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}; ^1H NMR (Me_2SO-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, $CHCH_3$), 1.21 (t, J = 7 Hz, 3 H, CH_2CH_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-Phenylpropenethial)(π-cyclopentadienyl)cobalt. (2-Phenylpropenethial)(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_5H5), 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}; ^1H NMR (Me_2SO-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.

Acknowledgment. This work was supported by the National Cancer Institute (Grant CA 08250) and by Syracuse University. We are indebted to Dr. B. H. Patwardhan for details of the preparation of aryl thietes and to Professor Alan Davison for helpful discussion. We thank Mariano Ruggeri for assistance with the elemental analyses.

Registry No. Va, 60015-46-5; Vb, 71986-72-6; Vc, 79992-53-3; Vd, 60030-58-2; Ve, 80010-12-4; VIa, 79992-55-5; VIb, 79991-97-2; VIb', 79991-99-4; VIc, 79992-57-7; VId, 79992-59-9; VId', 80010-14-6; VIe, 79992-61-3; VII, 79992-63-5; VIIIa, 80145-56-8; VIIIb, 80145-57-9; (S-methyl-2-ethyl-2-butenethial)cobalt iodide, 79992-64-6; (S-methyl-2-phenylpropenethial)cobalt iodide, 79992-65-7; cyclopentadienylcobalt dicarbonyl, 12078-25-0; 3-phenylthiete, 72000-02-3.

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

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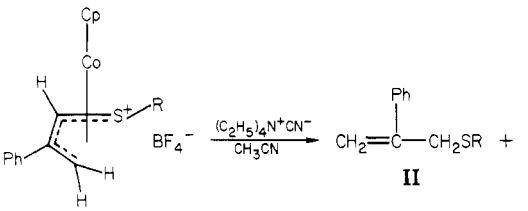
Treatment of the cation (π-cyclopentadienyl)[*S*-methyl(or *S*-ethyl)-2-phenylpropenethial]cobalt tetrafluoroborate with cyanide ion in organic solvents apparently generates an anion of methyl (or ethyl) 2-phenylpropenyl sulfide which can be protonated by reaction with deuterated nitromethane. A similar 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.

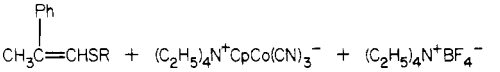
Results and Discussion

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 cyclopentadienyltricyanocobaltate. This compound has been obtained by treatment of (π-cyclopentadienyl)cobalt dicarbonyl with excess cyanide ions.[3]



II

1b, R = CH_3
b', R = C_2H_5



III

Vinyl sulfide III is obtained as the *E* isomer since it lacks the absorption at δ 5.95 in the ^1H NMR spectrum of the *Z* isomer.[4] An independent synthesis of II (R = C_2H_5) was achieved by treatment of α-bromomethylstyrene with ethanethiol in the presence of base. Its ^1H 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).

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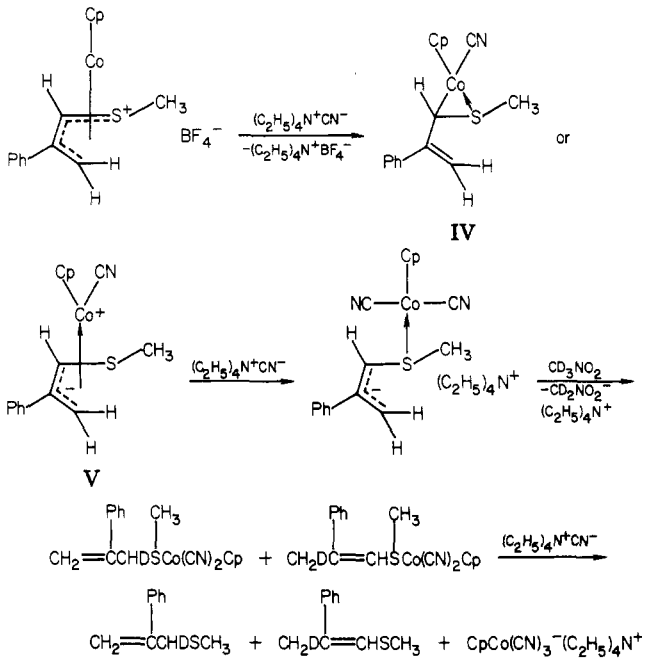
spectra are identical with those obtained for the product of the cyanide reaction. An elemental analysis for the solid mercuric chloride derivative of II (R = C_2H_5) was satisfactory. The spectroscopic data for the *S*-methyl derivative II are similar in every respect except for the absorptions originating from the methyl group.

