

left column referring to the case of equal reactivity for tertiary and secondary hydrogen abstraction, the right column to the more realistic case.<sup>19</sup> We find that with either set of values the probability that a side chain ethyl radical abstracts a secondary hydrogen,  $P_4$ , must exceed  $P_2$  greatly if the substantial proportion of ethyl groups is to be accounted for. This was already noted by Willbourn, who did not consider the decompositions of secondary and tertiary radicals, however. If  $P_4$  is made greater than 0.1, a succession of ethyl branches spaced two chain carbons apart results and simple solutions become inadequate. It can be seen qualitatively that  $P_4$  must, however, be allowed to exceed 0.1 if ethyl/butyl values of 2, as reported by Willbourn, are to be accounted for. Note that in either column of Table I,  $3P_1$  is substantially less than unity. If set equal to unity, as required by the low temperature coefficient of the vinylidene content, hydrogen abstraction would have to proceed with greater ease from a secondary than from a tertiary hydrogen radical ( $P_2 > P_3$ ,  $P_4 > P_5$ ). It would therefore appear that the low experimental activation energy for vinylidene formation together with accepted data of relative rates of secondary and tertiary hydrogen abstractions

(19) K. O. Kutschke and E. W. R. Steacie in "Vistas in Free Radical Chemistry," Pergamon Press, New York, N. Y., 1959, p. 176.

cannot be satisfied simultaneously. One possible rationalization for  $P_1$  being less than unity over the entire temperature range would, however, be provided if the activation energy for vinylidene formation in the present case were far less than that for  $\beta$ -elimination in a simple system as indicated in reaction 1. Conceivably,  $\beta$ -elimination and monomer addition to the radical which is split off is a concerted process, resulting in a lowering of the activation energy.

The data of this study, therefore, although not necessarily in disagreement with previous ideas on the origin of branching and unsaturation in high pressure polyethylene, cannot provide a quantitative confirmation for the mechanisms which have been proposed, without additional postulates which at the moment appear to be of doubtful validity. It is quite possible that these difficulties will be resolved with a more detailed knowledge of polymer structure. The conclusion that, under the conditions described, vinylidene formation is associated with the principal mechanism responsible for molecular termination is, however, independent of these uncertainties.

**Acknowledgments.**—We are indebted to C. Crofoot for the molecular weight measurements, to Dr. G. A. Mortimer for providing data on one of his samples, and to Prof. W. H. Urry for discussions.

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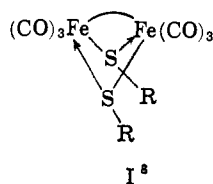
## Organosulfur Derivatives of the Metal Carbonyls. IV. The Reactions between Certain Organic Sulfur Compounds and Iron Carbonyls<sup>1</sup>

BY R. B. KING<sup>2</sup>

RECEIVED NOVEMBER 6, 1962

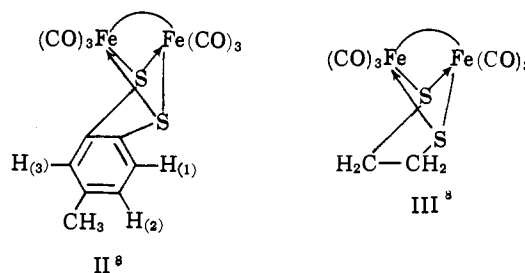
Iron pentacarbonyl was found to react with the sulfur derivatives 3,4-toluenedithiol, 1,2-ethanedithiol and bis-(trifluoromethyl)-dithietene to give the compounds  $C_7H_6S_2Fe_2(CO)_6$ ,  $C_2H_4S_2Fe_2(CO)_6$  and  $C_4F_6S_2Fe_2(CO)_6$ , respectively. Triiron dodecacarbonyl reacted with either  $(CF_3)_2S_4$  or  $(CF_2)_4S_3$  to give  $C_2F_4S_2Fe_2(CO)_6$ . These new iron complexes are red, volatile, crystalline, diamagnetic and air-stable solids. The reaction between  $C_3F_7Fe(CO)_4I$  and  $CF_3S_2Ag$  in benzene solution was found to give yellow crystalline volatile  $[C_3F_7Fe(CO)_3SCF_3]_2$ . The structures of these new compounds are discussed.

