

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 π -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.^{10b} 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 elsewhere²⁰ 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).

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

Chemistry of the Metal Carbonyls. XV. Fluorocarbon Derivatives of Iron Carbonyl^{1,2}

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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 perfluoroalkyl chlorides to yield bis-(perfluoroalkyl)-iron tetracarbonyl compounds. Some properties of the new perfluoroalkyl 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,⁵ 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.^{5a,6} The small range

of metals known to form perfluoroalkyl derivatives recently has been extended by preparation of the two series of compounds $C_nF_{2n+1}M(CO)_5$ [$M = Mn, Re$]^{7a} and $C_3H_5Co(C_nF_{2n+1})(CO)I$ ^{7b} and the compound $(CO)_4CoCF_2CF_2Co(CO)_4$.⁸ 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).

(2) This research was supported by the United States Air Force under Contract No. AF 49(638)-518, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

(3) National Science Foundation Predoctoral Research Fellow.

(4) Natvar Corporation Fellow at Harvard University.

(5) (a) J. J. Lagowski, *Quart. Revs. Chem. Soc.*, **13**, 233 (1959);

(b) H. J. Emeléus, *J. Chem. Soc.*, 2979 (1954).

(6) (a) H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chemistry and Industry*, 1409 (1959); (b) H. C. Clark and C. J. Willis, *J. Am. Chem.*

Soc., **82**, 1888 (1960); (c) H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *ibid.*, **82**, 6228 (1960).

(7) (a) H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 763 (1960); (b) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

(8) K. F. Watterson and G. Wilkinson, *Chemistry and Industry*, 1358 (1960).

cause of the highly electronegative character of perfluoroalkyl groups. Indeed, the electronegativities of perfluoroalkyl groups are of such a magnitude^{6a} that perfluoroalkyl iodides may in some respects be regarded as *pseudo*-interhalogen compounds. It therefore seemed possible that perfluoroalkyl iodides might react directly with suitable metal carbonyls to afford perfluoroalkylmetal carbonyl iodides, provided the resulting product has a favorable coordination number for the metal, and the effective atomic number formalism is obeyed. Since iron pentacarbonyl is known to react with iodine to give iron tetracarbonyl diiodide, it seemed worthwhile to study the reaction between iron pentacarbonyl and perfluoroalkyl iodides. From this reaction two series of compounds were synthesized: perfluoroalkyliron tetracarbonyl iodides $[R_FFe(CO)_4I]$,⁹ analogous to iron tetracarbonyl dihalides; and perfluoroalkyliron tricarbonyl iodides $[(R_FFe(CO)_3I)_2]$, analogous to the large number of known metal carbonyl halides having metal-halogen-metal bridges.¹⁰ Formation of the perfluoroalkyliron compounds from perfluoroalkyl iodides and iron pentacarbonyl occurs below 100° in the absence of light, in contrast to the usual behavior of perfluoroalkyl iodides, which normally have to be irradiated with ultraviolet light or heated to temperatures near 200° before they become reactive.

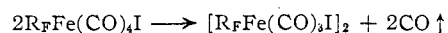
The perfluoroalkyliron tetracarbonyl iodides (Table I) are remarkably stable for compounds in which an organo-group is bonded to iron by a σ -bond. The compounds appear to be stable indefinitely under nitrogen but are decomposed in varying degrees by moisture. In the presence of moist air a clear red dichloromethane solution of $CF_3Fe(CO)_4I$ turns yellow and brown material precipitates after about 30 minutes. Under the same conditions the complex $C_2F_5Fe(CO)_4I$ showed no evidence of decomposition after 2 hr., but after standing overnight no perfluoroethyliron tetracarbonyl iodide could be recovered. On the other hand, approximately one-third of a sample of perfluoropropyliron tetracarbonyl iodide was recovered after exposure as a dichloromethane solution to air overnight. In the solid state the compounds are much less sensitive to moisture. It is interesting to note that these decompositions involve rupture of iron-iodine bonds rather than removal of perfluoroalkyl groups, since the formation of iodide ion could be demonstrated, although formation of fluorocarbons was not detected. Fluorocarbon groups are removed from perfluoroalkyliron tetracarbonyl iodides to some extent by heating the compounds with base at elevated temperatures for prolonged periods. Thus a sample of the derivative $C_2F_5Fe(CO)_4I$ with concentrated sodium hydroxide at 120° for 12 hr.

