

POLYFLUOROAROMATIC DERIVATIVES OF METAL CARBONYLS II*. REACTIONS OF DECAFLUOROBENZHYDRYL BROMIDE AND RELATED COMPOUNDS

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INTRODUCTION

Reaction of perfluoroalkyl iodides with iron pentacarbonyl gives (perfluoroalkyl)iron tetracarbonyl iodides, $R_fFe(CO)_4I^2$. Similar reactions with polyfluoroaromatic compounds have not yet been reported, and it was hoped that some stable organometallic complexes could be isolated from the reaction between decafluorobenzhydryl bromide, $(C_6F_5)_2CHBr$ (I), and metal carbonyls. Coffey³ has found that *gem*-dihalides, such as $(C_6H_5)_2CCl_2$, react with iron pentacarbonyl to give highly-coloured solutions, but only the products of coupling reactions, such as $(C_6H_5)_2C=C(C_6H_5)_2$ in the case mentioned, could be isolated from these solutions. More recently Corey and co-workers^{4,5} have used the ability of nickel carbonyl to remove halogen from allylic halides to form complexes whose degradation leads to cyclisation, and have used the reaction in an elegant one-step synthesis of 1,4,7-trimethylene-cyclononane from 1,1-bis(chloromethyl)ethylene⁵.

We have previously reported¹ the reactions of metal carbonyl anions with a variety of substituted polyfluoroaromatic compounds to give complexes in which the metal is attached to the fluorinated ring. Herein we describe further reactions of these anions with fluoroaromatic compounds containing a halogen in a side-chain, such as (I), pentafluorobenzyl bromide, and related compounds.

DISCUSSION

Treatment of iron pentacarbonyl with (I) gave no organo-iron complex, but rather a mixture of two fluorocarbons, bis(pentafluorophenyl)methane, $(C_6F_5)_2CH_2$ (II), and 1,1,2,2-tetrakis(pentafluorophenyl)ethane, $(C_6F_5)_2CHCH(C_6F_5)_2$ (III). The formation of (II), found in small amounts, probably occurs by replacement of bromine by hydrogen, perhaps by traces of moisture in the carbonyl or solvents. The major reaction leads to the substituted ethane (III), and is completely analogous to the reactions described by Coffey³ earlier.

Both fluorocarbons have been reported recently by Russian workers, who obtained (II) by reduction of decafluorobenzophenone (50% yield) or decafluorobenzhydrol (60% yield) with hydriodic acid and red phosphorus. The ethane was obtained

* Ref. 1 is considered to be Part I.

from (I) by treatment with lithium aluminium hydride, copper (I) cyanide or C_6F_5MgBr (77% yield)⁶.

The same compounds were formed in the reactions between (I) and the anion formed from cyclopentadienyliron dicarbonyl dimer. A similar reaction with benzhydriyl chloride gave $[CpFe(CO)_2]_2^*$ and traces of a white material identified as tetraphenylethane from its mass spectrum. Pentafluorobenzyl bromide reacts with the same anion to give three products, identified as decafluorobibenzyl, and the iron complexes $CpFe(CO)_2CH_2C_6F_5$ (IV) and $CpFe(CO)_2C_6F_4CH_2Fe(CO)_2Cp$ (V). The pentafluorobenzyl complex is unstable, both in solution and thermally; recrystallisation from petroleum ether gives a mixture of the complex and $C_6F_5CH_2CH_2C_6F_5$, which may be separated by careful sublimation. On heating, some decomposition occurs at the melting point and the sample does not liquefy completely until some way above the melting point of decafluorobibenzyl.

Compounds of the type $RM(CO)_5$ ($M = Mn$ or Re) appear to be very unstable where R is a secondary or tertiary alkyl group.⁷ Reaction of tert-butyl chloride with $[CpFe(CO)_2]^-$ gave only the hydride $CpFe(CO)_2H$ together with isobutene⁸. Reactions between secondary or tertiary alkyl halides and $[Mn(CO)_5]^-$ gave $Mn_2(CO)_{10}$ and a hydrocarbon. A similar case is the reaction between $[Mn(CO)_5]^-$ and tropylium bromide, which gives bitropyl and $Mn_2(CO)_{10}$ ⁹.