Comparison of the allyl and vinyl sulfide products with the initial cobalt salt shows that an extra hydrogen atom has become attached to the ligand backbone. That this proton does not originate from the acetonitrile solvent was established by the use of deuterated acetonitrile, $pK_a \approx 25$;[5] no deuterium incorporation into the products was indicated by the proton NMR spectra. The extra proton was not introduced during the aqueous workup of the reaction mixture since no deuterium incorporation was observed when D_2O was used. Proton donation via an E_2 elimination reaction from the tetraethylammonium ion is unlikely since switching to the tetramethylammonium salt did not change the results. Since the α-protons of sulfonium salts are acidic, we suggest that the extra proton in the products may originate from the *S*-methyl or *S*-ethyl group in Ib or b′. If this is so, half of the starting material is playing proton donor to the other half and the yields of sulfide products should not be greater than 50%. Significantly, the yields were typically 40–48%. Addition of a better proton donor than the *S*-alkyl groups should increase the yields in proportion to the extent to which the added proton donor is involved. Nitromethane ($pK_a \approx 10$)[5] is presumably a stronger carbon acid than the sulfonium salts;[6] and when the reaction was done in nitromethane–methylene chloride, the yields improved to 85–90%. Finally, when deuterated nitromethane is used, deuterium is found in the allylic position in the sulfide products. These results imply that treatment of the *S*-alkyl enethial salts with cyanide ion yields an allyl sulfide carbanion which abstracts a proton from an available acidic site ($>^+S—CH_2R$ or CH_3NO_2). This is a somewhat unique way of generating allyl sulfide anions since they normally are obtained by treating an allyl sulfide with a very strong base such as an alkyllithium reagent.[7] By comparison, cyanide ion is a very weak base. The ylide presumably formed by proton abstraction from the *S*-alkyl group in the salt is apparently unstable and could not be isolated or trapped. Scheme I gives a rationalization of the results. A key intermediate may involve a cobalt–carbon σ bond (e.g., IV) although a cobalt allyl sulfide anion complex (V) may be written also. Displacements by cyanide ion involving cobalt–carbon σ bonds in vitamin B_{12} were once thought to be direct but are now believed to be more complex.[8] Much of vitamin B_{12} chemistry probably involves radical intermediates.[8] We do not think that allyl sulfide radicals are involved in our reactions since they presumably should have abstracted deuterium atoms from CD_3CN since cyanoalkyl radicals are relatively stable. The *Q* value, which is related to the stability of radicals, for acrylonitrile is +0.60 (i.e., for $RCH_2\dot{C}HCN$),[9] and the cyano group is known to remove spin density (14.5%) from an alkyl carbon radical site.[10]

When the *S*-methyl salt Ib was treated with 1 equiv of tetraethylammonium cyanide, an unstable red oil was

Scheme I



obtained which showed absorption for cyanide in the infrared at 2090 cm^{-1} which may be attributable to a cobalt–cyanide bond.[11] Strong absorption at 1050 cm^{-1} for the tetrafluoroborate anion was absent. The UV spectrum of the red oil differed from that of the starting material. The proton NMR spectrum showed absorption at δ 7.13–7.52 and a singlet at δ 5.05 possibly representing absorption for the phenyl and cyclopentadienyl groups, respectively. The absorption of the latter group is intermediate between that of (π-cyclopentadienyl)(2-phenylpropenethial)cobalt (δ 4.83)[2] and the *S*-alkyl salt Ib (δ 5.37),[2] indicating a possible decrease in the electron withdrawal from cobalt effected by complexing with cyanide ion. These data are consistent with those of a monocyano complex, IV or V (Scheme I). A monocyano cobalt cyclopentadienyl diiodide complex, obtained by treatment of (π-cyclopentadienyl)cobalt carbonyl diiodide with cyanide ion, is reported to be unstable also.[3]

