Iron and Cobalt Complexes of Thioacroleins Derived from Thietes[1]

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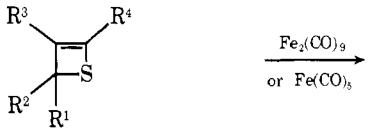
Abstract: Treatment of thietes (thiacyclobutenes) with several iron or cobalt carbonyls yields complexes of thioacroleins as indicated by an x-ray analysis of an iron dicarbonyl triphenylphosphine derivative. Dimers containing an essentially square Fe_2S_2 array are obtained from iron thioacrolein tricarbonyl complexes. The structure of one dimer has been determined by x-ray analysis. Both iron and cobalt complexes of thioacrolein and also the iron dimers yield *S*-oxides on mild oxidation with peracids or oxygen. Treatment of cobalt η^5-cyclopentadienyl thioacrolein complexes with triphenylmethyl or tropylium salts yields stable cations containing two cobalt atoms. These cations undergo reversible one-electron reductions. A mononuclear cation is obtained from iron thioacrolein triphenylphosphine dicarbonyl.

Thietes are four-membered, unsaturated sulfur-containing heterocycles, of which several examples have been synthesized recently.[3] They exhibit the hydrolytic tendencies of thioenol ethers and the electrocyclic ring-opening tendencies of cyclobutenes.[3,4] The latter type of ring-opening reaction of thietes would yield thioacroleins, expected to be highly reactive molecules and whose formation from thietes has hitherto been made plain only by polymer formation or by trapping with 2,4-dinitrophenylhydrazine. Thioacrolein, itself, has been obtained by thermolysis of diallyl sulfide at 923 K, the product being trapped at 77 K and examined spectroscopically.[5] The dianion of thioacrolein, obtained by treatment of allyl mercaptan with *n*-butyllithium, has been investigated recently.[6]

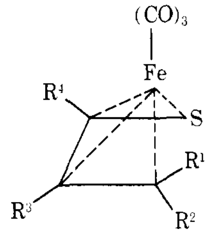
Monomeric Iron Complexes. Treatment of thietes **1–3** with diiron nonacarbonyl (thermal) or with iron pentacarbonyl (photochemical) gave complexes **4–6**, respectively, of thioacroleins, whose structures are based on an x-ray analysis of triphenylphosphine complex, **7**, derived from **4** by replacement of one carbon monoxide ligand.[1,7] A triethoxyphosphine complex (**8**) also was prepared. Thiobenzophenones, which may be considered as a special variety of α,β-unsaturated thio ketones, behave differently on complexation with metals: an ortho hydrogen of the aromatic ring is replaced by the metal.[8]

These complexes are red to orange crystalline solids or oils (mp of **4** is 28°). Compound **4** appears to be weakly dimeric in hexane as indicated by an osmometric molecular weight determination, but no evidence for a stable dimer in the solid state was obtained by mass spectrometry. In **7**, the iron atom is 1.669 Å above the plane of the ligand and the overall geometry is similar to that in butadiene iron tricarbonyl.[9] Bond angles in the ligand approximate 120° and the protons of the terminal methylene group are ca. 20° out of the plane of the ligand's backbone.[7] As mentioned in a preliminary communication, HMO calculations on the dianion of thioacrolein (back-donation of two electrons from iron is assumed) give bond orders in good agreement with those obtained by the x-ray analysis.[1] The pattern of long, short, long bonds observed for the three bonds of the thioacrolein ligand in **7** is analogous to that observed for a tungsten complex of methyl vinyl ketone.[10]

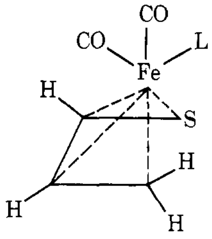
Infrared spectra of the complexes show absorption around 1450 cm^{-1}, presumably caused by vibrations of the methylene group, and at about 820 cm^{-1}, whose origin is unknown but may be associated with carbon–hydrogen vibrations. No appreciable absorption occurs in the vicinity of 1600 cm^{-1} such as was reported for a molybdenum complex of acrolein[11] and for the free thioacrolein molecule.[5] Absorptions around 1060 and 1180 cm^{-1}, which occur in thioacrolein,[5] occur also with variable intensity in the complexes. No evidence for bridging carbonyl ligands was observed.



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^4 = H$; $R^2 = CH_3$; $R^3 = C_2H_5$
3, $R^1 = R^4 = H$; $R^2 = R^3 = (CH_2)_5$



4, $R^1 = R^2 = R^3 = R^4 = H$
5, $R^1 = R^4 = H$; $R^2 = CH_3$; $R^3 = C_2H_5$
6, $R^1 = R^4 = H$; $R^2 = R^3 = (CH_2)_5$

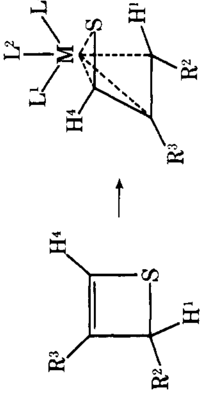


7, $L = Ph_3P$
8, $L = (C_2H_5O)_3P$

The mass spectrum (70 eV) of **7** is typical of the monomeric complexes. The parent ion and ions formed by the sequential loss of carbon monoxide and triphenylphosphine are observed; other ions correspond to the composition, thioacrolein plus iron. Ions always are observed with masses equivalent to those seen in the mass spectra of the parent thietes.

Proton NMR chemical shifts of the complexes **4–8** are given in Table I and are compared with several cobalt complexes whose preparation and properties will be discussed in a later section. Since the ^1H NMR spectrum of thioacrolein has not been reported, the chemical shifts of the thiete precursors are included in the table for comparison. Complexation of acrolein with molybdenum causes the absorption of all the protons to shift upfield (δ values for acrolein: 9.55 (CHO), 6.39 (vinyl H)).[11] The high field at which the endo proton (i.e., the one more or less directly under the iron atom) of the methylene

Table I. ^{1}H NMR Chemical Shifts[a] of Iron and Cobalt Complexes and Their Thiete Precursors



	1, $R^2 = R^3 = H^b$	4, $R^2 = R^3 = H$; M = Fe; L^1 = $L^2 = L^3$ = CO	8, $R^2 = R^3 = H$; M = Fe; L^1 = L^2 = CO; $L^3 = P(OEt)_3$	7, $R^2 = R^3 = H$; M = Fe; L^1 = L^2 = CO; $L^3 = PPh_3$	11, $R^2 = R^3 = H$; M = Co; L^1, L^2, L^3 = Cp	2, $R^2 = CH_3{}^b$ $R^3 = CH_2CH_3$	5, $R^2 = CH_3$; $R^3 = CH_2CH_3$; M = Fe; L^1 = $L^2 = L^3$ = CO	12, $R^2 = CH_3$; $R^3 = CH_2CH_3$; M = Co; L^1, L^2, L^3 = Cp	3, $R^2 = R^{3b} = (CH_2)_5$	6, $R^2 = R^3 = (CH_2)_5$; M = Fe; $L^1 = L^2 = L^3$ = CO
H^1	3.80	1.38	1.05	0.90	1.19	4.10	1.95	1.64	3.40	(1.2–3.1)
R^2	3.80	2.43	2.19	1.95	2.78	1.55	1.46	1.27	1.4–2.5	(1.2–3.1)
R^3	5.60	5.94	5.71	5.60	5.57	1.97, 1.00	~2.5, 1.3	2.45, 1.25	1.4–2.5	(1.2–3.1)
H^4	6.50	7.06	6.68	6.10	7.38	6.16	6.62	7.01	6.05	6.62

[a] δ, ppm downfield from internal Me_4Si. Solvent $CDCl_3$. [b] Data taken from ref 3.

group absorbs has an analogy in the ^{1}H NMR spectra of diene iron tricarbonyl complexes.[12] Substitution of a carbon monoxide ligand by triethoxyphosphine or triphenylphosphine results in progressively higher field absorptions of the protons which correlates with the greater electron-donating ability of the phosphine ligands. Phosphine complexes **7** and **8** show long range coupling between phosphorus and the methylene proton at high field (endo proton). Decoupling of the other protons in **7** left a residual doublet ($J \sim 3$ Hz). The coupling of only one of the two methylene protons with phosphorus may be the result of greater proximity of the endo proton to the phosphorus atom or of an especially felicitous arrangement of bonding orbitals from phosphorus to the proton.[13]

The ^{13}C NMR spectrum of **7** is compared with that of butadiene iron tricarbonyl[14] in Figure 1.

