text{-}Me_2C_4H_2)(CO)_6$ (2.5%) were isolated. For $Fe_2(2,5\text{-}Me_2C_4H_2S)(CO)_6$: ^1H NMR ($CDCl_3$) δ 5.91 (d, 1 H), 4.39 (d, 1 H), 2.89 (s,

Table II. Crystal Data Collection and Refinement Parameters

formula	$C_{31}H_{21}Fe_2PO_5S$
cryst system	triclinic
space group	$P\bar{1}$
cell const	
a, Å	12.498 (2)
b, Å	13.138 (2)
c, Å	10.618 (2)
α, deg	113.00 (1)
β, deg	111.22 (1)
γ, deg	100.37 (1)
cell vol, V, Å^3	1386.1 (4)
formula units/cell, Z	2
ρ(calcd), g cm^{-3}	1.552
abs coeff, cm^{-1}	12.14 (numerical correctn)
transmissn factors	0.8126–0.6922 (SHELX-76)
cryst dimens, mm	0.2 × 0.3 × 0.36
radiatn	Mo Kα ($\bar{\lambda}$ = 0.71073 Å)
scan technique	$\omega/2\theta$
2θ scan range, deg	3–46
2θ scan angle, deg	$K\alpha_1 - 0.8$ to $0.9 + K\alpha_2$
intensities measd ($\pm h, \pm k, +l$)	4276 (R_i = 0.016)
unique intensities	4121 (3389, $I > 2.58\sigma(I)$)
$R = \sum \lVert F_o - F_c \rVert / \sum F_o$	0.030
$R_w = (\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$	0.031 (p = 0.01)
max shift/error	0.056

3 H), 1.64 (s, 3 H); FDMS, m/e 360. For $Fe_2(2,5\text{-}Me_2C_4H_2)(CO)_6$: ^1H NMR ($CDCl_3$) δ 5.90 (d, 2 H), 2.36 (s, 6 H); FDMS, m/e 392.

$Fe_2[CpFe(CO)_2(2\text{-}C_4H_3S)](CO)_6$. A benzene solution (300 mL) of 900 mg of $CpFe(CO)_2(2\text{-}C_4H_3S)$ (3.46 mmol)[33] and 3.48 g of $Fe_3(CO)_{12}$ (6.92 mmol) was heated at 75 °C for 18 h. At this point, the $Fe_3(CO)_{12}$ had decomposed and the ^1H NMR spectrum of an aliquot showed unreacted $CpFe(CO)_2(2\text{-}C_4H_3S)$, $Fe_2[CpFe(CO)_2(2\text{-}C_4H_3S)](CO)_6$, and $Cp_2Fe_2(CO)_4$ in an approximate 2:1:2 ratio. A further 3.3 g of $Fe_3(CO)_{12}$ was added and heating continued at 50 °C for 12 h after which no change in product distribution was observed by NMR. The solution was refluxed 12 h further, cooled, and filtered through Celite leaving a dark solid. A CH_2Cl_2 rinse dissolved most of the solid that was later identified as $Cp_2Fe_2(CO)_4$. The dark red filtrate was evaporated and dried in vacuo. Flash column chromatography eluting with hexane removed residual $Fe_3(CO)_{12}$ and very small amounts of the ferrole and thiaferrole derived from dithienyl. The mobile phase was changed to 33% CH_2Cl_2/hexane to elute $Fe_2[CpFe(CO)_2(2\text{-}C_4H_3S)](CO)_6$. The dark red powder was isolated in 11.0% yield (205 mg): ^1H NMR ($CDCl_3$) δ 8.81 (d, 1 H), 5.96 (d, 1 H), 5.03 (q, 1 H), 4.89 (s, 5 H); IR (hexane) ν(CO) 2071, 2037, 1998, 1987 (sh) cm^{-1}. Anal. Calcd for $C_{17}H_8Fe_3O_8S$: C, 37.79; H, 1.49. Found: C, 38.24; H, 1.45.

Thermolysis of 2-Methylthiaferrole. A benzene solution (8 mL) of $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$ (53 mg) was refluxed for 21 h. The color turned from red to reddish orange and a brown solid precipitated. The mixture was filtered, chromatographed (pentane), and concentrated in vacuo to obtain 9 mg of $Fe_2(2\text{-}MeC_4H_3)(CO)_6$ and 30.8 mg of unreacted $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$ (42% conversion). This reaction was repeated with similar results.

Stability Studies on 2-Methylferrole. A heptane (6 mL) solution of $Fe_2(2\text{-}MeC_4H_3)(CO)_6$ (25 mg) was refluxed 15 h. The bright yellow solution contained no solids, only starting material was observed by TLC (hexane). Triiron dodecacarbonyl (115 mg, 0.23 mmol) was added to the flask and the green solution refluxed 8 h further after which time it was filtered, chromatographed (hexane), and concentrated in vacuo. Approximately 24 mg (96%) of $Fe_2(2\text{-}MeC_4H_3)(CO)_6$ was recovered and identified by TLC and ^1H NMR. No $Fe_3(CO)_{12}$ remained (TLC and IR).

X-ray Crystallography. A well-formed opaque reddish hexagonal crystal was grown from CH_2Cl_2/hexane. Positions of the two iron atoms, the sulfur atom, and the phosphorus atom were found by direct methods using MULTAN. A weighted difference Fourier summation revealed the remaining 36 non-hydrogen atoms, and subsequent least-squares difference Fourier calculations (SHELX) gave positions for the two vinyl hydrogen atoms. The rest of the hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, the two vinyl hydrogen atoms were independently refined with isotropic thermal coefficients, and a group isotropic thermal parameter was varied for the remaining hydrogen atoms. Succesful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant feature. There were no apparent systematic errors among the final observed and calculated structure factors. Data collection details and positional parameters are presented in Tables II and III.

