tellurides in 1.5 mL of deuteriochloroform (~0.2M). All tellurium-125 spectra were obtained with a Varian Associates Model FT80 NMR spectrometer equipped with a broad-band probe tuned to 25.104 MHz. About 1000–3000 average transients were required to obtain satisfactory signal to noise ratios using sweep widths of either 8 KHz (~318 ppm) or 4 KHz (~159 ppm) stored in 8K data points. With these spectral parameters, proton-noise-decoupled tellurium resonances were 5–10 Hz wide at half-height. All tellurium-125 shifts are referenced to dimethyl telluride at 25 094 885 Hz and are believed to be precise to at least ±1 ppm. Positive shifts are downfield and negative shifts are upfield from dimethyl ditelluride. The differences between shifts of dialkyl ditellurides reported in the literature and those presented in Table I (Me$_2$Te, δ 63[25] vs. δ 69; Et$_2$Te$_2$, δ 188[25] vs. δ 186; and i-Pr$_2$Te$_2$, δ 303[25] vs. δ 313) are probably due to solvent. In the previous work, the spectra were obtained for neat liquids or for solutions in benzene.

Addition of Electrophiles to the Sulfur Atom of Cobalt Complexes of α,β-Unsaturated Thioaldehydes (Enethials)[1]

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Cyclopentadienylcobalt complexes of α,β-unsaturated thioaldehydes (enethials) can be alkylated on the sulfur atom to give complexes involving the new ligands, formally S-alkyl enethial cations or S-alkyl allylcarbenium ions. A Hg II complex has been obtained. Silver tetrafluoroborate oxidizes the complexes to fluoroborate salts containing two cobalt atoms.

Introduction

Complexation with transition metals stabilizes a variety of exotic ligands whose existence otherwise would be in jeopardy.[3] Thioaldehydes are extremely rare[4] as are α,-β-unsaturated thioaldehydes. Stable examples of the latter involve extensive conjugation of the thiocarbonyl group with a nitrogen[5] or a sulfur[6] atom. The unstable molecule, thioacrolein or propenethial, has been obtained by flash vacuum thermolysis of diallyl sulfide; it decomposes slowly at −196 °C.[7] However, propenethial and other α,β-unsaturated thioaldehydes have been obtained as stable complexes with iron or cobalt (e.g., I, II).[8] An X-ray analysis has been performed on II.[9] These complexes are derived from thietes which are readily prepared.[8b,10]

I   II
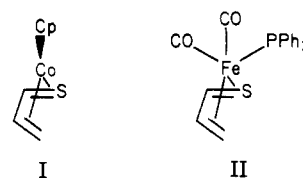
Cp = π-C$_5$H$_5$

In order to determine how complexation affects the chemical properties of the enethial ligand, we decided at

(1) Reported in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, April, 1979, Abstract ORGN 343.

(2) Taken in part from the Ph.D. Thesis of E. J. Parker, Syracuse University, Dec 1979.

(3) A partial list of examples includes cyclobutadienes [reviewed by A. Efraty, *Chem. Rev.*, **77**, 691 (1977)], pentalene [T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **94**, 3281 (1972)], carbenium ions (OC)$_9$Co$_3$CCO$^+$ [reviewed by D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976)], carbenes and carbynes [reviewed by E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976)], vinyl alcohols [C. H. de Puy, R. N. Greene, and T. E. Schroer, *J. Chem. Soc., Chem. Commun.*, 1225 (1968)], and trimethylenemethane [K. Ehrlich and G. F. Emerson, *J. Am. Chem. Soc.*, **94**, 2464 (1972)].

(4) A. Ohno, "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press, New York, 1977, p 196.

(5) R. B. Woodward, W. A. Ayer, J. M. Beaton, F. Bickelhaupt, R. Bonnett, P. Buchschacher, G. L. Closs, H. Dutler, J. Hannah, F. P. Hauck, S. Ito, A. Langemann, E. LeGoff, W. Leimgruber, W. Lwowski, J. Sauer, Z. Valenta, and H. Volz, *J. Am. Chem. Soc.*, **82**, 3800 (1960); S. McKenzie and D. H. Reid, *J. Chem. Soc. C*, 145 (1970); J. Dabrowski and K. Kamienska-Trela, *Org. Magn. Reson.*, 4, 421 (1972); S. C. Tang, G. N. Weinstein, and R. H. Holm, *J. Am. Chem. Soc.*, **95**, 613 (1973).

(6) H. Davy and J. Vialle, *Bull. Soc. Chim Fr.*, 1435 (1975); D. M. McKennon and J. M. Buchshriber, *Can. J. Chem.*, 49, 3299 (1971).

(7) W. J. Bailey and M. Isogawa, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 14, 300 (1973); [*Chem. Abstr.*, **82**, 74136 (1975)]; H. G. Giles, R. A. Marty, and P. de Mayo, *Can. J. Chem.*, **54**, 537 (1976).

(8) (a) D. C. Dittmer, K. Takahashi, M. Iwanami, A. I. Tsai, P. L. Chang, B. B. Blidner, and I. K. Stamos, *J. Am. Chem. Soc.*, **98**, 2795 (1976); (b) B. H. Patwardhan, E. J. Parker, and D. C. Dittmer, *Phosphorus Sulfur*, 7, 5 (1979).

(9) R. L. Harlow and C. E. Pfluger, *Acta Crystallogr., Sect B*, **B29**, 2633 (1973).

(10) D. C. Dittmer, P. L. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, 37, 1111 (1972).

Table I. S-Alkyl Enethial Fluoroborate Salts

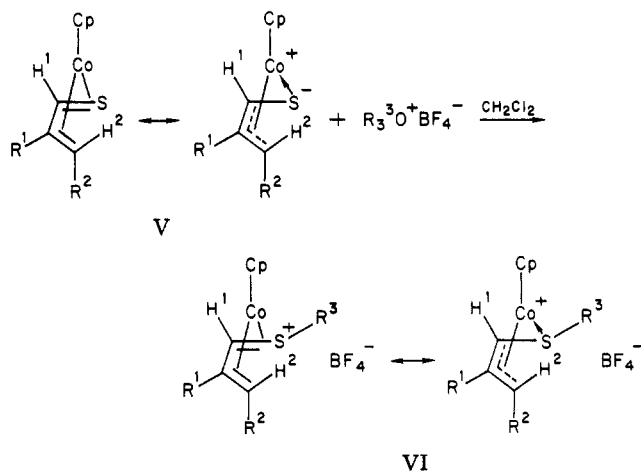|	R^1	R^2	R^3	appearance	mp, °C
VIa	H	H	CH_3	black	86-88
b	Ph	H	CH_3	brick red	128-131
b'	Ph	H	C_2H_5	brick red	130-134
c	β-naphthyl	H	CH_3	brick red	57-60
d	C_2H_5	CH_3	CH_3	purple	138-141
d'	C_2H_5	CH_3	C_2H_5	purple	87-91
e	$(CH_2)_5$		CH_3	black	165-166

