Metal Carbonyl Chemistry. Part XXVI.[1] Preparation, Spectroscopic Properties, and Mode of Decomposition of some Halogenoethylene Complexes of Tetracarbonyliron, and the Reaction of Nonacarbonyldi-iron with Iodotrifluoroethylene[2]

By **Roy Fields, Graham L. Godwin,** and **Robert N. Haszeldine,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Nonacarbonyldi-iron reacts under very mild conditions with a range of halogenoethylenes to give complexes of the form $[(olefin)Fe(CO)_4]$ [olefin = $CH_2{:}CHF$, $CH_2{:}CF_2$, $CHF{:}CF_2$, $CHBr{:}CF_2$, $CHCl{:}CF_2$, $CF_3{\cdot}CF{:}CF{\cdot}CF_3$, $CF_3{\cdot}CH{:}CH{\cdot}CF_3$ $(CF_3)_2C{:}C(CF_3)_2$, $CCl_2{:}CCl_2$, *etc.*]. Thermal decomposition gives the original olefin and pentacarbonyliron; traces of the geometric isomer of the olefin {*e.g. cis*-$CF_3{\cdot}CH{:}CH{\cdot}CF_3$ from the complex [(*trans*-$CF_3{\cdot}CH{:}CH{\cdot}CF_3$)$Fe(CO)_4$]} may arise *via* an intermediate zwitterion in which rotation about the original double-bond is possible. The spectroscopic properties of the complexes are more in accord with the ' ferracyclopropane ' model structure than the ' complexed olefin ' structure.

Trifluoroiodoethylene reacts anomalously with nonacarbonyldi-iron to give a dimer $[\{(C_2F_3I)Fe(CO)_4\}_2]$, of unknown structure, and a low yield of tetracarbonyliodo(trifluorovinyl)iron.

FLUORO-OLEFIN complexes $[(olefin)Fe(CO)_4]$ of tetracarbonyliron have been prepared [3] by the photochemical reaction of pentacarbonyliron or, in two cases, of nonacarbonyldi-iron with polyfluoro-olefins. Complexes with other olefins [olefin = (*e.g.*) C_2H_4,[4] maleic acid,[5] dimethyl fumarate,[5,6] $CH_2{:}CHCN$,[7] or $CH_2{:}CHCl$ [8]] have also been prepared by thermal or photochemical methods. In contrast to the fluoro-olefin complexes, the latter compounds show i.r. bands attributable to a co-ordinated double-bond, and are usually considered to involve σ-donation of π-electron density from the olefin to iron as the important factor in bond formation. We report here the preparation under very mild conditions of a series of halogenoethylene complexes which forms a link between the polyfluoro-olefin complexes and the other olefin complexes.

Preparation of the Complexes.—Although trifluoroethylene is reported [9] not to react with iron carbonyls at temperatures up to 150 °C, when a mixture of the olefin, light petroleum, and nonacarbonyldi-iron was allowed to warm to room temperature from −196 °C in the dark the yellow solution obtained after a few hours indicated that some reaction was occurring, and during a month at room temperature the nonacarbonyldi-iron disappeared to give pentacarbonyliron and tetracarbonyl(trifluoroethylene)iron in good yield. Bromotrifluoroethylene also reacted

$$CHF{:}CF_2 + [Fe_2(CO)_9] \longrightarrow [Fe(CO)_5] + \underset{57\%}{[(CHF{:}CF_2)Fe(CO)_4]}$$

cleanly in the dark with nonacarbonyldi-iron to give the olefin complex which had previously been prepared rather more rapidly (1 day *vs.* 6 days) under u.v. irradiation with pentacarbonyliron or nonacarbonyldi-iron. The dark reaction with 1,1-dichlorodifluoroethylene also gave the known olefin complex in fair yield, but hexafluoropropene, which readily forms tetracarbonyl(hexafluoropropene)iron under u.v. irradiation with pentacarbonyliron or with nonacarbonyldi-iron, failed to react appreciably with nonacarbonyldi-iron in the dark at room temperature, and less than 2% of the complex was formed under these conditions during ten months. Fluoro-olefins thus show a wide range of reactivity towards nonacarbonyldi-iron, and the reactions of some further fluoro-olefins were investigated under a range of conditions in order to find the mildest conditions compatible with efficient complex formation. The complexes, and suitable conditions for their formation, are given in Table 1. With the exception of the olefins mentioned above, and the probable exception of perfluoro-2,3-dimethylbut-2-ene, for which the optimum reaction time was not established, longer reaction time, or more powerful or higher energy irradiation than shown in Table 1, led to lower yields; decomposition of the complex was usually accompanied by formation of carbon monoxide, which was absent in the clean reactions, and unidentified involatile material which was usually insoluble in common organic solvents. Similar material was also obtained when some of the isolated complexes were allowed to decompose (see also Table 2).