The Mössbauer spectrum of **4** is comparable with those of other iron carbonyl-olefin complexes[15] and is consistent with a zero valence state for iron: isomer shift = 0.0806 mm s^{-1}; quadrupole splitting = 1.49 mm s^{-1} (natural iron standard).

Iron Dimers with Fe_2S_2 Arrays. Iron tricarbonyl complexes **4** and **5** lose carbon monoxide on gentle heating or on prolonged photolysis to yield orange or brown crystalline dimers. In some cases they are by-products in the preparation of monomers. Treatment of **4** at room temperature with diphenyl sulfide also results in a good yield of dimer. X-Ray analysis of dimer **10** reveals a nearly square array of two iron and two sulfur atoms, the iron atoms being coordinated further to the three carbon atoms of the ligand. One ligand backbone is above and one is below the plane of the Fe_2S_2 square (Figure 2) and a center of symmetry exists.[16] The bond distances in this dimer are similar to those of monomer **7** and points of similarity exist with a dithiolene iron tricarbonyl dimer, $[(CF_3)_2C_2S_2(CO)_3Fe]_2$,[17a] whose Fe–S bond distances in the Fe_2S_2 array are 2.28 and 2.31 Å and bond angles Fe–S–Fe, 95°, and S–Fe–S, 85°.[18] A number of other dithiolene iron dimers are known,[17b,c] some of which show appreciable differences in iron-sulfur bond distances in the Fe_2S_2 moiety.[19] The iron-sulfur bond distances (2.31 Å) in **10** are slightly greater than the corresponding distances (2.19–2.23 Å) in synthetic analogues of the active sites of Fe_2S_2 iron-sulfur proteins.[20]

The dimers decompose at their melting points and are stable in the solid state but less stable in solutions exposed to air.

A noteworthy difference appears in the chemical shifts of the methylene protons (H^1, H^2) in the dimers and monomers. The absorption for H^1 in **9** is at δ −0.10 (vs. 1.38 for **4**) and in **10**, at δ +0.52 (vs. 1.95 for **5**). For H^2 in **9** the chemical shift is 1.20 (vs. 2.43 for **4**). There is relatively little difference between monomer and dimer in chemical shifts for H^3 and H^4, e.g., **4**, δ H^3 5.94, δ H^4 7.06, **9** δ H^3 5.85, δ H^4 7.02. In **10**, and by analogy in **9**, protons H^1 are oriented toward and over (or under) the plane of the Fe_2S_2 array so that perhaps the observed chemical shifts for H^1 result from a ring current. The shielding of H^2 in **9** is more difficult to explain since that proton is expected to be directed away from the Fe_2S_2 ring although it may still be relatively close to it. Alternatively, these high field shifts may result from some change in the bonding of the terminal methylene group to iron on going from monomer to dimer. If so, this change is not reflected in the bond distance which is the same in both monomer **7** and dimer **10.**

The proton NMR spectrum of **10** indicates that the two methylene protons of the ethyl group are nonequivalent, a ten-line multiplet being observed. Irradiation of the methyl protons of the ethyl group causes the ten-line multiplet to collapse to a pair of doublets. Nonequivalent methylene protons in NMR are not uncommon and the origins of this type of nonequivalence have been reviewed.[21]

Equivalence of the two iron atoms in **9** are demonstrated by the Mössbauer spectrum, only one species of iron being present. The Mössbauer data are consistent with an iron(0) complex:

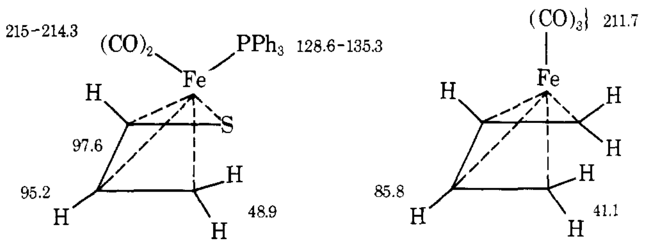
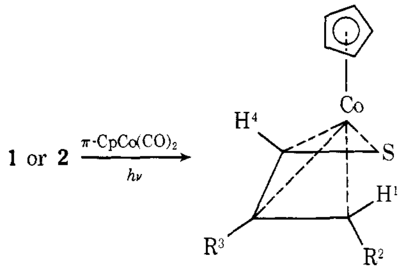


Figure 1. ^{13}C NMR chemical shifts (δ in ppm downfield from internal tetramethylsilane).

isomer shift 0.058 mm s^{-1}; quadrupole splitting 1.36 mm s^{-1} (natural iron standard).

No carbon-carbon double bond absorption was seen in the infrared spectrum of **9** and **10**, and no absorption for bridging carbonyl groups was observed. The mass spectra of **9** and **10** show the parent ions and fragments resulting from the stepwise loss of four carbon monoxide ligands. An ion corresponding to the mass of Fe_2S_2 is observed. Ions derived from the thioacrolein ligands also are prominent in the mass spectra.[3]

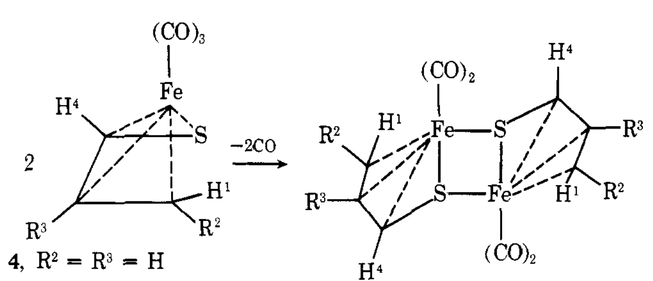
Monomeric Cobalt Complexes. Irradiation of a hexane solution of thietes **1** or **2** with η^5-cyclopentadienylcobalt dicarbonyl[22] yields dark green or green-brown compounds which apparently are cobalt analogues of the iron-thioacrolein complexes (Cp = π-C_5H_5).



11, $R^2 = R^3 = H$
12, $R^2 = CH_3$; $R^3 = C_2H_5$

The proton NMR patterns of absorption and chemical shifts are similar to those of the iron complexes (see Table I) and of several cobalt cyclopentadienyl diene complexes.[23] The two protons of the methylene group (in C_2H_5) of **12** appear as a complex multiplet and are nonequivalent as are similar protons in dimer **10**. The ^{13}C NMR spectra of these complexes (Figure 3) also are similar to that of iron complex **7**.

