535. *Transition-metal Fluorocarbon Complexes. Part I. Derivatives of Perfluoro-olefins.*

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The interaction of tri-iron dodecacarbonyl, $Fe_3(CO)_{12}$, with octafluorocyclohexa-1,3- or -1,4-diene forms a compound $C_6F_8Fe(CO)_3$ which must be formulated as a π-bonded olefin complex. In contrast, the interaction of tetrafluoroethylene with $Fe_3(CO)_{12}$ gives a compound $C_4F_8Fe(CO)_4$ in which the iron atom is bound to carbon by σ-bonds in a perfluorocycloalkane ring. Infrared, high-resolution nuclear magnetic resonance, and mass-spectroscopic studies support these formulations.

Products from the interaction of tetrafluoroethylene with $Co_2(CO)_8$ and $(\pi\text{-}C_5H_5)_2Co$ and of the latter with trifluoroiodomethane are described.

Although a very large number of olefin complexes of transition metals are known, no halogenated olefin complexes have been characterised and the interaction of chlorinated olefins with transition-metal carbonyls, a successful preparative method for hydrocarbon complexes, results in chlorination to give the metal chloride. A similar reaction to give the metal fluoride appeared to be less likely with fluorinated olefins. Further, since Dewar's view of the bonding of olefins to transition metals would imply stronger acceptor behaviour of the carbon anti-bonding π-orbitals for electron density in filled metal orbitals than for the hydrocarbons, we have studied the interactions of several fluoro-olefins with metal carbonyls.

The iron carbonyl complex isolated from the reaction products of tetrafluoroethylene with tri-iron dodecacarbonyl, $Fe_3(CO)_{12}$, was first believed [1a] to be an olefin derivative, but further work [1b] has shown that it is a cyclic perfluoroalkyl compound, $C_4F_8Fe(CO)_4$. The interaction of octafluorocyclohexa-1,3- or -1,4-dienes and $Fe_3(CO)_{12}$ gives $C_6F_8Fe(CO)_3$,[1a] which we have now shown to be the first true perfluoro-olefin–metal complex. At the present time we have failed to obtain isolable complexes from the reactions of tetrafluoroethylene and octafluorocyclohexadiene with the compounds $Mo(CO)_6$, $Mn_2(CO)_{10}$, $HMn(CO)_5$, $Ni(CO)_4$, $(\pi\text{-}C_5H_5)_2Ni$, $\pi\text{-}C_5H_5Co(CO)_2$ at temperatures up to 150°, or from these metal compounds or iron carbonyls with perfluorocyclohexene, trifluoroethylene, 1,2-difluorethylene, or perfluoro-propene or -buta-1,3-diene, although some rather air-sensitive products are formed from the perfluorobutadiene with iron and cobalt carbonyls.

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[1] Watterson and Wilkinson, *Chem. and Ind.*, (*a*) 1959, 991; (*b*) 1960, 1358.

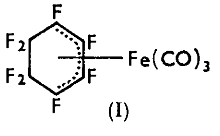
The extension of these studies to fluorinated acetylene derivatives has allowed several complexes, *e.g.*, $C_4F_6Co_2(CO)_6$, to be obtained.[2]

Octafluorocyclohexa-1,3-*dieneiron Tricarbonyl*.—From the products of the reaction of octafluorocyclohexa-1,3- or 1,4-diene with tri-iron dodecacarbonyl, can be readily isolated the same colourless crystalline compound, $C_6F_8Fe(CO)_3$. The spectroscopic evidence shows that in the iron compound the bound olefin is the 1,3-diene, so that the formation of the compound from the 1,4-diene must involve migration of fluorine. Examination of the surplus diene from the reaction with the 1,3- or 1,4-diene by infrared spectroscopy showed a strong absorption band at 1536 cm.$^{-1}$ which is characteristic of hexafluorobenzene; iron pentacarbonyl is also present. It was not possible to detect the 1,3-diene in surplus from the 1,4-diene reaction either spectroscopically or by vapour-phase chromatography.