It is evident that the stability of the radical or ion, R^\cdot or R^+ , which can be formed from RX in reaction with a metal carbonyl anion, determines the nature of the products isolated. If the radical can be stabilised, then R_2 is likely to be isolated from the reaction; examples are tropylium giving bitropyl and in the present case $(C_6F_5)_2CH^\cdot$, giving $(C_6F_5)_2CHCH(C_6F_5)_2$. On the other hand, if the radical cannot be stabilised, then an R -metal bond will be formed, such as with methyl iodide and $[Mn(CO)_5]^-$, when methylmanganese carbonyl is formed.

The greater stabilities of the fluorinated radicals compared with the hydrocarbon analogues are evident from the present study. Thus, reaction of the metal carbonyl anion with benzhydriyl chloride only gives traces of $(C_6H_5)_2CHCH(C_6H_5)_2$, whereas the fluorinated compound affords much larger amounts of the coupling product. Even the radical with only one fluorinated ring appears to possess considerable stability, if the ease of formation of decafluorobibenzyl is any guide; this fluorocarbon is isolated from the reaction mixture and is formed very readily by decomposition of the metal complex. Such a reaction is not found in the hydrocarbon case, where as discussed below no bibenzyl could be found, even though the complex was unstable.

The binuclear complex (V) is obtained in small amounts by treating pentafluorobenzyl bromide with $[CpFe(CO)_2]^-$, as a bright yellow solid, which is thermally quite stable, and may be sublimed at $\sim 200^\circ$ (0.1 mm). It was easily characterised by its characteristic infrared, ¹⁹F NMR and mass spectra, as described below. King¹⁰ has described complexes of the type $CpFe(CO)_2(CH_2)_nFe(CO)_2Cp$ ($n = 3-6$), and also the fluorinated analogue ($n = 3$)²². Reaction of hexafluorobenzene with excess of metal carbonyl anion gives only the monosubstituted derivative, although similar reactions with octafluoronaphthalene have given very small yields of a disubstituted compound¹¹. Presumably attachment of one metal atom to the ring deactivates it towards further substitution. Our complex thus represents an intermediate type,

* $Cp = \pi-C_5H_5$.

linking two metal atoms by means of a methylene group and fluorinated ring.

Reaction between benzyl chloride and $[\text{CpFe}(\text{CO})_2]^-$ gives the expected σ -benzyl complex as a volatile bright yellow solid which is not very stable in air, and rapidly decomposes in solution. However, in contrast to the fluorinated complex, no bibenzyl was isolated either from the reaction mixture or from the decomposition products. After this work was completed, Bibler and Wojcicki described the same complex¹².

RESULTS

Infrared spectra

The infrared spectra of the various compounds reported in this Paper are listed in Table 1. The fluorocarbon derivatives show the expected strong bands due to