(9) The reaction between perfluoroalkyl iodides and iron pentacarbonyl was first observed in these Laboratories by Dr. T. A. Manuel. For a preliminary communication see T. A. Manuel, S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 249 (1961). (In the preliminary communication the ¹⁹F n.m.r. spectrum of the compound $C_3F_7Fe(CO)_4I$ was incorrectly expressed as c.p.s. rather than p.p.m.)

(10) For a recent review see J. Chatt, P. L. Pauson and L. M. Venanzi, Chapter 10. "Organometallic Chemistry," Am. Chem. Soc. Monograph (Ed. H. Zeiss), Reinhold Publ. Corp., New York, N. Y., 1960.

afforded a 20% yield of pentafluoroethane, as well as traces of trifluoromethane and 1,1-difluoroethylene. Such stability toward base is remarkable compared with that of perfluoroalkyl derivatives of the main group elements tin,⁶ lead,^{6a,c} silicon¹¹ and arsenic,¹² which release their perfluoroalkyl groups quantitatively under much milder conditions.

When perfluoroalkyliron tetracarbonyl iodides are heated strongly they decompose forming fluoroolefins and carbon monoxide. If the $R_FFe(CO)_4I$ derivatives are heated at temperatures below 75°, however, they decompose quantitatively according to the equation



Formation of perfluoroalkyliron tricarbonyl iodides in small quantities in the reaction of iron pentacarbonyl with perfluoroalkyl iodides is thus understandable in terms of partial decomposition of the perfluoroalkyliron tetracarbonyl iodides. Formation of the $[R_FFe(CO)_3I]_2$ derivatives by decarbonylation of the $R_FFe(CO)_4I$ compounds is analogous to the preparation of substances of the type $[M(CO)_4X]_2$ ($M = Mn, Re$) by heating manganese or rhenium pentacarbonyl halides.¹³

Consideration of the infrared spectra of the perfluoroalkyliron tetracarbonyl and tricarbonyl iodides in the carbonyl region makes it possible to assign reasonable structures to the two series of compounds. With the resolution obtainable using a spectrophotometer fitted with a calcium fluoride prism all compounds of type $R_FFe(CO)_4I$ show four carbonyl stretching bands. For example, in $C_3F_7Fe(CO)_4I$ these bands are at 2145(m), 2111(vw), 2088(vs) and 2054(m) cm^{-1} in the tetrachloroethylene solution.¹⁴ Simple group theory suggests that four carbonyl stretching bands are to be expected if the perfluoroalkyl groups and iodine atoms in octahedral $R_FFe(CO)_4I$ compounds are in *cis*-positions (I). The more symmetrical *trans*-configuration would be expected to give rise to only two infrared active carbonyl stretching modes.

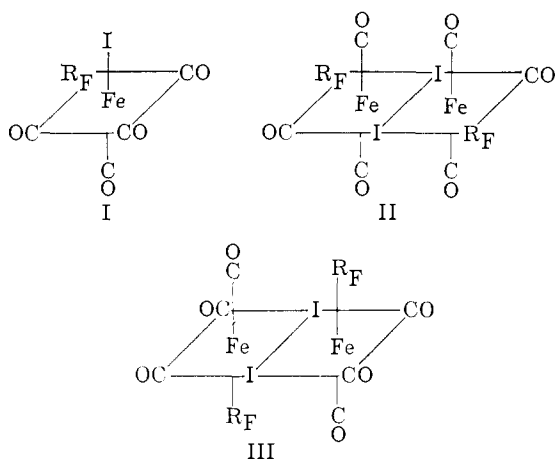
Using a spectrophotometer having a calcium fluoride prism three carbonyl stretching absorptions were observed in the infrared spectra of the dimeric perfluoroalkyliron tricarbonyl iodides. For example, in the complex $[C_2F_5Fe(CO)_3I]_2$ in tetrachloroethylene solution these bands are at 2110(m), 2075(vs) and 2053(s) cm^{-1} .¹⁴ Since none of these bands is in the region for a bridging carbonyl group and since perfluoroalkyl groups are unlikely to act as bridging groups, dimerization of perfluoroalkyliron tricarbonyl iodides is most likely to occur through iron-iodine-iron bridges, for which there is ample precedent.¹⁰ Of the numerous geometrical isomers which are possible for the perfluoroalkyliron tricarbonyl iodides only the two shown (II and III) have sufficient symmetry to show only