The most intense ions in the mass spectra of **11** and **12** are the molecular ions. Many ion fragments are observed which correspond to those observed for the thietes (e.g., *m/e* 71 for $C_3H_3S^+$). Ions of composition C_5H_5Co also are very numerous but those of thioacroleincobalt (C_3H_4SCo) were not observed, an indication that the thioacrolein ligand is more labile than η^5-cyclopentadienyl in mass spectrometry. Ions of *m/e* 66 in the spectra of both **11** and **12** correspond to $C_5H_6^+$ which suggests the possibility of a hydrogen transfer from the thioacrolein to the cyclopentadienyl ligand, perhaps via a cobalt-hydrogen intermediate analogous to those postulated for hydrogen transfers involving various iron and cobalt complexes.[24] In **12**, ions of *m/e* 125 are observed which may correspond to $(C_5H_5CoH)^+$. Hydrogen transfers have been observed in the mass spectrum of cyclohexadienylcyclopentadienyliron, ions of *m/e* 66 ($C_5H_6^+$) and 122 $(C_5H_5FeH)^+$ being formed.[25]



4, $R^2 = R^3 = H$
5, $R^2 = CH_3$; $R^3 = C_2H_5$

9, $R^2 = R^3 = H$
10, $R^2 = CH_3$; $R^3 = C_2H_5$

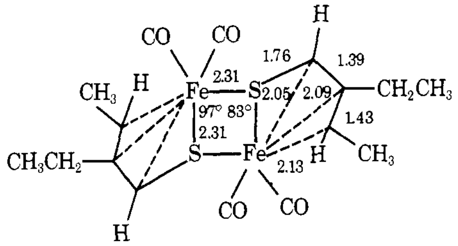


Figure 2. Structure and bond distances (Å) for dimer **10**.

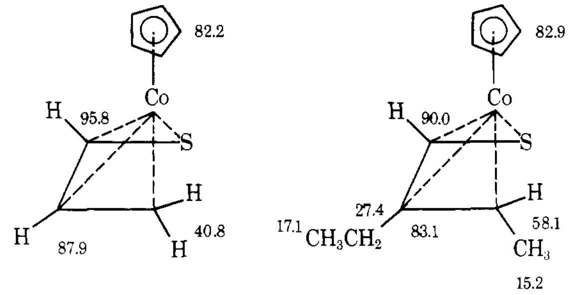
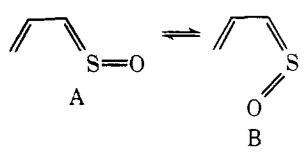


Figure 3. ^{13}C NMR chemical shifts (δ in ppm downfield from internal tetramethylsilane).

Thioacrolein *S*-Oxide (Vinyl Sulfine) Complexes of Iron and Cobalt. Oxidation of the sulfur atom in preference to the iron atom occurs on oxidation of iron complexes **4**, **5**, **7**, **9**, and **10** and cobalt complexes **11** and **12**. The oxidizing agent for **4**, **5**, and **7** was hydrogen peroxide in acetic acid and for **9**, **10**, **11**, and **12**, *m*-chloroperbenzoic acid. The iron compounds vary in color from yellow to red-orange; the cobalt compounds are red. These metals appear to be complexed with a new ligand, vinyl sulfine or thioacrolein *S*-oxide;[26] evidence for the presence of an *S*-oxide group is the strong absorption at 1020–1070 cm^{-1} in the infrared. These complexes are somewhat analogous to complexes of vinyl ketene.[27] Donation of electrons from iron or cobalt to the thioacrolein ligand is expected to create considerable electron density on sulfur, which may account for its facile oxidation. Two *S*-oxide isomers are obtained in the oxidation of **4** and **12** and the products from oxidation of **7** and **11** also may be mixtures of isomers. Since vinylsulfine can exist in two isomeric forms,[28] A and B, the formation of isomeric complexes (from exo isomer A and endo isomer B) is understandable.



Although the structures of these *S*-oxide complexes have not been established by x-ray analysis, they are probably similar to the thioacrolein complexes which are their precursors. Spectroscopic data tend to support this assumption.

The proton NMR spectra of **13**, **16**, and **17** show two absorptions for H^1; the ratio of areas of the high field absorption to the low field absorption is 3:2, 8.5:1.5, and 7:3, respectively. The low field absorption is ascribed to isomer **b** because of the known deshielding of a sulfoxide group in proximity to a more

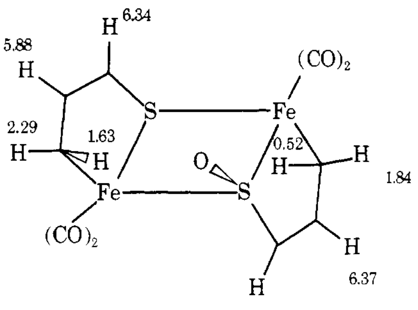
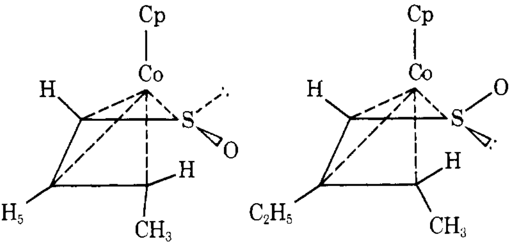
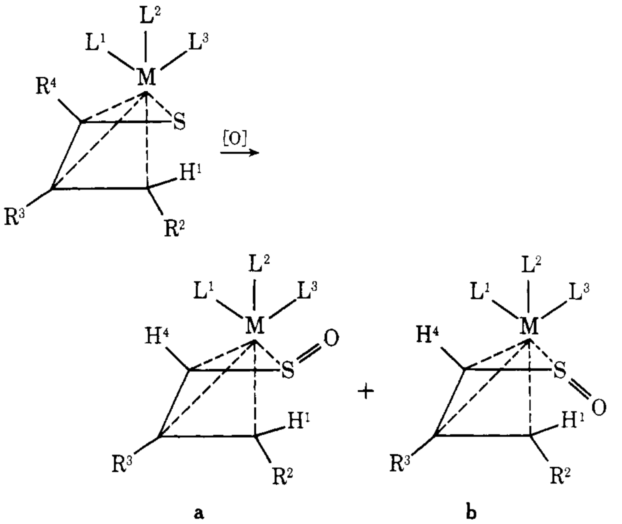


Figure 4. ^{1}H NMR chemical shifts for **18** (δ values in ppm downfield from internal tetramethylsilane).



m-ClC$_6$H$_4$CO$_3$H	30%	70%
O$_2$	75%	25%

Figure 5. Relative amounts of S-oxide formed by oxidation of **12** with m-chloroperbenzoic acid and with air (Cp = π-C$_5$H$_5$).



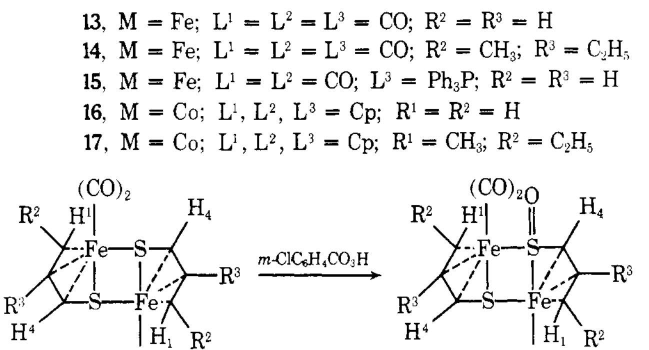
13, M = Fe; $L^1 = L^2 = L^3$ = CO; $R^2 = R^3$ = H

14, M = Fe; $L^1 = L^2 = L^3$ = CO; R^2 = CH$_3$; R^3 = C$_2$H$_5$

15, M = Fe; $L^1 = L^2$ = CO; L^3 = Ph$_3$P; $R^2 = R^3$ = H

16, M = Co; L^1, L^2, L^3 = Cp; $R^1 = R^2$ = H

17, M = Co; L^1, L^2, L^3 = Cp; R^1 = CH$_3$; R^2 = C$_2$H$_5$



18, $R^2 = R^3$ = H

19, R^2 = CH$_3$; R^3 = C$_2$H$_5$

or less collinear proton.[29] The pattern of chemical shifts in **13–17**, δ $H^4 > H^3 > H^2 > H^1$, and coupling constants is similar to that observed with the monomeric precursors. Absorption at ca. 1450 and 1170 cm^{-1} in the infrared is characteristic of the thioacrolein moiety. The possibility of a metal-oxygen-sulfur bond is suggested by absorption at 995 and 950 cm^{-1} in **16** and **17**.[30]