The iron compound—which is volatile, subliming readily at room temperature in a vacuum, and is soluble in common organic solvents—is stable in air in the solid state indefinitely but decomposes within a few hours in cold solutions or quite rapidly in boiling benzene even in absence of air. Since conventional molecular-weight procedures (cryoscopic, ebullioscopic or isopiestic) gave obviously unreliable results, the stoicheiometry and molecular weight have been obtained by other methods. Mass-spectroscopic measurements show that the ion of greatest mass, 364, is due to $C_6F_8Fe(CO)_3^+$, while molecular-weight determination by the *X*-ray method gives a value of 361 ($\pm 2\%$). In addition, measurements of the relative peak areas in the high-resolution fluorine nuclear magnetic resonance spectrum of a known weight of the compound compared with a known weight of benzotrifluoride in acetone were taken; if eight fluorine atoms are assumed per molecule of the iron compound, the ratio of the integrated peak areas gave a molecular weight = 370 ± 5.

Infrared and nuclear magnetic resonance spectra. The infrared spectrum of $C_6F_8Fe(CO)_3$ is given in detail in the Experimental section; few assignments are possible except for the three strong carbonyl stretching frequencies at 2108, 2054, and 2018 cm.$^{-1}$, which are displaced to higher wavenumbers than in the carbonyls or the hydrocarbon complex, presumably owing to the electronegativity of the fluorine atoms which would tend to have a similar effect to that of placing a positive charge on a carbonyl complex in reducing the multiple-bond contribution in the metal–carbon bond of the M–C–O group.[3] The only other useful piece of information concerns the strong band at 1550 cm.$^{-1}$, which can be assigned as a C=C stretching frequency associated with a conjugated double-bond system. Hexafluorobenzene has an absorption at 1536 cm.$^{-1}$;[4] octafluorocyclohexa-1,4-diene absorbs at 1740 cm.$^{-1}$, and the 1,3-diene at 1750 and 1710 cm.$^{-1}$, the two bands for the latter arising from splittings due to conjugation. Since the fluoroalkyl–metal derivatives discussed below do not show a band in this region, the presence of a co-ordinated conjugated diene system seems a reasonable assumption and the downward shift of *ca.* 200 cm.$^{-1}$ is in the direction to be expected for the effect of co-ordination to the metal atom.

The high-resolution fluorine nuclear magnetic resonance spectra (at 56·45 Mc./sec.) for the iron compound and also for the two dienes are shown in the Figure; the details of the spectra and assignments are listed in the Experimental section. The spectrum of the iron compound is consistent with a structure based on a co-ordinated 1,3-diene group (I), but a similar structure with two Fe–C σ-bonds plus a co-ordinated double bond cannot be rigorously excluded.



(I)

As in the parent 1,3-diene, the pentuplet band (intensity *ca.* 2) at the highest field can be assigned to the terminal co-ordinated olefinic fluorine atoms (F_1 and F_4) and the " triplet " band (intensity *ca.* 2) next to this represents the central (F_2, F_3) olefinic fluorine atoms. The component structure is produced by spin-coupling between non-equivalent

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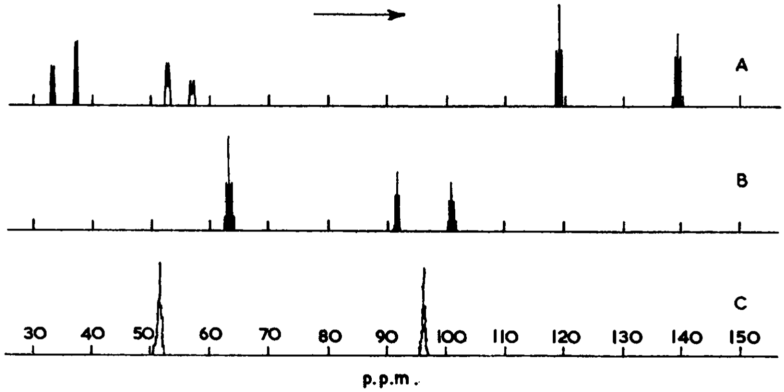
[2] Boston, Sharp, and Wilkinson, *Chem. and Ind.*, 1960, 1137.