first to investigate the nucleophilicity or Lewis base character of the sulfur atom. Since cobalt frequently donates electrons to ligands (back-bonding), the sulfur atom may be relatively nucleophilic. For example, the carbonyl oxygen atom in cyclopentadienylcobalt tetrasubstituted cyclopentadienones is easily protonated, indicating an enhanced basicity which has been attributed to donation of electrons from cobalt to the dienone as illustrated by the two resonance structures III and IV.[11]
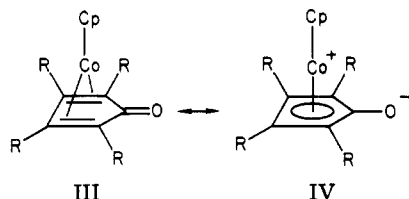
Attachment of electrophiles to the sulfur atom might yield new and unusual ligand types, and another goal of this investigation was the study of the free ligand by removing the transition metal, if possible. Such ligands might have diene or dienophilic properties of use in synthesis.

Results and Discussion

S-Alkyl Enethial Cationic Complexes. Thiobenzophenone has been S-alkylated by melting it with triethyloxonium tetrafluoroborate.[12] Derivatives of (propenethial)(π-cyclopentadienyl)cobalt (V) react readily with

a, $R^1 = R^2 = H$; b, $R^1 = Ph$, $R^2 = H$; c, $R^1 = 2$-naphthyl, $R^2 = H$; d, $R^1 = C_2H_5$, $R^2 = CH_3$; e, $R^1 = R^2 = (CH_2)_5$

trimethyloxonium or triethyloxonium tetrafluoroborate in

methylene chloride at room temperature. Salts (VI) were obtained (Table I) in essentially quantitative yield. Two of several possible resonance structures are given for V and VI. The salts are hygroscopic.

The ^{1}H NMR spectra of the salts, VI, and their precursors, V, are compared in Table II. Since the protons of the $^+SCH_3$ group in simple sulfonium salts absorb in the range δ 2.52-3.02 and those of the $^+SCH_2CH_3$ group in the ranges δ 3.03-3.58 and δ 1.38-1.51,[13] it is reasonable to assume S-alkylation of V since the protons of these two groups in salts VI have chemical shifts in the above ranges. Methylation of the cobalt atom would be expected to result in somewhat deshielded methyl protons.[14,15] Alkylation of the sulfur atom results in downfield shifts for the cyclopentadienyl protons of 0.47-0.74 ppm. Protonation of the oxygen atom in the cyclopentadienone complexes III (R = CH_3, Ph) gives downfield shifts of the cyclopentadienyl protons of 0.45 and 0.74 ppm, respectively.[11a] The proton chemical shifts associated with the π-cyclopentadienyl group have been used as a measure of the electron density on the cobalt atom,[16] and our results are in accord with electron withdrawal from cobalt. Inspection of Table II reveals that while introduction of a positive charge into Va by S-alkylation leads to a downfield shift of 0.95 ppm for $R^2 = H$, it leads to *upfield* shifts for H^1 and H^2 of 0.43 and 0.07 ppm, respectively. A somewhat similar shielding effect is observed on protonation of the sulfur atom of the thiocarbonyl group of 3-benzyl-3-phenylthiophthalimidine. The upfield shifts observed were attributed to a diminution of the usual deshielding effect caused by the anisotropy of electron circulations in the thiocarbonyl group.[17] In the S-alkyl salts, the effect is expected to be felt most by the protons, H^1 and H^2, nearer the complexed thiocarbonyl group where the expected downfield shift due to the positive charge is more than offset by the upfield shift caused by a decrease in the normal anisotropic contribution of the thiocarbonyl group. The proton, $R^2 = H$, more distant from the thiocarbonyl group, apparently is affected mainly by the positive charge and less by the anisotropic effect since its absorption shifts downfield.

Ultraviolet and infrared spectral data, to be briefly discussed, are given in the Experimental Section. The absorption at highest wavelength in the UV spectrum of the precursors, V, in the range 453-495 nm (ϵ 850-1300) is lost on going to the salts VI (highest wavelength 250-393 nm) which may signify a more electronically stabilized ground state due to the positive charge or may signify the cancellation of an n $\rightarrow$ π^* transition of the lone pair of electrons on sulfur which becomes bonded to the alkyl group on the conversion of V to VI.

The infrared spectra of both precursors and salts show bands attributable to the η^5-cyclopentadienyl ring.[18] However, absorption bands at ca. 1460 cm^{-1} tentatively assigned to carbon-carbon double-bond stretching in the

(11) (a) J. E. Sheats, W. Miller, M. D. Rausch, S. A. Gardner, P. S. Andrews, and F. A. Higbie, *J. Organomet. Chem.*, **96**, 115 (1975); (b) J. E. Sheats and M. D. Rausch, *J. Org. Chem.*, **35**, 3245 (1970); (c) G. N. Schrauzer and G. Kratal, *J. Organomet. Chem.*, **2**, 336 (1964); (d) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)* 1381 (1959).

(12) L. Carlsen and A. Holm, *Acta Chem. Scand., Ser. B*, **B30**, 277 (1976).

(13) G. A. Olah, J. R. DeMember, J. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc.*, **96**, 884 (1974); M. C. Caserio, R. E. Pratt, and R. J. Holland, *Ibid.* **88**, 5747 (1966); T. E. Young and R. A. Lazarus, *J. Org. Chem.*, **33**, 3770 (1968).

(14) R. G. Kidd in "Characterization of Organometallic Compounds", M. Tsutsui, Ed., Part II, Wiley-Interscience, New York, 1971, p 379 ff. H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Faraday Discuss. Chem. Soc.*, **47**, 165 (1969).

(15) That the alkyl group is on the sulfur atom is proved subsequently by the reaction with cyanide ion: E. J. Parker and D. C. Dittmer, following paper in this issue.