The nature of the decomposition products found [3] after u.v. irradiation of tetrachloroethylene and pentacarbonyliron suggested that a complex had been formed but had decomposed under further irradiation. Attempts were therefore made to intercept the complex by the reaction of the olefin with nonacarbonyldi-iron. No reaction was

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[9] H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2738.

evident at 18 °C after $2\frac{1}{2}$ h in the dark or under irradiation from a tungsten lamp, but a low yield of tetracarbonyl(tetrachloroethylene)iron was isolated after irradiation at 40 °C for 2 h. Longer reaction times even at room temperature led only to decomposition products similar to those obtained previously.[3] In contrast, perfluoro-2,3-dimethylbut-2-ene, prepared[10] by the high temperature reaction of perfluorobut-2-yne with trifluoroiodomethane, reacted only slowly with nonacarbonyldi-iron even under u.v. irradiation, and the complex gave no indication of any mode of decomposition other than reversal of its formation.

TABLE 1

Preparation of $[(\text{olefin})Fe(CO)_4]$ complexes

Olefin	Conditions [a]	Time	Yield (%) [b]	M.p. or b.p. (t/°c)	Found (%) C	Found (%) H	Required (%) C	Required (%) H
$CHF{:}CF_2$	A	33 days	57	15	28.5	0.7	28.8	0.4
$CH_2{:}CF_2$	B	14 h	37	30/5 mmHg	31.7	1.0	31.0	0.9
$CH_2{:}CHF$	B	19 h	6	27/4 mmHg	34.9	1.6	33.6	1.4
$CF_3{\cdot}CH{:}CH_2$	B	9 h	53	41/3 mmHg	31.0	1.2	31.8	1.1
$CHBr{:}CF_2$	B [c]	7.5 h	21	32/1 mmHg	22.8	0.3	23.15	0.3
$CHCl{:}CF_2$	B [c]	23 h	49	38/3 mmHg	27.2	0.4	27.0	0.4
$CFBr{:}CF_2$	A [c]	6 days	30	27/4 mmHg [d]				
$CF_2{:}CF_2$	A	39 days	Trace [e]					
$CF_3{\cdot}CF{:}CF_2$	A [c]	10 months	<2					
$(CF_3)_2C{:}C(CF_3)_2$	C	7 days	6 [f]	46 (decomp.)	25.9	0.3	25.6	0.0
$CF_2{:}CBr_2$	B [c]	19.5 h	2	50	17.8	0.8	18.5	0.0
$CF_2{:}CCl_2$	A	16 days	40	29 [g]				
$CCl_2{:}CCl_2$	B [h]	2 h	<1	41				

[a] Nonacarbonyldi-iron, an excess of olefin, and light petroleum or n-hexane solvent: A, in the dark at room temperature; B, irradiation with a 300 W tungsten filament lamp; C, irradiation with a Hanovia UVS 500 medium-pressure arc. [b] Based on initial nonacarbonyldi-iron. [c] No solvent. [d] Ref. 3 gives b.p. 27 °C/4 mmHg. [e] Tetracarbonyl(octafluorotetramethylene)iron (4%) also isolated. [f] 78% Based on nonacarbonyldi-iron consumed. [g] Ref. 3 gives m.p. 30 °C. [h] At 40 °C, no solvent.

Perfluorobut-2-ene (a 3 : 1 mixture of *trans*- and *cis*-isomers) gave a white solid complex with i.r. and ^{19}F n.m.r. spectra corresponding to those reported briefly[11] for the complex formed in ' low and highly erratic yield ' by u.v. irradiation of pentacarbonyliron with these olefins, and a lower yield of a yellow liquid complex, separated with difficulty from the crystals, in combined 59% yield. Pyrolysis experiments suggest strongly that the crystalline complex is that with the CF_3 groups *trans*, and this is in accord with the greater shielding of the CF_3 signals in the ^{19}F spectrum of the crystalline complex, and also with the recovery of an approximately 3 : 1 olefin ratio from an experiment in which only a small excess of olefin over nonacarbonyldi-iron was used. Pure *trans*-1,1,1,4,4,4-hexafluorobut-2-ene also gave a low-melting solid complex in which the CF_3 groups apparently remained *trans*. Unequivocal assignment of the configuration of this and of the solid complex from perfluorobut-2-ene is, however, not possible without *X*-ray diffraction studies of the complexes themselves.