TABLE I

INFRARED SPECTRA OF SEVERAL POLYFLUOROAROMATIC DERIVATIVES (cm^{-1})^a

$(\text{C}_6\text{F}_5)_2\text{CH}_2$	1656 m(sh) 1650 m 1524 vs 1512 vs 1506 vs(sh) 1407 m 1331 m 1310 w 1304 w 1270 w 1237 w 1180 w 1143 w 1122 vs 1066 w 1030 w 1001 vs 963 w 901 m 806 m 772 m 748 w 703 w 678 m
$(\text{C}_6\text{F}_5)_2\text{CHCH}(\text{C}_6\text{F}_5)_2^b$	1660 m 1654 m(sh) 1590 vw 1527 vs 1512 vs 1500 vs 1424 m 1317 m 1307 m 1290 w 1234 m 1144 vs 1124 vs 1035 w 1021 w 1006 m 988 vs 970 vs 945 s 908 w 792 w 778 m 764 m 737 w 730 w 684 m 649 w 630 m
$\text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{C}_6\text{F}_5$	1660 m 1523 s 1510 vs 1367 m(br) 1318 w 1310 w 1189 m 1171 w 1126 s 1120 s 1056 m 994 m 973 m 960 vs 940 m 918 w
$\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$	2025 vs 1975 vs $[\nu(\text{CO})]$ 1656 s 1515 vs(sh) 1500 vs 1440 w 1376 w 1310 w 1303 w 1185 m 1125 s 1055 m 994 s 973 s 960 vs 940 s 919 w 828 w (C_5H_5) 710 w
$\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_4\text{Fe}(\text{CO})_2\text{Cp}$	2043 vs 2019 vs 1998 vs 1968 vs $[\nu(\text{CO})]^c$ 1660 w 1503 w 1434 w 1384 w 1359 w 1138 w(br) 1063 w 1007 w 995 w 914 s 839 m(sh) (C_5H_5) 834 m $(\text{C}_5\text{H}_5)^f$

^a Cyclohexane solution. ^b Nujol mull. ^c Chloroform solution.

C–F stretching modes, and also the strong absorption at $\sim 1500 \text{ cm}^{-1}$ that has been assigned to the aromatic ring vibration¹³. The metal complexes do not show this band, presumably because of some interaction with the conjugated system.

The mononuclear metal complexes show the usual two carbonyl stretching modes in the 2000 cm^{-1} region. The binuclear complex(V) shows four bands of approximately equal intensity in this region (Fig. 1). Comparison of the carbonyl stretching frequencies in this complex with those shown by the related complexes $\text{C}_6\text{F}_5\text{Fe}(\text{CO})_2\text{Cp}^{14}$ and $\text{C}_6\text{F}_5\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}$ allows an assignment of these bands as shown, since no vibrational coupling of these modes would be expected in this molecule.

	$\text{C}_6\text{F}_5\text{Fe}(\text{CO})_2\text{Cp}$	$\text{C}_6\text{F}_5\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}$	$\text{CpFe}(\text{CO})_2\text{C}_6\text{F}_4\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}$	
$\nu(\text{CO})$	2045	2025	2043	2019 cm^{-1}
	1997	1975	1998	1968

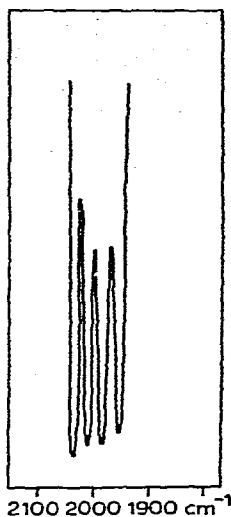
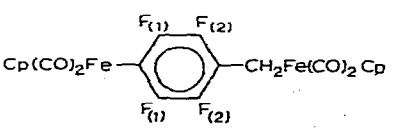


Fig. 1. Carbonyl stretch region of the infrared spectrum of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_4\text{Fe}(\text{CO})_2\text{Cp}$.

Fluorine-19 NMR spectra

The ^{19}F NMR spectra of the products are listed in Table 2. As expected, the pentafluorophenyl derivatives show three resonances with the intensity ratio 2 : 1 : 2,