Table III. Atomic Coordinates for $Fe_2(C_8H_6S)(CO)_5(PPh_3)$

	x/a	y/b	z/c
Fe1	0.83996 (4)	0.66894 (4)	0.42757 (5)
Fe2	0.73456 (4)	0.81223 (4)	0.39245 (5)
S	0.67335 (7)	0.62418 (7)	0.20171 (9)
P	0.65065 (7)	0.89239 (7)	0.24989 (9)
O9	0.9441 (2)	0.4865 (2)	0.3335 (3)
O10	1.0126 (3)	0.8107 (3)	0.7623 (3)
O11	0.6593 (3)	0.5457 (3)	0.4855 (4)
O12	0.8718 (3)	1.0235 (3)	0.7016 (3)
O13	0.5255 (2)	0.7406 (3)	0.4453 (3)
C1	0.9012 (3)	0.8244 (3)	0.4140 (4)
C2	0.9378 (3)	0.7494 (3)	0.3342 (4)
C3	0.7442 (3)	0.6200 (3)	0.0825 (3)
C4	0.6792 (3)	0.5606 (3)	−0.0778 (4)
C5	0.7433 (3)	0.5468 (3)	−0.1616 (4)
C6	0.8701 (4)	0.5918 (3)	−0.0859 (4)
C7	0.9356 (3)	0.6549 (3)	0.0753 (4)
C8	0.8735 (3)	0.6725 (3)	0.1616 (3)
C9	0.9023 (3)	0.5557 (3)	0.3682 (4)
C10	0.9483 (3)	0.7550 (3)	0.6307 (4)
C11	0.7307 (3)	0.5955 (3)	0.4659 (4)
C12	0.8143 (3)	0.9417 (3)	0.5775 (4)
C13	0.6042 (3)	0.7691 (3)	0.4199 (4)
C21	0.4817 (3)	0.8461 (3)	0.1649 (3)
C22	0.4085 (3)	0.7273 (3)	0.0996 (4)
C23	0.2807 (3)	0.6891 (3)	0.0320 (4)
C24	0.2245 (3)	0.7700 (3)	0.0294 (4)
C25	0.2943 (3)	0.8862 (3)	0.0922 (4)
C26	0.4230 (3)	0.9254 (3)	0.1602 (4)
C31	0.6996 (3)	1.0552 (3)	0.3503 (3)
C32	0.6953 (3)	1.1134 (3)	0.4892 (4)
C33	0.7248 (3)	1.2356 (3)	0.5634 (4)
C34	0.7586 (3)	1.3010 (3)	0.5007 (5)
C35	0.7620 (3)	1.2452 (3)	0.3637 (5)
C36	0.7333 (3)	1.1231 (3)	0.2888 (4)
C41	0.6764 (3)	0.8591 (3)	0.0812 (3)
C42	0.5808 (3)	0.8099 (3)	−0.0681 (4)
C43	0.6061 (3)	0.7873 (3)	−0.1915 (4)
C44	0.7256 (4)	0.8153 (3)	−0.1661 (4)
C45	0.8225 (3)	0.8658 (3)	−0.0172 (4)
C46	0.7981 (3)	0.8864 (3)	0.1062 (4)
H1	0.968 (3)	0.888 (3)	0.504 (4)
H2	1.020 (3)	0.766 (2)	0.381 (3)

Acknowledgment. This research was supported by the National Science Foundation. Initial stages of this investigation were also supported by the Illinois Coal Research Board. We thank Professor A. Gellman for many helpful discussions.

Registry No. 1, 12086-84-9; 2, 113646-75-6; $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$, 63249-22-9; $Fe_2(2,5\text{-}Me_2C_4H_2S)(CO)_6$, 113646-77-8; $Fe_2[CpFe(CO)_2(2\text{-}C_4H_3S)](CO)_6$, 113646-78-9; $Fe_3(CO)_{12}$, 17685-52-8; $Fe_2(C_8H_6S)(CO)_4(PPh_3)_2$, 113646-76-7; $(NH_4)_2Ce(NO_3)_6$, 10139-51-2; $Fe(CO)_5$, 13463-40-6; $Cu_2(OOCCH_3)_4(H_2O)_2$, 4465-79-6; $2\text{-}MeC_4H_3S$, 554-14-3; $Fe_2(2,5\text{-}Me_2C_4H_2)(CO)_6$, 60285-90-7; $2,5\text{-}Me_2C_4H_2S$, 638-02-8; $CpFe(CO)_2(2\text{-}C_4H_3S)$, 59307-97-0; $Cp_2Fe_2(CO)_4$, 12154-95-9; $Fe_2(2\text{-}MeC_4H_3)(CO)_6$, 61300-81-0; benzothiophene, 95-15-8; 1-thiocoumarin, 1075-14-5; ethylbenzene, 100-41-4; 2-ethylbenzenethiol, 4500-58-7; 1-bromo-2-ethylbenzene, 1973-22-4; bis(2-ethylphenyl) disulfide, 4500-66-7.

Supplementary Material Available: For the crystallographic study of $Fe_2(C_8H_6S)(CO)_5(PPh_3)$, thermal parameters, "idealized" coordinates, and a complete listing of bond lengths and bond angles (4 pages); a listing of structure factor tables (15 pages). Ordering information is given on any current masthead page.