2,3-Dichlorotetrafluoropropene unexpectedly failed to give any identifiable complex with pentacarbonyliron, nonacarbonyldi-iron, or combinations of the two under any conditions investigated (in the dark at temperatures from 23 to 100 °C, irradiation with tungsten filament or medium-pressure mercury arc); the olefin was recovered almost quantitatively and carbon monoxide (up to 15%) was the only identifiable product. Tetracyanoethylene displaced 92% of the carbon monoxide from nonacarbonyldi-iron during 43 days in the dark at room temperature, but the solid black product remained unidentified. In none of these reactions was any trace found of a five-membered heterocycle analogous to tetracarbonyl(octafluorotetramethylene)iron, which is formed in comparable reactions with tetrafluoroethylene (see Table 1 and refs. 3, 9, and 12). In contrast, perfluorobut-2-yne and nonacarbonyldi-iron or pentacarbonyliron reacted slowly in the dark at room temperature, but gave only the known[13] tricarbonylcyclopentadienonetetrakis(trifluoromethyl)-iron, and no mono-acetylene complex could be intercepted.

Stability.—The complexes show a wide variation in stability. Solid tetracarbonyl(perfluoro-2,3-dimethylbut-2-ene)iron is stable for several days in air at room temperature, and tetracarbonyl(perfluorobut-2-ene)iron and tetracarbonyl(trifluoroethylene)iron are stable under nitrogen at room temperature for several days. In contrast, tetracarbonyl(fluoroethylene)iron and tetracarbonyl(1,1-difluoroethylene)iron decomposed rapidly under nitrogen at room temperature, forming dodecacarbonyltri-iron, and were difficult to purify.

Table 2 shows the conditions under which some of the complexes decomposed *in vacuo* in a sealed tube, and the products isolated. All the evidence suggested that the complexes formulated as $[(trans\text{-}CF_3CH{:}CH{\cdot}CF_3)Fe(CO)_4]$ and $[(cis\text{-}CHF{:}CF{\cdot}CF_3)Fe(CO)_4]$ were pure, and the identification amongst the pyrolysis products of small amounts of the geometric isomers of the olefins may

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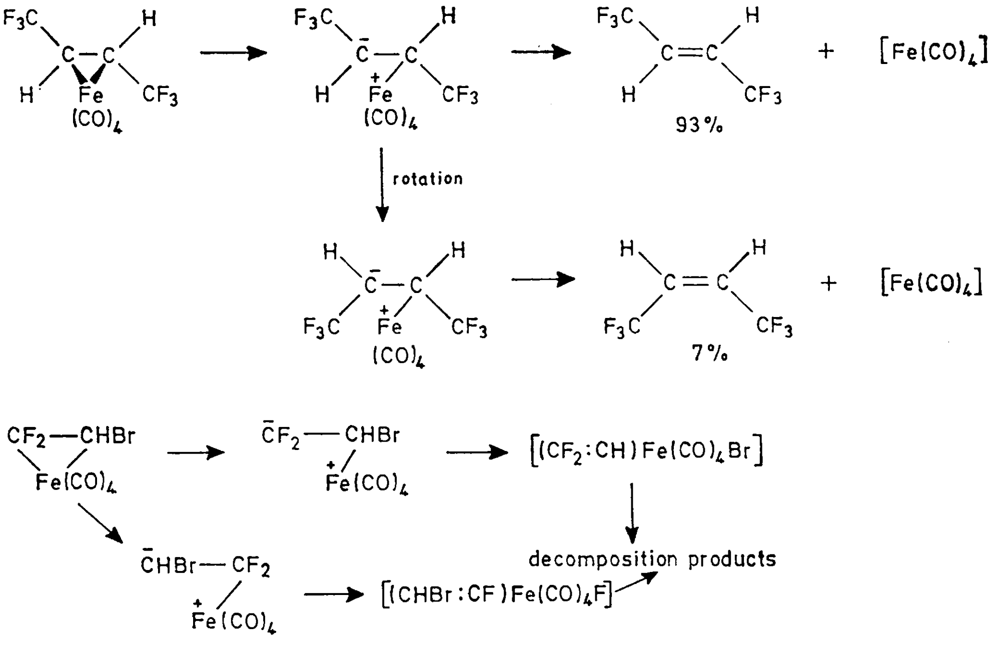
indicate that the decomposition involves an intermediate with single-bond character, in which rotation about the former carbon–carbon double-bond may occur, analogous to that suggested [14] for the formation of certain iridium and platinum complexes. Control experiments showed that isomerisation of preformed *trans*-hexafluorobut-2-ene under the reaction conditions is unlikely. Similar intermediates could also be involved in the decomposition of the bromine- and chlorine-containing complexes, in which halogen transfer (including fluorine transfer) to iron is indicated by the identification of the halide ions amongst the involatile material (see Scheme) and also by a number of rearrangement ions in the mass spectra (see below).

