

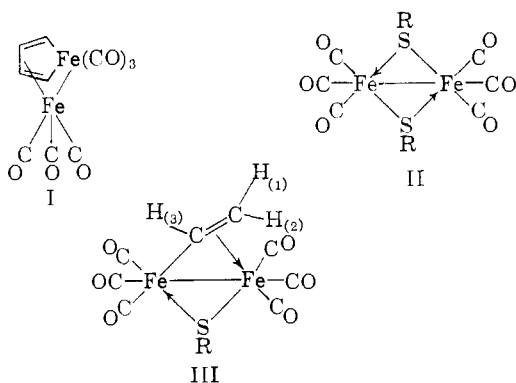
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. XIV. New Organosulfur Derivatives of Iron and Cobalt<sup>1, 2</sup>BY R. B. KING,<sup>3</sup> P. M. TREICHEL<sup>3</sup> AND F. G. A. STONE

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Vinyl sulfides  $\text{RSCH}:\text{CH}_2$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}:\text{CH}_2$  and  $\text{CH}(\text{CH}_3)_2$ ) react with triiron dodecacarbonyl to afford red volatile complexes of composition  $[\text{RSCH}:\text{CH}_2]\text{Fe}_2(\text{CO})_8$ . On the basis of chemical and spectroscopic evidence a structure for these compounds is proposed in which the two iron tricarbonyl groups are joined by a bridging vinyl group, a bridging  $\text{RS}$ -group and an iron-iron bond. An improved preparation of the thianaphthene-iron carbonyl complex is reported and evidence is presented for the stoichiometry  $\text{C}_8\text{H}_6\text{S}\cdot\text{Fe}_2(\text{CO})_8$ , and for a structure analogous to the vinyl sulfide complexes mentioned above. Reactions between dimethyl disulfide and the cyclopentadienyl metal carbonyls  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and  $[\text{C}_5\text{H}_5\text{Co}(\text{CO})_2]_2$  give the sulfur compounds  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2$  and  $[\text{C}_5\text{H}_5\text{CoSCH}_3]_2$ , respectively.

It has been shown recently that the main product of the reaction between iron carbonyls and thiophene is the organoiron compound I.<sup>4</sup> In this desulfurization of thiophene rupture of carbon-sulfur bonds takes place. A similar cleavage of carbon-sulfur bonds is observed in reactions between dialkyl sulfides and iron pentacarbonyl.<sup>5a</sup> However, in this case sulfur-containing iron complexes (II) are isolated, although these substances are best obtained by treating iron carbonyls with the appropriate mercaptan or organo-disulfide.<sup>5</sup>



In order to shed more light on iron carbonyl reactions of this kind, a study was made of the reaction between triiron dodecacarbonyl and divinyl sulfide, a compound structurally similar to thiophene. A deep red liquid of composition  $(\text{CH}_2:\text{CH})_2\text{S}\cdot\text{Fe}_2(\text{CO})_8$  was obtained. Spectroscopic studies showed that the diiron compound contained vinyl groups in two different environments, one being involved in bonding to iron atoms while the other remained uncomplexed. This result led to a study of reactions between triiron dodecacarbonyl and some alkylvinyl sulfides to determine whether these substances would form similar complexes.

Experimental<sup>6</sup>

1. Apparatus and Starting Materials.—Infrared spectra were recorded using a Perkin-Elmer Model 21 spectro-

photometer. Nuclear magnetic resonance spectra of saturated carbon disulfide solutions were recorded at 60 megacycles by a Varian Model 4300B high resolution spectrometer fitted with a super stabilizer. Chemical shifts are referred to tetramethylsilane as standard (0.0 p.p.m.).

Divinyl sulfide was obtained by dehydrohalogenation of  $(\text{BrCH}_2\text{CH}_2)_2\text{S}$  with potassium hydroxide.<sup>7a</sup> The various alkylvinyl sulfides were obtained by treating the appropriate alkyl hydroxyethyl sulfides with solid potassium hydroxide at 200–300°.<sup>7</sup> Triiron dodecacarbonyl was prepared from iron pentacarbonyl by the method previously described.<sup>8</sup> Cyclopentadienyliron dicarbonyl dimer was synthesized from iron pentacarbonyl and dicyclopentadiene at 130–140°,<sup>9</sup> and cyclopentadienylcobalt dicarbonyl was prepared by carbonylation of benzene solutions of bis-(cyclopentadienyl)-cobalt(II) at elevated temperatures and pressures.<sup>10</sup>