Recently a variety of organosulfur derivatives of general formula  $[Fe(CO)_3SR]_2$  (I) (R = methyl, ethyl, isopropyl, phenyl, or naphthyl)<sup>3-7</sup> have been prepared by reactions between triiron dodecacarbonyl and appropriate mercaptans, sulfides, or disulfides. In



view of the existence of these compounds it seemed of interest to synthesize related compounds such as II or III in which the two sulfur atoms are joined by a carbon chain. Such compounds might be expected to be especially readily formed and to exhibit special stability due to an effect similar to that responsible for the stabilization of various chelate derivatives.

The most obvious route for the synthesis of compounds such as II and III is the reaction between an appropriate 1,2-dithiol derivative and iron pentacar-



bonyl or triiron dodecacarbonyl. In this connection the reaction between the commercially available 3,4-toluenedithiol and iron pentacarbonyl was investigated and found to give stable, volatile red crystals of the composition  $C_7H_6S_2Fe_2(CO)_6$  expected for II. The yield was about 20% when iron pentacarbonyl was used. In order to obtain yields of this order of magnitude in the preparation of the  $[Fe(CO)_3SR]_2$  compounds where the R group does not act as a bridge between the two sulfur atoms, it is necessary to use the more reactive triiron dodecacarbonyl.

The properties of this new organosulfur derivative

(8) Recent X-ray studies on  $[Fe(CO)_3SC_2H_5]_2$  have indicated the presence of a bent iron-iron bond and a molecular geometry similar to that of  $Co_2(CO)_8$ .<sup>10</sup> The analogous compounds described in this paper undoubtedly possess a similar structure and are therefore depicted in the structures with bent iron-iron bonds.

(9) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(10) Work of O. S. Mills quoted by R. S. Nyholm, *Proc. Chem. Soc.*, 287 (1961).

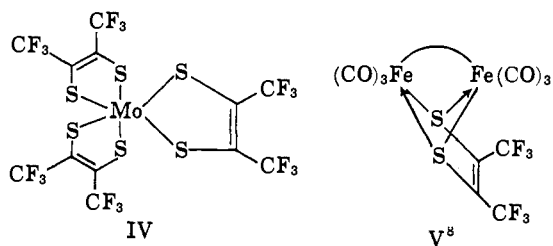
- (1) For part III see R. B. King, *Inorg. Chem.*, **2**, 641 (1963).
- (2) Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Penna.
- (3) W. Hieber and P. Spacu, *Z. anorg. Chem.*, **233**, 353 (1937).
- (4) W. Hieber and C. Scharfenberg, *Ber.*, **73**, 1012 (1940).
- (5) W. Hieber and W. Beck, *Z. anorg. Chem.*, **305**, 265 (1960).
- (6) S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960).
- (7) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

of iron carbonyl are entirely in accord with structure II. The red color, the volatility ( $\sim 80^\circ$  (0.1 mm.)), and the infrared spectrum in the carbonyl region are entirely comparable to those of the known  $[\text{Fe}(\text{CO})_3\text{SR}]_2$  compounds. The proton n.m.r. spectrum shows a sharp methyl resonance at 2.07 p.p.m. due to the three methyl protons of the 3,4-toluenedithiol system and resonances at 6.89 (two protons) and 6.39 p.p.m. (one proton) due to the aromatic protons,  $\text{H}_{(1)}$ ,  $\text{H}_{(2)}$ , and  $\text{H}_{(3)}$ . The resonance at 6.39 p.p.m. is a doublet,  $J = 8$  cycles, which would be due to either  $\text{H}_{(2)}$  split by  $\text{H}_{(1)}$  or to  $\text{H}_{(1)}$  split by  $\text{H}_{(2)}$ . The other doublet due to these protons is undoubtedly contained in the resonance at 6.89 p.p.m. but is obscured by the resonance of  $\text{H}_{(3)}$  which occurs in the same position.

It also proved possible to synthesize the compound  $\text{C}_2\text{H}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  (III) by reaction between 1,2-ethanedithiol and iron pentacarbonyl, but in this case the yield was extremely low ( $\sim 0.3\%$ ). This drastically reduced yield may be due to the lower acidity of the aliphatic mercaptan as compared with the aromatic mercaptan, 3,4-toluenedithiol. Substitution of triiron dodecacarbonyl for iron pentacarbonyl would be expected to improve the yield in the preparation of III, but the malodorous character of 1,2-ethanedithiol discouraged such attempts.