Mass spectra of all S-oxide complexes show an ion corresponding to the loss of one oxygen, a behavior also observed with free sulfines.[31]

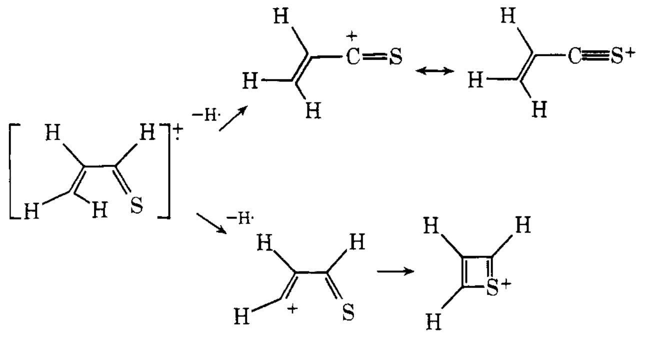
The proton NMR spectrum of **18** and **19** reveals the nonequivalence of the two ligands (Figure 4). The spectrum of **19** is complicated by overlapping absorptions which make assignments difficult.

Autooxidation of Cobalt Complex 12. Cobalt complex **12** decomposes when heated in air above its melting point or in acetone solution. From the acetone solution a red oil was obtained which spectroscopic data indicated was a mixture of two isomeric S-oxide complexes, **17a** and **17b**. The ratio of the amounts of the two isomers obtained from the autooxidation is different from that obtained by oxidation with m-chloroperbenzoic acid (Figure 5). Proton NMR analysis indicates that more of the syn isomer is obtained in the autooxidation which may indicate some involvement of a cobalt-oxygen complex in which the oxygen attached to the cobalt atom is in greater proximity to one side of the sulfur atom.

This autooxidation reaction may be analogous to the sensitized photooxidation of sulfides to sulfoxides[32] provided that ambient light can provide access to a triplet state of **12**. On the other hand, an uncatalyzed complexation with oxygen may occur either via cobalt or by formation of a peroxide. There are a number of analogies to the reaction of **12** with oxygen. Phosphine-cobalt complexes have been reported to yield phosphine oxides with molecular oxygen via a cobalt-oxygen complex,[33] and the autooxidations of triphenylphosphine[34a] and of benzyl mercaptan[34b] are catalyzed by several anionic transition metal complexes of dithiolenes. A sulfur atom in a copper sulfinate complex is oxidized by atmospheric oxygen to yield a sulfonate complex.[35] A cobalt dithiolene complex has been reported to be a powerful antioxidant and a good stabilizer of polypropylene to ultraviolet light.[36] At low temperatures cobaltocene reacts with oxygen to give a peroxide bridge between two cyclopentadienyl rings,[37a] and a cobalt-oxygen complex is believed to be involved in the cleavage of α-diketones.[37b]

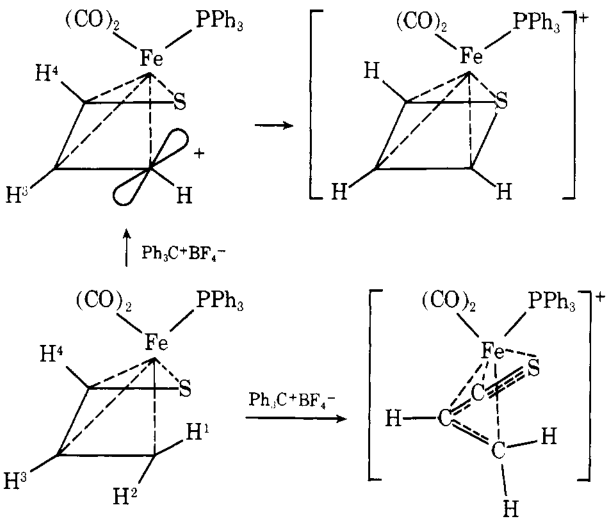
Iron and Cobalt Cationic Complexes. The mass spectra of thietes show abundant ions corresponding to the parent ions minus a hydrogen atom.[3] These cations might involve stabilization by the sulfur atom:

Alternatively, the cation might have a structure derived by loss of a hydrogen atom from a thioacrolein radical ion; the cation derived by loss of a hydrogen atom from the terminal methylene group might cyclize to the thiete cation.



Treatment of complexes **4**, **7**, **11**, and **12** with triphenylmethyl fluoroborate (and in some cases with tropylium salts) gave fluoroborate salts containing the sulfur ligand. The formation of triphenylmethane or cycloheptatriene was further evidence for hydride ion abstraction.[38] Although definite structures for these compounds have not been established, salts obtained from **7**, **11**, and **12** gave satisfactory elemental analyses for structures which are consistent with other physical and chemical data.

The yellow, hygroscopic salt obtained by treatment of **7** with triphenylmethyl fluoroborate contains, in addition to the fluoroborate anion (ir 1050 cm^{-1}), an iron atom, a C_3H_3S moiety, and the original triphenylphosphine and carbon monoxide ligands. The proton NMR spectrum showed that absorptions for all three protons of the sulfur-containing ligand had shifted downfield; detailed analysis was difficult because these absorptions are under the absorption of the aromatic protons (δ 7–7.9) of the triphenylphosphine ligand. Several possibilities exist for the structure of the cation. If H^1 or H^2 is removed, cyclization to a complexed 4-π electron cation may occur. Loss of H^4 would yield a complex of a thioalkenoyl cation.



The cation obtained from **4** was unstable and the best elemental analysis for $(C_3H_3S)Fe(CO)_3{}^+BF_4{}^-$ was 1.3% high in carbon and 1.6% high in hydrogen. It was very soluble in sulfur dioxide, acetonitrile, acetone, dimethylformamide, and dimethyl sulfoxide and insoluble in most other organic solvents. It appears to react with water and with pyridine. The instability of the salt may be related to the increased lability of the carbon monoxide ligands because of reduced electron donation to them by iron. Mössbauer data on this impure material were obtained: isomer shift 0.103 mm s^{-1}; quadrupole splitting 1.76 mm s^{-1} (natural iron standard).

Treatment of cobalt complexes **11** and **12** with triphenylmethyl or tropylium fluoroborate or tropylium hexafluorophosphate was a different story. Dark brown salts, **20** and **21**, were obtained which are composed of two cobalt atoms, two nonequivalent η^5-cyclopentadienyl ligands, and one C_3H_3S moiety in addition to one tetrafluoroborate anion. The proton and ^{13}C NMR spectra of **20** and **21** provide important information about the structures. In the proton NMR spectrum of the salt from **11**, three absorptions are observed: δ 10.40 (two doublets, J = 2.6, 5.5 Hz), 6.68 (triplet, J = 2.6 Hz), and 5.98 (two doublets, J = 2.6, 5.5 Hz). Spin-tickling experiments indicated that all the proton–proton coupling constants have the same sign so that the common distinction of opposite signs for three- and four-bond couplings[39] does not hold in this case. The chemical shift of δ 10.40 is analogous to that for protons situated on a positive carbon in allylic systems,[40] but this large downfield shift also may be caused by contact interactions arising from the electronic properties of the salt.[41] No broadened resonances, indicative of strong paramagnetism, were observed, however. The carbon absorption of the methyl group in **21**, $R^2 = CH_3$, appears at 34 ppm downfield from tetramethylsilane, a chemical shift analogous to those for methyl groups on positive carbons.[42] The chemical shifts of the other two protons in **20** are in the region expected for vinyl protons and are not greatly shifted from their positions in **11**. The NMR absorption of the protons of the methyl group in **21** is a singlet, whereas in **12** it is a doublet. Therefore, the hydrogen that was abstracted is most probably H^1 and not H^4. The proton NMR spectrum of **20** in acetonitrile is unchanged from −35 to +58°. Higher temperatures cause decomposition. Although there is no fluxional behavior of **20** that can be observed, the possibility of its occurrence at higher temperatures cannot be ruled out. A solvent in which decomposition does not occur is required for further investigation.