2. Complexes of Type III Obtained from Reactions between Triiron Dodecacarbonyl and Some Vinyl Sulfides.—In the general procedure, triiron dodecacarbonyl (36 mmoles), a vinyl sulfide (100 mmoles) and thiophene-free benzene (500 ml.) were refluxed together under nitrogen until the green color of the iron carbonyl had disappeared and the supernatant liquid was red-orange. Reaction times ranged from 5 to 18 hr. After the reaction period was over, the mixture was cooled to room temperature and filtered. The red filtrate was evaporated (20 mm.) to a red oil. The latter was dissolved in pentane and chromatographed on alumina. The chromatogram was developed and the red band eluted with pentane. Except for the methyl derivative which is an orange solid, evaporation of the pentane from the eluate (20 mm.) left a red liquid, which was purified further by sublimation at 60° (0.1 mm.) onto a  $-78^\circ$  probe. The sublimate was pumped on (0.1 mm.) for several hours before being submitted for analysis. Analytical data for the various complexes are summarized in Table I.

3. Trifluoroacetic Acid Degradation of the Organoiron Compounds of Type III.—The effect of trifluoroacetic acid on the parent sulfides was first investigated. Samples of methylvinyl sulfide, ethylvinyl sulfide and isopropylvinyl sulfide were heated with trifluoroacetic acid at 70° for about 12 hr. No ethylene was detected as a product of such treatments. In the reactions described below the ethylene formed was identified by its infrared spectrum.

(a) Compound IIIa.—A mixture of 251.4 mg. (0.710 mmole) of IIIa and 0.8 ml. (10.7 mmoles) of trifluoroacetic acid was heated in a sealed Pyrex bulb at 69° for 13 hr. The reaction bulb was attached to the vacuum line and opened. Volatile material was fractionated to give 4.26 mmoles of carbon monoxide (100% of theor.) and 0.684 mmoles of ethylene (96.3% of that expected for the presence of one  $\text{CH}_2:\text{CH}-\text{Fe}$  in IIIa).

(1) Previous paper in this series, T. A. Manuel, S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3597 (1961).

(2) We are indebted to the National Science Foundation for support of this work.

(3) National Science Foundation predoctoral fellow.

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

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(6) Microanalyses were performed by Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany.

(7) (a) C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2672 (1959); (b) C. C. Price and R. G. Gillis, *ibid.*, **75**, 4750 (1953).

(8) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961); and references cited therein.

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TABLE I  
 SULFUR-CONTAINING ORGANOIRON COMPOUNDS

Composition of product	Parent sulfide	Yield, %	Carbon, %		Hydrogen, %		Iron, %		Sulfur, %		CO groups <sup>a</sup>	Mol. wt. <sup>b</sup>	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		Calcd.	Found
C <sub>2</sub> H <sub>6</sub> O <sub>8</sub> SFe <sub>2</sub> (IIIa) <sup>c</sup>	CH <sub>3</sub> :CHSCH <sub>2</sub>	10.3	30.5	30.2	1.69	1.80	31.6	31.3	9.05	9.28	5.7	354	340
C <sub>10</sub> H <sub>10</sub> O <sub>8</sub> SFe <sub>2</sub> (IIIb)	CH <sub>2</sub> :CHSC <sub>2</sub> H <sub>5</sub>	11.6	32.6	32.1	2.18	2.24	30.4	30.2	8.70	9.03	5.5	368	363
C <sub>10</sub> H <sub>10</sub> O <sub>8</sub> SFe <sub>2</sub> (IIIc)	(CH <sub>2</sub> :CH) <sub>2</sub> S	6.0	32.8	33.3	1.64	1.80	..	..	8.75	9.12	..	..	..
C <sub>11</sub> H <sub>10</sub> O <sub>8</sub> SFe <sub>2</sub> (IIId)	CH <sub>2</sub> :CHSCH(CH <sub>3</sub> ) <sub>2</sub>	9.8	34.6	33.9	2.62	2.78	29.3	29.0	8.38	8.58	5.6	382	351

<sup>a</sup> Determined by heating weighed samples of the iron compounds with excess iodine in evacuated bulbs at 150–180° for 18 hr. Carbon monoxide evolved was measured using a high vacuum system. <sup>b</sup> Determined by the isopiestic method. <sup>c</sup> M.p. 46.5–48.0°. Sublimes at 30° (0.1 mm.).