Reaction with Thiocyanate. Potassium thiocyanate also reacts with Ib. The organic products were complex as indicated by spectroscopic data. A blue, inorganic solid was obtained which appears to be $K_2Co(NCS)_4$ by comparison of its infrared and UV spectrum with those of tetraethylammonium or tetramethylammonium tetrakis(isothiocyanato)cobaltate(II).[12] The difference in the reaction of cyanide ion, which yields a cobalt(III) derivative, and thiocyanate, which yields a cobalt(II) derivative, may be related to the observation that cobalt(III) is generally stable only when complexed to strong field ligands; otherwise, it acts as an oxidizing agent (toward the ligand or other species present), and reactions involving it result in isolation of cobalt(II) salts.[13] Since cyanide ion is a strong field ligand whereas thiocyanate is not, the differ-

(5) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).
(6) C. J. M. Stirling in "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press, New York, 1977, p 486.
(7) E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978, Chapter 2.
(8) For a review see R. H. Abeles and D. Dolphin, *Acc. Chem. Res.*, **9**, 114 (1976).
(9) L. J. Young in "Polymer Handbook", J. Brandrup and E. H. Immergut, Eds., Interscience, New York, 1966, pp II-352.
(10) H. Fischer, *Z. Naturforsch., A*, **19A**, 866 (1964); **20A**, 428 (1965).
(11) T. Funabiki and K. Tarama, *Bull. Chem. Soc. Jpn.*, **45**, 2945 (1972).
(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley-Interscience, New York, 1970, p 188. A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965); F. A Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).
(13) J. E. Huheey, "Inorganic Chemistry", Harper and Row, New York, 1972, p 306 ff, 449 ff. P. J. Durant and B. Durant, "Introduction to Advanced Inorganic Chemistry", 2nd ed., Wiley, New York, 1970, pp 970, 1083.

ence in the two reactions is understandable. Any cobalt(III) formed in the thiocyanate reaction is probably converted to cobalt(II) with concomitant oxidation of the organic ligands or thiocyanate to unknown materials.

Treatment of Ib with sodium methoxide, potassium *tert*-butoxide and lithium aluminum hydride decomposed the salt to unidentified materials.

Experimental Section

Elemental analyses were obtained from Micro-Analysis, Inc., Wilmington, DE. Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 710B infrared spectrometer; absorptions are classified as very strong (vs), strong (s), medium (m), or weak (w). Ultraviolet and visible spectra were recorded on a Cary 118 ultraviolet and visible spectrometer. The proton NMR spectra were obtained on a Varian T-60 spectrometer. The chemical shifts are reported in parts per million downfield from the internal standard tetramethylsilane (Me_4Si). Tetraethylammonium cyanide (Fluka), and potassium thiocyanate (J. T. Baker Chemical Co) were used as obtained.

Reaction of (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Excess Cyanide. (A) (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (Ib) (270 mg, 0.696 mmol) was dissolved in dry, degassed methylene chloride (40 mL). Tetraethylammonium cyanide (652 mg, 4.17 mmol) was added, and the solution was stirred for 30 min at room temperature, during which it became dark brown. The reaction mixture was poured into water (100 mL)–methylene chloride (150 mL). The methylene chloride layer was separated, washed with water (2 × 50 mL), and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure (water aspirator) to give a brown oil which was extracted with pentane. Removal of the pentane gave a mixture of methyl 2-phenyl-2-propenyl sulfide, II, and (*E*)-methyl 2-phenyl-1-propenyl sulfide as a yellow oil (51.4–54.7 mg, 45.0–47.9%; II/III from 73:27 to 100:0): IR (thin film) 3400 (w, br, H_2O), 3080 (m), 3050 (m), 3030 (m), 2960 (s), 2910 (s), 2880 (m), 2860 (m), 2830 (w), 1790 (w, C=CH_2), 1720 (m), 1660 (w), 1615 (m, C=CC_6H_5), 1580 (m), 1565 (w), 1485 (s), 1435 (s), 1415 (s, C=CH_2), 1395 (w), 1370 (m), 1305 (m), 1290 (m), 1225 (m), 1150 (w), 1120 (w), 1095 (w), 1065 (w), 1020 (m), 975 (m), 950 (w), 895 (s, C=CH_2), 800 (w, C=CHR[3]), 765 (s), 740 (s), 685 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.13–7.55 (m, 5 H, C_6H_5), 6.21 (s, 0.27 H, =C*H*SCH_3), 5.40 (s, 0.73 H, =CH_2 hydrogen cis to phenyl group), 5.14 (s, 0.73 H, =CH_2 hydrogen trans to phenyl group), 3.55 (s, 1.46 H, CH_2SCH_3), 2.33 (s, 0.81 H, =CHSC*H*$_3$), 2.12 (s, 0.81 H, CH_3C=), 2.02 (s, 2.19 H, CH_2SCH_3).