The properties of III are consistent with those of related organosulfur compounds such as II. III is also a volatile red crystalline solid with similar infrared bands in the carbonyl region. The proton n.m.r. spectrum shows a single sharp peak at 2.36 p.p.m. due to the single type of protons in the molecule. No evidence for the existence of isomers of  $\text{C}_2\text{H}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  was observed in contrast to the observation of two isomers for the compound  $[\text{Fe}(\text{CO})_3\text{SCH}_3]_2$ .<sup>11</sup>

Recently the reaction between molybdenum hexacarbonyl and the novel organosulfur derivative bis-(trifluoromethyl)-dithietene<sup>12</sup> was reported as giving the molybdenum(VI) chelate derivative  $\text{Mo}(\text{C}_4\text{F}_6\text{S}_2)_3$  (IV).<sup>1</sup> In a further investigation of the chemistry of this ligand, bis-(trifluoromethyl)-dithietene was heated with iron pentacarbonyl. From the resulting reaction mixture, a dark red volatile compound of composition  $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$  was isolated in  $\sim 50\%$  yield.

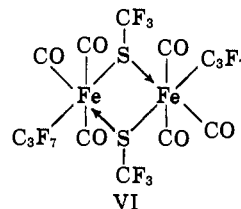


The infrared spectrum of this new iron complex shows bands in the carbonyl region similar to those of the organosulfur derivatives of iron carbonyl described above. The  $\text{F}^{19}$  n.m.r. spectrum shows only a single type of  $\text{CF}_3$  group. In view of these data, structure V, entirely analogous to II and III, is proposed for the compound  $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$ .

The existence of iron compounds containing  $\text{RS}$ -bridging groups (I), where R represents an alkyl or aryl group such as methyl, ethyl, or phenyl, made it of interest to attempt to prepare an iron carbonyl complex containing an  $\text{R}_f\text{S}$ -bridging group where  $\text{R}_f$  is a perfluoroalkyl group such as  $\text{CF}_3$  or  $\text{C}_3\text{F}_7$ . However, attempts to prepare such a compound by heating iron pentacarbonyl or triiron dodecacarbonyl with such compounds as  $\text{CF}_3\text{SSCF}_3$ ,  $\text{C}_3\text{F}_7\text{SSC}_3\text{F}_7$ ,  $(\text{CF}_3\text{S})_2\text{Hg}$  or

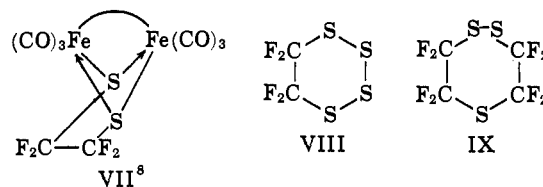
$\text{CF}_3\text{SAg}$  gave no product with the exception of a single experiment involving the reaction between  $(\text{CF}_3\text{S})_2\text{Hg}$  and  $\text{Fe}_3(\text{CO})_{12}$ . Here a deep red, very volatile compound was observed but in insufficient quantity for characterization.

As a different approach to the preparation of an iron complex with  $\text{R}_f\text{S}$ -bridging groups, the reaction between  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4$ <sup>13</sup> and  $\text{CF}_3\text{SAg}$ <sup>14</sup> was investigated. This led to the isolation of a complex of composition  $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{SCF}_3]_2$ . This new heptafluoropropyliron carbonyl complex, the first metal carbonyl complex containing  $\text{R}_f\text{S}$ -bridging groups to be isolated, is an air-stable yellow crystalline solid subliming at  $\sim 70^\circ$  (0.2 mm.) with significant decomposition. The  $\text{F}^{19}$  n.m.r. spectrum is consistent with structure VI possibly with isomers depending on the relative orientations of the  $\text{C}_3\text{F}_7$  group and the  $\text{CF}_3\text{S}$ -bridges. The spectrum is too poor to reach any definite conclusion about the existence of such isomers. This compound,  $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{SCF}_3]_2$ , may be regarded as analogous to compounds such as  $[\text{Re}(\text{CO})_4\text{SC}_6\text{H}_5]_2$ ,<sup>15,15a</sup> where the  $\text{C}_3\text{F}_7$  group replaces one of the carbonyl groups with the necessary change in the atomic number of the central metal atom. As in  $[\text{Re}(\text{CO})_4\text{SC}_6\text{H}_5]_2$ <sup>15</sup> and  $[\text{C}_5\text{H}_5\text{FeCOCH}_2\text{S}]_2$ <sup>7</sup> no metal-metal bond is necessary to account for the observed diamagnetism of  $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{SCF}_3]_2$ , which may also be considered as analogous to the compound  $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{I}]_2$ <sup>13</sup> with  $\text{CF}_3\text{S}$ -bridges replacing the iodine bridges.