TABLE 2

Thermal decomposition of $[LFe(CO)_4]$

L	Decomp. time/temp (t/°C)	Products (%) CO [a]	Fe$(CO)_5$ [a]	L	Other products [b]
$CH_2{:}CHF$	25 days/23 [c]	5	47	38	F^-, Cl^-, Fe^{2+}, $CDCl_3$
	63 days/23 [d]	<1	19	42	F^-, Cl^-, Fe^{2+}, CH_2Cl_2
$CHBr{:}CF_2$	20 days/23	56	14	11	$CH_2{:}CF_2$ (32%), F^-, Br^-, Fe^{2+}
$CHCl{:}CF_2$	32 days/23 [d]	0	81	65	$CH_2{:}CF_2$ (19%), $[LFe(CO)_4]$ (13%), F^-, Cl^-, Fe^{2+}
	3 days/100	8	70	72	$CH_2{:}CF_2$ (5%), F^-, Cl^-, Fe^{2+}
trans-$CF_3{\cdot}CH{:}CH{\cdot}CF_3$	5 days/100	3	94	93	*cis*-$CF_3{\cdot}CH{:}CH{\cdot}CF_3$ (7%), Fe^{2+}
cis-$CHF{:}CF{\cdot}CF_3$	7 days/180	87	13	79	*trans*-$CHF{:}CF{\cdot}CF_3$ (4%), F^-, Fe^{2+}
trans-$CF_3{\cdot}CF{:}CF{\cdot}CF_3$ [e]	17 h/112	53	48	100 [f]	Fe^{2+}

[a] % Of total CO. [b] Ionic products listed were detected after the involatile residue had been dissolved in dilute nitric acid. [c] In $CDCl_3$ solution. Recovered olefin contained ^1H only (i.r.). [d] In CH_2Cl_2 solution. [e] Contaminated by a small amount of the *cis*-isomer. [f] The recovered olefin contained some of the *cis*-isomer, detected by i.r. spectroscopy, but although the proportion was less than in the olefin mixture used in the preparation of the complexes the precise ratio could not be established.



SCHEME

Most of the thermal-decomposition reactions were carried out with the pure complexes, but the reaction of tetracarbonyl(fluoroethylene)iron in the presence of deuteriochloroform and of methylene chloride resulted in the formation of chloride ion, showing that the solvent was also involved in the decomposition, in accord with previous experience that solutions of metal complexes in halogenated solvents are unstable. The mode of formation of 1,1-difluoroethylene in the thermal decomposition of $[(CHCl{:}CF_2)Fe(CO)_4]$ and of $[(CHBr{:}CF_2)Fe(CO)_4]$ is not known. Although hydrolysis by water is unlikely in view of the stringent precautions taken to exclude moisture, it cannot be completely ruled out, making further speculation groundless.

Spectroscopic Properties.—(a) *Mass spectra*. Although only the four solid complexes $[L = (CF_3)_2C{:}C(CF_3)_2$,

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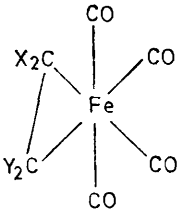
[14] J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1970, 1847.

trans-$CF_3{\cdot}CF{:}CF{\cdot}CF_3$, $CF_2{:}CCl_2$, or $CF_2{:}CBr_2$], which were inserted directly into the spectrometer, showed detectable molecular ions, all except those from vinyl fluoride, 1-chloro-2,2-difluoroethylene, 3,3,3-trifluoropropene, and 1,1-difluoroethylene showed ions corresponding to $LFe(CO)_n$ ($n < 4$) and/or $(L{-}X)Fe(CO)_n$ ($n \leqslant 4$, X = H, Cl, F, or Br), providing evidence for the formulation [$LFe(CO)_4$]. [$(CF_2{:}CH_2)Fe(CO)_4$] showed ions corresponding to $C_2Fe(CO)$ and CH_2Fe, but the others showed mainly ions due to the free olefin and its breakdown products and to $Fe(CO)_n$. Transfer of halogen from carbon to iron in the decomposition is indicated by the identification of ions such as FeX^+ and $FeX(CO)^+$ (X = F, Cl, or Br), but there is, unfortunately, no evidence at what stage the rearrangement takes place.