(B) Salt Ib (100 mg, 0.267 mmol) was treated with tetraethylammonium cyanide (250 mg, 1.6 mmol) in dry acetonitrile (20 mL). A mixture of methyl 2-phenyl-2-propenyl sulfide, II, and (*E*)-methyl 2-phenyl-1-propenyl sulfide, III, was obtained as a yellow oil (20.5 mg, 46.8%, II/III = 90:10); the ^1H NMR spectrum of the mixture was similar to that obtained from the previous reaction.

The reaction was repeated in deuterated acetonitrile. A mixture of II and III was obtained as a yellow oil (19 mg, 43%, II/III = 80:20). The relative areas of the absorptions in the ^1H NMR spectrum were unchanged, indicating no deuterium incorporation.

(C) Salt Ib (100 mg, 0.267 mmol) was treated with tetraethylammonium cyanide (250 mg, 1.6 mmol) in methylene chloride (15 mL) as previously described. The reaction mixture was poured into methylene chloride–deuterium oxide. Separation of the methylene chloride layer, and removal of the solvent gave a brown oil. The oil was extracted with pentane and the solvent was removed. The sulfide mixture was obtained as a yellow oil (21 mg, 48%); the relative areas of the absorptions in the ^1H NMR spectrum were unchanged, indicating no deuterium incorporation.

(D) Salt Ib (125 mg, 0.334 mmol) was treated with tetramethylammonium cyanide (120 mg, 2.01 mmol) in dry acetonitrile (20 mL) as previously described. A mixture of allylic sulfide II and vinylic sulfide III was obtained as a yellow oil (22 mg, 40.1%, II/III = 75:25).

(E) Salt Ib (70 mg, 0.187 mmol) was treated with tetraethylammonium cyanide (175 mg, 1.12 mmol) in methylene chloride (15 mL)–nitromethane (5 mL), as previously described. A mixture of II and III was obtained as a yellow oil (27.8 mg, 90%, II/III = 95:5).

(F) The above reaction was repeated with deuterated nitromethane in place of nitromethane. A mixture of allylic sulfide II and vinylic sulfide III was obtained as a yellow oil (27.4 mg, 88.3%, II/III = 95:5): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.13–7.55 (m, 5 H, C_6H_5), 6.21 (s, 0.05 H, =C*H*SCH_3, E), 5.40 (s, 0.95 H, =CH_2 hydrogen cis to phenyl group), 5.14 (s, 0.95 H, =CH_2 hydrogen trans to phenyl group), 3.55 (s, 0.95 H, =CC*H*DS), 2.33 (s, 0.15 H, =CHSC*H*$_3$), 2.12 (s, 0.10 H, =CCH_2D), 2.02 (s, 2.85 H, CH_2DSCH_3). The reaction mixture was poured into water–methylene chloride. The aqueous layer was separated and the water was removed to give an orange solid. The infrared and ^1H NMR data indicate the orange solid is a mixture of tetraethylammonium cyanide, tetraethylammonium tetrafluoroborate, and tetraethylammonium (π-cyclopentadienyl)tricyanocobaltate(III)[3] (combined weight 140 mg, 80%). The components could not be separated by chromatography (silica gel): IR (KBr), 3370 (s, br, H_2O), 3100 (w), 2980 (m), 2950 (w), 2890 (w), 2130 (m, CN), 2100 (s, CN), 2060 (m, CN), 1700–1590 (s), 1480–1430 (s), 1390 (s), 1360 (m), 1330 (w), 1310 (w), 1240 (w), 1220 (m), 1175 (m), 1165 (m), 1090–1000 (s, BF_4^-), 995 (s), 955 (m), 840 (m), 825 (w), 780 (s) cm^{-1}; ^1H NMR (D_2O, 60 MHz) δ 5.50 (s, 5 H, C_5H_5), 3.20 (q, J = 8 Hz, 45 H, NCH_2CH_3), 1.20 (triplet of triplets, J = 8, 2 Hz, 67.5 H, NCH_2CH_3).