The synthesis of metal carbonyl derivatives with  $\text{R}_f\text{S}$ -bridges is difficult and the compounds are thermally unstable. However, it seemed probable that compounds with a fluorocarbon residue joining the two sulfur bridges might be more stable and more readily synthesized. Therefore, the synthesis of the compound VII in which the two sulfur bridges are themselves bridged by a  $-\text{CF}_2\text{CF}_2-$  residue was attempted.

Two possible precursors to VII are the cyclic polysulfides VIII and IX, both of which may be obtained from tetrafluoroethylene and sulfur under appropriate conditions.<sup>16</sup> It was found that the reaction between either VIII or IX and triiron dodecacarbonyl gave a red,



volatile crystalline solid of composition  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$ .

The infrared spectrum of this new compound in the carbonyl region is similar to that of the compounds obtained from iron pentacarbonyl and 1,2-dithiols described above. The  $\text{F}^{19}$  n.m.r. spectrum at 56.4 Mc.

(13) R. B. King, S. L. Stafford, P. M. Treichel and F. G. A. Stone, *ibid.*, **88**, 3604 (1961).

(14) H. J. Emeléus and D. E. MacDuffie, *J. Chem. Soc.*, 2597 (1961).

(15) W. Hieber and L. Schuster, *Z. anorg. Chem.*, **285**, 205 (1956).

(15a) Recently syntheses of several analogous manganese compounds of general formula  $[\text{Mn}(\text{CO})_3\text{SR}]_2$  (R = methyl, ethyl, and *n*-butyl) have been accomplished by the reactions between the appropriate disulfides and manganese pentacarbonyl hydride: P. M. Treichel, J. H. Morris and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

(16) C. G. Krespan and W. R. Brasen, *J. Org. Chem.*, **27**, 3995 (1962).

(11) R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

(12) C. G. Krespan and B. C. McKusick, *ibid.*, **83**, 3434 (1961).

exhibits a single sharp resonance at +230 cycles relative to internal  $(\text{CFCl}_2)_2$ , indicating the presence of only one kind of fluorine atom. This is in complete agreement with what would be expected for a compound of structure VII.

It will be noted that VIII gave a 14% yield of  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  with  $\text{Fe}_3(\text{CO})_{12}$ , whereas IX gave only a 7% yield of  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  under similar reaction conditions. Moreover, VIII gave detectable amounts of  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  when heated with iron pentacarbonyl, whereas IX gave no detectable amounts of  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  when heated with iron pentacarbonyl. This greater reactivity of VIII over IX in this type of reaction is in agreement with expectations since to form  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_2(\text{CO})_6$  from VIII only sulfur-sulfur bonds need to be broken, whereas to form the same iron complex from IX carbon-sulfur as well as sulfur-sulfur bonds need to be broken. In general, the breaking of sulfur-sulfur bonds is much more facile than the breaking of carbon-sulfur bonds.

### Experimental

Infrared spectra were taken in KBr pellets and recorded on a Perkin-Elmer Infracord machine. Proton n.m.r. spectra were in general taken in carbon disulfide solution and recorded on a Varian Associates Model A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane and were reproducible to  $\pm 0.02$  p.p.m.  $\text{F}^{19}$  n.m.r. spectra were in general taken at 56.4 Mc. in dichloromethane solution. Chemical shifts are given in cycles relative to internal  $(\text{CFCl}_2)_2$ . All of the compounds reported in this paper were indicated by n.m.r. to be diamagnetic. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Bis-(trifluoromethyl)-dithietene was prepared from hexafluorobutene-2 and sulfur by the method of Krespan and McKusick.<sup>12</sup>  $\text{CF}_3\text{SAg}$  was prepared from silver(I) fluoride and carbon disulfide by the method of Emeléus and MacDuffie.<sup>14</sup> Heptafluoropropyl-iron tetracarbonyl iodide was prepared from iron pentacarbonyl and heptafluoropropyl iodide by the method of King, Stafford, Treichel and Stone.<sup>13</sup> 3,4-Toluenedithiol was purchased from Eastman Kodak Co. and 1,2-ethanedithiol from Columbia Organic Chemicals.

**Reaction between Iron Pentacarbonyl and 3,4-Toluenedithiol.**—A mixture of 1 ml. (~7 mmoles) of 3,4-toluenedithiol, 3 ml. (4.2 g., 21.5 mmoles) of iron pentacarbonyl and 50 ml. of methylcyclohexane was refluxed under nitrogen 3 hr. with magnetic stirring. The reaction mixture was allowed to cool to room temperature and then filtered. Solvent was removed from the red filtrate at ~30 mm. leaving red crystals. These were dissolved in 25 ml. of pentane and the solution cooled in a  $-78^\circ$  bath. The resulting red crystals were filtered.