(b) *I.r. spectra.** All the complexes showed either three or four bands in the terminal carbonyl stretching region. Four bands are expected for the C_{2v} or C_s symmetry of structure (1), and in view of the ^{19}F n.m.r. spectra, and of a recent electron-diffraction study of [$(C_2F_4)Fe(CO)_4$],[15] the observation in some instances of only three bands is most probably due to overlap of two of the bands. The more stable complexes generally have higher frequencies than the less stable ones, implying that the iron is relatively electron deficient in the more stable complexes, and that the structures more closely approach the σ-bonded three-membered-ring model than the co-ordinated-olefin model. Conversely, the less stable, and generally less halogenated, complexes more closely approach the co-ordinated-olefin model. In accord with this, if it is assumed that the band at the next highest frequency to the carbonyl absorptions can be assigned to the co-ordinated double-bond, the ' co-ordination shift ' (*i.e.* difference in frequency between this band and the C=C stretching frequency in the free olefins) is similar for vinyl fluoride (184 cm^{-1}) and for 3,3,3-trifluoropropene (180 cm^{-1}) to those reported, with the same assumption, for vinyl chloride [8] (160 cm^{-1}) and propene [8] (154 cm^{-1}), but considerably higher than that for ethylene [4] (72 cm^{-1}). The shift for 1,1-difluoroethylene, however, is much bigger (268 cm^{-1}), and those for the more highly substituted olefins are greater than 300 cm^{-1}, suggesting that there is little double-bond character in the complexes.



(1)

(c) *N.m.r. spectra.** Although the CF_3 groups are consistently to low field in the complexes compared with the free olefins, the ' vinylic ' fluorines having a geminal hydrogen or CF_3 group appear to high field of their positions in the free olefins, in contrast to the low-field shift noted previously [3] in [$(C_2F_4)Fe(CO)_4$] and in most of the perhalogenoethylene complexes. It was suggested [3] that the high-field shift in the complexes formed from cyclic olefins was due to the vinylic fluorines of the cyclo-olefins becoming bridgehead fluorines in the complexes, but this is clearly not so for the olefins reported here. The high-field shift apparently results from cancellation of the low-field shift due to proximity of the metal by a high-field shift due to conversion of the olefin into a ferracyclopropane. For instance, the ^{19}F shift for the CHF group in vinyl fluoride [16] is −36 p.p.m.; in 1,1,2-trifluorocyclopropane [17] it is −144.5 p.p.m., an upfield shift of 108.5 p.p.m., and in the complex, −81 p.p.m. Similarly, in trifluoroethylene,[18] the CHF group absorbs at −109 p.p.m., in pentafluorocyclopropane [17,19] at −163.4 p.p.m., and in the complex at −127 p.p.m. The low-field shift observed [3] for the $CF{\cdot}CF_3$ group when hexafluoropropene forms the complex may arise simply because this fluorine already absorbs well to high field in the olefin [δ_F −115.5 in C_3F_6, −132.8 in perfluoro(methylcyclopropane), an upfield shift of only 17.3 p.p.m., −105 p.p.m. in $C_3F_6{\cdot}Fe(CO)_4$]. The ' very large upfield shift ' reported [11] for the vinylic fluorines in the complex formed from perfluorobut-2-ene arises from the mistaken assignment of the CF_3 absorption of the less-abundant isomer in the commercial perfluorobut-2-ene to the vinylic fluorine of the major component. The absorption is shifted upfield on complex formation by 10 p.p.m. for *trans*-perfluorobut-2-ene, but vinylic fluorine of the complex from the *cis*-isomer could not be detected.

The loss of double-bond character on formation of the complexes is also shown by the high values (109—138 Hz) for the fluorine–fluorine coupling, which is identified unambiguously in the complexes [$(CF_2{:}CHCl)Fe(CO)_4$], [$(CF_2{:}CHBr)Fe(CO)_4$], and [$(CF_2{:}CFH)Fe(CO)_4$], and also [3] in [$(CF_3{\cdot}CH{:}CF_2)Fe(CO)_4$], as due to geminal fluorine atoms; the low value for the *trans*-vicinal fluorine–fluorine coupling in [$(CF_2{:}CFH)Fe(CO)_4$] (the largest possible value being 78 Hz compared with the 109—123 Hz commonly associated [18,20] with *trans*-vinylic fluorines) is also in accord with this.