[3] Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

[4] Birchall and Haszeldine, *J.*, 1959, 13.

fluorine atoms. The low-field bands arise from the aliphatic fluorine atoms; in the parent compound, as expected, these are all equivalent, producing a band of intensity 4. In the iron compound, however, the presence of two chemically shifted bands in this region shows that two of the aliphatic fluorine atoms are different from the other two; the large doublet splitting of *ca.* 250 c./sec. between them shows that it is the two fluorine atoms of each CF_2 group which are not equivalent, *i.e.*, we have CFF′, probably because one of them is necessarily closer to the metal atom in the $Fe(CO)_3$ group. Since the splitting between the fluorine atoms of the CF_2 group is of the same order of magnitude as the chemical shift between them, their spectrum has the symmetrical appearance of an "AB" pair. A similar difference between two fluorine atoms in a cyclic CF_2 group when one of the atoms is closer to another atom is found in the monosubstituted tetrafluorocyclobutanes,[5] and in the case of protons we have observed several cases of a similar nature [6] when one of the atoms is closer to a metal atom than the other.

^{19}F *magnetic resonance spectra at* 56·45 *Mc./sec.* (*external reference, benzotrifluoride*); *fields increase to the right.*



A, *Complex* $C_6F_8Fe(CO)_3$. B, *Perfluorocyclohexa*-1,3-*diene*. C, *Perfluorocyclohexa*-1,4-*diene*.

The small additional doublet splitting on the aliphatic fluorine lines probably results from the coupling between these atoms and the terminal olefinic fluorine atoms. This splitting is different for the two fluorines in each CFF′ group, suggesting that the C–F bonds make different angles with the $\underset{\text{F}}{\diagdown}\text{C}=$ bond.

The octafluorocyclohexa-1,4-diene shows only one high-field line due to the four equivalent fluorine atoms, and it would be expected that an iron complex containing a 1,4-diene co-ordinated symmetrically would show no separations of the magnitude observed. Hence we consider that the nuclear magnetic resonance data are consistent with a structure of type (I), where the double bonds are either localized and donating independently, or, more probably, are delocalized so that the $C_{(1)}$–$C_{(2)}$ and $C_{(2)}$–$C_{(3)}$ distances are about the same as has been found in butadieneiron tricarbonyl.[7] It may be noted that the separation of the olefinic fluorine resonance lines is somewhat increased in the complex, as compared with the olefin; with the conjugated hydrocarbon complexes [6] such as those of cyclopentadiene or butadiene, there is a very much larger separation of the olefinic proton resonance lines than with the olefin itself. While this separation could imply localization of electron density in the double-bond positions, and this view seems reasonable for the cycloheptatriene metal complexes,[8] this explanation may be an oversimplification if the

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[5] Phillips, *J. Chem. Phys.*, 1956, **25**, 949.

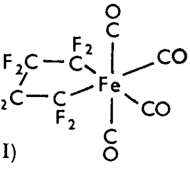
[6] Cf. Green, Pratt, and Wilkinson, *J.*, 1959, 3753; 1960, 989.

[7] Mills and Robinson, *Proc. Chem. Soc.*, 1960, 421.

[8] Bennett, Pratt, and Wilkinson, *J.*, 1961, 2037.

carbon–carbon distances in co-ordinated conjugated olefins are the same, and we cannot be certain on this point with the evidence to hand. Certainly, however, proton resonances are more susceptible both to small electron-density effects and also to long-range shielding effects of π-electron systems than are fluorine resonances, so that the large separations observed are not necessarily inconsistent with the view that the carbon–carbon distances are the same in the co-ordinated conjugated diene system.

Perfluorotetramethyleneiron Tetracarbonyl.—The reaction of tetrafluoroethylene with tri-iron dodecacarbonyl leads to a colourless crystalline compound of properties very similar to the diene derivative noted above. On the basis of analytical data which are now known to have been unreliable, mainly owing to difficulties in removing traces of impurities by sublimation with the small quantities of the material originally available, this compound was first believed to be the tricarbonyl. Mass-spectroscopic measurements unequivocally showed that the compound is a tetracarbonyl, as did the *X*-ray molecular-weight determination. Further, a comparison of the fluorine resonance integrated peak areas for known weights of the compound and benzotrifluoride in acetone gave a molecular weight of 373. Thus the stoicheiometry and the spectroscopic studies are consistent with the structure (II) in which a $[-CF_2-]_4$ chain is bound to the iron atom by σ-bonds. The nuclear magnetic resonance spectrum shows two lines of equal intensity (2 : 2) in the region of other aliphatic C–F bonds. Both lines appear to be approximately triplets with a splitting of *ca.* 2·5 c./sec., which is consistent with the spin-coupling between non-equivalent aliphatic CF_2 groups.