TABLE 2
FLUORINE-19 CHEMICAL SHIFTS OF SOME POLYFLUOROAROMATIC COMPOUNDS^a

	<i>o</i> -F	<i>m</i> -F	<i>p</i> -F
$(\text{C}_6\text{F}_5)_2\text{CHBr}$	138.3	161.1	152.9
$(\text{C}_6\text{F}_5)_2\text{CH}_2$	145.2	167.8	160.8
$(\text{C}_6\text{F}_5)_2\text{CH}\cdot\text{CH}(\text{C}_6\text{F}_5)_2$	150.1	166.1	158.2
$\text{C}_6\text{F}_5\text{CH}_2\text{Br}$	144.7	163.9	155.5
$\text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{C}_6\text{F}_5$	149.1	167.3	159.1
$\text{C}_6\text{F}_5\text{CH}_2\text{Fe}(\text{CO})_2\text{Cp}$	146.6	165.6	159.6
		$\text{F}_{(1)}$	111.3
		$\text{F}_{(2)}$	145.3

^a In ppm upfield from CFCl_3 as internal reference.

assignable to the fluorines *ortho*, *para* and *meta* respectively to the substituent. The chemical shifts of the fluorines *ortho* to the iron atom in the binuclear complex show the characteristic deshielding associated with fluorines in this position; the pentafluorobenzyl complex IV does not show this effect, since the iron is separated from the ring by the methylene group, and is similar to the fluorines *meta* to the iron in complex V. The resonances were poorly resolved in most cases, and determination of coupling constants was not possible; in the decafluorobenzhydryl derivatives, this was perhaps due to interactions between two C_6F_5 groups attached to the same carbon atom.