(16) R. B. King, *Inorg. Chim Acta*, **2**, 454 (1968); E. S. Bolton, G. R. Knox, and C. G. Robertson, *J. Chem. Soc., Chem. Commun.*, 664 (1969).

(17) I. D. Rae, *Aust. J. Chem.*, **27**, 2621 (1974).

(18) V. T. Aleksanyan and B. V. Lokshin, *J. Organomet. Chem.*, **131**, 113 (1977).

Table II. Proton Chemical Shifts (δ) of Enethial Complexes (V) and S-Alkyl Salts (VI)[a]

|	Va	VIa	Vb	VIb	VIb'	Vc	VIc	Vd	VId	VId'	Ve	VIe
H^1	7.38	6.95	7.10-7.80	7.20-7.97	7.15-8.02	7.22-8.07	7.20-8.30	7.01	6.95	7.00	6.93	6.62
H^2	1.19	1.12	1.12	0.90	0.91	1.18	0.88	1.64	1.58	1.13-1.80	1.07-3.13	1.07-3.13
R^1	5.57	5.37-6.10	7.10-7.80	7.20-7.97	7.15-8.02	7.22-8.07	7.20-8.30	2.41-1.25	2.59-1.32	2.13-3.12 } 1.13-1.80	1.07-3.13	1.07-3.13
R^2	2.78	3.73	3.23	4.12	4.17	3.36	4.23	1.27	1.58	1.13-1.80		
C$_5$H$_5$	4.81	5.55	4.83	5.37	5.37	4.83	5.33	4.81	5.28	5.33	4.80	5.34
R^3	...	2.40	...	2.67	3.07-1.50	...	2.65	...	2.47	2.13-3.12 1.13-1.80	...	2.30

[a] Solvents: CDCl$_3$, Va-d, VIb-d; CD$_3$CN, Ve; VIa,e.

precursors V are missing in the salt complexes VI, which may reflect a change in the bonding description of the enethial ligand caused by electron donation from cobalt.

Alkylation of the sulfur atom of Vd with methyl iodide was slower than with the oxonium salts. When a onefold excess of methyl iodide was used, the reaction was complete after 4 h at room temperature as indicated by thin-layer chromatography. The product was unstable, but ^{1}H NMR, UV–visible, and IR spectra suggest a structure similar to that of VId. The ^{1}H NMR spectrum of the iodide salt is essentially identical with that of VId. If the absorption at 207 and 245 nm due to iodide ion is subtracted from the observed UV spectrum of the iodide salt, a spectrum similar to that of VId is obtained: iodide salt corrected for iodide ion absorption, 207 (ε 14 400), 277 (10 700), 304 (4480); fluoroborate salt VId, 207 (14 600), 278 (13 200), 305 (5840). The instability of the iodide salt probably is related to the nucleophilic power of iodide ion which may attack the complex. Treatment of crude iodide salt (obtained with 1 equiv of methyl iodide) with excess silver tetrafluoroborate gave VId in 59% yield, thus establishing the similarity of the two compounds. A similar result was obtained with the complex of 2-phenyl-propenethial (Vb) although it reacted more slowly with methyl iodide.

VId
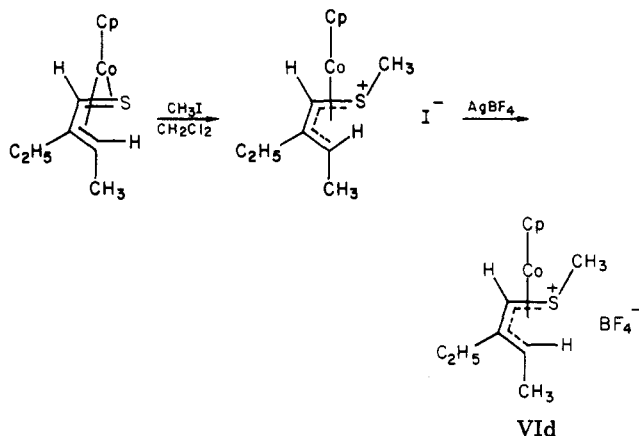
When silver tetrafluoroborate was used in conjunction with methyl iodide in an attempt to effect a one-step conversion to the tetrafluoroborate salt, a dicobalt salt, VII,


VII
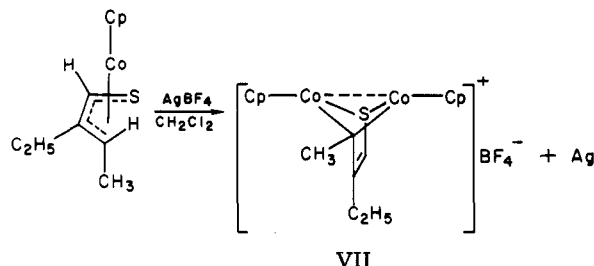
previously obtained by treatment of Vd with trityl or

tropylium tetrafluoroborate,[8a] was obtained. Silver tetrafluoroborate alone gave the same result, the silver ion being reduced to free silver. This reaction represents another manifestation of the ease with which electrons are donated from the complexes, V.

Complex Ve also reacted with α-bromoacetophenone and with dimethyl diazomalonate (photochemically). The reactions seemed complex and the products were not identified.

Reaction with HgCl$_2$. Stable green complexes (VIII)

VIIIa, R^1 = C$_2$H$_5$, R^2 = CH$_3$
b, R^1 = Ph, R^2 = H
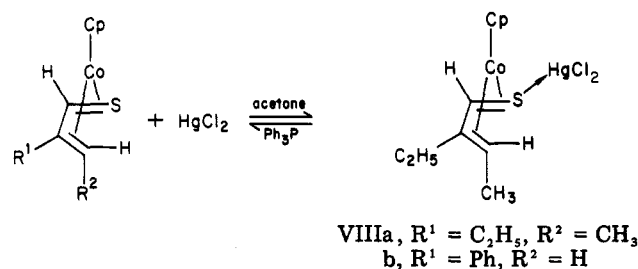
are formed when the (2-ethyl-2-butenethial)- or (2-phenylpropenethial)cobalt complexes are treated with mercuric chloride. Their proton NMR spectra are similar to those of other S-substituted salts (e.g., VId). The mercuric chloride may be removed by treatment with triphenylphosphine. Mercury(II) sulfate and phenyl-mercuric chloride did not react.