(II)

Mass spectra of $C_6F_8Fe(CO)_3$ *and* $C_4F_8Fe(CO)_4$.—A partial mass spectrum of the key ion fragments, detected when $C_4F_8Fe(CO)_4$ was sublimed into a mass spectrometer at 25°, is shown in Table 1.

TABLE 1. *Partial mass spectrum of* $C_4F_8Fe(CO)_4$.

Mass no.	Fragment ion	Peak intensity *	Mass no.	Fragment ion	Peak intensity *
368	$C_4F_8Fe(CO)_4^+$	2·3	284	$C_4F_8Fe(CO)^+$	9·1
340	$C_4F_8Fe(CO)_3^+$	34·1	256	$C_4F_8Fe^+$	2·0
312	$C_4F_8Fe(CO)_2^+$	17·1	162	$C_4F_6^+$	100·0

* Relative to $C_4F_6^+$ ion peak as 100.

The fragment ion of mass 368 is an important one in that it determines the molecular weight of the compound. This result is of special interest because many of the conventional methods for determination of molecular weight give unreliable values for the iron carbonyl derivative. The detection of an ion assignable to $C_4F_8Fe(CO)_4$ is unique since metal carbonyl compounds often lose carbon monoxide so easily that the ion required for the molecular weight is not seen in the mass spectrum.

The ions of mass 340, 312, 284, and 256 corresponding to $C_4F_8Fe(CO)_3^+$, $C_4F_8Fe(CO)_2^+$, $C_4F_8Fe(CO)^+$, and $C_4F_8Fe^+$, respectively, are formed by a stepwise loss of carbon monoxide from the parent compound. One might expect the $C_4F_8Fe^+$ ion to break up stepwise also, to give $C_4F_8^+$ and $C_4F_7^+$ ions, but these fragments do not appear in the mass spectrum. The largest iron-free fragment in the spectrum is the $C_4F_6^+$ ion. This fragment of mass 162 is one of the major ions in the spectrum, and its abundance appears to be related to the ease with which $C_4F_8Fe(CO)_4$ decomposes to give perfluorocyclobutene when heated. It was found, for example, that introduction of $C_4F_8Fe(CO)_4$ into the mass spectrometer through an inlet maintained at 150° gives the mass spectrum of perfluorocyclobutene and no ions of mass larger than 162.

A partial mass spectrum of the ion fragments observed when $C_6F_8Fe(CO)_3$ was sublimed into a mass spectrometer is shown in Table 2.

The mass spectrum of $C_6F_8Fe(CO)_3$ is similar to that of $C_4F_8Fe(CO)_4$ in the appearance of the ions $C_6F_8Fe(CO)_3^+$, $C_6F_8(CO)_2^+$, $C_6F_8Fe(CO)^+$, and $C_6F_8Fe^+$ that correspond to the

TABLE 2. *Partial mass spectrum of* $C_6F_8Fe(CO)_3$.

Mass no.	Fragment ion	Peak intensity *	Mass no.	Fragment ion	Peak intensity *
364	$C_6F_8Fe(CO)_3^+$	4·0	224	$C_6F_8^+$	1·1
336	$C_6F_8Fe(CO)_2^+$	4·0	205	$C_6F_7^+$	2·5
308	$C_6F_8Fe(CO)^+$	0·1	186	$C_6F_6^+$	100·0
280	$C_6F_8Fe^+$	0·36			

* Relative to $C_6F_6^+$ ion peak at 100.

parent compound and the fragments formed by successive loss of carbon monoxide. Formation of $C_6F_6^+$ as the major fluorocarbon ion is also similar to that of $C_4F_6^+$ from $C_4F_8Fe(CO)_4$. It should be noted, however, that $C_6F_8Fe(CO)_3$ shows important differences from $C_4F_8Fe(CO)_4$ in fragmentation behaviour. For example, the fragments $C_6F_8Fe(CO)_2^+$, $C_6F_8Fe(CO)^+$, and $C_6F_8Fe^+$ are not as abundant in the mass spectrum of $C_6F_8Fe(CO)_3$ as the corresponding ions derived from $C_4F_8Fe(CO)_4$. Another significant feature of the behaviour of $C_6F_8Fe(CO)_3$ is the formation of the ions $C_6F_8^+$ and $C_6F_7^+$ as well as $C_6F_6^+$. There is also a sharp contrast between these two iron compounds with regard to the ease with which $Fe(CO)_x^+$ fragments are formed. The partial mass spectrum shown in Table 3

TABLE 3. *Partial mass spectrum of* $C_6F_8Fe(CO)_3$ *and* $C_4F_8Fe(CO)_4$.