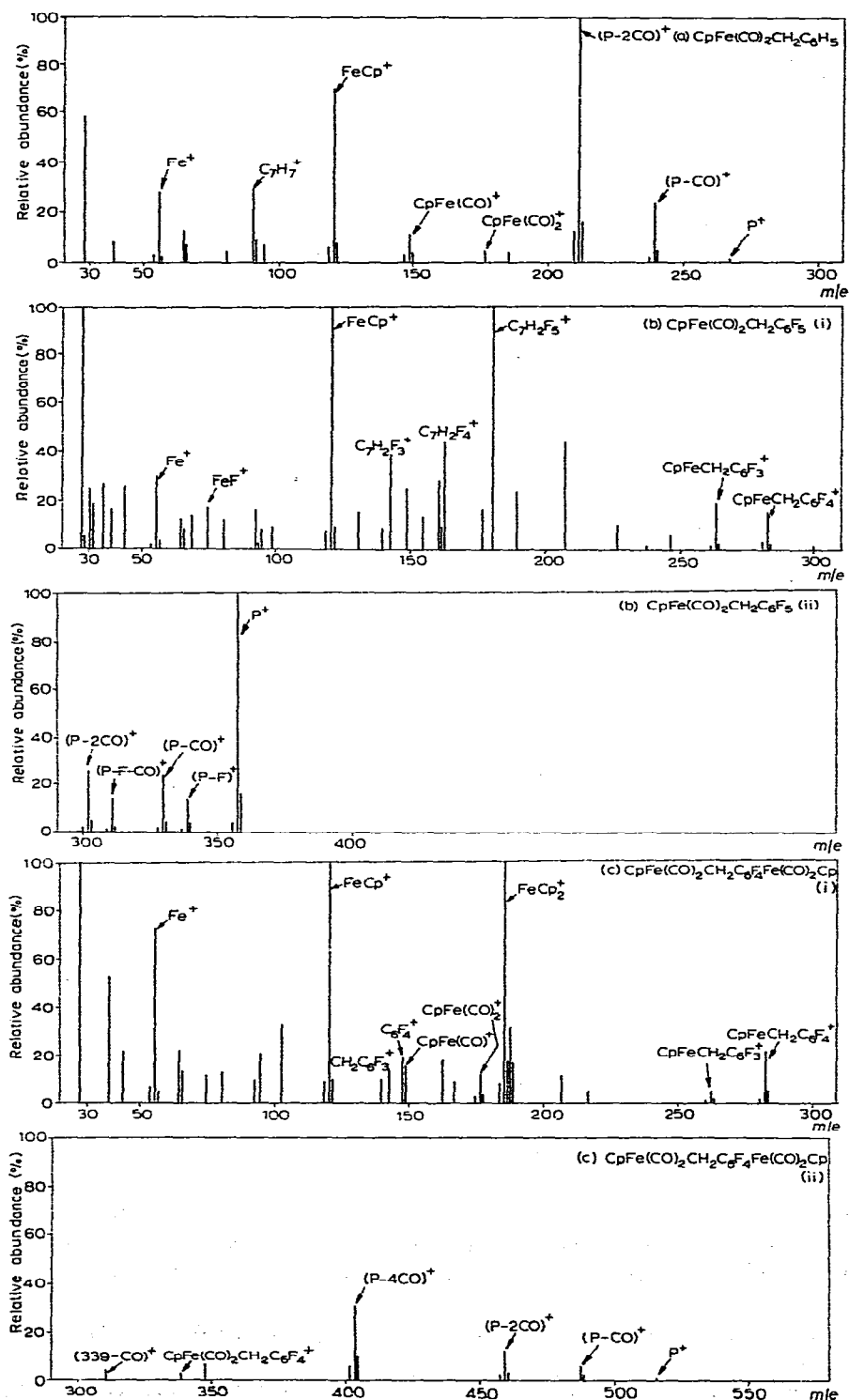


Fig. 2. Mass spectra of (a) $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$, (b) $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ and (c) $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_4\text{Fe}(\text{CO})_2\text{Cp}$.

TABLE 3

METASTABLE PEAKS PRESENT IN MASS SPECTRA OF SOME IRON COMPLEXES

Obsd. <i>m/e</i>	Calcd. <i>m/e</i>	Process
(a) CpFe(CO)₂CH₂C₆H₅		
69.1	69.1	CpFeCH ₂ C ₆ H ₅ ⁺ → CpFe ⁺ + CH ₂ C ₆ H ₅
92.5	92.5	CpFe(CO)CH ₂ C ₆ H ₅ ⁺ → CpFe(CO) ⁺ + CH ₂ C ₆ H ₅
98.3	98.3	CpFe(CO) ⁺ → CpFe ⁺ + CO
125.4	125.5	CpFe(CO) ₂ ⁺ → CpFe(CO) ⁺ + CO
187.2	187.3	CpFe(CO)CH ₂ C ₆ H ₅ ⁺ → CpFeCH ₂ C ₆ H ₅ ⁺ + CO
~215	215.0	CpFe(CO) ₂ CH ₂ C ₆ H ₅ ⁺ → CpFe(CO)CH ₂ C ₆ H ₅ ⁺ + CO
Also unidentified metastable transitions at <i>m/e</i> 46.5, 84.6		
(b) CpFe(CO)₂CH₂C₆F₅		
126.5	126.2	CH ₂ C ₆ F ₅ ⁺ → CH ₂ C ₆ F ₃ ⁺ + F
145.0	145.0	CH ₂ C ₆ F ₅ ⁺ → CH ₂ C ₆ F ₄ ⁺ + F
~246	246.3	CpFeCH ₂ C ₆ F ₄ ⁺ → CpFeCH ₂ C ₆ F ₃ ⁺ + F
Also unidentified metastable transitions at <i>m/e</i> 102.6, 149.5		
(c) CpFe(CO)₂CH₂C₆F₄Fe(CO)₂Cp		
77.7	77.4	CpFe(CO) ₂ CH ₂ C ₆ F ₄ ⁺ → CH ₂ C ₆ F ₄ ⁺ + CpFe(CO) ₂
168.8	168.0	CpFeCH ₂ C ₆ F ₄ ⁺ → CH ₂ C ₆ F ₄ Fe + Cp

Mass spectra

We have briefly reported¹⁶ the major features of the mass spectra of the benzyl and pentafluorobenzyl complexes described in this Paper. These spectra, together with that of the binuclear complex, are shown in Fig. 2, and metastable peaks observed are listed in Table 3.