A number of other metal ions and Lewis acids react with the brown cobalt complex of 2-ethyl-2-butenethial, but no definite products were identified. The observations may be summarized as follows: PtCl$_2$, yellow to green solid; PdCl$_2$, red-brown solid; ZnCl$_2$, green → black solution; Zn(NO$_3$)$_2$, brown-black solution; CdCl$_2$, green solution; AlCl$_3$, black solution; FeCl$_3$, black solution; BF$_3$, black solution. Photolysis of (2-ethyl-2-butenethial)(π-cyclo-pentadienyl)cobalt with iron pentacarbonyl in ether gave an unstable red oil. Its infrared spectrum showed strong absorption at 1860–2070 cm^{-1} in the region for terminal carbonyl stretching. The ^{1}H NMR spectrum showed broad singlets at δ 5.01 and 5.73 and a broad multiplet at δ 0.77–1.80. A reaction apparently had occurred since no absorption remained at δ 4.81 for the cyclopentadienyl protons of the starting material; but the unstable, red oil resisted further characterization.

Experimental Section

Pentane and hexane were washed successively with sulfuric acid, water, saturated aqueous sodium bicarbonate, and water, dried (MgSO$_4$), and distilled from Linde molecular sieves, type 4A. Ethyl ether and nitromethane were distilled from calcium hydride and stored over Linde molecular sieves, type 4A. Acetone, acetonitrile, chloroform, methylene chloride, and methanol were dried over Linde molecular sieves, type 4A. Solvents were degassed by passing nitrogen or argon through them for 15–30 min prior to use.

Trimethyloxonium tetrafluoroborate (Alfa-Ventron, freshly opened sample), triethyloxonium tetrafluoroborate (Alfa-Ventron), triethyloxonium hexafluorophosphate (Alfa-Ventron), silver tetrafluoroborate (Alfa-Ventron), iron pentacarbonyl (Strem Chemicals, Inc.), and (π-cyclopentadienyl)cobalt dicarbonyl (Strem Chemicals, Inc.) were used as obtained.

The photochemical irradiation was done by means of a 450-W high-pressure mercury arc lamp (Hanovia 679A/36). The cooling system used for the photolyses consisted of a Blue M Electric Co. portable cooling unit (Model PCC-13A-3) and an ethylene glycol bath.

(Propenethial)(π-cyclopentadienyl)cobalt, (2-ethyl-2-butenethial)(π-cyclopentadienyl)cobalt, and (2-phenylpropenethial)(π-cyclopentadienyl)cobalt were prepared as previously described.[8] However, ether is the preferred solvent for the preparation of the complexes instead of the hexane used earlier.[8a] Its use is illustrated in the following preparations which include a more detailed procedure for the synthesis of the 2-phenylpropenethial complex.

(π-Cyclopentadienyl)(2-phenylpropenethial)cobalt (Vb). 3-Phenylthiete (1.30 g, 8.87 mmol) and cyclopentadienylcobalt dicarbonyl (3.2 g, 17.6 mmol) were disolved in dry, degassed ether (500 mL) in a photolysis vessel cooled in a bath at –10 °C. The reaction mixture was photolyzed with a high-pressure mercury lamp (Corex filter) under argon for 20 h after which it was filtered through a plug of glass wool and the solvent removed under reduced pressure (water aspirator) at 20 °C. The resulting dark oil was chromatographed on Woelm neutral alumina (activity II). Unreacted cyclopentadienylcobalt dicarbonyl (1.2–1.5 g) was eluted with pentane as a reddish brown band. Elution with ether gave the enethial complex (brown band); the solution was concentrated to give a brown solid (2.0–2.2 g, 7.4–8.1 mmol, 83.3–91.7%). The material could be purified by sublimation (75 °C (0.02 mm)) to give a light brown, crystalline solid: mp 58–60 °C; IR (KBr) 3080 (m), 3050 (m, C$_5$H$_5$), 3000 (m), 2950 (m), 1600 (w), 1500 (m), 1460 (m, C=C), 1440 (m, C$_5$H$_5$), 1415 (m), 1380 (w, C$_5$H$_5$), 1360 (w, C=CH$_2$), 1230 (m), 1120 (m, C$_5$H$_5$), 1060 (m, C=S), 1020 (m, C$_5$H$_5$), 1000 (m, C$_5$H$_5$), 920 (m), 900 (w, C=CH$_2$), 880 (s), 820 (s, C$_5$H$_5$), 785 (s), 770 (s), 700 (s), 655 (m) cm^{-1}; UV max (95% ethanol) 453 nm (ε 1.11 × 10^3), 306 (sh) (5.86 × 10^3), 248 (2.04 × 10^4), 223 (1.96 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.80–7.10 (m, 6 H, C$_6$H$_5$, CHS), 4.83 (s, 5 H, C$_5$H$_5$), 3.23 (s, 1 H, =CH anti to cobalt), 1.12 (s, 1 H, =CH syn to cobalt).

Anal. Calcd for C$_{14}$H$_{13}$CoS: C, 61.76; H, 4.78. Found: C, 62.01; h, 4.98.

(π-Cyclopentadienyl)(2-β-naphthylpropenethial)cobalt (Vc). The (2-β-naphthylpropenethial)cobalt complex was obtained as a metallic golden crystalline solid in 80.9% yield according to the above procedure: mp 96–98 °C; IR (KBr) 3450 (w, H$_2$O), 3100 (m), 3055 (s, C$_5$H$_5$), 2960 (s), 2900 (s), 2880 (s), 2860 (s), 1595 (m), 1500 (m), 1460 (m, C=C), 1450 (m, C$_5$H$_5$), 1410 (w), 1380 (m, C$_5$H$_5$), 1360 (m, C=CH$_2$), 1285 (s), 1270 (s), 1120 (s), 1110 (s, C$_5$H$_5$), 1070 (m, C=S), 1010 (m, C$_5$H$_5$), 990 (m, C$_5$H$_5$), 945 (m, C$_5$H$_5$), 890 (m, C=CH$_2$), 855 (m), 805 (s, C$_5$H$_5$), 740 (s), 695 (m), 670 (m) cm^{-1}; UV max (hexane) 453 nm (ε 1.06 × 10^3), 294 (sh) (1.28 × 10^4), 245 (sh) (2.72 × 10^4), 225 (4.8 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 8.07–7.22 (m, 8 H, C$_{10}$H$_7$, CHS), 4.83 (s, 5 H, C$_5$H$_5$), 3.36 (s, 1 H, =CH anti to cobalt), 1.18 (s, 1 H, =CH syn to cobalt).

Anal. Calcd for C$_{18}$H$_{15}$CoS: C, 67.08; H, 4.66. Found: C, 67.55; H, 4.87.