Reaction with Trifluoroiodoethylene.—Under u.v. irradiation, or at 50 °C in the dark, trifluoroiodoethylene and

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* Detailed spectroscopic data (i.r. and ^{19}F n.m.r.) are deposited as a Supplementary Publication (SUP No. 21372; 4 pp.); for details of this scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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nonacarbonyldi-iron reacted readily to give carbon monoxide and a pyrophoric solid, but after a week at room temperature in the dark a purple solid was obtained from the reaction mixture and was resolved with difficulty into brown plates of tetracarbonyliodo(trifluorovinyl)iron and purple needles of a dimeric compound.

$$\begin{array}{l} CF_2{:}CFI + [Fe_2(CO)_9] \longrightarrow \\ \qquad [(CF_2{:}CF)Fe(CO)_4I] + [\{(C_2F_3I)Fe(CO)_4\}_2] \\ \qquad\qquad 3\% \qquad\qquad\qquad\qquad 24\% \end{array}$$

The trifluorovinyl compound was identified by analysis and its mass spectrum, and by its ^{19}F n.m.r. and i.r. spectra, which were in good agreement with those reported [20,21] for other trifluorovinyl–transition-metal compounds. The high intensity of the molecular ion in the mass spectrum (relative intensity 45% of the $[Fe(CO)_4]^+$) contrasted sharply with the low intensity of the molecular ions from the $[(olefin)Fe(CO)_4]$ complexes. Migration of iodine from iron to carbon was indicated by peaks corresponding to $C_2F_3I^+$, $C_2F_2I^+$, and C_2FI^+, the latter almost as strong as the peak due to $[Fe(CO)_4]^+$.

The structure of the purple needles remains unknown. Microanalysis was in accord with the empirical formula $C_2F_3IFe(CO)_4$. The mass spectrum obtained with the source at 70 °C showed peaks corresponding to $[C_4F_6I_2Fe_2(CO)_n]^+$ (n = 2—8), $[C_4F_5I_2Fe(CO)_n]^+$ (n = 3—8), and $[C_2F_3IFe_2(CO)_n]^+$ (n = 0—6), the peak at highest mass corresponding to a dimeric formulation $[\{(C_2F_3I)Fe(CO)_4\}_2]$. The first two series of ions were undetectable when source temperatures of 110 and 150 °C were used. The i.r. spectrum showed five bands in the terminal carbonyl region (2 096s, 2 066vs, 2 035vs, 2 032vs, and 2 021m cm^{-1}), and no bands attributable to bridging or acyl carbonyl groups. The ^{19}F spectrum consisted of three doublets of doublets, with coupling constants 103, 73, and 6.3 Hz, suggesting a structure analogous to the $[(olefin)Fe(CO)_4]$ complexes, but the chemical shifts were markedly to low field of those for the complexes [3] $[(CF_2{:}CFX)Fe(CO)_4]$ (X = Cl or Br), and if it is assumed that the chemical-shift change on complex formation would be similar to that for these olefin complexes the geminal coupling constant for the purple crystals would be 6.3 rather than 103 Hz. The Mössbauer spectrum showed only one iron environment with an isomer shift considerably larger (0.28 *vs.* 0.14 mm s^{-1}) than that of the olefin complex $[(CF_2{:}CCl_2)Fe(CO)_4]$, or of the complexes from dimethyl maleate or fumarate.[22]

Reaction with bromine at 150 °C resulted in quantitative evolution of carbon monoxide according to the equation:

$$[\{(C_2F_3I)Fe(CO)_4\}_2] \xrightarrow{Br_2} 8CO$$

With iodine at 90 °C, some 75% of the carbon monoxide was evolved. Pyrolysis of the crystals (100 °C) gave carbon monoxide (70%), pentacarbonyliron (65% of carbon monoxide), traces of trifluoroiodoethylene, perfluorocyclobutene, perfluorobutadiene, iodine, and an unidentified residue containing iron, fluorine, and iodine, which showed a broad carbonyl absorption in its i.r. spectrum. No structure in accord with all these results has yet been devised, and it appears that an *X*-ray structure determination will be necessary.

EXPERIMENTAL

Volatile materials were manipulated in a conventional vacuum system. I.r. spectra were obtained on a Perkin-Elmer model 21 spectrometer with calcium fluoride optics and expanded scale calibrated with deuterium chloride for the carbonyl region, or on a Perkin-Elmer model 257 grating spectrometer. N.m.r. spectra were obtained with Perkin-Elmer R10 or Hitachi–Perkin-Elmer R20A spectrometers (60.0 MHz for ^1H, 56.46 MHz for ^{19}F) or with a Varian Associates HA 100 spectrometer (100.0 MHz for ^1H, 94.1 MHz for ^{19}F). Chemical shifts are reported in p.p.m. to low field (positive values) of tetramethylsilane (^1H) or external trifluoroacetic acid (^{19}F). Mass spectra were determined on an A.E.I. MS 902 instrument at 70 eV, at the lowest possible inlet temperature. Nonacarbonyldi-iron was prepared essentially by King's [23] method; incorporation of a water-cooled finger to cool the liquid apparently prevented the formation of dodecacarbonyltri-iron. Light petroleum is the fraction boiling in the range 40—60 °C, and irradiations were with a 300 W tungsten filament lamp unless otherwise stated.