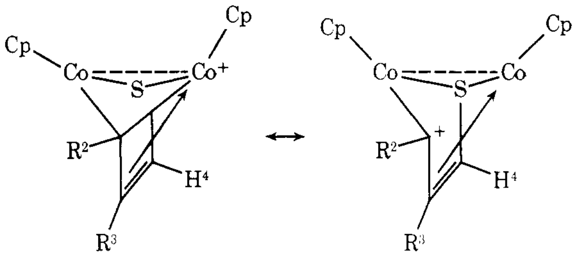
One carbon of the ligand framework is not observable in the ^{13}C NMR spectra of **20** and **21** which suggests the possibility of a carbon–cobalt bond, the large quadrupole moment of cobalt causing extensive broadening of the carbon resonance line. The resonance of the apical carbon in the cation, $[Co_3(CO)_9CCHR]^+$, is not observed for this reason.[43] The resonance of the cyano carbon atom of the solvent, acetonitrile, is broadened in the spectra of **20** and **21**. This broadening may be caused by a fluctuating coordination of the acetonitrile to cobalt. The chemical shifts of the other two carbons of the ligand framework in the two salts indicate that no large amount of positive charge is associated with them, thus supporting involvement of the π-bond between these two carbons in coordination with cobalt.

$$\mathbf{11} \xrightarrow[CH_2Cl_2]{Ph_3C^+BF_4^-} \underset{\mathbf{20}}{(C_3H_3S)Co_2(\pi\text{-}C_5H_5)_2BF_4}$$

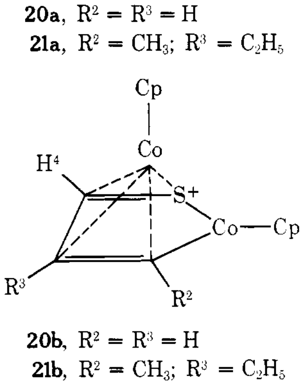
$$\mathbf{12} \xrightarrow[\substack{\text{or } C_7H_7^+X^- \\ CH_2Cl_2}]{Ph_3C^+X^-} (C_6H_9S)Co_2(\pi\text{-}C_5H_5)_2X^-$$

21a, $X^- = BF_4^-$
21b, $X^- = PF_6^-$

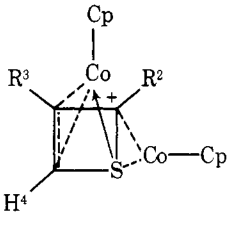
Three structures for **20** and **21** may be considered, **20a**, **b**, and **c** and **21a**, **b**, and **c**. Structures **a** are used in Figure 6 for presentation of the proton and carbon chemical shifts. The assignments of chemical shifts to the carbons and the protons of the vinyl group may be reversed. Structures have been proposed analogous to **20a** or **21a** for certain dithiolene iron



20a, $R^2 = R^3 = H$
21a, $R^2 = CH_3$; $R^3 = C_2H_5$



20b, $R^2 = R^3 = H$
21b, $R^2 = CH_3$; $R^3 = C_2H_5$



20c, $R^2 = R^3 = H$
21c, $R^2 = CH_3$; $R^3 = C_2H_5$

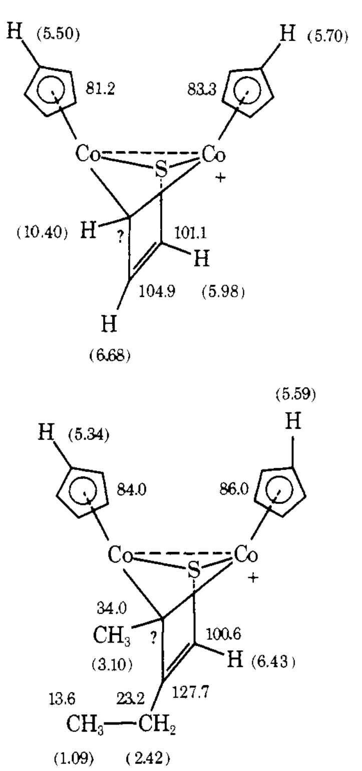


Figure 6. ^1H NMR and ^{13}C NMR chemical shifts (ppm downfield from Me_4Si) for cobalt salts. ^1H NMR shifts are in parentheses.

complexes.[44] An uncharged biscobalt complex, obtained by photolysis of a mixture of cyclobutadiene(π-cyclopentadienyl)cobalt and cyclopentadienylcobalt dicarbonyl, has a structure analogous to **20b** or **21b**.[45]

Magnetic susceptibility measurements on **20** at 24.5° gave effective magnetic moments of 2.52, 2.56, and 2.62 μ_B at three different field strengths. The paramagnetism of **20** was confirmed by electron spin resonance; the spectrum, although complex, showed coupling with cobalt. The low value of the magnetic moment is consistent with a weak cobalt-cobalt bond as in **20a** and **21a**, but because the magnetic and ESR data could arise from an impurity or decomposition product, the significance of the data may be dubious. However, an ESR spectrum of a decomposition product (structure unknown) of **20** was not identical with that observed for the salt.

Direct and alternating current polarograms and cyclic voltammograms were obtained from solutions of **20** and **21** in nitromethane. The data were consistent with a reversible one-electron reduction process ($E_{1/2} = -0.636$ and -0.680 V, vs. standard calomel electrode, respectively). The monomeric cobalt complex, **11**, did not undergo any well-defined redox reactions in nitromethane solution. Cyclic voltammetry of **20** and **21** gave symmetric curves. No complicating reactions were observed.

Treatment of salt **21** with sodium methoxide in acetonitrile or with aqueous sodium azide did not alter the ultraviolet-visible spectrum. Treatment with methanolic sodium cyanide resulted in decomposition, no stable compound being isolated. It may be noted that the nucleophilicity parameters, n_{Pt}, for the three nucleophiles, methoxide, azide, and cyanide, are <2.4, 3.58, and 7.14 respectively.[46] Decomposition also occurred when **20** was treated with *n*-butyllithium in ether. Although triphenylphosphine did not appear to react with **20**, a black solid roughly corresponding to a 1:1 adduct was obtained with triethoxyphosphine. No absorption could be detected in the proton NMR spectrum of this black adduct and paramagnetism was demonstrated by electron spin resonance.

Experimental Section

Elemental analyses were obtained from Microanalysis, Inc., Wilmington, Del. Molecular weights (determined by osmometry) were performed at Galbraith Laboratories, Knoxville, Tenn. Melting points were measured on a Kofler micro hot stage apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 137 infrared spectrometer; ultraviolet and visible spectra were obtained on a Perkin-Elmer 202 ultraviolet spectrometer. The ESR spectra were obtained on a Varian E-9 EPR spectrometer and the proton NMR spectra were obtained on Varian A-60 or Varian XL-100-15 NMR spectrometer. The proton-decoupled ^{13}C NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped for both frequency sweep and pulsed Fourier transform (FT) operation. In all cases, the FT mode was utilized. The chemical shifts are reported in parts per million downfield from the internal standard, tetramethylsilane (Me_4Si). The mass spectra were measured on a Perkin-Elmer Hitachi Model RMU-6E single focusing spectrometer. Mössbauer spectra were obtained on an Austin Science Associates spectrometer and 0.001 in. natural iron foil was used for calibration.

Pentane and hexane were washed successively with sulfuric acid, saturated aqueous sodium bicarbonate, and water, dried ($MgSO_4$), and distilled from Linde molecular sieves, type 4A, prior to use. Benzene was dried over sodium or Linde molecular sieves, type 4A. Ether (ethyl ether) was distilled from lithium aluminum hydride or dried over molecular sieves (4A). Acetonitrile and nitromethane were distilled from calcium hydride.