 TABLE II  
 INFRARED SPECTRA OF SOME ORGANOIRON-SULFUR COMPOUNDS

Compound	Band positions in the carbonyl region, <sup>a</sup> cm. <sup>-1</sup>	Band positions in the C-H stretching region, <sup>b</sup> cm. <sup>-1</sup>	Other bands, <sup>b</sup> cm. <sup>-1</sup>
I	2079(s), 2042(vs), 2006(vs), 1998(vs) <sup>c</sup>	.....	.....
II (R = CH <sub>3</sub> )	2072(m), 2036(vs), 1996(s), 1990(s) <sup>c</sup>	2899(m)	1312(m), 1302(m), 949(m)
II (R = C <sub>2</sub> H <sub>5</sub> )	2073(m), 2037(vs), 2000(s), 1991(s) <sup>d,e</sup>	2941(m), 2899(m), 2841(w)	1376(m), 1253(m), 1045(w), 970(w)
II (R = (CH <sub>3</sub> ) <sub>2</sub> CH)	2069(m), 2032(vs), 1998(s), 1987(s) <sup>c</sup>	2950(m), 2900(m), 2850(w)	1382(w), 1365(m), 1238(m), 1150(m), 1044(m)
II (R = C <sub>6</sub> H <sub>5</sub> )	2078(m), 2041(vs), 2009(s), 2001(s) <sup>d,e</sup>	.....	.....
IIIa <sup>f</sup>	2073(m), 2038(vs), 2002(s), 1995(s) <sup>c</sup>	2940(w,sh), 2890(m)	1313(m), 1292(m), 985(w), 956(m), 948(m), 925(w), 744(m), 702(m)
IIIb <sup>f</sup>	.....	2950(m), 2906(m), 2849(w)	1377(m), 1295(m), 1253(m), 1044(m), 982(w), 971(m), 926(m), 772(m), 742(m)
IIIc <sup>g</sup>	2077(m), 2043(s), 2005(vs), 2003(vs) <sup>c</sup>	3000(w), 2952(w), 2907(m)	1370(m), 1290(m), 1270(m), 1018(m), 983(w), 955(s), 920(s), 741(m)
IIId <sup>f</sup>	2071(m), 2037(vs), 2000(s), 1992(s) <sup>c</sup>	2924(m), 2889(m), 2834(m)	1381(m), 1366(m), 1293(m), 1241(m), 1148(m), 1069(s), 1045(s), 1025(s), 929(m), 877(w), 742(m)
IV	2076(m), 2044(vs), 2004(s), 1992(m) <sup>c</sup>	3012(m), 2924(m), 2890(m)	1274(m), 1252(m), 1122(w), 1058(w), 1027(w), 986(w), 931(w), 874(m), 831(w), 753(s), 735(s), 690(w)

<sup>a</sup> Taken using a fluorite prism and sodium chloride cell. When a sodium chloride prism is used only three carbonyl bands are observed. <sup>b</sup> Taken in carbon disulfide solution using a sodium chloride prism. <sup>c</sup> Tetrachloroethylene solution. <sup>d</sup> Data taken from ref. 20. <sup>e</sup> Carbon tetrachloride solution. <sup>f</sup> A tetrachloroethylene solution showed no bands in the carbon-carbon double bond stretching region. <sup>g</sup> A tetrachloroethylene solution showed a carbon-carbon double bond stretching band at 1590(s) cm.<sup>-1</sup>.

(b) Compound IIIb.—A mixture of 285.4 mg. (0.777 mmole) of IIIb and 0.8 ml. (10.7 mmole) of trifluoroacetic acid was heated in a bulb at 67° for 24 hr. In the manner just described, 0.495 mmole of ethylene (64% of theor. for one CH<sub>2</sub>:CH-Fe group in IIIb), as well as some carbon monoxide (not measured) was obtained.

The solid residue from the trifluoroacetic acid treatment was extracted with dichloromethane and filtered. After solvent had been removed, sublimation at 35° (0.01 mm.) gave red-orange crystals (m.p. 73.0–73.5°) of the known compound<sup>5</sup> [C<sub>2</sub>H<sub>5</sub>SFe(CO)<sub>3</sub>]<sub>2</sub> (II, R = C<sub>2</sub>H<sub>5</sub>). Identity was established by comparison with an authentic sample of [C<sub>2</sub>H<sub>5</sub>SFe(CO)<sub>3</sub>]<sub>2</sub>, prepared from triiron dodecacarbonyl and diethyl disulfide. The infrared spectra, the melting points and the mixed melting points of the two samples were the same.

(c) Compound IIIc.—A sample (227.7 mg., 0.596 mmole) of IIIc was heated at 60° for 5 hr. with 1 ml. (13.3 mmole) of trifluoroacetic acid. Fractionation of the volatile reaction products gave 0.666 mmole of carbon monoxide (18.6% of theor.) and 0.345 mmole of ethylene (58.2% of that expected for presence of one CH<sub>2</sub>:CH-Fe group in IIIc).