(11) A. M. Geyer and R. N. Haszeldine, *J. Chem. Soc.*, 1038 (1957).

(12) G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *ibid.*, 2552 (1952).

(13) (a) E. W. Abel, G. B. Hargreaves and G. Wilkinson, *ibid.*, 3149 (1958); (b) E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

(14) Further details of the infrared spectra of perfluoroalkyliron compounds will be given in a forthcoming publication by E. Pitcher and F. G. A. Stone.



three carbonyl bands in the infrared, all other isomers having lower symmetry and hence requiring more than three carbonyl stretches. A reasonable decision between II and III can be made by considering the "trans-effect" and the capability of the various ligands to partake in π -bonding.¹⁵ Since a carbonyl group is more strongly *trans* directing than an iodine atom or a perfluoroalkyl group the compound most likely to form will be that which is obtained by displacement of the carbonyl of a perfluoroalkyliron tetracarbonyl iodide (I) which is opposite another carbonyl, rather than a carbonyl group opposite a perfluoroalkyl group or an iodine atom. These considerations suggest that the structure of the perfluoroalkyliron tricarbonyl iodide dimers will be III rather than II.

In addition to the perfluoroalkyliron carbonyl iodides one other fluorocarbon derivative of iron has been described, being formed by heating tetrafluoroethylene with iron carbonyls. This compound was actually the first fluorocarbon derivative of any transition metal to be reported, although it was originally formulated as bis-(tetrafluoroethylene)-iron tricarbonyl, being regarded as a novel variety of olefin complex.¹⁶ However, an independent study of the reaction between iron carbonyls and tetrafluoroethylene led to assignment of a different stoichiometry to this fluorocarbon-iron compound, and it was shown on the basis of chemical and spectroscopic properties to have a structure with four CF_2 groups and an iron atom in a heterocyclic ring, a structure also supported by preliminary results of an X-ray diffraction study.¹⁷ Existence of the stable compound $(\text{CF}_2)_4\text{Fe}(\text{CO})_4$ suggested that it should be possible to prepare compounds of the type $(\text{R}_F)_2\text{Fe}(\text{CO})_4$ and that such iron carbonyl derivatives should be quite stable. This would be of special interest since the analogous compounds $\text{R}_2\text{Fe}(\text{CO})_4$ are not known, attempts¹⁸ to synthesize $(\text{CH}_3)_2\text{Fe}(\text{CO})_4$ by a similar method to that used to prepare the unstable cobalt compound $\text{CH}_3\text{Co}(\text{CO})_4$ ¹⁹ giving