Excess of 3,4-toluenedithiol was removed from the crude product by sublimation for 1.5 hr. at  $50-60^\circ$  (0.1 mm.) on to an ice-cooled probe. After the probe was cleaned, the product was isolated by sublimation at  $70-150^\circ$  (0.1 mm.) for 16 hr. and purified by resublimation at  $70-100^\circ$  (0.1 mm.) for 4 hr. giving 600 mg. (20% yield) of red crystals, m.p.  $123-124^\circ$ ; infrared spectrum: carbonyl bands at 2080(s), 2045(vs), 2030(vs), 2000(vs), and 1990(s)  $\text{cm}^{-1}$ ; other bands at 1580(w), 1453(w), 1382(vw), 1260(w), 890(w) and 820(m)  $\text{cm}^{-1}$ ; proton n.m.r. spectrum: resonances at 6.89 p.p.m. (doublet with superimposed singlet), 6.39 p.p.m. (doublet, 8 cycles separation) and 2.07 p.p.m. (sharp singlet).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_6\text{O}_6\text{S}_2\text{Fe}_2$ : C, 35.9; H, 1.4; S, 14.8; Fe, 25.8; mol. wt., 434. Found: C, 35.8; H, 1.4; S, 14.8; Fe, 25.5; mol. wt., 403 (isopiestic in chloroform).

**Reaction between Iron Pentacarbonyl and 1,2-Ethanedithiol.**—(Note: 1,2-Ethanedithiol is so malodorous that despite carrying out the experiment in a hood, an extremely vile odor was created which infected the whole laboratory.) A mixture of 16.7 ml. (18.8 g., 200 mmoles) of 1,2-ethanedithiol, 62 ml. (88.5 g., 450 mmoles) of iron pentacarbonyl and 250 ml. of methylcyclohexane was refluxed 5 hr. under nitrogen with magnetic stirring. After having been cooled to room temperature, the reaction mixture was filtered and solvent removed from the red filtrate at ~30 mm. Volatile materials were collected in a trap cooled in a  $-78^\circ$  bath in order to minimize spreading of the malodorous 1,2-ethanedithiol. A dark red liquid residue remained which was treated with 20 ml. of pentane and cooled in a  $-78^\circ$  bath. The resulting red crystals were filtered and purified further by two sublimations at  $100^\circ$  (0.25 mm.). The yield was only 200 mg. (0.27%) of red crystals, m.p.  $76-77^\circ$ ; infrared spectrum: carbonyl bands at 2080(s), 2045(vs) and 2000(vs)  $\text{cm}^{-1}$ ; other bands at 1439(w), 1420(vw), 1240(w), 1209(vw), 1113(w),

770(vw), and 736(w)  $\text{cm}^{-1}$ ; proton n.m.r. spectrum: single sharp peak at 2.36 p.p.m.

*Anal.* Calcd. for  $\text{C}_6\text{H}_4\text{O}_6\text{S}_2\text{Fe}_2$ : C, 25.8; H, 1.1; mol. wt., 372. Found: C, 25.9; H, 1.3; mol. wt., 378 (Mechrolab vapor pressure osmometer in benzene).

**Reaction between Iron Pentacarbonyl and Bis-(trifluoromethyl)-dithietene.**—A mixture of 1.0 ml. (1.6 g., 7 mmoles) of bis-(trifluoromethyl)-dithietene, 2.0 ml. (2.8 g., 14.3 mmoles) of iron pentacarbonyl and 40 ml. of methylcyclohexane was refluxed 3 hr. 15 min. under nitrogen with magnetic stirring. After the reaction period was over the reaction mixture was allowed to cool to room temperature and then in a  $-78^\circ$  bath. The dark colored crystals which separated were filtered and purified further by sublimation at  $40-100^\circ$  (1 mm.) for 1.5 hr. to give 1.56 g. (44% yield) of red-black crystals of  $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$ , m.p.  $80.5-81.5^\circ$ .