Preparation of Olefin Complexes.—Nonacarbonyldi-iron and an excess of the olefin were sealed together *in vacuo* with n-hexane or light petroleum (*ca.* 10 ml) for reactions with low-boiling olefins, and kept under the conditions indicated for straightforward cases in Table 1. The excess of olefin, the solvent, and pentacarbonyliron were removed *in vacuo*, and the complex was isolated by distillation at low pressure in an atmosphere of dry nitrogen or by sublimation at low pressure. Conventional microanalytical techniques, with the sample sealed *in vacuo* in a small Pyrex ampoule which was broken in the microanalytical train, were satisfactory for the more stable complexes, but some complexes decomposed while samples were being transferred to the ampoules and the results were outside the normal tolerance.

Reaction of Nonacarbonyldi-iron with 1,2,3,3,3-*Pentafluoropropene.*—Nonacarbonyldi-iron (2.28 g, 6.26 mmol), n-hexane (10 ml), and 1,2,3,3,3-pentafluoropropene (2.58 g, 19.5 mmol), shown by g.l.c. to contain 95% of the *cis*-isomer, were irradiated *in vacuo* (45 h). The olefin (1.9 g, 75%), hexane, and pentacarbonyliron were removed *in vacuo*, and the green liquid was distilled to give pale yellow tetracarbonyl(1,2,3,3,3-pentafluoropropene)iron (0.86 g, 46% on initial nonacarbonyldi-iron) (Found: C, 29.1; H, 0.6. Calc. for $C_7HF_5FeO_4$: C, 28.0; H, 0.3%), b.p. 36 °C/5 mmHg, and a residue containing nonacarbonyldi-iron and docecacarbonyltri-iron.

Reaction of Nonacarbonyldi-iron with trans-1,1,1,4,4,4-*Hexafluorobut-2-ene.*—Nonacarbonyldi-iron (2.15 g, 5.91 mmol), n-hexane (10 ml), and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (1.87 g, 11.4 mmol) were irradiated *in vacuo* (6

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[22] K. Laszlo and B. Kalman, *Magyar Kém. Folyóirat*, 1968, **74**, 434.

[23] R. B. King, *Organometallic Syntheses*, 1965, **1**, 93.

days), to give olefin (1.10 g, 59%), hexane, pentacarbonyliron, *tetracarbonyl*(1,1,1,4,4,4-*hexafluorobut*-2-*ene*)*iron* (0.82 g, 42% on initial nonacarbonyldi-iron) (Found: C, 29.2; H, 0.7. $C_8H_2F_6FeO_4$ requires C, 28.9; H, 0.6%) as a yellow liquid, b.p. 30 °C/5 mmHg, which subsequently crystallised, m.p. 21 °C, and a solid residue containing nonacarbonyldi-iron.

Reaction of Nonacarbonyldi-iron with Perfluorobut-2-*ene*.—Nonacarbonyldi-iron (2.27 g, 6.24 mmol), n-hexane (10 ml), and perfluorobut-2-ene (4.18 g, 20.9 mmol), shown by its n.m.r. spectrum to contain 25% of the *cis*- and 75% of the *trans*-isomer, showed no observable change after 65 h in the dark. After irradiation (70 h), the olefins (3.60 g, 86%), hexane, and pentacarbonyliron were removed, and the residual brown liquid was distilled under reduced pressure to give pentacarbonyliron, and, by a combination of repeated distillation and sublimation, white crystals of (*tetracarbonyl*-trans-*perfluorobut*-2-*ene*)*iron* (0.62 g, 27% on initial nonacarbonyldi-iron) (Found: C, 25.9; H, 0.2%; M^+, 368. $C_8F_8FeO_4$ requires C, 26.1; H, 0.0%; M, 368), m.p. 47 °C, b.p. 50 °C/4 mmHg, a mixture of tetracarbonyl (*cis*-and *trans*-perfluorobut-2-ene) iron (0.71 g, 31%), and a small amount of yellow liquid free from solid which the n.m.r. spectrum suggested was pure tetracarbonyl(*cis*-perfluorobut-2-ene)iron (0.02 g, 1%), m.p. 20 °C, b.p. 50 °C/*ca*. 5 mmHg.