In all cases, the characteristic peaks due to the CpFe(CO)₂ group are found. These occur at *m/e* 39 (C₃H₃⁺), 56 (Fe⁺), 65 (C₅H₅⁺), 93 (FeC₃H₃⁺), 121 (FeC₅H₅⁺), 149 (C₅H₅FeCO⁺) and 177 (C₅H₅Fe(CO)₂⁺), and will not be discussed further here. Peaks due to successive loss of the carbonyl groups are found, except in (V), where (P-3 CO)⁺ is not observed. In this spectrum, ions corresponding to the CpFe(CO)₂ group are present in fairly high abundance, and a metastable peak (Table 2) shows that loss of this group as a whole unit occurs in preference to its gradual fragmentation.

The base peak in the spectrum of the benzyl complex is (P-2 CO)⁺, and other predominant ions comprise C₇H₇⁺ and one at *m/e* 186, which may be assigned to ferrocene, Fe(C₅H₅)₂⁺, formed by decomposition, or to C₃H₃FeC₇H₇⁺. In contrast, the fluorinated complex loses fluorine easily to give (P-F)⁺, and ions resulting from loss of CO groups from this ion. Below *m/e* 150, various fluorocarbon ions are found. Similar ions have also been observed in many aromatic fluorocarbon derivatives¹⁷. The base peak is C₇H₂F₅⁺; both this ion and C₇H₂F₄⁺ seem to be formed by loss of FeCp from (P-2 CO)⁺ and (P-F-2 CO)⁺ respectively. The low relative abundance of FeC₇H₂F₅⁺ (2%) suggests that the Fe-C₅H₅ bond is much stronger than the Fe-C₇H₂F₅ bond.

As previously mentioned¹⁶, the most abundant ion in the spectrum of (VI) is

assumed to be the π -tropylium- π -cyclopentadienyliron cation, formed in a manner similar to $C_7H_7^+$ from many benzylic compounds. It is interesting to note that $C_7H_7^+$ has only 30% intensity of the base peak and that $C_7H_7Fe^+$ is not observed. This indicates fragmentation of $C_5H_5FeC_7H_7^+$ occurs by fission of the weaker Fe- C_7H_7 bond. In contrast, the ion $C_7H_2F_5^+$ is much more intense than $C_5H_5FeC_7H_2F_5^+$, and suggests that further stabilisation of the pentafluorotropylium ion cannot occur by metal-complex formation. This is further supported by the ready loss of fluorine from the parent ion. The high abundance of $C_7H_2F_5^+$ suggests, however, that ring enlargement to the substituted tropylium cation has occurred, and the absence of ions $C_6F_5^+$ and $C_6F_4^+$ supports this view, these ions normally being found in the spectra of C_6F_5X compounds.

These observations are in keeping with the idea that fluorocarbons do not form π -complexes of the same type as do the corresponding hydrocarbons. Thus, no π -complexes of hexafluorobenzene analogous to $Cr(C_6H_6)_2$ have been reported, and structural differences occur between complexes of butadiene and of butadienes substituted with electronegative groups¹⁸.

The spectrum of the binuclear complex (V) shows a strong peak due to ferrocene, perhaps formed by decomposition, and the ion formed by loss of the four carbonyl groups is relatively intense. The subsequent breakdown of this ion involves loss of the iron groups: an ion at m/e 348 can be assigned to $CpFeCH_2C_6F_4Cp^+$. Similar extrusion of iron has been found¹⁹ with ferrocene, giving ions such as $C_5H_5-C_5H_5^+$ and $C_5H_4=C_5H_4^+$. The presence of ions such as $C_6F_4^+$ may imply that ring expansion has not occurred in this case.

Both fluorocarbon complexes show ions such as FeF^+ (m/e 75) and $CpFeF^+$ (m/e 140), although similar carbonyl-containing ions are absent. This type of ion appears to be quite common in the spectra of fluorocarbon-metal complexes; loss of a metal fluoride as a neutral species has previously been reported by King²⁰, and by Miller²¹.