negative results. A possible route to bis-(perfluoroalkyl)-iron tetracarbonyl derivatives, treatment of $\text{Na}_2\text{Fe}(\text{CO})_4$ with perfluoroacyl chlorides, was suggested by the method of synthesis of $\text{R}_F\text{M}(\text{CO})_5$ [$\text{M} = \text{Mn, Re}$] compounds.^{7a} In extending this kind of chemistry to iron a difficulty arises in that although the anion $\text{Fe}(\text{CO})_4^{-2}$ has been known for many years, all syntheses of its salts, *e.g.*, $\text{Na}_2\text{Fe}(\text{CO})_4$, have involved the use of aqueous, alcoholic or liquid ammonia media, solutions unsuitable for reactions with acid chlorides. This difficulty was circumvented by forming $\text{Na}_2\text{Fe}(\text{CO})_4$ in tetrahydrofuran. When triiron dodecacarbonyl is treated with sodium dispersion in tetrahydrofuran, the intense green color of the carbonyl rapidly turns to red and finally brown. Treatment of the tetrahydrofuran solutions with perfluoropropionyl chloride or perfluorobutyryl chloride led to an exothermic reaction, with evolution of carbon monoxide. The new compounds $(\text{C}_2\text{F}_5)_2\text{Fe}(\text{CO})_4$ and $(\text{C}_3\text{F}_7)_2\text{Fe}(\text{CO})_4$ were recovered from these reactions, the intermediate perfluoroacyliron carbonyls not being isolated. These new bis-(perfluoroalkyl)-iron compounds are physically similar to the heterocyclic iron complex $(\text{CF}_2)_4\text{Fe}(\text{CO})_4$ mentioned above, being exceedingly volatile solids, which show three carbonyl bands in their infrared spectra under the resolution obtainable with a calcium fluoride prism. Bis-(perfluoroethyl)-iron tetracarbonyl sublimes readily at 25° (0.1 mm.) and shows carbonyl bands at 2151(w), 2098(s,d), 2080(m,d) cm^{-1} (tetrachloroethylene solution).¹⁴ Like the perfluoroalkyliron tetracarbonyl iodides, bis-(perfluoroalkyl)-iron tetracarbonyl compounds are hydrolyzed by base only with difficulty. Thus upon heating bis-(perfluoroethyl)-iron tetracarbonyl with 20% potassium hydroxide solution for 3 hr. at 60° only a trace of pentafluoroethane was obtained. Hydrolysis of bis-(perfluoroethyl)-iron tetracarbonyl with concentrated hydrochloric acid for 12 hr. at 60° leads to about a 15% removal of C_2F_5 groups as pentafluoroethane.

All perfluoroalkyliron carbonyl compounds undergo a fluoride shift on strong heating, with formation of fluoro-olefins and release of carbon monoxide. When bis-(perfluoroethyl)-iron tetracarbonyl is heated at 100° a mixture of the two perfluorobutenes $\text{CF}_3\text{CF}:\text{CFCF}_3$ and $\text{CF}_3\text{CF}_2\text{CF}:\text{CF}_2$ is produced. The pyrolysis of $(\text{CF}_2)_4\text{Fe}(\text{CO})_4$ to afford perfluorocyclobutene quantitatively⁹ suggests that shift of an α -fluorine is preferred to a β -shift in the decomposition of fluoroalkyl-iron groups. Thus we might expect the carbene $:\text{CF}_2\text{CF}_3$ to be formed from pyrolysis of a perfluoroethyl-iron compound. Pyrolysis in the presence of excess of tetrafluoroethylene gives essentially the same mixture of butenes. These reactions are under further study.

Pyrolysis of perfluoromethyliron tetracarbonyl iodide affords tetrafluoroethylene, together with lesser amounts of perfluoropropene. The latter may have been produced *via* perfluorocyclopropane as an intermediate, formed by combination of some of the tetrafluoroethylene with the difluorocarbene, $:\text{CF}_2$. Support for this idea comes from

(15) (a) J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955); (b) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

(16) K. F. Watterson and G. Wilkinson, *Chemistry and Industry*, 991 (1959).

(17) Results of R. Mason quoted by K. F. Watterson and G. Wilkinson in reference 8.

(18) G. Braun, Thesis, Technischen Hochschule, München, 1960.