(1-Cycloheptenethiocarboxaldehyde)(π-cyclopentadienyl)cobalt (Ve). The enethial cobalt complex was obtained in 81.5% yield as a brown solid. The material was purified by sublimation (85 °C (0.02 mm)): mp 91–93 °C; IR (KBr) 3090 (w, C$_5$H$_5$), 2980 (m), 2950 (s), 2870 (m), 1580 (w), 1460 (m, C=C), 1430 (m, C$_5$H$_5$), 1380 (m, C$_5$H$_5$), 1360 (w), 1290 (s), 1275 (s), 1220 (w), 1165 (w), 1140 (m), 1120 (m, C$_5$H$_5$), 1080 (m,

C=S), 1040 (w), 1020 (w, C$_5$H$_5$), 995 (w, C$_5$H$_5$), 960 (m, C$_5$H$_5$), 895 (w), 840 (m), 830 (m), 815 (m, C$_5$H$_5$), 805 (w), 740 (m), 750 (w) cm^{-1}; UV max (hexane) 459 nm (ε 9.55 × 10^2), 343 (sh) (1.80 × 10^3), 296 (sh) (6.43 × 10^3), 267 (1.18 × 10^4), 215 (2.05 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 6.93 (s, 1 H, CHS), 4.80 (s, 5 H, C$_5$H$_5$), 3.13–1.07 (complex multiplet, 11 H, -(CH$_2$)$_5$-, =CH).

Anal. Calcd for C$_{13}$H$_{17}$CoS: C, 59.09; H, 6.44. Found: C, 59.25; H, 6.36.

(S-Methylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VIa). (Propenethial)(π-cyclopentadienyl)cobalt (100 mg, 0.51 mmol) was dissolved in dry, degassed methylene chloride (20 mL) in an Erlenmeyer flask which was equipped with a magnetic stirrer. A nitrogen atmosphere was maintained. Trimethyloxonium tetrafluoroborate (75 mg, 0.51 mmol) was added and the suspension stirred at room temperature for 90 min. A small amount of black solid was removed by filtration, and the solvent was removed under reduced pressure (water aspirator) to give a black solid (149 mg, 0.50 mmol, 98.0%) which was recrystallized from acetone–ether: mp 86–88 °C dec; IR (thin film) 3100 (m), 3070 (m, C$_5$H$_5$), 3020 (w), 2970 (w), 2930 (w), 1600 (m, br), 1420 (s, C$_5$H$_5$), 1400 (s), 1370 (w, C$_5$H$_5$), 1320 (w), 1280 (m), 1050 (vs, br, BF$_4^-$), 900 (w), 820 (s, C$_5$H$_5$) cm^{-1}; UV max (CH$_3$CN) 393 (sh) nm (ε 3.04 × 10^3), 267 (1.10 × 10^4), 231 (7.90 × 10^3); ^{1}H NMR (CD$_3$CN, 60 MHz) δ 6.95 (doublet of doublets, J = 5, 2 Hz, 1 H, CHS), 6.10–5.37 (m, 1 H, CHCHS), 5.55 (s, 5 H, C$_5$H$_5$), 3.73 (AMX multiplet, J = 8, 2, 2 Hz, 1 H, =CH anti to cobalt), 2.40 (s, 3 H, S$^+$-CH$_3$), 1.12 (doublet of doublets, J = 10, 2 Hz, 1 H, =CH syn to cobalt).

Anal. Calcd for C$_9$H$_{12}$BCoF$_4$S: C, 36.28; H, 4.03. Found: C, 35.83; H, 4.05.

(S-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VIb). (2-Phenylpropenethial)(π-cyclopentadienyl)cobalt (300 mg, 1.10 mmol) was treated with trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol) in the same manner as described for the synthesis of VIa. The (S-methyl-2-phenylpropenethial)cobalt salt was obtained as a dark red solid (402.9 mg, 1.08 mmol, 98.0%): mp 128–131 °C; IR (KBr) 3100–2800 (w), 1410 (m, C$_5$H$_5$), 1380 (m, C$_5$H$_5$), 1300 (w), 1270 (w), 1020 (vs, br, BF$_4^-$), 830 (m, C$_5$H$_5$), 755 (m) cm^{-1}; UV max (CH$_3$CN) 316 nm (ε 4.56 × 10^3), 257 (2.06 × 10^4), 227 (1.42 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.97–7.20 (m, 6 H, CHS, C$_6$H$_5$), 5.37 (s, 5 H, C$_5$H$_5$), 4.12 (doublet of doublets, J = 4, 2 Hz, 1 H, =CH anti to cobalt), 2.67 (s, 3 H, S$^+$-CH$_3$), 0.90 (d, J = 4 Hz, 1 H, syn to cobalt).

Anal. Calcd for C$_{15}$H$_{16}$BCoF$_4$S: C, 48.15; H, 4.28. Found: C, 48.38; H, 4.54.

(S-Ethyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VIb'). The salt obtained by the treatment of (2-phenylpropenethial)(π-cyclopentadienyl)cobalt (300 mg, 1.10 mmol) with triethyloxonium tetrafluoroborate (163 mg, 1.10 mmol) was a brick red solid (419 mg, 1.08 mmol, 98.0%): mp 130–134 °C; IR (KBr) 3400 (m, br, H$_2$O), 3100 (w), 3050 (w, C$_5$H$_5$), 2960 (w), 2920 (w), 1440 (m, C$_5$H$_5$), 1400 (m), 1380 (m, C$_5$H$_5$), 1260 (m), 1030 (vs, br, BF$_4^-$), 840 (s, C$_5$H$_5$), 755 (s), 680 (m) cm^{-1}; UV max (CH$_3$CN) 317 nm (ε 4.47 × 10^3), 259 (2.13 × 10^4), 226 (1.59 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 8.02–7.15 (m, 6 H, C$_6$H$_5$, CHS), 5.37 (s, 5 H, C$_5$H$_5$), 4.17 (doublet of doublets, J = 4, 2 Hz, 1 H, =CH anti to cobalt), 3.07 (q, J = 7 Hz, 2 H, S$^+$CH$_2$CH$_3$), 1.50 (t, J = 7 Hz, 3 H, S$^+$CH$_2$CH$_3$), 0.91 (d, J = 4 Hz, 1 H, =CH syn to cobalt).

Anal. Calcd for C$_{16}$H$_{18}$BCoF$_4$S + 0.6H$_2$O: C, 48.17; H, 4.82. Found: C, 48.64; H, 5.32.