Triphenylmethyl fluoroborate was prepared from triphenylmethanol and fluoroboric acid, recrystallized from acetonitrile, and vacuum dried. Tropylium fluoroborate (Cationics, Inc.), tropylium hexafluorophosphate (Cationics, Inc.), iron pentacarbonyl (Strem Chemicals, Inc.), and π-cyclopentadienylcobalt dicarbonyl (Strem Chemicals, Inc.) were used as obtained. In handling the organometallic compounds, all the reactions were done in an atmosphere of argon or nitrogen.

The photochemical irradiation was done by means of a 450-W high pressure mercury arc lamp (Hanovia 679A/36).

Thioacroleiniron Tricarbonyl (4). Iron pentacarbonyl (6 g, 0.031 mol) and thiete[3] (0.8 g, 0.011 mol) were dissolved in pentane (500 ml) and irradiated under nitrogen in a cylindrical apparatus with a high pressure mercury arc lamp and a Corex filter contained in a water-cooled quartz tube in the center. The photolysis vessel was kept in a −15 to −20° acetone bath. After the reaction mixture was irradiated for 3.25 h, insoluble material was removed by filtration and the filtrate was concentrated and chromatographed (Florisil, pentane) under nitrogen. The main fraction was concentrated by evaporation to give a red oil. Orange-red crystals of thioacroleiniron tricarbonyl (0.690 g, 0.00325 mol, 30%) could be obtained by chilling the concentrated pentane solution in a freezer: mp 28°; mol wt calcd for $(C_6H_4O_3SFe)_2$ 424, found 466 in hexane (osmometrically). Anal. ($C_6H_4FeO_3S$) C, H.

(2-Ethylthiocrotonaldehyde)iron Tricarbonyl (5). A mixture of 3-ethyl-4-methylthiacyclobutene[3] (0.817 g, 7.15 mmol) and diiron nonacarbonyl (2.60 g, 7.15 mmol) under dry nitrogen in ether (50 ml) at 0° was allowed to warm gradually to 23-25° with stirring over a period of 4 h. An insoluble brown powder was removed by filtration, and the filtrate was concentrated under reduced pressure without heat. The residue from the filtrate was dissolved in pentane and any solid material was removed by filtration. The pentane solution was concentrated under reduced pressure and the residue was chromatographed (Florisil) with elution by pentane. An orange band was collected and the material was chromatographed twice to give an orange-red syrup (0.5 g, 1.6 mmol, 22%): $n^{26}D$ 1.5900. Anal. ($C_9H_{10}FeO_3S$) C, H.

1-Cycloheptenethioaldehydeiron Tricarbonyl (6). In a procedure identical with that for the preparation of **5**, diiron nonacarbonyl (2.6 g, 7.15 mmol) and 8-thiabicyclo[5.2.0]-1(9)-octene[3] (0.99 g, 7.15 mmol) gave orange-red crystals of complex **6**: mp 28–29°. Anal. ($C_{11}H_{12}FeO_3S$) C, H.

(Thioacrolein)(triphenylphosphine)iron Dicarbonyl (7). A solution of thioacroleiniron tricarbonyl (0.47 g, 2.2 mmol) and triphenylphosphine (0.58 g, 2.2 mmol) in benzene (10 ml) was stirred at 50° under nitrogen for 4 h. Solvent was removed and **7** was obtained as red crystals (1.1 g, 2.2 mmol, 100%) which were recrystallized from hexane-benzene (4:1): mp 131–133°. Anal. ($C_{23}H_{19}FeO_2PS$) C, H

(Thioacrolein)(triethoxyphosphine)iron Dicarbonyl (8). Thioacroleiniron tricarbonyl (0.353 g, 1.67 mmol) and triethoxyphosphine (0.277 g, 1.67 mmol) in dichloromethane (15 ml) were stirred under argon at room temperature for 20 h. The solution was concentrated under reduced pressure without heating and was chromatographed on a Florisil column. Elution with distilled pentane gave two yellow bands: the first yellow band was bis(thioacroleiniron dicarbonyl) (**9**) (ca. 10 mg, 0.055 mmol, 3.3%); the second band was unreacted thioacroleiniron tricarbonyl (80 mg, 0.38 mmol, 23%), the compounds being identified by ir spectra and melting point. Finally, the column was washed with pentane containing a few drops of ether. The orange solution remaining after removal of pentane gave an orange-red syrup, **8** (0.180 g, 0.49 mmol, 30%). Anal. ($C_{11}H_{19}FeO_5PS$) C, H.

Bis(thioacroleiniron dicarbonyl) (9). Thioacroleiniron tricarbonyl (0.20 g, 0.95 mmol) was heated in a nitrogen atmosphere on an oil bath at 130° for 5 min. After the reaction flask was cooled to room temperature, some volatile material was removed under vacuum (pump). The residue in the flask was dissolved in acetone and insoluble material was removed by filtration. The acetone was removed by a rotary evaporator without heating and the residue was recrystallized from acetone (2 ml). Yellow-brown crystals of **9** were obtained on chilling the acetone solution (0.060 g, 0.16 mmol, 34%): mp 155–157° dec. Anal. ($C_{10}H_8Fe_2O_4S_2$) C, H.

Bis(2-ethylcrotonthioaldehydeiron dicarbonyl) (10). 3-Ethyl-4-methylthiacyclobutene (**3**) (1.8 g, 0.0158 mol) and iron pentacarbonyl (9.5 g, 0.05 mol) were dissolved in degassed (N_2 bubbled into the solution for 0.5 h), purified hexane in a 500-ml photolysis reaction vessel which was equipped with a Corex filter. The reaction mixture was irradiated under nitrogen at 10–15° for 6 h.

The reaction mixture was filtered and concentrated. Column chromatography (Florisil, pentane) eluted dark red, volatile crystals of $Fe_3S_2(CO)_9$: mp 112° (lit.[47] mp 114°) (0.1 g, 0.0003 mol, 2%); ir (KBr) 2060–1950 (s, CO); mass spectrum (70 eV) *m/e* 484. A small amount of monomeric complex **5** (0.5 g, 0.002 mol, 13%) also was obtained. Continued elution of the column with 2% ether in hexane gave a yellow fraction. After removal of the solvent with a rotary evaporator, orange crystals of dimer **10** were obtained (0.7 g, 0.0016 mol, 20%): mp 164–166°. Anal. Calcd for $C_{16}H_{20}Fe_2O_4S_2$: C, 42.50; H, 4.46; S, 14.18. Found: C, 43.00; H, 4.52; S, 13.59.

Thioacrolein(π-cyclopentadienyl)cobalt (11). A solution of thiete (0.72 g, 10 mmol) and π-cyclopentadienylcobalt dicarbonyl (1.80 g, 10 mmol) in hexane (1 l.) was irradiated (Corex filter) under nitrogen at −15 to −20° for 24 h. The reaction mixture was filtered and the filtrate concentrated. Column chromatography (Woelm alumina grade 1, ether) in a nitrogen atmosphere gave a dark brown fraction which was concentrated and triturated with a small amount of hexane. Complex **11** was obtained as dark brown crystals (1.62 g, 8.26 mmol, 83%): mp 80–82°. Anal. (C_8H_9CoS) C, H.

(2-Ethylcrotonthioaldehyde)(π-cyclopentadienyl)cobalt (12). A solution of 3-ethyl-4-methylthiacyclobutene (2.0 g, 17.5 mmol) and π-cyclopentadienylcobalt dicarbonyl (6 g, 33 mmol) in hexane (1 l.) was irradiated under nitrogen at −15 to −20° for 24 h. The reaction mixture was concentrated under a reduced pressure and chromatographed (Woelm alumina grade III, hexane, ether-hexane, ether). The main fraction (ether) was concentrated to yield a dark green, crystalline solid, mp ~80°. The solid could be purified by sublimation (50%/0.025 mm), and dark green needles of **12** (1.9 g, 8 mmol, 47%) were obtained: mp 89–91° dec. Anal. ($C_{11}H_{15}CoS$) C, H, mol wt.