(19) W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

TABLE I
 PERFLUORO-ORGANOIRON COMPOUNDS

Compound	M.p., °C.	Carbon, %		Fluorine, %		Iodine, %		Iron, %		CO groups ^a		Mol. wt. ^b	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CF ₃ Fe(CO) ₄ I	91-94 dec.	16.5	16.2	15.6	15.5	34.9	34.8	15.4	15.5	4.0	3.9	364	350
C ₂ F ₅ Fe(CO) ₄ I	15-16 ^c	17.4	17.6	22.9	22.7	30.7	30.9	13.5	13.2	4.0	4.0
C ₃ F ₇ Fe(CO) ₄ I	69-70	18.1	18.3	28.6	28.9	27.4	27.6	12.1	12.2	4.0	4.0	464	480
[C ₂ F ₅ Fe(CO) ₃ I] ₂	110-112 dec.	15.5	15.3	24.6	24.3	32.9	32.8	14.5	14.8	3.0	3.0	772	760
[C ₃ F ₇ Fe(CO) ₃ I] ₂	140-142 dec.	15.6	16.0	30.5	29.9	29.1	28.8
(C ₂ F ₅) ₂ Fe(CO) ₄	62-63.5	23.6	23.8	46.8	46.5	13.8	13.9	4.0	3.8	406	428
(C ₃ F ₇) ₂ Fe(CO) ₄	88-90	23.7	23.9	52.6	52.4	11.1	11.3	4.0	4.0	506	501

^a Determined by heating weighed samples with excess of iodine at 150° and measuring carbon monoxide evolved. ^b Isopiestic method. ^c Incorrectly listed in ref. 9 as 105-106°.

the observation that when perfluoromethyliron tetracarbonyl iodide is heated at lower temperatures (100°) in the presence of tetrafluoroethylene, perfluorocyclopropane is formed, and when heated in the presence of ethylene, 1,1-difluorocyclopropane is produced. Although other sources of difluorocarbene are known, use of perfluoromethyliron tetracarbonyl iodide may have some advantages, and the subject is under further investigation.

Recently the reaction between perfluoroalkyl chloride and the salt NaMn(CO)₅ has been investigated and found to yield a compound of composition C₃F₅Mn(CO)₅.^{7a} The ¹⁹F magnetic resonance spectrum of this compound established that the C₃F₅ moiety present was a perfluoropropenyl group and not a perfluoroalkyl group as might be expected. In view of this interesting rearrangement it seemed worthwhile to investigate the reaction of perfluoroalkyl chloride with sodium derivatives of other metal carbonyls. It was found that the sodium salt of cyclopentadienyliron dicarbonyl reacted with perfluoroalkyl chloride to produce an orange-yellow solid of composition C₅H₅Fe(CO)₂C₃F₅. Both the infrared and the ¹⁹F n.m.r. spectra of this complex showed it to be a perfluoropropenyl derivative. Thus the iron compound, in carbon disulfide solution, showed a band at 1645 cm.⁻¹ in the C=C stretching region; perfluoropropenylmanganese pentacarbonyl has a corresponding band at 1647 cm.⁻¹. The positions of these bands are as expected for the degree of fluorine atom substitution at the double bond²⁰ and from observations of C=C stretching frequencies in perfluorovinylmetal compounds²¹ and are significantly shifted from the observed position (1789 cm.⁻¹) in perfluoroalkyl chloride. The ¹⁹F magnetic resonance spectrum, as in the case of the manganese compound,^{7a} showed a 3:1:1 ratio of intensities, rather than the 2:1:1:1 ratio of peak intensities expected for a perfluoroalkyl group σ-bonded to a metal.

Experimental²²

Infrared spectra were recorded using a Perkin-Elmer Model 21 double-beam spectrophotometer. Fluorine n.m.r. spectra were recorded at 56.4 megacycles in tetrahydrofuran solution, with trichlorofluoromethane as an internal stand-

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen, London, 1958, p. 42.

(21) S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, **17**, 412 (1961).

(22) Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institut für Kohlenforschung, Mülheim, Germany, and by the Schwarzkopf Microanalytical Laboratories, Woodside New York.

ard, using a Varian Model 4300B high-resolution spectrometer fitted with a super stabilizer.

Triiron dodecacarbonyl was prepared essentially by the same procedure as described elsewhere,²³ except that use of bromine was avoided, manganese dioxide being prepared by treating potassium permanganate with an excess of 25% ethanol. Perfluoroacyl chlorides and perfluoroalkyl iodides were commercial samples.²⁴ Perfluoroalkyl chloride was prepared by dechlorination of the halide ClF₂C-CFCl-CF₂Cl with mossy zinc in absolute ethanol. Cyclopentadienyliron dicarbonyl was prepared as described elsewhere.²⁵ Tetrahydrofuran was freshly distilled over lithium aluminum hydride before use.