Larger quantities of  $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$  can readily be obtained by scaling up the reaction. Thus, from 7.5 g. (33 mmoles) of bis-(trifluoromethyl)-dithietene and 10 ml. (14.3 g., 73 mmoles) of iron pentacarbonyl in 100 ml. of methylcyclohexane, 8.0 g. (53% yield) of  $\text{C}_4\text{F}_6\text{S}_2\text{Fe}_2(\text{CO})_6$  was obtained; infrared spectrum: carbonyl bands at 2120(vs), 2080(vs) and 2030(vs)  $\text{cm}^{-1}$ ;  $\text{C}=\text{C}$  at 1635(m)  $\text{cm}^{-1}$ ;  $\text{C}-\text{F}$  bands at 1260(vs), 1250(vs), 1182(vs) and 1170(sh)  $\text{cm}^{-1}$ ; other bands at 882(w), 712(m) and 688(w)  $\text{cm}^{-1}$ ;  $\text{F}^{19}$  n.m.r. spectrum: single sharp peak at  $-375$  cycles relative to internal  $(\text{CFCl}_2)_2$ .

*Anal.* Calcd. for  $\text{C}_{10}\text{F}_6\text{O}_6\text{S}_2\text{Fe}_2$ : C, 23.7; H, 0.0; F, 22.5; S, 12.7; Fe, 22.1; mol. wt., 506. Found: C, 23.3; H, 0.4; F, 22.5; S, 12.9; Fe, 21.3; mol. wt., 490 (isopiestic in chloroform).

**Reaction between Heptafluoropropyliron Tetracarbonyl Iodide and Trifluoromethylthiosilver.**—A mixture of 4.64 g. (10 mmoles) of  $\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$ ,<sup>15</sup> 2.09 g. (10 mmoles) of  $\text{CF}_3\text{SAg}$ <sup>14</sup> and 50 ml. of thiophene-free benzene was stirred at room temperature for 16 hr. under nitrogen. A yellow precipitate of silver(I) iodide soon formed. The reaction mixture was filtered and the residue washed with two 20-ml. portions of dichloromethane. The solvent was removed from the combined filtrates at ~30 mm. to give yellow crystals. These were best recrystallized from hexane-dichloromethane to give 700 mg. (17% yield) of yellow crystals of  $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{SCF}_3]_2$ ; infrared spectrum: carbonyl bands at 2140(s), 2110(s) and 2090(s)  $\text{cm}^{-1}$ ; bands in the  $\text{C}-\text{F}$  region at 1325(s), 1253(s), 1233(s), 1209(s), 1187(s), 1162(s), 1151(s), 1093(s), 1089(s), 1042(m) and 1015(m)  $\text{cm}^{-1}$ ; other bands at 813(s), 760(m) and 726(s)  $\text{cm}^{-1}$ ;  $\text{F}^{19}$  n.m.r. spectrum: only a relatively weak spectrum was observed in which peaks were found at  $-2015$ ,  $-1960$ ,  $-121$ ,  $+625$ ,  $+2680$  and  $+2740$  cycles relative to  $(\text{CFCl}_2)_2$ . A better spectrum is necessary before a reasonably reliable interpretation can be given. On heating, the yellow crystals did not melt but began to darken at about  $170^\circ$ . Sublimation at  $70^\circ$  (0.25 mm.) may also be used for purification, but in this case the losses are greater.

*Anal.* Calcd. for  $\text{C}_{14}\text{F}_{20}\text{O}_6\text{S}_2\text{Fe}_2$ : C, 20.5; H, 0.0; F, 46.3; S, 7.8; Fe, 13.6; mol. wt., 820. Found (sublimed sample): C, 20.6; H, 0.5. Found (recrystallized sample): C, 20.8; H, 0.6; F, 45.1; S, 8.1; Fe, 14.0; mol. wt., 809 (Mechrolab vapor pressure osmometer in benzene).

**Reaction between  $(\text{CF}_2)_2\text{S}_4$  (VIII) and Triiron Dodecacarbonyl.**—A mixture of 4.0 ml. (~30 mmoles) of  $(\text{CF}_2)_2\text{S}_4$  (VIII), 10.0 g. (~20 mmoles) of triiron dodecacarbonyl and 250 ml. of thiophene-free benzene was refluxed under nitrogen with magnetic stirring for 3 hr. After ~1 hr. the reaction mixture appeared reddish and contained a black precipitate. After the reaction period was over the reaction mixture was allowed to cool to room temperature and then filtered by suction. Solvent was removed from the resulting red filtrate at ~30 mm. leaving a red crystalline residue. This residue was treated with ~30 ml. of pentane and the resulting dark red solution cooled in a  $-78^\circ$  bath. The red crystals which separated were filtered and dried. The crude product weighed 1.3 g. (21% yield based on  $\text{Fe}_3(\text{CO})_{12}$  and based on the removal of the extra sulfur atoms as  $\text{FeS}$ ).