(S-Methyl-2-β-naphthylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VIc). (2-β-Naphthylpropenethial)(π-cyclopentadienyl)cobalt (300 mg, 0.93 mmol) was treated with trimethyloxonium tetrafluoroborate (138 mg, 0.93 mmol) to give a brick red solid (387 mg, 0.913 mmol, 98.0%): mp 57–60 °C; IR (KBr) 3100 (w), 3050 (w, C$_5$H$_5$), 2900 (w), 1420 (m, C$_6$H$_5$), 1400 (w), 1390 (w, C$_5$H$_5$), 1030 (vs, br, BF$_4^-$), 840 (w, C$_5$H$_5$), 800 (w) cm^{-1}; UV max (CH$_3$CN) 250 (sh) nm (ε 2.71 × 10^4), 226 (4.22 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.20–8.30 (m, 8 H, C$_{10}$H$_7$, CHS), 5.33 (s, 5 H, C$_5$H$_5$), 4.23 (doublet of doublets, J = 4, 2 Hz, 1 H, =CH anti to cobalt), 2.65 (s, 3 H, S$^+$-CH$_3$), 0.88 (d, J = 4 Hz, 1 H, syn to cobalt).

Anal. Calcd for C$_{19}$H$_{18}$BCoF$_4$S: C, 53.80; H, 4.28. Found: C, 54.30; H, 4.86.

(S-Methyl-2-ethyl-2-butenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VId). Treatment of (2-ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (300 mg, 1.26 mmol) with trimethyloxonium tetrafluoroborate (185 mg, 1.26 mmol) gave a dark oil. The oil was dissolved in dry dichloromethane (5 mL) and added rapidly to dry, stirred ether (100 mL). The suspension was filtered, giving VId as a purple solid (419.6 mg, 1.23 mmol, 98.0%): mp 138–141 °C; IR (KBr) 3100 (w), 3075 (w, C_5H_5), 2970 (w), 2875 (w), 1420–1400 (m), 1375 (m, C_5H_5), 1350 (w), 1315 (w), 1040 (vs, br, BF_4^-), 845 (s), 840–810 (s), 760 (w) cm^{-1}; UV max (CH$_3$CN) 305 (sh) nm (ε 5.84 × 10^3), 278 (1.32 × 10^4), 207 (1.46 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 6.95 (s, 1 H, CHS), 5.28 (s, 5 H, C_5H_5), 2.59 (q, J = 7 Hz, 2 H, CH_2CH_3), 2.47 (s, 3 H, S^+CH_3), 1.58 (br s, 4 H, =$CHCH_3$), 1.32 (t, J = 7 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{12}H_{18}BCoF_4S$: C, 42.38; H, 5.30. Found: C, 42.53; H, 5.56.

(S-Ethyl-2-ethyl-2-butenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VId'). (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (300 mg, 1.26 mmol) was treated with triethyloxonium tetrafluoroborate (239 mg, 1.26 mmol) as described for the synthesis of VIa. The (S-ethyl-2-ethyl-2-butenethial)cobalt salt was obtained as a purple solid (437.0 mg, 1.235 mmol, 98.0%): mp 87–91 °C; IR (KBr) 3040 (w, C_5H_5), 2960 (w), 2930 (w), 2870 (w), 1440 (w, C_5H_5), 1400 (w), 1380 (w, C_5H_5), 1030 (vs, br, BF_4^-), 840 (m), 820 (m, C_5H_5) cm^{-1}; UV max (CH$_3$CN) 305 (sh) nm (ε 4.79 × 10^3), 277 (1.13 × 10^4), 208 (1.24 × 10^4); ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.00 (s, 1 H, CHS), 5.33 (s, 5 H, C_5H_5), 2.13–3.12 (m, 4 H, $S^+CH_2CH_3$, CH_2CH_3), 1.13–1.80 (m, 10 H, $S^+CH_2CH_3$, CH_2CH_3, $CHCH_3$).

Anal. Calcd for $C_{13}H_{20}BCoF_4S$: C, 44.10; H, 5.65. Found: C, 44.33; H, 5.29.

(S-Methyl-1-cycloheptenethiocarboxaldehyde)(π-cyclopentadienyl)cobalt Tetrafluoroborate (VIe). (1-Cycloheptenethiocarboxaldehyde)(π-cyclopentadienyl)cobalt (300 mg, 1.14 mmol) was treated with trimethyloxonium tetrafluoroborate (168 mg, 1.14 mmol) in degassed methylene chloride (20 mL) under nitrogen. Removal of the solvent gave VIe as a black solid (411.5 mg, 1.125 mmol, 99.0%) which was recrystallized from acetone–ether: mp 165–166 °C; IR (KBr) 3050 (w, C_5H_5), 2900 (m), 2830 (w), 1420 (m, C_5H_5), 1390 (m, C_5H_5), 1310 (w), 1040 (vs, br, BF_4^-), 830 (m, C_5H_5), 810 (w), 780 (w) cm^{-1}; UV max (CH$_3$CN) 304 (sh) nm (ε 6.01 × 10^3), 279 (1.12 × 10^4), 219 (1.25 × 10^4); ^{1}H NMR (CD$_3$CN, 60 MHz) δ 6.62 (s, 1 H, CHS), 5.34 (s, 5 H, C_5H_5), 2.30 (s, 3 H, S^+CH_3), 3.13–1.07 (complex multiplet, 11 H, –(CH$_2$)$_5$–, =CH).

Anal. Calcd for $C_{14}H_{20}BCoF_4S$: C, 45.94; H, 5.47. Found: 46.64; H, 5.52.