Extraction of the solid residue with dichloromethane was followed by filtration and removal of solvent. Sublimation at 35° (0.01 mm.) gave red crystals (m.p. 88.0–88.5°) of the new compound [(CH<sub>3</sub>)<sub>2</sub>CHSFe(CO)<sub>3</sub>]<sub>2</sub> (II, R = CH(CH<sub>3</sub>)<sub>2</sub>).

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>8</sub>S<sub>2</sub>Fe<sub>2</sub>: C, 33.5; H, 3.26; S, 14.9; Fe, 26.0; mol. wt., 430. Found: C, 33.5; H, 3.26; S, 14.7; Fe, 26.3; mol. wt., 396.

The compound [(CH<sub>3</sub>)<sub>2</sub>CHSFe(CO)<sub>3</sub>]<sub>2</sub> was independently synthesized from isopropyl mercaptan and triiron dodecacarbonyl. The melting point and infrared spectrum (Table

II) were the same as those of the compound recovered after trifluoroacetic acid degradation of complex IIIc.

4. Spectroscopic Studies on Compounds of Type III.—(a) Infrared Spectra.—The infrared spectral bands are listed in Table II.

(b) Proton Nuclear Magnetic Resonance Spectra.—Compound IIIa.—Peaks were observed at 8.16 (quartet, separations 9, 5 and 9 cycles), 3.81 (doublet, separation 9 cycles, some evidence of further splitting), 2.85 (doublet, separation 14 cycles, some evidence of further splitting) 2.15, 2.07 and 1.62 p.p.m. The quartet and the two complex doublets each have about the same intensity. The three high field peaks are in the region of the spectrum for methyl group protons. The presence of several lines may be due to isomeric forms of IIIa. The structure proposed for compounds of type III could give rotational and/or geometrical isomers. Similar behavior might be possible in compounds of structure type II. It is interesting, therefore, that the n.m.r. spectrum of the compound [CH<sub>3</sub>SFe(CO)<sub>3</sub>]<sub>2</sub> shows peaks at 2.14, 2.08 and 1.61 p.p.m., implying the presence of methyl protons in more than one kind of environment.

Compound IIIb.—Peaks occur at 8.15 (quartet, separations 9, 6 and 9 cycles), 3.78 (doublet, separation 9 cycles, evidence of further splitting), 2.83 (doublet, separation 15 cycles, evidence of further splitting), 2.31 (complex multiplet) and 1.30 (triplet, separation 7 cycles) p.p.m. The quartet and the two doublets each have about the same relative intensity.

Compound IIIc.—Peaks were observed at 8.16 (quartet, separations 9, 6 and 9 cycles), 5.70 (complex multiplet), 3.82 (quartet, separations 1, 8 and 1 cycles), and 2.78 (quartet, separations 1, 14 and 1 cycles) p.p.m., with approximate relative intensities 1:3:1:1, respectively.

**Compound III<sub>d</sub>.**—Peaks were recorded at 8.35 (quartet, separations 8, 6 and 8 cycles), 3.78 (doublet, separation 8 cycles, evidence of further splitting), 2.85 (doublet, separation 14 cycles, evidence of further splitting), 2.52 (broad complex multiplet) and 1.32 (complex multiplet, strongest feature a doublet, separation 7 cycles) p.p.m., with approximate relative intensities 1:1:1:1:6, respectively.

**5. The Reaction between Thianaphthene and Iron Carbonyls.**—The previously described method for obtaining the thianaphthene-iron carbonyl complex gives the compound in only very small amounts.<sup>11</sup> The improved method here described affords the complex in more substantial quantities, permitting a greater degree of purification than was possible in the earlier work.

A mixture of triiron dodecacarbonyl (15.0 g., 29.8 mmoles), thianaphthene (13.4 g., 100 mmoles) and 500 ml. of thiophene-free benzene was refluxed under nitrogen for 18 hr., during which time the green color of the iron carbonyl was discharged. The mixture was cooled to room temperature and filtered, a red-orange filtrate being obtained. The residue was washed with 50 ml. of benzene. Solvent was removed from the combined filtrate and washings at 20 mm. leaving a dark red-orange semi-solid residue. The latter was dissolved in 100 ml. of pentane and the solution chromatographed on alumina. The sharp red-orange band was eluted with pentane, and solvent was removed (20 mm.) from the intense red-orange eluate to give red-orange crystals of the iron derivative, contaminated with thianaphthene.

Sublimation yielded thianaphthene at 50° (0.01 mm.) and the desired complex at 80° (0.01 mm.). In this manner 3.0 g. (16% yield) of fairly pure thianaphthene-iron carbonyl complex (IV) was obtained. Final purification was accomplished by re-sublimation to give a center cut (1.8 g.) of m.p. 103–104° (lit.<sup>11</sup> 100–101°), used for analyses and proton n.m.r. studies.