		Peak intensity relative to				Peak intensity relative to	
Mass no.	Fragment ion	$C_6F_6^+$ from $C_6F_8Fe(CO)_3$	$C_4F_6^+$ from $C_4F_8Fe(CO)_4$	Mass no.	Fragment ion	$C_6F_6^+$ from $C_6F_8Fe(CO)_3$	$C_4F_6^+$ from $C_4F_8Fe(CO)_4$
168	$Fe(CO)_4^+$	—	0·4	84	$Fe(CO)^+$	103·2	61·9
140	$Fe(CO)_3^+$	49·1	2·2	56	Fe^+	79·9	56·5
112	$Fe(CO)_2^+$	192·1	60·5	28	CO^+	10·6	185·6

shows that $Fe(CO)_2^+$ and $Fe(CO)^+$ are the major ions in the fragmentation of $C_6F_8Fe(CO)_3$. The situation with regard to the abundance of CO^+ ion in the two spectra is just the reverse. These differences in fragmentation behaviour of $C_6F_8Fe(CO)_3$ and $C_4F_8Fe(CO)_4$ indicate a fundamental difference in the bonding of the iron to the fluorocarbon part of the molecule, in accord with the other evidence presented above.

Other Derivatives.—Reaction of tetrafluoroethylene with cobalt carbonyl gives a compound $(CO)_4Co[CF_2]_2Co(CO)_4$ which is like the iron compound in being a normal σ-bonded derivative. With di-π-cyclopentadienylcobalt a binuclear species is also obtained but here the $-[CF_2]_2-$ group bridges the *endo*-positions of two π-cyclopentadienylcobalt cyclopentadiene units; this structure is confirmed by results of nuclear resonance measurement, and a comparison can readily be made with similar cyclopentadiene compounds [6] and particularly with the compound $\pi\text{-}C_3H_5CoC_5H_5{\cdot}CF_3$ resulting from the interaction of trifluoromethyl iodide and $(\pi\text{-}C_5H_5)_2Co$. For the latter, the fluorine resonance [6] is a doublet split by the H_β proton, and conversely the H_β proton resonance line (triplet) is further split into a quadruplet by the three fluorine nuclei. In $[\pi\text{-}C_5H_5CoC_5H_5{\cdot}CF_2-]_2$, the fluorine resonance is again a doublet split by H_β and occurs in the normal aliphatic C–F region; the proton spectrum shows a single line from the $\pi\text{-}C_5H_5$ protons, a " triplet " band from the central diene protons, and a band at higher field from the terminal diene protons. The remaining band is assigned to the H_β proton, and it would have been expected that it would show splitting by both CF_2 groups and that the terminal diene protons would give a triple triplet, but it was not possible to resolve this structure.

EXPERIMENTAL

Microanalyses and molecular-weight measurements (ebullioscopic in benzene) were made by the Microanalytical Laboratory, Imperial College, and, together with mass-spectrometric analyses, also by the Physical and Analytical Division, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.

*Octafluorocyclohexa-*1,3*-dieneiron Tricarbonyl.*—In a typical preparation $Fe_3(CO)_{12}$ (2 g.) was sealed with octafluorocyclohexa-1,3- or -1,4-diene (*ca.* 3 g.) in a thick-walled glass tube. During the heating at 120—130° for *ca.* 12 hr., the contents of the tube became dark brown. After cooling in liquid oxygen, the tube was opened and the excess of olefin and other volatile products removed. Extraction of the solid residue with light petroleum (b. p. 40—60°) gave a yellow-orange solution from which at −80° pale yellow crystals separated. The *product* was purified by recrystallisation and sublimation in a vacuum from *ca.* 30° to a probe at −80° [yield, *ca.* 1·38 g., *ca.* 31% based on $Fe_3(CO)_{12}$; m. p. 45°] [Found: C, 29·6, 28·5, 28·2; F, 40·7, 41·2; Fe, 15·0, 15·9. $C_6F_8Fe(CO)_3$ requires C, 29·7; F, 41·8; Fe, 15·3%]. Solutions in organic solvents undergo extensive decomposition in a few hours, even in the absence of air; ebullioscopic molecular-weight determinations gave values *ca.* 500, presumably owing to loss by volatilisation or decomposition.