(Thioacrolein *S*-oxide)iron Tricarbonyl (13). Hydrogen peroxide (30%, 640 mg) was added slowly to a solution of thioacroleiniron tricarbonyl (0.996 g, 4.69 mmol) in acetic acid (7 ml) at 5–10°. The chilled reaction mixture was stirred for 30 min. Chloroform (100 ml) was added and the chloroform solution was washed successively with water (10 ml), twice with saturated, aqueous sodium bicarbonate (30 ml), 5% aqueous sodium thiosulfate (20 ml), and water. The chloroform solution was dried ($MgSO_4$) and the solvent removed by a rotary evaporator without heating. The residue was chromatographed (Florisil; pentane, ethyl acetate). The main fraction (ethyl acetate) was concentrated by a rotary evaporator and ether (5 ml) was added. Yellow crystals of **13** separated from the ether solution on cooling (freezer) (0.850 g, 3.72 mmol, 79%): mp 112–114°. Anal. ($C_6H_4FeO_4S$) C, H.

(2-Ethylcrotonthioaldehyde *S*-oxide)iron Tricarbonyl (14). Hydrogen peroxide (peroxide content determined by titration with $KMnO_4$ solution,[48] 30%, 0.147 g, 1.3 mmol) was added slowly at 0° to an acetic acid solution (2 ml) of **5** (331 mg, 1.3 mmol). The reaction mixture was stirred at 5° for 30 min after which chloroform (50 ml) was added. The chloroform solution was washed successively with water (10 ml), saturated sodium bicarbonate (10 ml × 2), 5% sodium thiosulfate solution (7 ml), and water and dried ($MgSO_4$). The solution was concentrated and chromatographed (Woelm alumina, dry column, CH_2Cl_2). The main fraction (yellow band) was collected to give an orange-yellow oil, **14** (314 mg, 1.16 mmol, 90%).

(Thioacrolein *S*-oxide)(triphenylphosphine)iron Dicarbonyl (15). A solution of thioacrolein(triphenylphosphine)iron dicarbonyl (0.446 g, 1.00 mmol) in benzene (6 ml)-acetic acid (4 ml) was stirred under nitrogen at 0–5°, and hydrogen peroxide (160 mg, 30% aqueous solution) in acetic acid (1 ml) was added dropwise during 5 min. The solution was stirred for an additional 20 min and chloroform (50 ml) was added. The chloroform solution was extracted with water (10 ml), twice with saturated aqueous sodium bicarbonate (15 ml), 5% sodium thiosulfate solution (15 ml), and water (20 ml). The chloroform layer was dried (sodium sulfate) and filtered through Florisil which was washed well with acetone. Solvent was removed by a rotary evaporator with heating to give an oil from which orange crystals of **15** were obtained on addition of a small amount of cold ether (0.372 g, 0.805 mmol, 80%). Two recrystallizations gave a pure sample: mp 188–190°. Anal. ($C_{23}H_{19}FeO_3PS$) C, H.

(Thioacrolein *S*-oxide)(π-cyclopentadienyl)cobalt (16a, b). *m*-Chloroperbenzoic acid (Aldrich Chem. Co., assay 85%,[48] 101.5 mg, 0.500 mmol) in dichloromethane (35 ml) was added slowly at −40° to a stirred dichloromethane solution (75 ml) of **11** (98 mg, 0.500 mmol) in a three-necked flask. The solution instantly changed its color from greenish brown to red. The reaction mixture was stirred for an additional 10 min at −30 to −40°, and ammonia gas (dried by passage through a sodium hydroxide tower) was passed into the reaction mixture for 10 min. Excess ammonia was removed by evacuation (water aspirator) of the solution for 30 min. A white precipitate formed during this period. The precipitate was removed by filtration and the filtrate was concentrated and chromatographed (Woelm alumina, dry column, elution with 1:1 v/v methylene chloride-chloroform). The main fraction was concentrated to a red oil which was triturated with a small amount of pentane to give red crystals of a mixture of isomers, **16a** and **16b** (74 mg, 0.35 mmol, 70%). The red crystals of the mixture of isomers were hygroscopic; on contact with air they liquified instantly. A red solid (mp ~107°) was obtained by storage of the oily crystalline mixture in a desiccator (over H_2SO_4) for a week. Anal. (C_8H_9CoOS) C, H.

(2-Ethylcrotonthioaldehyde *S*-oxide)(π-cyclopentadienyl)cobalt (17a, b). 2-Ethylcrotonthioaldehyde(π-cyclopentadienyl)cobalt (127 mg, 0.500 mmol) was oxidized as described for the preparation of **16a** and **16b**. The main fraction from chromatography was concentrated to a red oil which was triturated with a small amount of pentane to give red crystals of a mixture of isomers **17a** and **17b** (102 mg, 0.400 mmol, 80%): mp 71–76°. Anal. ($C_{11}H_{15}CoOS$) C, H.

Autooxidation of (2-Ethylcrotonthioaldehyde)(π-cyclopentadienyl)cobalt (12). A sample of **12** (ca. 0.5 g) was dissolved in warm acetone and any undissolved material was removed by filtration through a plug of glass wool. The sample was not degassed. A ^{13}C NMR spectrum was taken on the sample after which the solvent was removed by evaporation. The recovered solid was not completely soluble in chloroform or dichloromethane. The solid (ca. 0.5 g) was redissolved in chloroform (60 ml) and a brown solid (ca. 0.1 g) was removed by filtration. The filtrate was concentrated on a rotary evaporator to give a brown oil (ca. 0.3 g). Column chromatography of this oil (Woelm alumina grade 1, ethyl ether) gave green crystals of **12** (ca. 0.2 g) and a new red band at the top of the column. This was eluted with chloroform and concentrated to give a red oil (ca. 0.1 g) whose properties indicate it is a mixture of isomers **17a** and **17b**.

Bis(thioacroleiniron dicarbonyl) *S*-Oxide (18). A solution of *m*-chloroperbenzoic acid (Aldrich Chemical Co., assay 85%,[48] 50 mg, 0.25 mmol) in dichloromethane (13 ml) was stirred into a solution of **6** (46 mg, 0.125 mmol) in dichloromethane (25 ml) at 0°. After 0.5 h the reaction mixture was warmed to room temperature and was washed with saturated sodium bicarbonate solution (15 ml) and dried (Na_2SO_4). The solution was concentrated and chromatographed on a Florisil column (dichloromethane). The main fraction was concentrated to give a red-orange solid. Recrystallization of the solid from a few drops of dichloromethane and pentane (3 ml) gave red-orange crystals of **18** (23 mg, 0.06 mmol, 48%): mp 122–125° dec. Anal. ($C_{10}H_8Fe_2O_5S_2$) C, H.

Bis((2-ethylcrotonthioaldehyde)iron dicarbonyl) *S*-Oxide (19). The procedure described above was used for the oxidation of **10** (118 mg, 0.260 mmol) and its purification. The monosulfoxide dimer, **19**, was obtained as red-orange crystals (87 mg, 0.13 mmol, 50%), mp 131–133° dec. Anal. Calcd for $C_{16}H_{20}Fe_2O_5S_2$: C, 41.03; H, 4.28; S, 13.68. Found: C, 40.97; H, 4.31; S, 11.07.[49]

Hydride Abstraction from (Thioacrolein)(triphenylphosphine)iron Dicarbonyl (7). Freshly prepared trityl fluoroborate[50] (0.0730 g, 0.221 mmol) was added to a solution of thioacrolein(triphenylphosphine)iron dicarbonyl (**7**) (0.0985 g, 0.221 mmol) in dichloromethane (7 ml, dried over Linde No. 4A molecular sieves and degassed by passing nitrogen through the solvent). The flask was stoppered and stirred for 20 h at room temperature. Dry ether (ca. 75 ml) was added dropwise to the stirred reaction mixture. A yellow precipitate (0.075 g, 0.141 mmol, 64%) was collected by filtration. It was very hygroscopic and was dissolved in acetonitrile and reprecipitated by slow addition of dry ether (ca. 75 ml) and pentane (25 ml) to give the salt (0.025 g, 0.037 mmol, 21%), mp 113–117° dec. Anal. Calcd for $C_{23}H_{18}BF_4O_2PS$: C, 51.88; H, 3.38. Found: C, 51.90; H, 3.68.