Reaction of (*S*-Ethyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Excess Cyanide. (*S*-Ethyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (230 mg, 0.593 mmol) was dissolved in dry, degassed methylene chloride (40 mL). Tetraethylammonium cyanide (560 mg, 3.56 mmol) was added, and the solution was stirred for 1 h at room temperature. After the workup described above, a yellow oil was obtained (50 mg, 0.281 mmol, 47.3%): IR (thin film), 3400 (w, br, H_2O), 3080 (m), 3060 (m), 3030 (m), 2960 (s), 2930 (s), 2860 (m), 1800 (w, C=CH_2), 1720 (m), 1615 (m, C=CC_6H_5), 1590 (m), 1570 (m), 1485 (m), 1440 (s), 1420 (w), 1375 (m), 1260 (m), 1225 (m), 1110 (m), 1070 (s), 1030 (m), 895 (s, C=CH_2), 800 (w, C=CHR), 770 (s), 750 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$ 60 MHz) δ 7.13–7.57 (m, 5 H, C_6H_5), 6.30 (s, 0.3 H, =C*H*SCH_2CH_3, *Z* isomer), 6.05 (s, 0.3 H, =C*H*SCH_2CH_3, *E* isomer), 5.38 (s, 0.7 H, =CH_2 hydrogen cis to phenyl group), 5.17 (s, 0.7 H, =CH_2 hydrogen trans to phenyl group), 3.58 (s, 1.4 H, =C-CH_2S), 3.46–2.00 (m, 4.4 H, =C-CH_3 *E* and *Z* isomers, =CSCH_2, *E* and *Z* isomers, SCH_2CH_3), 1.50–0.96 (m, 3.9 H, S-CH_2CH_3). The mixture was chromatographed on silica gel (pentane, ether). Ethyl 2-phenyl-2-propenyl sulfide (elution with pentane) was obtained as a yellow oil (15 mg, 14.2%) ^1H NMR ($CDCl_3$, 60 MHz) δ 7.15–7.55 (m, 5 H, C_6H_5), 5.38 (s, 1 H, =CH_2 hydrogen cis to phenyl group), 5.17 (s, 1 H, =CH_2 hydrogen trans to phenyl group), 3.58 (s, 2 H, $CH_2SCH_2CH_3$), 2.50 (q, J = 7 Hz, 2 H, $CH_2SCH_2CH_3$), 1.22 (t, J = 7 Hz, 3 H, $CH_2SCH_2CH_3$).

Ethyl 2-Phenyl-2-propenyl Sulfide (II, R = C_2H_5). α-Bromomethylstyrene[14] (1.97 g, 10.0 mmol) was added dropwise to a solution of ethanethiol (620 mg, 10.0 mmol) and 10 N aqueous sodium hydroxide (1 mL, 10.0 mmol) in methanol (15 mL). The solution was stirred at room temperature for 1.5 h. Ether (75 mL) was added, and the precipitated sodium bromide was removed by filtration. The filtrate was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure (water aspirator). Ethyl 2-phenyl-2-propenyl sulfide was obtained as a yellow oil (1.65 g, 9.27 mmol, 92.7%): IR (thin film) 3080 (w), 3050 (w), 3325 (w), 2960 (m), 2920 (m), 2860 (w), 1600 (w, br), 1480 (m), 1435 (m), 1415 (m), 1390 (w), 1360 (w), 1290 (w), 1255 (m), 1220 (m), 1050 (s, br), 1020 (s), 970 (w), 890 (s), 790 (m), 760 (s), 740 (m), 680 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.58–7.13 (m, 5 H, C_6H_5), 5.44 (s, 1 H, =CH cis to phenyl group), 5.19 (s, 1 H, =CH trans to phenyl group), 3.59 (s, 2 H, =CCH_2S), 2.50 (q, J = 7 Hz, 2 H, SCH_2CH_3), 1.22 (t, J = 7 Hz, 3 H, SCH_2CH_3).