The density was determined by the standard flotation method in aqueous barium mercuric iodide solutions and a value of 2·133 ± 0·007 g./c.c. was obtained; *X*-ray diffraction studies gave the dimensions of the orthorhombic unit cell as $a = 13{\cdot}38$, $b = 6{\cdot}85$, $c = 11{\cdot}88$ Å; the molecular weight is 361, the space group being $Pca2_1$.

Octafluorotetramethyleneiron Tetracarbonyl.—Tetrafluoroethylene was prepared by cracking polytetrafluoroethylene (I.C.I. powder) at *ca.* 500°. The gas was condensed and then taken off from a trap at −80° through soda-lime before use. About 3 g. of tetrafluoroethylene were condensed on to *ca.* 2 g. of $Fe_3(CO)_{12}$ in a thick-walled glass tube. After the sealed tube had been heated at 110—120° for 10—15 hr. it was cooled in liquid oxygen and opened and the excess of olefin and volatile material [mainly $Fe(CO)_5$] were removed. The residue was dissolved and the product crystallised from light petroleum (b. p. 40—60°) at −80° and finally sublimed in a vacuum from 40° to a probe at −80° (yield, *ca.* 100 mg.; m. p. 77—78°). On a larger scale the compound is best extracted from the residues with ethyl acetate (in which it is very soluble); the solution is filtered, methylcyclohexane is added, and the ethyl acetate (which distils first) is removed in a vacuum, whereupon the *product* separates as snow-white crystals [Found: C, 26·5, 26·5; F, 41·7; Fe, 15·4. $C_4F_8Fe(CO)_4$ requires C, 26·1; F, 41·3; Fe, 15·2%]. The density by flotation in aqueous solutions of barium mercuric iodide was 2·097 ± 0·001 g./c.c. and *X*-ray diffraction showed a monoclinic cell, with $a = 12{\cdot}86$, $b = 7{\cdot}55$, $c = 13{\cdot}58$ Å, $\beta = 116{\cdot}4°$, leading to a molecular weight of 373. The compound decomposes within a few hours in organic solvents; it is stable to dilute acids but is decomposed by sodium hydroxide. From molten $C_4F_8Fe(CO)_4$ gas evolution begins at 150° and is rapid at 185°; this is consistent with the pyrolysis of the compound to perfluorocyclobutane, mentioned in connection with the mass-spectrometric studies.

Octacarbonyl-μ-tetrafluorodimethylenedicobalt.—Cobalt carbonyl (1 g.) was sealed with an excess of tetrafluoroethylene and held at 25° for 10 days. After removal of the excess of olefin and carbonyl at 60° in a vacuum the residue crystallised from light petroleum (b. p. 30—40°) at −80°. Sublimation in a vacuum gave the *compound* as orange crystals [*ca.* 30%, based on $Co_2(CO)_8$], m. p. 80° (decomp.) (Found: C, 27·0; F, 16·4; Co, 26·2. $C_{10}F_4Co_2O_8$ requires C, 27·2; F, 17·2; Co, 26·7%). The compound is moderately stable in air but decomposes in solution in organic solvents (in which it is quite soluble), quite rapidly in air though in absence of air the solutions are stable for some hours; the compound decomposes in boiling benzene in absence of air.

Di-(π-cyclopentadienylcobalt)-endo-*μ-tetrafluorodimethylenecyclopentadiene.*—Di-π-cyclopentadienylcobalt (2 g.) in tetrahydrofuran (10 ml.) was sealed with tetrafluoroethylene (10 ml.; liquid) for 2 days at 25°. The volatile materials were removed and the residue was extracted (Soxhlet) with light petroleum (b. p. 30—80°); cooling to −80° gave a crystalline red-brown *product* (0·5 g.), decomp. 140° without melting (Found: C, 55·2; H, 4·4; F, 16·3; Co, 25·7%; *M*, 500. $C_{22}H_{20}Co_2F_4$ requires C, 55·25; H, 4·2; F, 15·9; Co, 24·65%; *M*, 478·3). The compound is sparingly soluble in light petroleum but is moderately soluble in carbon tetrachloride, chloroform, carbon disulphide, and acetone. It is stable in air and moderately so (several hours) in solution.