The product was purified further by sublimation at  $\sim 70^\circ$  (0.5 mm.) for 2.5 hr. to give 860 mg. (13.9% yield) of dark red crystals of  $\text{C}_2\text{F}_4\text{S}_2\text{Fe}_3(\text{CO})_6$ , m.p.  $70-72^\circ$ ; infrared spectrum: carbonyl bands at 2110(s), 2070(vs) and 2030(vs)  $\text{cm}^{-1}$ ; other bands at 1222(s), 1131(w,sh), 1119(m), 1109(m), 985(s), 921(w), and 700(vw)  $\text{cm}^{-1}$ ;  $\text{F}^{19}$  n.m.r. spectrum: single sharp resonance at +230 cycles relative to internal  $(\text{CFCl}_2)_2$ .

*Anal.* Calcd. for  $\text{C}_8\text{F}_4\text{O}_6\text{S}_2\text{Fe}_3$ : C, 22.8; H, 0.0; S, 15.2; Fe, 26.7; mol. wt., 420. Found: C, 22.5; H, 0.6; S, 15.0; Fe, 27.4; mol. wt., 458 (Mechrolab vapor pressure osmometer in benzene).

**Reaction between  $(\text{CF}_2)_4\text{S}_3$  (IX) and Triiron Dodecacarbonyl.**—A mixture of 25 g. (~50 mmoles) of triiron dodecacarbonyl, 20 g. (67.6 mmoles) of  $(\text{CF}_2)_4\text{S}_3$  (IX) and 500 ml. of thiophene-free benzene was refluxed under nitrogen. The refluxing was allowed to continue for 21 hr., the green color of the  $\text{Fe}_3(\text{CO})_{12}$  gradually

becoming red but at a much slower rate than in the analogous reaction with  $(CF_2)_2S_4$ .

After 21 hr. the refluxing was discontinued and the reaction mixture allowed to cool to room temperature and filtered by gravity. Solvent was removed from the deep red filtrate at  $\sim 30$  mm. leaving a deep red liquid. This liquid was dissolved in  $\sim 50$  ml. of pentane and the solution chromatographed on a  $2 \times 60$  cm. alumina column. The single orange band was eluted with pentane and the red eluate evaporated to dryness at  $\sim 50$  mm. A red crystalline solid remained which weighed 1.67 g. (8% yield based on  $Fe_3(CO)_{12}$ ).

For further purification the product was sublimed at  $60^\circ$  (0.1 mm.) to give 1.46 g. (7% yield) of red crystals of  $C_2F_4S_2Fe_2(CO)_6$ , m.p.  $64-66^\circ$ .

The infrared and  $F^{19}$  n.m.r. spectra both indicated the product to be the same as that obtained from  $(CF_2)_2S_4$  and  $Fe_3(CO)_{12}$ . Analytical data were also in agreement with the  $C_2F_4S_2Fe_2(CO)_6$  formula. The slightly lower melting point is presumably attributable to trace amounts of impurities.

*Anal.* Calcd. for  $C_8F_4O_6S_2Fe_2$ : C, 22.8; H, 0.0; F, 18.1. Found: C, 22.7; H, 0.3; F, 17.6.

**Acknowledgment.**—The author is indebted to Dr. C. G. Krespan of the Central Research Department for helpful advice and to Dr. W. R. Brasen for generous samples of the cyclic sulfides VIII and IX.

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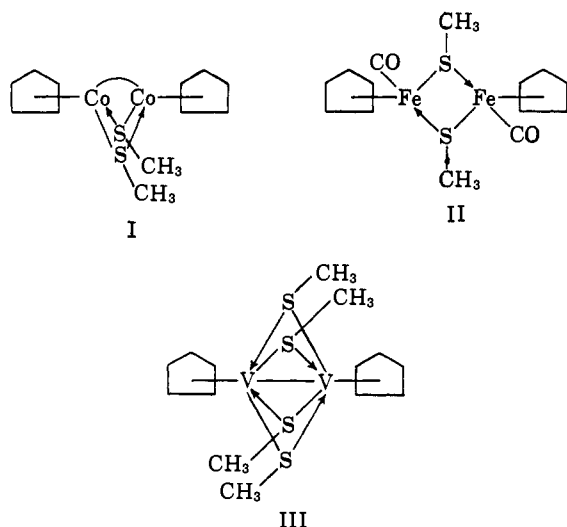
## Organosulfur Derivatives of the Metal Carbonyls. V. The Reactions between Certain Organic Sulfur Compounds and Various Cyclopentadienyl Metal Carbonyl Derivatives<sup>1</sup>