Preparation of Perfluoroalkyliron Tetracarbonyl Iodides (I).—In the earlier work⁹ the reaction between perfluoroalkyl iodides and iron pentacarbonyl was carried out in a solvent at normal pressures under nitrogen. The method described here gives the compounds in much better yield.

Iron pentacarbonyl (12 ml., ca. 85 mmoles) and perfluoropropyl iodide (27 g., 91 mmoles) were placed in a 150-ml. steel bomb, which was evacuated and then heated at 70° for 15 hr. After cooling, carbon monoxide was vented and the bomb was rinsed with portions of dichloromethane until the rinsings were colorless. All operations were carried out with minimum exposure to air. Dichloromethane was removed at reduced pressure (100 mm.) leaving orange solid. Sublimation at 30° (1 mm.) onto a 0° probe gave 31.5 g. (80% yield based on iron pentacarbonyl taken) of orange red C₃F₇Fe(CO)₄I (Table I). Continued sublimation at 110° (0.1 mm.) gave 240 mg. of pale orange [C₃F₇Fe(CO)₃I]₂ (Table I).

In an analogous manner, the perfluoroethyliron carbonyl iodides (Table I) were obtained from 14 ml. (ca. 100 mmoles) of iron pentacarbonyl and 27 g. (110 mmoles) of perfluoroethyl iodide heated in the bomb at 65° for 14 hr. Removal of dichloromethane used to rinse out the bomb left a dark red liquid which readily sublimed at 25° (1 mm.) onto a 0° probe, forming dark red crystals. In this manner 20.9 g. (50% yield) of C₂F₅Fe(CO)₄I was obtained. Further sublimation at 90° (0.1 mm.) gave 380 mg. of orange-red [C₂F₅Fe(CO)₃I]₂.

Perfluoromethyliron tetracarbonyl iodide (2.8 g., 6% yield), subliming at 35° (0.1 mm.), was obtained by heating iron pentacarbonyl (20 ml., ca. 140 mmoles) with perfluoromethyl iodide (22 g., 155 mmoles) in a bomb at 70° for 100 hr.

Formation of Perfluoroalkyliron Tricarbonyl Iodides (III) from Perfluoroalkyliron Tetracarbonyl Iodides (I).—A 0.81-g. (1.9 mmoles) sample of perfluoroethyliron tetracarbonyl iodide was sealed in an evacuated reaction bulb and heated at 50° for 21 hr. On opening the bulb 40 cc.²⁶ (1.8 mmoles) of carbon monoxide was recovered, as would be expected in the formation of a compound of type III from a complex of type I. Solid material in the bulb was removed with dichloromethane and sublimed. The infrared spectrum and melting point of the sublimate showed it to be identical with the dimer obtained in the original synthesis.

In a parallel experiment, a sample (3.55 g., 7.65 mmoles) of perfluoropropyliron tetracarbonyl iodide was heated in

(23) W. Hieber, *Z. anorg. Chem.*, **204**, 165 (1932); W. Hieber and G. Brendel, *ibid.*, **289**, 324 (1957).

(24) From Columbia Organic Chemicals, Columbia, South Carolina.

(25) B. F. Hallam, O. S. Mills and P. L. Pauson, *J. Inorg. Nucl. Chem.*, **1**, 313 (1955).

(26) Throughout this paper the term cc. refers to volume at S.T.P.

an evacuated bulb at 75° for 22 hr. On opening the bulb, carbon monoxide (168 cc., 7.50 mmoles) and perfluoropropyliron tricarbonyl iodide dimer were obtained.