*π-Cyclopentadienyl(*endo*trifluoromethylcyclopentadiene)cobalt.*—$(\pi\text{-}C_5H_5)_2Co$ (0·7 g.) and trifluoromethyl iodide (2 ml.; liquid) were sealed and left at 25°. After 4 days the excess of iodide was removed and the residue extracted with light petroleum (b. p. 40—60°). The blood-red solution was evaporated in a stream of nitrogen and the residual oil distilled to a probe at −80°, giving blood-red crystals [*ca.* 40% based on $(\pi\text{-}C_5H_5)_2Co$] of *complex*, m. p. −10° (Found: C, 50·1; H, 3·8; Co, 23·2. $C_{11}H_{10}CoF_3$ requires C, 51·1; H, 4·0; Co, 22·8%). The compound decomposes above 110° and is readily oxidised in air in the pure state and even more rapidly in solution in organic solvents. It is stable in hydrocarbon and other solvents in absence of air.

Infrared Spectra.—Spectra were taken on a Perkin–Elmer model 21 instrument with sodium chloride, calcium fluoride, and potassium iodide prisms in the appropriate regions.

Octafluorocyclohexa-1,3-*diene* (5 mm. Hg; 10-cm. gas cell): 1750m, 1710m (C=C str.), 1400s, 1352s, 1278m, 1223w, 1176w, 1152s, 1105s, 1020w, 988s, 945m cm.$^{-1}$.

Octafluorocyclohexa-1,4-*diene* (as above): 2195w, 1785w, 1741s (C=C str.), 1410w, 1375w, 1330s, 1282w, 1242s, 1204w, 1176w, 1150m, 1100s, 1025s, 975s cm.$^{-1}$. The spectra of these olefins in the C=C region only have been reported previously,[9] the values quoted being 1713, 1753 (1,3-), and 1739 (1,4-) cm.$^{-1}$.

$C_6F_8Fe(CO)_3$ (CCl_4, CS_2, and C_2Cl_4 mulls): 2480w; 2108s, 2054vs, 2018m (C–O str.); 1550s (C=C str.); 1455m, 1407m, 1278vs, 1138s, 1105m, 1068m, 1047s, 974s, 941vs, 805w, 723s cm.$^{-1}$.

$C_4F_8Fe(CO)_4$ (CCl_4, CS_2, and C_2Cl_4 mulls): 2480w; 2160s, 2108vs, 2088vs, 2055s (C–O str.); 1332m, 263m, 1228m, 1170s, 1103s, 1060s, 968s, 910s, 720m, 647s, 628w, 610w, 575s, 520m, 492m, 437m cm.$^{-1}$.

$(CO)_4Co(CF_2)_2Co(CO)_4$ (CCl_4 and CS_2): 2480w, 2430w; 2130s, 2070vs, 2025vs, 1940m (C–O) str.); 1218s, 1048m, 925w, 785s, 767vs, 675s cm.$^{-1}$.

(π-$C_5H_5CoC_5H_5$-*endo*-CF_2–$)_2$ (CCl_4, CS_2 and C_2Cl_4 mull): 3090m (C–H str. of π-C_5H_5), 2940w (C–H_β str.), 1420w, 1383w, 1346w, 1336w, 1322m, 1250w, 1220m, 1146s, 1108m, 1088s, 1070m, 1050m, 1007m, 998m, 962m, 912w, 908w, 875w, 853w, 836m, 805s, 692s, 655m cm.$^{-1}$.

π-$C_5H_5CoC_5H_5CF_3$ (CCl_4): 3070w (C–H str. of π-C_5H_5), 2930w (C–H_β str.), 1835m, 1785m, 1340m, 1255m, 1230m, 1203m, 1183m, 1142s, 1127s, 1077m, 1033m, 938m, 675m cm.$^{-1}$.

Mass-spectrometric Analysis.—A Consolidated 21-103C mass spectrometer was used to record the mass spectra of $C_4F_8Fe(CO)_4$ and $C_6F_8Fe(CO)_3$. The conditions employed for $C_4F_8Fe(CO)_4$ were as follows: inlet temperature 25°, source temperature 250°, and current 10·5 microamp. The following conditions were used for obtaining the mass spectrum of $C_6F_8Fe(CO)_3$: inlet temperature 25°, source temperature 250°, current 15 and 60 microamp. The sample holder was heated at 55° in the analysis of $C_6F_8Fe(CO)_3$, but no heating of the sample was required for $C_4F_8Fe(CO)_4$.