The liquid sulfide (30 mg, 0.168 mmol) was converted to a solid derivative by dissolving it in methylene chloride (2 mL) and shaking the mixture with a saturated, aqueous solution of mercuric

(14) S. F. Reed, Jr., *J. Org. Chem.*, **30**, 3258 (1965).

chloride (20 mL). A white solid precipitated within 1 min. The suspension was filtered and the solid washed with methylene chloride (20 mL) to give the bis(mercuric chloride) adduct of ethyl 2-phenyl-2-propenyl sulfide as a white solid (110 mg, 0.152 mmol, 90.9%): mp 123–124 °C; ^{1}H NMR (Me_2SO-d_6, 60 MHz) δ 7.13–7.62 (m, 5 H, C_6H_5), 5.43 (s, 1 H, $=CH_2$ hydrogen cis to phenyl group), 5.21 (s, 1 H, $=CH_2$ hydrogen trans to phenyl group), 3.65 (s, 2 H, $CH_2SCH_2CH_3$), 2.52 (q, J = 7 Hz, 2 H, $CH_2SCH_2CH_3$), 1.12 (t, J = 7 Hz, 3 H, $CH_2SCH_2CH_3$).

Anal. Calcd for $C_{11}H_{14}Cl_4Hg_2S$: C, 18.31; H, 1.94; Cl, 19.67. Found: C, 18.05; H, 1.62; Cl, 17.15.[15]

Reaction of (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Equimolar Cyanide Ion. (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (Ib) (175 mg, 0.468 mmol) was dissolved in dry, degassed acetonitrile (15 mL). Tetraethylammonium cyanide (73 mg, 0.468 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. During this time the solution became light red. The solvent was removed under reduced pressure (water aspirator). The resulting brown oil was chromatographed (silica gel, ether, acetone). A red oil (200 mg eluted with acetone) was obtained after solvent removal. The red oil is believed to be an impure monocyano adduct of Ib: IR (thin film) 3400 (s, br, H_2O), 2970 (s), 2940 (m), 2890 (m), 2090 (m, CN), 1685 (s), 1670 (s), 1660 (s), 1650 (s), 1635 (s), 1615 (s), 1450 (m), 1430 (m), 1415 (m), 1360 (s), 1340 (m), 1300 (m), 1215 (m), 1165 (m), 1135 (s), 1015 (s), 1000 (m), 945 (m), 905 (m), 890 (m), 820 (m), 780 (m), 750 (m) cm^{-1}; UV max (CH_3CN)[16] 544 nm (ϵ 28), 408 (144), 253 (3070); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.52–7.13 (m, 30 H, C_6H_5), 7.32 (s), 5.05 (s, 5 H, C_5H_5), 3.36 (s), 2.62 (s), 2.40 (s), 2.17 (s), 1.42 (s), 1.35 (s), 1.24 (s), 0.85 (s).