Bis-(perfluoroalkyl)-iron Tetracarbonyls.²⁷—A mixture of triiron dodecacarbonyl (17 g., 33 mmoles) and 50% sodium dispersion in mineral oil (9.2 g., 0.2 mole of sodium)²⁸ was stirred for 12 hr. under nitrogen in 500 ml. of tetrahydrofuran in a 1-liter three-necked flask. During the last 90 minutes of the reaction the mixture was refluxed. A Dry Ice condenser then was attached to the reaction flask and the mixture was stirred with pentafluoropropionyl chloride (36.9 g., 0.2 mole) for 90 minutes and then heated at 50° for 3 hr., carbon monoxide evolution occurring. Volatile material was removed (20 mm.), and the brown residue obtained was extracted with dichloromethane. After filtration the dichloromethane was removed (20 mm.) and the residual oil was distilled (4 mm.) against a Vigreux column with the pot temperature slowly rising to 150°. Yellow crystals which collected in the column were removed with dichloromethane. Dichloromethane was evaporated from the resulting solution (20 mm.), and the product was sublimed at 25° (0.1 mm), giving 5.45 g. (13% yield) of $(C_2F_5)_2Fe(CO)_4$ (Table I) as a very pale yellow solid.

Bis-(perfluoropropyl)-iron tetracarbonyl (Table I) was obtained (15% yield) as very pale yellow crystals subliming at 25° (0.1 mm.), by a similar procedure.

Pyrolysis of Perfluoroalkyliron Compounds. (a) $(C_2F_5)_2Fe(CO)_4$.—A 342.0-mg. (0.843 mmole) sample was heated in an evacuated bulb at 100° for 10 hr. Fractionation of the gaseous products gave 64.5 cc. (85% of theor.) of carbon monoxide and 19 cc. (0.848 mmole) of a mixture of the fluorolefins $CF_3CF_2CF_2CF_2$ and $CF_3CF_2CF_2CF_2$ (identified spectroscopically).

Pyrolysis of $(C_2F_5)_2Fe(CO)_4$ (0.369 g., 0.911 mmole) in the presence of tetrafluoroethylene (100 cc., 4.47 mmoles) also was studied. After 16 hr. at 100°, 98% of the tetrafluoroethylene was recovered. The bulb was re-sealed and heated at 120° for 6 hr. Fractionation in the high vacuum system afforded 78 cc. of carbon monoxide (95% of theor.), 75.2 cc. of C_2F_4 (identified spectroscopically) and 19.6 cc. of a mixture of $CF_3CF_2CF_2CF_2$ and $CF_2CF_2CF_2CF_2$ (identified spectroscopically). If tetrafluoroethylene had not entered into reaction only 10.2 cc. of the perfluorobutene mixture could have formed. The volume of perfluorobutenes produced (19.6 cc.) is very close to that expected (20.4 cc.) if the carbenes formed all reacted with tetrafluoroethylene.

(b) $C_3F_7Fe(CO)_4I$.—A 0.661-g. (1.42 mmoles) sample was heated in a sealed bulb at 180° for 48 hr. In addition to carbon monoxide, 3 cc. of perfluoropropene (identified spectroscopically) was recovered.

(c) $CF_3Fe(CO)_4I$.—A 0.344-g. (0.94 mmole) sample was heated at 180° for 96 hr. On opening the reaction bulb carbon monoxide was removed, 5 cc. of gas condensing at -196°. This was shown by its infrared spectrum to be principally tetrafluoroethylene containing a little perfluoropropene.

Infrared Spectra.—Using carbon disulfide solutions and sodium chloride optics the various perfluoro-organoiron compounds were observed to have infrared bands in the C-F and C-C stretching regions as follows:

(27) For a preliminary mention of compounds of this type see R. B. King, P. M. Treichel and F. G. A. Stone, *Proc. Chem. Soc.*, 69 (1961).

(28) Sodium amalgam may be used instead of sodium dispersion.