Hydride Abstraction from (Thioacrolein)iron Tricarbonyl (4). A solution of thioacroleiniron tricarbonyl (0.655 g, 3.10 mmol) and triphenylmethyl fluoroborate[50] (1.02 g, 3.10 mmol) in methylene chloride (17 ml) was stirred at room temperature under nitrogen for 24 h. A brown precipitate (0.16 g) was removed by filtration. A similar precipitate was obtained in sulfur dioxide as solvent. Triphenylmethane (0.65 g, 2.7 mmol) and thioacroleiniron tricarbonyl (0.1 g, 0.5 mmol) were recovered from the filtrate. The brown salt was unstable at room temperature and was impure, mp 90–110°. Anal. Calcd for $C_6H_3BF_4FeO_3S$: C, 24.20; H, 1.03; Found: C, 25.53; H, 2.66.

Reaction of Thioacrolein(π-cyclopentadienyl)cobalt (11) with Triphenylmethyl Fluoroborate. Compound **11** (254.8 mg, 13.00 mmol) and freshly prepared triphenylmethyl fluoroborate[50] (225 mg, 0.681 mmol) were placed in an Erlenmeyer flask equipped with a stirring bar. Dry, degassed dichloromethane (8 ml) was added and the flask was stoppered under nitrogen. The reaction mixture was stirred for 20 h at room temperature. Dry diethyl ether (75 ml) was added slowly to the stirred reaction mixture. The dark precipitate of crude salt **20** was collected by filtration. The brown salt **20** (100 mg, 0.25 mmol, 36.8%) was obtained by three reprecipitations from acetonitrile-dry ether: mp above 300°; magnetic moments, 24.5°, three different field strengths, $\mu_{\text{eff}} = 2.52$, 2.56, and 2.62 μ_B (a correction of 175×10^{-6} cgs per mole for the diamagnetic susceptibilities of other elements in the molecule was applied). Anal. Calcd for $C_{13}H_{13}BCo_2F_4S$: C, 38.42; H, 3.20; Co, 29.06. Found: C, 38.34; H, 3.22; Co, 22.31, 23.2 (by atomic absorption or by oxidation and titration with EDTA).

Hydride Abstraction from (2-Ethylthiocrotonaldehyde)(π-cyclopentadienyl)cobalt (12). (A) With Triphenylmethyl Fluoroborate. Compound **12** (107.4 mg, 0.451 mmol) was treated with triphenylmethyl fluoroboate (74.3 mg, 0.225 mmol) in the same manner as for the preparation of **20**. The precipitate of salt was dissolved in dry acetone (10 ml) or acetonitrile (5 ml) and insoluble material removed by filtration. Dry ether (100 ml) was added slowly to the filtrate to give a brown precipitate. Two repetitions of this process gave a brown solid, **21a** (75 mg, 0.17 mmol, 75%), free of triphenylmethane and triphenylmethyl fluoroborate, decomposition above 300°. Anal. Calcd for $C_{16}H_{19}BCo_2F_4S$: C, 42.86; H, 4.24; Co, 26.34. Found: C, 42.60; H, 4.29; Co, 25.07 (by oxidation and titration with EDTA).

(B) With Tropylium Fluoroborate. A solution of compound **12** (384 mg, 1.613 mmol) and tropylium fluoroborate (Cationics, Inc., 144 mg, 0.81 mmol) in dry degassed nitromethane (12 ml) and dichloromethane (2 ml) was stirred at room temperature for 24 h under argon. Solvent was removed by vacuum distillation (room temperature and 0.2 mmHg). GC analysis (10% Carbowax 20 M) of the liquid removed by the distillation and collected in a dry ice-acetone bath showed it contained nitromethane, dichloromethane, and cycloheptatriene (ca. 50 mg, 0.54 mmol, 67%). The analysis was accomplished by the chromatography of a known mixture of nitromethane, dichloromethane, and cycloheptatriene. The solid residue in the distillation flask was dissolved in acetonitrile (15 ml) and the solution was filtered. Dry ether (ca. 100 ml) was added slowly to the stirred filtrate. A dark brown precipitate of **21a** (239 mg, 0.534 mmol, 64.5%) was removed by filtration. The ^1H NMR and ir spectra of this compound were identical with those of the salt prepared by treatment of **12** with trityl fluoroborate.

Table II. Polarographic Results on Salts **20** and **21a**[a]

Current	Compound	$E_{1/2}$[b]	Slope[c]	n[d]
dc	**20**	-0.579 ± 0.020	0.085[e]	1
ac	**20**	-0.636 ± 0.005	0.123[f]	1
dc	**21a**	-0.662 ± 0.010	0.072[e]	1
ac	**21a**	-0.680 ± 0.005	0.128[f]	1

[a] These results are not corrected for the voltage drop caused by the resistance of the solution. [b] Half-wave potentials, V vs. aqueous SCE. [c] Accurate determination of slope was difficult. [d] Taken as the nearest integral number of electrons (calculated). [e] Reciprocal of the slope derived from plot of log $i/(i_d - i)$ vs. E. [f] Slope from plot of E vs. log $(I_p/I)^{1/2} \pm ((I_p - I)/I)^{1/2}$ should be $120/n$ mV for a reversible reaction.

(C) With Tropylium Hexafluorophosphate. Treatment of **12** (93.1 mg, 0.391 mmol) with tropylium hexafluorophosphate (Cationics, Inc. 46.30 mg, 0.196 mmol) in the manner described above gave a dark brown precipitate (67 mg, 0.132 mmol, 68%) of hexafluorophosphate salt, **21b**: decomposition above 300°. The ^1H NMR spectrum was identical with that reported for **21a**. Anal. ($C_{16}H_{19}Co_2F_6PS$) C, H.

Electrochemical Measurements on Salts 20 and 21a. The direct current (dc) and alternating current (ac) polarograms were obtained with an instrument designed and built by John Potts from Analog Devices which utilizes solid-state operational amplifiers and standard electric components. The ac polarograph was modified after instruments described by Hayes and Reilley[51a] and Smith.[51b] A Moseley Model 7001 X-Y recorder was used to obtain permanent dc and ac polarographic records. Cyclic voltammograms were taken with the same instrument.

Nitromethane (Eastman spectroscopic grade) was used as solvent. It was purified by a method described by Olah and-co-workers.[52] A conventional polarographic cell was used for the measurement. Tetraethylammonium hexafluorophosphate (TEAHFP, K and K Laboratories, Inc.) was used as background electrolyte. The sample solutions in nitromethane containing 0.20 M TEAHFP were degassed by passing a stream of nitrogen through the solution for 2 h before the polarograms were taken. A saturated sodium chloride calomel electrode (SCE) or a saturated potassium chloride, silver–silver chloride reference electrode was used as the reference electrode for the dc and ac runs and a spinning platinum electrode for cyclic voltammetric runs.

The electrochemical data are given in Table II.

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Supplementary Material Available: details of the ir, uv, ^1H NMR, ^{13}C NMR, and mass spectra (7 pages). Ordering information is given on any current masthead page.

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