*Anal.* Calcd. for hexacarbonyl derivative, C<sub>14</sub>H<sub>6</sub>O<sub>6</sub>Fe<sub>2</sub>: C, 40.6; H, 1.45; S, 7.74; Fe, 27.0; mol. wt., 414. Calcd. for pentacarbonyl derivative, C<sub>13</sub>H<sub>6</sub>O<sub>5</sub>Fe<sub>2</sub>: C, 40.4; H, 1.55; S, 8.29; Fe, 29.0; mol. wt., 386. Found: C, 41.0, 40.9; H, 1.42, 1.61; S, 7.57, 7.45; Fe, 27.1, 27.0; mol. wt., 420.

In an attempt to determine by analysis for carbonyl groups whether IV is a diiron pentacarbonyl or a diiron hexacarbonyl derivative samples were heated with iodine at 180° for 12–20 hr. periods. Carbon monoxide gas released by such treatments was measured. Five separate determinations were made giving volumes of carbon monoxide ranging from 98.9–100.8% of the expected volume for five carbonyl groups, or 88.2–90.8% of the expected volume for six carbonyl groups.

In the proton n.m.r. spectrum of IV peaks occur at 8.90 (doublet, separation 9 cycles), 6.95 and 5.40 (doublet, separation 9 cycles) p.p.m., with relative intensities 1:4:1, respectively. In the earlier work<sup>11</sup> the spectrum of IV was reported as consisting of a single line, the two weak doublets apparently being lost in the noise as a result of an insufficient concentration of the complex. The infrared spectrum of IV in the carbonyl region, recorded with a spectrometer fitted with a calcium fluoride prism, is given in Table II.

**6. Reaction of Cyclopentadienyliron Dicarboxyl with Dimethyl Disulfide.**—A mixture of 3.55 g. (10 mmoles) of cyclopentadienyliron dicarbonyl dimer, 5 ml. of dimethyl disulfide and 40 ml. of 2,2,4-trimethylpentane was refluxed for 2.5 hr. under nitrogen, the reaction mixture soon becoming a dark brown. After cooling to room temperature, the mixture was filtered. The filtrate was evaporated at 20 mm., leaving a brown residue which was washed with 20 ml. of pentane cooled to –78°. The resulting residue was purified by sublimation at 110° (0.1 mm.) giving 340 mg. (8.7% yield) of V as brown-black crystals, m.p. 104–105°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub>Fe<sub>2</sub>: C, 42.9; H, 4.08; S, 16.3; mol. wt., 392. Found: C, 42.9; H, 4.23; S, 16.2; mol. wt., 390.

The n.m.r. spectrum of V showed peaks at 4.23 and 1.32 p.p.m., of relative intensities 5:3, respectively.

The infrared spectrum of V (carbon disulfide solution, NaCl optics) showed a carbonyl stretching band at 1958(s) cm.<sup>-1</sup>. No bridging carbonyl bands were observed. Other bands occur at 943(w) and 803(m) cm.<sup>-1</sup>.

(11) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960)

**7. Reaction of Cyclopentadienylcobalt Dicarboxyl with Dimethyl Disulfide.**—A mixture of 1.0 g. (5.55 mmoles) of cyclopentadienylcobalt dicarbonyl, 5 ml. of dimethyl disulfide and 40 ml. of 2,2,4-trimethylpentane was refluxed for 20 hr., the reaction mixture turning black. After cooling to room temperature solvent was removed at 20 mm. The product was isolated by sublimation at 110–140° (0.1 mm.) giving 100 mg. (10.5% yield) of VI as black air-stable crystals.

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>S<sub>2</sub>Co<sub>2</sub>: C, 42.1; H, 4.68; S, 18.7; Co, 34.5; mol. wt., 342. Found: C, 41.8; H, 4.69; S, 18.4; Co, 35.1; mol. wt., 330.

The n.m.r. spectrum of VI shows peaks at 4.82 and 2.52 p.p.m. with relative intensities 5:3. The infrared spectrum of VI shows broad weak bands at 948 and 797 cm.<sup>-1</sup> (carbon disulfide solution).