Alkylations with Methyl Iodide. (A) (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (50 mg, 0.21 mmol) was dissolved in dry, degassed methylene chloride (20 mL) in an Erlenmeyer flask which had been flushed with argon. Methyl iodide (60 mg, 0.42 mmol) was added and the solution stirred for 4 h at room temperature. The excess methyl iodide and the solvent were removed under reduced pressure (water aspirator) to give a dark brown oil. The oil was dissolved in dry methylene chloride (2 mL) and poured rapidly into dry ether (100 mL). The suspension was filtered giving the (S-methyl-2-ethyl-2-butenethial)cobalt iodide salt as a brown solid (40 mg, 0.105 mmol, 50.0%). The solid decomposes on standing to a dark brown solid which is insoluble in organic solvents (e.g., ether, acetone, dimethyl sulfoxide) and in water. The material decomposed without melting: IR (KBr) 3050 (m, C_5H_5), 2960 (m), 1445 (m, C=C), 1420 (m, C_5H_5), 1395 (m), 1370 (m, C_5H_5), 1305 (m), 1100 (w, C_5H_5), 1070 (w, C=S), 1030 (m), 1005 (m, C_5H_5), 970 (m, C_5H_5), 940 (w), 845 (s), 820 (m, C_5H_5), 800 (w), 760 (w) cm^{-1}; UV max (CH$_3$CN) 304 (sh) nm (ε 4.48 × 10^3), 277 (1.07 × 10^4), 245 (1.59 × 10^4), 207 (3.03 × 10^4); ^{1}H NMR (CD$_3$CN, 60 MHz) δ 6.67 (s, 1 H, CHS), 5.30 (s, 5 H, C_5H_5), 2.47 (q, J = 7 Hz, 2 H, CH_2CH_3), 2.28 (s, 3 H, S^+CH_3), 1.57 (br s, 4 H, $CHCH_3$), 1.26 (t, J = 7 Hz, 3 H, CH_2CH_3).

(B) (2-Phenylpropenethial)(π-cyclopentadienyl)cobalt (100 mg, 0.368 mmol) was treated with methyl iodide (156 mg, 1.10 mmol) as above, and the solution was stirred for 5 h at room temperature. A black solid was removed by filtration. The solvent and excess methyl iodide were removed under reduced pressure (water aspirator) to give the (S-methyl-2-phenylpropenethial)cobalt iodide salt as a brown solid which on standing became insoluble in organic

solvents (e.g., ether, acetone, dimethyl sulfoxide) and in water: IR (KBr) 3440 (s, br, H$_2$O), 3070 (s), 3045 (s, C_5H_5), 2970 (s), 2900 (m), 1480 (w), 1450 (w, C=C), 1430 (m, C_5H_5), 1410 (m), 1395 (s), 1380 (m, C_5H_5), 1305 (m), 1250 (m), 1200 (w), 1090 (m), 1070 (s, C=S), 1030 (s), 1010 (s, C_5H_5), 990 (s, C_5H_5) 890 (s), 820 (s, C_5H_5), 755 (s), 680 (s), 640 (w) cm^{-1}; UV max (CH$_3$CN) 313 (sh) nm (ε 4.67 × 10^3), 247 (2.52 × 10^4), 230 (sh) (1.70 × 10^4); ^{1}H NMR (CD$_3$CN, 60 MHz) δ 8.02–7.25 (m, 6 H, C_6H_5, CHS), 5.35 (s, 5 H, C_5H_5), 4.25 (doublet of doublets, J = 4, 2 Hz, 1 H, =CH anti to cobalt), 2.58 (s, 3 H, S$^+$CH$_3$), 0.93 (d, J = 4 Hz, 1 H, syn to cobalt).

(2-Phenylpropenethial)(π-cyclopentadienyl)cobalt (50 mg, 0.184 mmol) was treated with methyl iodide (26 mg, 0.184 mmol) as described above. After the solution had stirred for 10 h at room temperature, silver tetrafluoroborate (39.6 mg, 0.202 mmol) was added and the suspension was stirred overnight. A brown solid was removed by filtration. The solvent was removed under reduced pressure (water aspirator) to give a brick red solid (32 mg, 0.086 mmol, 46.5%) which was identified as the (S-methyl-2-phenylpropenethial)cobalt tetrafluoroborate salt VIb from its infrared and ^{1}H NMR spectra.[8a]

Reactions of (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt with Methyl Iodide and Silver Tetrafluoroborate. (A) (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (50 mg, 0.21 mmol) and methyl iodide (29.8 mg, 0.21 mmol) were dissolved in dry, degassed methylene chloride (20 mL) in an Erlenmeyer flask, which had been flushed with argon. Silver tetrafluoroborate (40.9 mg, 0.21 mmol) was added, and the suspension was stirred for 1 h at room temperature. A brown solid was filtered from the reaction mixture, and the solvent was removed under reduced pressure (water aspirator) to give a dark oil. The oil was dissolved in dry methylene chloride (3 mL) and the mixture added rapidly to stirred, dry ether (100 mL). A brown solid was removed by filtration. The infrared, ultraviolet–visible, and ^{1}H NMR spectra are identical with those of the (2-ethyl-2-butenethial)dicobalt salt VII which was obtained from the reaction of (2-ethyl-2-butenethial)(π-cyclopentadienyl)cobalt with trityl tetrafluoroborate.[8a] No (S-methyl-2-ethyl-2-butenethial)cobalt salt was obtained.[8a]

(B) (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (50 mg, 0.21 mmol) was dissolved in dry, degassed methylene chloride (15 mL). Methyl iodide (29.8 mg, 0.21 mmol) was added and the solution stirred for 4 h at room temperature. Silver tetrafluoroborate (50.9 mg, 0.26 mmol) was added, and the suspension was stirred overnight. A brown solid was filtered from the reaction mixture, and the solvent was removed under reduced pressure (water aspirator) to give a brown oil. The oil was dissolved in dry acetone (2 mL) and the mixture poured into stirred, dry ether (100 mL). Filtration of the resulting suspension gave a purple solid (42 mg, 0.12 mmol, 58.8%) which was identified as the (S-methyl-2-ethyl-2-butenethial)cobalt tetrafluoroborate salt VId from its infrared and ^{1}H NMR spectra.

Reaction of (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt with Silver Tetrafluoroborate. (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (100 mg, 0.42 mmol) was dissolved in dry, degassed methylene chloride (15 mL) in an Erlenmeyer flask, which was equipped with a magnetic stirrer and which had been flushed with nitrogen. Silver tetrafluoroborate (40.9 mg, 0.21 mmol) was added and the suspension stirred for 4 h at room temperature. Solid impurities were removed by filtration. The filtrate was concentrated to ca. 3 mL and poured into stirred, dry ether (150 mL). Filtration of the suspension gave a brown solid which was precipitated twice from acetone–ether to give (2-ethyl-2-butenethial)dicobalt salt VII as a brown solid (61 mg, 0.136 mmol, 64.9%). Ultraviolet–visible, infrared, and ^{1}H NMR spectra are identical with those of VII obtained from treatment of the (2-ethyl-2-butenethial)cobalt complex with trityl ion.[8a]

Mercuric Chloride Adduct (VIIIa) of (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt. (2-Ethyl-2-butenethial)(π-cyclopentadienyl)cobalt (Vd) (50 mg, 0.21 mmol) was dissolved in dry, degassed acetone (10 mL) in an Erlenmeyer flask, which was equipped with a magnetic stirrer and which had been flushed with nitrogen. Mercuric chloride (57 mg, 0.21 mmol) was added. The reaction mixture immediately turned dark green and within a few seconds a precipiate formed. After being stirred for 15 min, the mixture was filtered and the solid was washed with acetone.