High-resolution Nuclear Magnetic Resonance Spectra.—The spectra were recorded with Varian spectrometers V-4311 and 4310C at frequencies of 56·45 and 40 Mc./sec. The samples were contained in 5-mm. (outside diameter) Pyrex spinning tubes. Line positions were measured by the conventional side-band technique. Tetramethylsilane was added to the solutions as an internal reference for protons, and shifts are given in τ-values. Fluorine resonance line positions are given in p.p.m. relative to benzotrifluoride, positive values representing lines on the high-field side of this reference.

Perfluorocyclohexa-1,3-*diene* (liquid, reference external): 63·20, approx. triplet (13·2 ± 1 c./sec.) with additional structure, including weak components at ±31 c./sec. from centre, CF_2 groups, split by F_1 and F_4; 91·55, " triplet " (15·2 ± 1 c./sec.), F_2 and F_3, each split by F_1 and F_4; $100{\cdot}9_5$, approx. pentuplet (inner components 13·4 c./sec., outer components 30·6 c./sec., from centre) with finer structure (? quartets) $\sim$1·5 c./sec., F_1 and F_4, split by F_2 and F_3, and by nearest CF_2 group.

Perfluorocyclohexa-1,4-*diene* (liquid, reference external): 51·43, complex multiplet, CF_2 groups; 96·30, complex multiplet, =CF groups.

$C_6F_8Fe(CO)_3$ (in CCl_4 solution, reference external): (*a*) 35·4; centre (calculated for "A" of an "AB " pair) of each of two equivalent ^{19}F nuclei, one in each CF_2 group, split into an unsymmetrical doublet (232·1 ± 1 c./sec.) by the non-equivalent " B " fluorine nucleus in the same CF_2 group, and again into a doublet (18·2 ± 0·7 c./sec.) by the adjacent fluorine nucleus F_1 or F_4. Each of the resulting four component lines has additional unresolved fine structure ($\frac{1}{2}$ width of lines $\sim$7 c./sec.).

(*b*) 54·70, centre (calculated for " B " of "AB " pair) of each of two equivalent ^{19}F nuclei, the others in each CF_2 group, doublet (232 ± 1 c./sec.) doublet (14·2 ± 1 c./sec.), latter by coupling with adjacent F_1 or F_4. Additional unresolved coupling (not identical with that of "A" nuclei) gives $\frac{1}{2}$ width of about 15 c./sec.

(*c*) 119·4, approx. triple (19·4 ± 1 c./sec.) triplet (3·4 c./sec.), $F_2 + F_3$ split by F_1 and F_4, and by the nearest CF_2 group (3·4 c./sec.).

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[9] Evans and Tatlow, *J.*, 1954, 3779.

(*d*) 139·5, approx. pentuplet (18·2 ± 1 c./sec.) with additional (? quartet) structure ($\sim$3—4 c./sec.), $F_1 + F_4$, split by F_2 and F_3 and by the adjacent CF_2 group.

$C_4F_8Fe(CO)_4$ (in CCl_4, internal reference): 9·25, approx. pentuplet (1 : 4 : 5 : 4 : 1), ($\sim$2·5 c./sec.), central CF_2 groups; 73·95, approx, pentuplet (1 : 5 : 10 : 5 : 1), ($\sim$2·6 c./sec.), terminal CF_2 groups.

$[(CO)_4CoCF_2\text{–}]_2$ (in CCl_4, internal reference): $-30{\cdot}7$, single fluorine resonance line, width $\leqslant 2$ c./sec.

$[\pi\text{-}C_5H_5CoC_5H_5CF_2\text{–}]_2$ (in CCl_4, external reference): fluorine resonance: 62·2, doublet (13·5 c./sec.), split by methylene proton H_β. Proton resonance: 5·08, " triplet " (2 c./sec.), $H_3 + H_4$ split by $H_2 + H_5$; 4·62, singlet, π-C_5H_5 group; $\sim$3·1 (very weak), H_β; 2·37, $H_2 + H_5$.

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