## Discussion

Compounds of Type III are deep red liquids at room temperature, except for the complex derived from methylvinyl sulfide. The complexes are readily soluble in organic solvents to afford deep red solutions and are fairly air stable, oxidation being observed only after keeping them in air for several days. The organoiron complex III<sub>c</sub>, derived from triiron dodecacarbonyl and divinyl sulfide, shows a carbon-carbon double bond stretching band at 1590 cm.<sup>-1</sup> in its infrared spectrum. This establishes that at least one vinyl group in III<sub>c</sub> is not  $\pi$ -complexed to an iron atom, since it is well known that if the  $\pi$ -electrons of a carbon-carbon double bond are complexed to a metal the C=C stretching band is both greatly reduced in intensity and shifted from the normal region of the spectrum.<sup>12</sup> The nuclear magnetic resonance spectrum of III<sub>c</sub> also indicates the presence of an uncomplexed vinyl group since a cluster of lines with a relative intensity corresponding to three protons arises around 5.70 p.p.m., in the region for normal olefinic hydrogen atoms. On the other hand, the n.m.r. spectrum also shows three distinct quartets at 8.16, 3.82 and 2.78 p.p.m., each corresponding in intensity to a single proton. As will be discussed further below, this band pattern corresponds to the presence in the complex of another kind of vinyl group.

The complexes III<sub>a</sub>,b,d, derived from alkylvinyl sulfides, although similar in stoichiometry to III<sub>c</sub>, unlike the parent sulfides or III<sub>c</sub> have no carbon-carbon double bond stretching bands in their infrared spectra, showing that the vinyl group in the original alkylvinyl sulfide has become  $\pi$ -complexed to iron.

The n.m.r. spectra of complexes of type III are sharp and the magnitudes of the chemical shifts are normal, thereby establishing that the compounds are diamagnetic. For this to occur each iron tricarbonyl group requires the donation of four electrons from the organic residue, or, if an iron-iron bond is present, three electrons. It will be noted that the complexes III show no bridging carbonyl groups in their infrared spectra, thereby ruling out any structure involving metal-carbonyl bridges. Furthermore, a CH<sub>2</sub>=CH—S group could donate a total of at least six electrons only if both lone pairs of the sulfur atom are involved in bonding to iron atoms, a situation without precedent.

(12) (a) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953);

(b) D. B. Powell and N. Sheppard, *Spectrochimica Acta*, **13**, 69 (1958); (c) *J. Chem. Soc.*, 2519 (1960).

An alternative solution to the structural problem is suggested by consideration of the previously observed desulfurization of thiophene,<sup>4</sup> as well as the analogous cleavage of organo-groups from dialkyl sulfides to give compounds of type II.<sup>5a</sup> These cleavage reactions suggest that in formation of complexes of type III a vinyl group may have been removed from sulfur, just as vinyl groups are cleaved from vinyltin compounds by iron carbonyls.<sup>13</sup> It is, therefore, proposed that the complexes may be represented in classical terms by structure III. In this structure the vinyl group acts as a bridging group and can be regarded as  $\sigma$ -bonded to one iron atom and  $\pi$ -complexed to the other. The structure suggested is similar to that proposed for compounds of type II. Like II, and the two compounds cyclopentadienyliron dicarbonyl dimer and iron enneacarbonyl, III has an iron-iron bond. Compounds of type III all show four bands in the carbonyl region of the infrared spectrum, under the resolution obtainable with a calcium fluoride prism. It is interesting to compare the similar carbonyl band pattern observed for the various organoiron sulfur compounds among themselves and with that of I (Table II). The latter also has an iron-iron bond. Compounds of type III, with a vinyl group  $\sigma$ -bonded to iron, can also be regarded as an unusual type of vinylmetallic derivative.<sup>14</sup> Indeed, if the structure proposed is correct the compounds should react with protonic acids to give ethylene.<sup>15</sup> In accord with this conclusion compounds IIIa,b,d gave ethylene in yields of from 58–96% on treatment with trifluoroacetic acid. Some carbon monoxide also was formed in these degradation reactions. When carbon monoxide formation was not quantitative, compounds of type II were recovered from the reaction residues.

The proton n.m.r. spectra are readily interpretable in terms of structure III. All four compounds show peaks attributable to the organo-group still bonded to sulfur. Of greater significance in the spectra of each of the four compounds are the three characteristic groups of peaks occurring near 8.2, 3.8 and 2.8 p.p.m. It is especially interesting that these three groups of peaks have such different chemical shifts. Because of this the spectrum of the  $\pi$ -complexed vinyl group appears as a simple pattern of three separated absorptions, rather than as the more complex pattern frequently observed in vinyl compounds and exemplified by the 5.70 p.p.m. multiplet of IIIc. The quartet centered near 8.2 p.p.m. in the spectrum of each of the compounds may reasonably be assigned to the protons  $H_{(3)}$  in III since the chemical shift is so very different from those of the other two groups of peaks. The simplicity of the spectra permits

(13) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 3833 (1960).