The mercuric chloride adduct VIIIa was obtained as a green solid (80.0 mg, 0.157 mmol, 74.8%): mp >300 °C; IR (KBr) 3080 (w), 3040 (w, C_5H_5), 2960 (w), 2860 (w), 1630 (w, br), 1455 (w), 1420 (w, C_5H_5), 1390 (w), 1380 (w, C_5H_5), 1360 (w), 1340 (w), 1100 (w, C_5H_5), 1050 (w), 1020 (m), 1010 (m, C_5H_5), 980 (w, C_5H_5), 950 (w, C_5H_5), 880 (w), 840 (s), 820 (s), 810 (s, C_5H_5), 790 (w) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6, 60 MHz) δ 7.08 (s, 1 H, CHS), 5.20 (s, 5 H, C_5H_5), 1.43 (br s, 4 H, C*H*C*H*$_3$), 1.21 (t, J = 7 Hz, 3 H, CH$_2$C*H*$_3$).

Anal. Calcd for $C_{11}H_{15}Cl_2CoHgS$: C, 25.90; H, 2.94. Found: C, 25.82; H, 2.86.

Mercuric Chloride Adduct (VIIIb) of (2-Phenyl-propenethial)(π-cyclopentadienyl)cobalt. (2-Phenyl-propenethial)(π-cyclopentadienyl)cobalt (Vb) (50 mg, 0.184 mmol) was treated with mercuric chloride (49.9 mg, 0.184 mmol) as described for the synthesis of VIII. Addition of the mercuric chloride caused an immediate change in color to green, and solid began to precipitate within 10 min. After having been stirred for 45 min at room temperature, the reaction mixture was filtered and the solid was washed with acetone. The mercuric chloride adduct VIIIb was obtained as a yellow-green solid (70.0 mg, 0.129 mmol, 70.1%): mp >300 °C; IR (KBr) 3080 (w), 3030 (w, C_5H_5), 2970 (w), 1640 (w, br), 1500 (w, br), 1430 (w, C_5H_5), 1390 (w, C_5H_5), 1190 (w), 1100 (w, C$_5$H5), 1070 (w), 1050 (w), 1030 (w), 1000 (m,

C_5H_5), 985 (m, C_5H_5), 920 (m), 860 (w), 840 (s), 815 (s, C_5H_5), 765 (s), 745 (s), 680 (s), 640 (m) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6, 60 MHz) δ 7.92–7.22 (m, 6 H, C_6H_5, CHS), 5.18 (s, 5 H, C_5H_5), 3.78 (br m, 1 H, =CH anti to cobalt), 0.93 (br s, 1 H, =CH syn to cobalt).

Anal. Calcd for $C_{14}H_{13}Cl_2CoHgS$: C, 30.90; H, 2.39. Found: C, 29.99; H, 2.62.

Cyanide Displacement of Allylic Sulfide Anions from Cobalt Complexes of *S*-Alkyl Salts of α,β-Unsaturated Thioaldehydes (Enethials)

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Treatment of the cation (π-cyclopentadienyl)[*S*-methyl(or *S*-ethyl)-2-phenylpropenethial]cobalt tetra-fluoroborate with cyanide ion in organic solvents apparently generates an anion of methyl (or ethyl) 2-phenylpropenyl sulfide which can be protonated by reaction with deuterated nitromethane. A similar treatment with potassium thiocyanate ion gave complex and unidentified organic products and an inorganic substance believed to be $K_2Co(NCS)_4$.

Introduction

As reported in the previous paper,[2] attachment of electrophiles to the sulfur atom in cobalt complexes of enethials yields new and unusual ligand types, and a goal of this investigation was the study of the free ligand by removing the transition metal.

Results and Discussion

Reaction of *S*-Alkyl Enethial Cations with Cyanide Ion. In an attempt to remove the cyclopentadienylcobalt moiety and to free the *S*-alkyl enethial cation, we treated complex Ib or Ib′with tetraethylammonium cyanide in acetonitrile at room temperature. When 6 equiv of cyanide ion were used, allyl sulfide II and vinyl sulfide III were obtained. Spectroscopic evidence also indicated the formation of tetraethylammonium cyclopentadienyltri-cyanocobaltate. This compound has been obtained by treatment of (π-cyclopentadienyl)cobalt dicarbonyl with excess cyanide ions.[3]

1b, R = CH$_3$
b′, R = C$_2$H$_5$

CH_3C=CHSR + $(C_2H_5)_4N^+CpCo(CN)_3^-$ + $(C_2H_5)_4N^+BF_4^-$

III
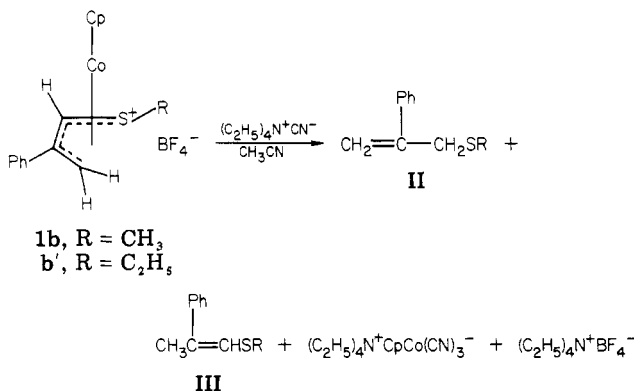
Vinyl sulfide III is obtained as the *E* isomer since it lacks the absorption at δ 5.95 in the ^{1}H NMR spectrum of the *Z* isomer.[4] An independent synthesis of II (R = C$_2$H$_5$) was achieved by treatment of α-bromomethylstyrene with ethanethiol in the presence of base. Its ^{1}H NMR and IR

(1) Taken from the Ph.D. Thesis of E. J. Parker, Syracuse University, Dec 1979.

(2) E. J. Parker, J. R. Bodwell, T. C. Sedergran, and D. C. Dittmer, preceding article in this issue.

(3) J. A. Dineen and P. L. Pauson, *J. Organomet. Chem.* **43**, 209 (1972).

(4) M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, *J. Org. Chem.*, **40**, 1979 (1975).