EXPERIMENTAL

Infrared spectra were recorded on Perkin-Elmer 237 or 257 grating spectrophotometers, and ¹⁹F NMR spectra on a Perkin-Elmer R 10 spectrometer. All reactions were run under nitrogen. Chromatography was performed on columns of "Florisil". Petroleum ether is a fraction b.p. 40-60° unless otherwise stated. The polyfluoroaromatic compounds were gifts from the Imperial Smelting Corporation which are gratefully acknowledged; other reagents were commercial products. The sodium salt of cyclopentadienyliron dicarbonyl dimer was made as has been previously described¹³.

Reactions of decafluorobenzhydryl bromide

(a) *With iron pentacarbonyl.* The carbonyl (5 ml) and decafluorobenzhydryl bromide (2 ml) were refluxed 3 h in petroleum ether (b.p. 100-120°) (5 ml), and after cooling, the reaction mixture was evaporated to dryness. Sublimation at room temperature (0.1 mm; probe at -78°) gave a white solid, which was recrystallised from petroleum ether to give long white needles of bis(pentafluorophenyl)methane, m.p. 55-56° (lit.⁶ m.p. 62°) (80 mg). [Found: C, 44.4; H, 0.45; F, 54.1; mol.wt. (mass

spectrum), 348. $C_{13}H_2F_{10}$ calcd.: C, 44.8; H, 0.55; F, 54.1%; mol.wt. 348.] The evaporated acetone extract of the residue was chromatographed, and petroleum ether/benzene mixtures slowly eluted a white solid, which was recrystallised from aqueous acetone to give white cubes of 1,1,2,2-tetrakis(pentafluorophenyl) ethane, m.p. 250° (mixed m.p. with a sample prepared by reaction of (I) with copper bronze¹⁵, $249\text{--}250^\circ$) (600 mg, 37%). [Found: C, 45.10; H, 0.25; F, 54.61; mol.wt. (mass spectrum), 694. $C_{26}H_2F_{20}$ calcd.: C, 44.95; H, 0.29; F, 54.79%; mol.wt., 694.]

In one experiment where the products were separated by chromatography rather than by sublimation, an intensely red fraction was eluted with ethanol. On evaporation, this gave an oil, which on heating gave a black infusible residue containing iron; its infrared spectrum showed no bands due to C-F vibrations, and it was not examined further.

(b) *With molybdenum hexacarbonyl.* In a similar experiment to (a) molybdenum carbonyl (1.3 g) and (I) (2 g) afforded the ethane (960 mg, 59%).

(c) *With manganese carbonyl.* The reaction between manganese carbonyl (1 g) and (I) (1 g) gave the same fluorocarbon (720 mg, 88%).

In both cases (b) and (c), the infrared spectrum of the carbonyl recovered by sublimation showed absorptions similar to those found in bis(pentafluorophenyl)-methane. No attempt was made to separate the mixtures into their components.

Reactions of $[CpFe(CO)_2]^-$

(a) *With decafluorobenzhydryl bromide.* The sodium salt prepared from $[CpFe(CO)_2]_2$ (1.8 g) in tetrahydrofuran (30 ml) was treated with (I) (4.3 g) in tetrahydrofuran (20 ml). After removal of solvent ($30^\circ/0.1$ mm) the residue was extracted with dichloromethane (2×5 ml) and the evaporated extract was chromatographed. Petroleum ether eluted a small amount of volatile white solid, identified (infrared spectrum) as $(C_6F_5)_2CH_2$; benzene/petroleum ether mixtures slowly eluted a fraction containing $(C_6F_5)_2CHCH(C_6F_5)_2$ (700 mg); and benzene eluted a small amount of an unstable unidentified yellow oil $[CpFe(CO)_2H?]$, which showed two terminal carbonyl stretching bands at 2007 and 2048 cm^{-1} . (Found: C, 49.2; H, 2.0%; $C_7H_6F_2O_2$ calcd.: C, 47.2; H, 3.37%.)