(a) $CF_3Fe(CO)_4I$.—1055(vs); 705(w) cm^{-1} . (b) $C_2F_5Fe(CO)_4I$.—1303(m); 1192, 1188(s); 1045(m); 915(m); 727(w) cm^{-1} . (c) $C_3F_7Fe(CO)_4I$.—1322(m); 1228(s); 1201(s); 1160(m); 1098(m); 1036(m); 813(m); 725(s); 665(w) cm^{-1} . (d) $[C_2F_5Fe(CO)_3]_2$.—1301(s); 1185, 1172(vs); 1048, 1024(m); 906(s); 727(m) cm^{-1} . (e) $[C_3F_7Fe(CO)_3]_2$.—1518(m); 1318(m); 1224(s); 1200(s); 1158(m); 1093(m); 806(m); 721(s) cm^{-1} . (f) $(C_2F_5)_2Fe(CO)_4$.—1300(s); 1205(s); 1182(vs); 1100(s); 1059(m); 1010(m); 910(m); 894(s); 757(s) cm^{-1} . (g) $(C_3F_7)_2Fe(CO)_4$.—Tetrachloroethylene solution. 1602 (w); 1321(s); 1228(s); 1200(s); 1159(m); 1058(w); 1002(w) cm^{-1} .

Reaction between the Sodium Salt $C_5H_5Fe(CO)_2Na$ and Perfluoroalkyl Chloride.—Cyclopentadienyliron dicarbonyl dimer (12.4 g., 35 mmoles) was stirred with an excess (0.1 g. atom) of 1% sodium amalgam in 300 ml. of tetrahydrofuran for 12 hr. under nitrogen. The red-brown color of the cyclopentadienyliron dicarbonyl dimer soon disappeared. Excess amalgam was removed, and the resulting solution was treated with perfluoroalkyl chloride (12.8 g., 77 mmoles) at 0°, using a Dry Ice cooled condenser to prevent loss of perfluoroalkyl chloride. After an hour at 0° the mixture was kept at 25° for an additional hour and then heated at 60° for 15 hr. Solvent was then removed (20 mm.) and the resulting sticky brown residue was extracted with benzene. Filtration of the extracts and evaporation of solvent (20 mm.) gave another sticky brown residue. This was dissolved in pentane (100 ml.) and the solution was chromatographed on alumina. The chromatogram was developed with benzene, two bands being observed. The first band, yellow in color, proved to be $C_5H_5Fe(CO)_2C_2F_5$, followed by a more strongly adsorbed red-brown band of cyclopentadienyliron dicarbonyl dimer. Benzene was removed from the yellowish eluate (20 mm.) leaving a yellow liquid which soon crystallized to a yellow-orange solid (1.0 g., 4.6% yield based on cyclopentadienyl-iron dicarbonyl dimer). Analytical samples were obtained by subliming twice at 40° (0.1 mm.) onto a probe cooled to 0°. The yellow-orange crystals (m.p. 69.5–70.5°) so obtained are readily soluble in organic solvents.

Anal. Calcd. for $C_{10}H_5F_5O_2Fe$: C, 39.0; H, 1.62; F, 30.85; Fe, 18.2; mol. wt., 308. Found: C, 39.1; H, 1.8; F, 31.1; Fe, 18.5; mol. wt., 307.

The infrared spectrum of the compound (carbon disulfide solution) shows strong carbonyl bands at 2040 and 1995 cm^{-1} (NaCl optics). Other principal bands occur at 1645(m), 1320(s), 1264(w), 1185(s), 1124(s), 1055(m), 1015(w), 844(m), 812(m) and 678(s) cm^{-1} . Throughout the region 1600–650 cm^{-1} , except for the band at 844 cm^{-1} , the infrared spectrum closely matches the spectrum of σ -perfluoropropenyilmanganese pentacarbonyl.^{7a} The band in the iron compound at 844 cm^{-1} is due to the cyclopentadienyl group, which in cyclopentadienyliron dicarbonyl iodide occurs at 830 cm^{-1} .

The ¹⁹F n.m.r. spectrum of $CF_3CF_2CFFe(CO)_2C_5H_5$ shows peaks of relative intensity 3:1:1 centered at 66 p.p.m. (quadruplet), 86 and 166 p.p.m.; the latter two absorptions are doublets of quadruplets with 135 cycle separations in the doublets. In the manganese compound $C_3F_5Mn(CO)_5$ corresponding resonances occur at 67, 95 and 164 p.p.m., and the fine structure is similar.⁷ Assignments of these absorptions and details of the fine structure of the spectra will be discussed in detail elsewhere.²⁹

(29) E. Pitcher and F. G. A. Stone, *Spectrochimica Acta*, in press.