By R. B. KING<sup>2</sup>

RECEIVED DECEMBER 10, 1962

Dimethyl disulfide was found to react with  $[C_5H_5Cr(CO)_3]_2$  and  $[C_5H_5Mo(CO)_3]_2$  to give the new compounds  $(C_5H_5)_2Cr_2(CH_3S)_3$  and  $[C_5H_5Mo(CH_3S)_2]_2$ , respectively. Reactions between bis-(trifluoromethyl)-dithietene and various cyclopentadienyl metal carbonyl derivatives gave the compounds  $[C_5H_5MC_4F_6S_2]_2$  ( $M = V, Cr$  and  $Mo$ ), and the compounds  $C_5H_5MC_4F_6S_2$  ( $M = Co$  and  $Ni$ ). The structures of some of these compounds are discussed.

Recently novel compounds obtained from reactions between dimethyl disulfide and several cyclopentadienyl carbonyl complexes of transition metals were described.<sup>3,4</sup> The reaction between cyclopentadienylcobalt dicarbonyl and dimethyl disulfide gave a black solid of composition  $[C_5H_5CoCH_3S]_2$ , structure I<sup>3</sup>; the reaction between cyclopentadienyliron dicarbonyl dimer and dimethyl disulfide gave a brown-black solid of composition  $[C_5H_5FeCOCH_3S]_2$ , structure II; and the reaction between cyclopentadienylvanadium tetracarbonyl and dimethyl disulfide gave a dark brown solid of composition  $[C_5H_5V(CH_3S)_2]_2$ , apparently structure III.<sup>4</sup> The vanadium compound III is especially unusual in that it appears to have four bridging  $CH_3S$ -groups and to be the first example of a complex containing four bridging groups. In view of the unusual



structure of the vanadium compound III it seemed of interest to investigate the reactions between dimethyl

disulfide and cyclopentadienyl carbonyl derivatives of metals near vanadium in the periodic table such as chromium and molybdenum.

In an attempt to prepare the molybdenum analog, the reaction between  $[C_5H_5Mo(CO)_3]_2$  and dimethyl disulfide was investigated. Heating the two reactants for several hours in refluxing methylcyclohexane gave a deep brown reaction mixture from which a brown solid sublimable at  $160^\circ$  (0.1 mm.) could be isolated. Analyses indicated this material to be  $[C_5H_5Mo(CH_3S)_2]_2$ , corresponding to the vanadium derivative  $[C_5H_5V(CH_3S)_2]_2$ .<sup>4</sup> The proton n.m.r. spectrum of the molybdenum compound indicated it to be diamagnetic and showed a resonance at 5.57 p.p.m. attributable to the protons of the  $\pi$ -bonded cyclopentadienyl groups and a second resonance at 1.26 p.p.m. attributable to the protons of the methyl groups. The diamagnetism of the compound, also confirmed by magnetic balance measurements, indicates that the molybdenum complex is dimeric like the analogous vanadium compound, since a monomer would have an odd number of electrons and would thus be paramagnetic. Unfortunately,  $[C_5H_5Mo(CH_3S)_2]_2$  like many of the other compounds described in this paper proved to be too insoluble in organic solvents for successful determination of the molecular weight.<sup>4a</sup>

It was found that when dimethyl disulfide was heated with either  $[C_5H_5Cr(CO)_3]_2Hg$ <sup>5</sup> or  $[C_5H_5Cr(CO)_3]_2$ <sup>5</sup> in refluxing methylcyclohexane, an intense purple solution was produced from which a dark purple solid

(4a) NOTE ADDED IN PROOF.—After this paper was accepted, Treichel, Morris and Stone<sup>4b</sup> reported the reaction between cyclopentadienylmolybdenum tricarbonyl hydride and dimethyl disulfide at room temperature to give a brown crystalline material  $[C_5H_5Mo(CO)_2SCH_3]_2$ . It thus appears that cyclopentadienylmolybdenum carbonyl derivatives and disulfides can form compounds of either the types  $[C_5H_5Mo(CO)_2SR]_2$  or  $[C_5H_5Mo(SR)_2]_2$  depending on the reaction conditions. In this connection, it is of interest that cyclopentadienyltungsten tricarbonyl hydride when heated with dimethyl disulfide even to temperatures as high as  $135^\circ$  for several hours still forms significant quantities of  $[C_5H_5W(CO)_2SCH_3]_2$ ,<sup>4b,4c</sup> indicating that displacement of all of the carbonyl groups of the tungsten compound is much more difficult than the analogous reaction of the molybdenum compound.

(4b) P. M. Treichel, J. H. Morris and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

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