Reaction of (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt Tetrafluoroborate with Thiocyanate Ion. (*S*-Methyl-2-phenylpropenethial)(π-cyclopentadienyl)cobalt tetrafluoroborate (Ib) (100 mg, 0.268 mmol) was dissolved in dry, degassed acetone (40 mL). Potassium thiocyanate (156 mg, 1.60 mmol) was added, and the solution was stirred for 30 min at room temperature. During this time the solution turned blue-green. The solvent was removed under reduced pressure (water aspirator) to give a green solid. The solid was chromatographed (silica gel, ether, acetone). A brown oil was obtained from the ether fraction after solvent removal. The acetone fraction yielded a blue solid, [$K_2Co(NCS)_4$]. The brown oil was rechromatographed (silica gel, pentane, ether). Pentane elution and solvent removal gave a yellow oil. A brown oil was obtained from the ether fraction. Yellow oil: IR (thin film) 3070 (m), 3050 (m), 3030 (m), 2950 (s), 2920 (s), 2860 (m), 1720 (s), 1680 (w, C=C), 1585 (m), 1615 (w, $C{=}CC_6H_5$) 1485 (m), 1435 (s), 1420 (m, $C{=}CH_2$), 1350 (w, C=CHR), 1310 (m), 1270 (s), 1115 (m), 1060 (m), 890 (m, $C{=}CH_2$), 815 (w, C=CHR), 800 (w, C=CHR), 740 (s) cm^{-1}, ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.13–7.43 (m), 6.39 (s), 6.20 (s), 5.48 (s), 4.73 (s), 4.30 (s), 4.22 (s), 3.07 (s), 2.77 (s), 2.38 (s), 2.30–1.97 (m). Brown oil: IR (thin film) 3400 (m, br, H_2O), 3070 (w), 3050 (m), 3030 (m), 2950 (s), 2910 (s), 2860 (m), 1710 (m), 1690–1640 (s, C=C), 1620 (w, $C{=}CC_6H_5$), 1590 (w), 1480 (w), 1430 (m), 1410 (m), 1250 (s), 1080 (m), 1060 (m), 1035 (m), 1010 (m), 790 (s), 770 (s), 740 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.87–7.23 (m), 4.40 (s), 4.32 (s), 2.90–2.07 (m), 1.73–1.27 (m). $K_2Co(NCS)_4$: IR (KBr) 3400 (s, br, H_2O), 2060 (s, SCN), 720 (m, br) cm^{-1}; visible (acetone), 620, 584 (sh) nm. Similar results were obtained with tetraethylammonium thiocyanate.

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Registry No. Ib, 79991-97-2; Ib′, 79991-99-4; II, R = CH_3, 79992-70-4; II, R = C_2H_5, 51876-02-9; III, R = CH_3, 25650-53-7; V, 79991-92-7; [$K_2Co(NCS)_4$], 19543-13-5; tetraethylammonium (π-cyclopentadienyl)tricyanocobaltate(III), 79991-93-8; α-bromomethylstyrene, 3360-54-1; ethanethiol, 75-08-1.

(15) Mercury often interferes with analysis for chlorine: C. Ayers in "Comprehensive Analytical Chemistry", C. L. Wilson and D. W. Wilson, Eds., Vol. 1B, Elsevier, New York, 1960, p 230.

(16) Molar absorptivities are low because of the presence of impurities.

Syntheses of Kinetically Unstable Neutral Formyl Complexes via $Li(C_2H_5)_3BH$ and "Transformylation" Reactions of Metal Carbonyl Cations

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Low-temperature syntheses of the kinetically unstable formyls (η-C_5H_5)Re(NO)(CO)(CHO) (**9**), (η-C_5H_5)Mn(NO)(CO)(CHO) (**10**), $Re(PPh_3)(CO)_4(CHO)$ (**11**), $Mn(PPh_3)_2(CO)_3(CHO)$ (**12**), $Ir(PPh_3)_2(CO)_2(CHO)$ (**13**), and (η-C_5H_5)$Mo(PPh_3)(CO)_2(CHO)$ (**14**) by reaction of $Li(C_2H_5)_3BH$ with the corresponding metal carbonyl cations are described. Formyls **9**, **10**, and **11** can also be synthesized by hydride transfer from the stable neutral formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (**1**) to the appropriate metal carbonyl cation precursor ("transformylation"); this procedure avoids formation of byproduct $(C_2H_5)_3B$. Whereas **9** (in dilute solution) and **13** decarbonylate to detectable metal hydrides upon warming, the decomposition chemistry of the other formyls is more complex and sometimes involves the dichloromethane cosolvent.

Introduction

Several simple neutral metal carbonyl complexes ($Co_2(CO)_8$, $Mn_2(CO)_{10}$, $Ru(CO)_5$) have been found to be catalyst precursors for the homogeneous reduction of CO/H_2 gas mixtures to oxygen-containing organic molecules.[2] For such transformations, a plausible initial step is the formation of a catalyst bound formyl (–CHO). Hence the synthesis of neutral, homogeneous transition metal formyl complexes has been an extremely active research area.[3]

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(2) (a) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45 and references therein. (b) Pruett, R. L *Ibid.* **1977**, *295*, 239. (c) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419. (d) Dombek, B. D. *Ibid.* **1980**, *102*, 6855. (e) Fahey, D. R. *Ibid.*, **1981**, *103*, 136. (f) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. (g) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 188.

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