(14) Apparently these compounds are the first vinyl derivatives of transition metals to be reported, although two perfluoropropenyl derivatives,  $CF_3CF:CFMn(CO)_5$  and  $CF_3CF:CFFe(CO)_2C_6H_5$ , have been described. See H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforschg.*, **15b**, 763 (1960), and R. B. King, P. M. Treichel and F. G. A. Stone, *Proc. Chem. Soc.*, 69 (1961).

(15) For a discussion of cleavage of vinylmetal compounds to give ethylene, see H. D. Kaesz and F. G. A. Stone, "Organometallic Chemistry," (Editor, H. Zeiss), American Chemical Society Monograph 147, Reinhold Publ. Corp., New York, N. Y., 1960, Chapter 3.

reasonable assignments of the three groups of peaks on the basis of the observed first-order multiplet splittings. The splittings of the quartets near 8.2 p.p.m. are 9 and 15 c.p.s. Since these values are of the magnitude expected for *cis* and *trans* proton-proton spin couplings, respectively,<sup>16</sup> this confirms assignment of the peaks near 8.2 p.p.m. to protons  $H_{(3)}$ . The 9 c.p.s. splitting occurs also in the lines near 3.8 p.p.m., and the 15 c.p.s. splitting in the lines near 2.8 p.p.m., permitting assignment of these peaks to protons  $H_{(1)}$  and  $H_{(2)}$ , respectively, since *trans*-coupling constants are invariably greater than *cis*-coupling constants.<sup>17</sup>

In a study of the n.m.r. spectra of a number of compounds  $CH_2:CHX$ , where  $X = C, O, Cl, Br$ , etc., Banwell and Sheppard<sup>16</sup> obtained results suggesting that chemical shifts in vinyl compounds are related to the  $\pi$ -electron distribution in the vinyl group. In this respect it is interesting to note that the chemical shifts between  $H_{(3)}$  and  $H_{(1)}$  or  $H_{(2)}$  in compounds of type III are much greater than those found between corresponding protons in most vinyl compounds.<sup>16</sup> Since formation of a donor bond from the vinyl group to an iron atom would greatly perturb the  $\pi$ -electron system, this may be responsible for the large chemical shifts observed.

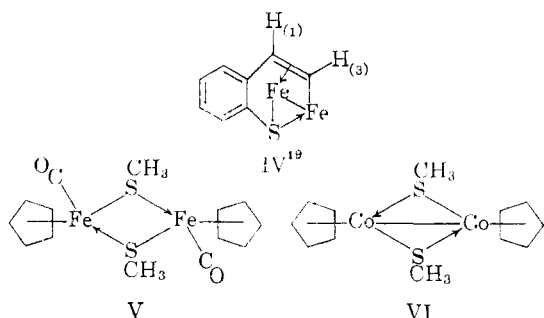
Recently we reported a binuclear iron carbonyl derivative of thianaphthene as being produced in very low yield from the reaction between triiron dodecacarbonyl and thianaphthene.<sup>11</sup> Analysis of this compound seemed to support a formulation  $C_8H_6S \cdot Fe_2(CO)_5$  rather than  $C_8H_6S \cdot Fe_2(CO)_6$ . This seemed reasonable at the time since thianaphthene has the same number of  $\pi$ -electrons available for complex formation as azulene, and the latter is reported to form a compound azulene-diiron pentacarbonyl.<sup>18</sup> Moreover, several analyses for sulfur content of the thianaphthene-iron carbonyl derivative eliminated the possibility of thianaphthene having undergone a desulfurization, as thiophene does in its reactions with iron carbonyls. Nevertheless, in view of the discovery of the organoiron derivatives III it seemed possible that the thianaphthene-iron complex might have an analogous structure IV and thus be a diiron hexacarbonyl derivative rather than a diiron pentacarbonyl compound. The new elemental analyses given in the Experimental section, particularly the crucial iron and sulfur analyses, are in accord with this idea. In an attempt to confirm independently the presence of six CO groups per molecule rather than five, samples of the compound were degraded with iodine and the volume of carbon monoxide measured. Results, however, were inconclusive.

The infrared and n.m.r. spectra of the thianaphthene-iron derivative strongly support structure IV, as do the new elemental analyses mentioned above. In the carbonyl region of the infrared the thianaphthene-iron compound shows a band pat-

(16) C. N. Banwell and N. Sheppard, *Molecular Phys.*, **3**, 351 (1960).

(17) Pople, Schneider and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 194.