(b) *With benzhydryl chloride.* A similar reaction using $[CpFe(CO)_2]_2$ (3.54 g) and benzhydryl chloride (4.0 g) gave, on chromatography, traces of a white solid and unreacted $[CpFe(CO)_2]_2$. The mass spectrum of the white solid showed a molecular ion at m/e 334, and an intense peak at m/e 167, which, together with its mode of formation, suggests that the material is 1,1,2,2-tetraphenylethane (calcd. for $C_{26}H_{22}$: mol.wt., 334).

(c) *With benzyl chloride.* Chromatography of the product from a reaction using $[CpFe(CO)_2]_2$ (3.54 g) and benzyl chloride (2.53 g) in the usual way gave, with 10% benzene/light petroleum, a yellow eluate, which rapidly darkened in air. Evaporation and sublimation gave σ -benzyl- π -cyclopentadienyliron dicarbonyl (2.8 g, 52%). The analytical sample was recrystallised from light petroleum at 0° and resublimed to give a bright yellow solid, m.p. $52\text{--}54^\circ$ (lit.¹² m.p. $55\text{--}57^\circ$). [Found: C, 63.0; H, 4.75%; mol.wt. (mass spectrum), 268. $C_{14}H_{12}FeO_2$ calcd.: C, 62.7; H, 4.5%; mol.wt., 268.]

(d) *With pentafluorobenzyl bromide.* The product from a similar reaction to (c), using $[CpFe(CO)_2]_2$ (1.77 g) and $C_6F_5CH_2Br$ (2.6 g) was chromatographed. Petroleum ether/benzene (80 : 20) eluted a yellow band, which was evaporated and sublimed

to give yellow σ -(pentafluorobenzyl)- π -cyclopentadienyliron dicarbonyl (IV), m.p. 70–72° (dec.) (240 mg, 3.4%). [Found: C, 46.4; H, 1.8; mol.wt. (mass spectrum), 358. $C_{14}H_7F_5FeO_2$ calcd.: C, 46.9; H, 1.95%; mol.wt., 358.] Recrystallisation from petroleum ether gave a product which was obviously a mixture of the desired complex and white crystals. The latter were purified by further crystallisation and sublimation to give decafluorobibenzyl, m.p. 101–102°. (Found: C, 46.6; H, 1.0. $C_{14}H_4F_{10}$ calcd.: C, 46.4; H, 1.1%.)

Further elution of the column with benzene/light petroleum (30:70) gave a second yellow material, which was sublimed at $\sim 200^\circ$ (0.1 mm), and identified as the binuclear complex V, m.p. 195–197° (dec.), with darkening above 180°. [Found: C, 49.28; H, 2.13; mol.wt. (mass spectrum), 516. $C_{21}H_{12}F_4Fe_2O_4$ calcd.: C, 48.85; H, 2.32%; mol.wt., 516.]

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SUMMARY

The reactions of $(C_6F_5)_2CHBr$ with metal carbonyls give mixtures of $(C_6F_5)_2CH_2$ and $(C_6F_5)_2CHCH(C_6F_5)_2$. The same products are formed in the reaction with $[CpFe(CO)_2]^-$, but only traces of the hydrocarbon analogue $(C_6H_5)_2CHCH(C_6H_5)_2$ are formed in a similar reaction using $(C_6H_5)_2CHCl$. With benzyl chloride, $C_6H_5-CH_2Fe(CO)_2Cp$ is formed; pentafluorobenzyl chloride affords a mixture of $C_6F_5-CH_2CH_2C_6F_5$ and the complexes $C_6F_5CH_2Fe(CO)_2Cp$ and $CpFe(CO)_2C_6F_4CH_2-Fe(CO)_2Cp$.

The infrared, fluorine-19 NMR and mass spectra of some of the products are described and discussed.

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