Reaction of Nonacarbonyldi-iron with Trifluoroiodoethylene.—Nonacarbonyldi-iron (3.16 g, 8.68 mmol) and trifluoroiodoethylene (10.60 g, 51.0 mmol) were kept (7 days) *in vacuo* in the dark (23 °C), carbon monoxide (0.014 g), pentacarbonyliron, trifluoroiodoethylene (9.3 g, 88%), and traces of trifluoroethylene and perfluorocyclobutene were removed, and repeated fractional sublimation of the purple residue, which did not react with mercury, gave: (i) brown plates of *tetracarbonyliodo*(*trifluorovinyl*)*iron* (0.1 g, 3%) (Found: C, 19.3; H, 0.0%; M^+, 376. $C_6F_3FeIO_4$ requires C, 19.2; H, 0.0%; M, 376), m.p. 62 °C, ^{19}F n.m.r. −6.3, −44.3, and −61.0 p.p.m. (each a doublet of doublets, equal intensities, J_{FFgem} 87.4, J_{FFcis} 46.5, and $J_{FFtrans}$ 115.6 Hz); i.r., $\bar{\nu}$(CO) 2 139, 2 090, 2 067, and 2 051; $\bar{\nu}$(C:C) 1 712; $\bar{\nu}$(:CF$_2$)asym. 1 258, sym 970; $\bar{\nu}$(:CF) 1 106 cm^{-1}; mass spectrum, major peaks corresponding to $[C_2F_3Fe(CO)_nI]^+$, $[C_2F_3Fe(CO)_n]^+$, and $[Fe(CO)_nI]^+$, each with n = 0—4; (ii) purple needles of the dimer (0.8 g, 24%) (Found: C, 19.5; H, 0.1%; M^+, 752. Calc. for $C_{12}F_6Fe_2I_2O_8$: C, 19.2; H, 0.0%; M, 752), m.p. 38 °C, ^{19}F n.m.r. +34 (d, 73, d, 6.3 Hz), +4 (d, 103, d, 6.3 Hz), and −20 p.p.m. (d, 103, d, 73 Hz); and (iii) involatile decomposition products.

Reaction of Nonacarbonyldi-iron with Tetracyanoethylene.—During 43 days in the dark (23 °C) *in vacuo*, nonacarbonyldi-iron (0.46 g, 1.26 mmol), toluene (15 ml), and tetracyanoethylene (0.64 g, 5.0 mmol) gave carbon monoxide (0.29 g, 92%), a trace of pentacarbonyliron, recovered toluene, and an unidentified black powder (0.7 g), i.r. (mull) doublet 2 205, and 2 140 cm^{-1}, which was insoluble in common organic solvents, and dissolved partially in water to give a solution containing Fe^{2+} and CN^- ions. U.v. irradiation (30 h) of nonacarbonyldi-iron (0.80 g, 2.20 mmol), light petroleum (25 ml), and tetracyanoethylene (0.32 g, 2.5 mmol) gave only traces of carbon monoxide and pentacarbonyliron, and the reactants were recovered.

Reaction of Nonacarbonyldi-iron with Perfluorobut-2-*yne*.—Nonacarbonyldi-iron (1.18 g, 3.24 mmol) and perfluorobut-2-yne (3.86 g, 24.0 mmol) were kept together *in vacuo* in a Pyrex tube (70 ml) in the dark (27 days) at 23 °C, to give a trace of carbon monoxide, perfluorobut-2-yne (3.40 g, 88%), and pentacarbonyliron (0.30 g, 47% on initial nonacarbonyldi-iron) as volatile products, together with yellow crystals of tricarbonylcyclopentadienonetetrakis(trifluoromethyl)iron (0.70 g, 98% on consumed alkyne, 44% on initial nonacarbonyldi-iron) (Found: C, 29.0; H, 0.1. Calc. for $C_{12}F_{12}FeO_4$: C, 29.3; H, 0.0%), m.p. 154 °C (decomp.) (lit.,[13] m.p. 157—157.5 °C), with i.r. and ^{19}F n.m.r. spectra identical with those reported,[13] and nonacarbonyldi-iron. In other experiments, no reaction was detectable after (a) 2 days at −78 °C with liquid alkyne, (b) 3.5 days at 0 °C with liquid alkyne, or (c) 13 days at 23 °C with gaseous alkyne.

Reaction of Pentacarbonyliron with Perfluorobut-2-*yne*.—Pentacarbonyliron (3.3 g, 16.8 mmol) and perfluorobut-2-yne (7.1 g, 43.8 mmol) slowly formed yellow crystals when kept in the dark *in vacuo* at 23 °C. After 47 days, perfluorobut-2-yne (6.7 g, 95%) and pentacarbonyliron were recovered, and tricarbonylcyclopentadienonetetrakis(trifluoromethyl)iron (0.52 g, 88% on consumed alkyne) was isolated.

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