(18) R. Burton, L. Pratt and G. W. Wilkinson, *J. Chem. Soc.*, 4290 (1960).



tern strikingly similar to the complexes of type II and III. In the n.m.r. spectrum the resonance at 6.95 p.p.m., relative intensity 4, is in a reasonable position for protons on a benzene ring not  $\pi$ -complexed to a metal. The group of peaks at 8.90 and at 5.40 p.p.m., with 9 cycle separations and relative intensities 1:1, may be ascribed to the two *cis*-protons on the olefinic double bond. Comparison with the spectra of the complexes III discussed above shows that the peaks centered at 8.90 p.p.m. are due to the proton  $H_{(3)}$  in IV and the peaks centered at 5.40 p.p.m. are due to the proton  $H_{(1)}$ .

Within the last few years metal carbonyl chemistry has been greatly expanded by the discovery of a series of cyclopentadienylmetal carbonyls. It seemed likely that cyclopentadienylmetal derivatives containing RS-bridges might exist, analogous to II. As described in the Experimental section we obtained V from dimethyl disulfide and

(19) For purposes of clarity the three carbonyl groups bonded to the iron atoms are not shown.

cyclopentadienyliron dicarbonyl. It is interesting that unlike in compounds II and III, it is not necessary to postulate an iron-iron bond to account for the diamagnetism of V. On the basis of relative intensity and position, the peak at 4.23 p.p.m. in the n.m.r. spectrum of V may be ascribed to the ten protons of the cyclopentadienyl rings, and the peaks at 1.32 p.p.m. to the six protons of the methyl groups.

We have commented previously on similarities in the chemical behavior of iron pentacarbonyl and cyclopentadienylcobalt dicarbonyl.<sup>10b</sup> It seemed probable that cyclopentadienylcobalt dicarbonyl would react with dialkyl disulfides to form compounds similar to II. As described in the Experimental part, VI can be obtained from dimethyl disulfide and cyclopentadienylcobalt dicarbonyl. The peak in the n.m.r. spectrum of VI at 4.82 p.p.m. can be ascribed to the cyclopentadienyl ring protons, while the peak at 2.52 p.p.m. must be due to the methyl group protons. The presence of a cobalt-cobalt bond is necessary in VI in order to give both metal atoms an inert gas electronic configuration. As stated elsewhere<sup>20</sup> it seems more reasonable to invoke metal-metal bonds in II, III, IV and VI rather than to account for diamagnetism by postulating that the organothio-groups contribute four electrons to the metal atoms.

**Acknowledgments.**—We are indebted to our colleagues Drs. T. D. Coyle and S. L. Stafford for stimulating discussions.

(20) S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960).

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## Chemistry of the Metal Carbonyls. XV. Fluorocarbon Derivatives of Iron Carbonyl<sup>1,2</sup>

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Perfluoroalkyl iodides react with iron pentacarbonyl at moderate temperatures to afford perfluoroalkyliron tetracarbonyl iodides, as well as lesser amounts of dimeric perfluoroalkyliron tricarbonyl iodides. Treatment of triiron dodecacarbonyl with sodium amalgam or dispersion in tetrahydrofuran gives brown solutions which react with perfluoroacetyl chlorides to yield bis-(perfluoroalkyl)-iron tetracarbonyl compounds. Some properties of the new perfluoroalkyliron compounds are described. Reaction between the salt  $C_3H_5Fe(CO)_2Na$  and perfluoroalkyl chloride yields an orange crystalline solid  $C_3H_5Fe(CO)_2C_3F_5$ , in which the  $C_3F_5$  moiety is present as the perfluoropropenyl group.

Many compounds are known wherein a perfluoroalkyl group is bonded to a non-metal or metalloid,<sup>5</sup> but relatively few perfluoroalkyl metal compounds have been described. Indeed, until recently well-defined perfluoroalkyl derivatives of metals were limited to compounds of lithium, magnesium, zinc, mercury, tin and lead.<sup>5a,6</sup> The small range

of metals known to form perfluoroalkyl derivatives recently has been extended by preparation of the two series of compounds  $C_nF_{2n+1}M(CO)_5$  [ $M = Mn, Re$ ]<sup>7a</sup> and  $C_3H_5Co(C_nF_{2n+1})(CO)I$ <sup>7b</sup> and the compound  $(CO)_4CoCF_2CF_2Co(CO)_4$ .<sup>8</sup> In this paper some perfluoroalkyl derivatives of iron are described, extending still further the range of transition metals known to form compounds of this type.

The chemical behavior of perfluoroalkyl iodides differs in many ways from that of alkyl iodides be-

(1) Previous paper in this series, R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

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(3) National Science Foundation Predoctoral Research Fellow.

(4) Natvar Corporation Fellow at Harvard University.

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