Polyfluoroaromatic Derivatives of Ferrocene

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The preparations of polyfluoroaromatic derivatives of ferrocene, $C_5H_5FeC_5H_4R$ and $(RC_5H_4)_2Fe$ (R = $CO{\cdot}C_6F_5$, $CH_2{\cdot}C_6F_5$, C_6F_5, or $C_6F_4{\cdot}OCH_3$-*p*), are described, and the spectroscopic properties of these compounds are discussed. The formation of two polynuclear ferrocene compounds is also reported.

IN spite of the recent widespread interest in the chemistry of polyfluoroaromatic compounds, the only reported fluoroaromatic derivatives of ferrocene are *o*-fluorophenylferrocene,[1] *m*-trifluoromethylphenylferrocene,[1-3] and 1,1′-bis-(*p*-fluorobenzoyl)ferrocene.[4,5] We here describe the syntheses of several pentafluorophenyl- and pentafluorobenzoyl-ferrocenes, and some reactions of these compounds.

Reactions of ferrocene with pentafluorobenzoyl chloride under Friedel–Crafts conditions gave a reddish-purple compound, readily identified as pentafluorobenzoylferrocene (I). Several experiments, with different conditions, gave evidence for the formation of a small

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[1] W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *J. Amer. Chem. Soc.*, 1964, **86**, 1376.

[2] W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *J. Amer. Chem. Soc.*, 1964, **86**, 1382.

[3] J. D. Johnson, *Diss. Abs.*, 1963, **23**, 4513.

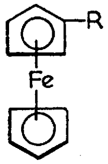
[4] R. L. Schaaf and C. T. Lenk, *J. Org. Chem.*, 1963, **28**, 3238.

[5] D. W. Fischer, *Acta Cryst.*, 1964, **17**, 619.

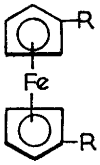
amount of the disubstituted product, but we were not able to isolate it in a pure state from these reactions. However, a high yield of 1,1'-bis(pentafluorobenzoyl)-ferrocene (II) was obtained from the reaction between acid chloride and dilithioferrocene, obtained from the n-butyl-lithium–tetramethyldiaminoethane (TMED) complex.[6]

The ketones (I) and (II) could not be sublimed successfully; similar fluoroaliphatic ketones, *e.g.* $FcCOCF_3$ (Fc = ferrocenyl), are reported to form viscous dark red oils which crystallise with difficulty.[7] The usual ketonic derivatives could not be obtained by use of semicarbazide, but the 2,4-dinitrophenylhydrazones formed in low yield as lustrous black crystalline solids. It has been reported[8] that decafluorobenzophenone does not form similar derivatives, probably for steric reasons.

A recent study[9] of the Clemmensen reduction of benzoylferrocene reported Fc(Ph)C:C(Ph)Fc as the major product (28%) accompanied by $PhCH_2Fc$ (7%), $Fc(Ph)CH{\cdot}CH(Ph)Fc$ (4%), and Fc_2CPhBz. Under similar conditions, compounds (I) and (II) gave the pentafluorobenzyl derivatives (III) and (IV). A small amount of a second yellow product was isolated from the reduction of (I); the mass spectrum showed a parent ion at *m*/*e* 728, with an accurate mass corresponding to $C_{34}H_{18}F_{10}Fe_2$, and in the absence of any further analytical and spectroscopic data, this compound is assumed to be 1,2-diferrocenyl-1,2-bis(pentafluorophenyl)ethylene.



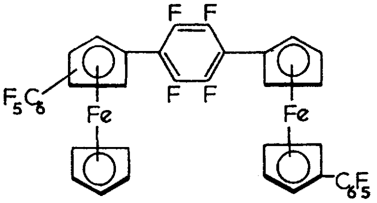
(I) R = $CO{\cdot}C_6F_5$
(III) R = $CH_2{\cdot}C_6F_5$
(V) R = C_6F_5
(VIII) R = $C_6F_4{\cdot}OMe$-*p*



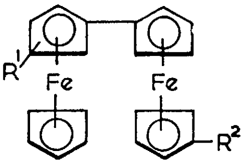
(II) R = $CO{\cdot}C_6F_5$
(IV) R = $CH_2{\cdot}C_6F_5$
(VI) R = C_6F_5
(IX) R = $C_6F_4{\cdot}OMe$-*p*

The reaction of lithioferrocene with bromopentafluorobenzene gave only ferrocene, together with some bromoferrocene, identified by mass spectrometry. Evidently a ready exchange occurs between ferrocenyllithium and bromopentafluorobenzene, rather than substitution to give the fluoroaromatic derivative. However, reaction of lithioferrocene with hexafluorobenzene gave a mixture of pentafluorophenyl- and 1,1'-bis(pentafluorophenyl)-ferrocenes [(V) and (VI), respectively], with the former predominant. Use of the n-butyl-lithium–TMED reagent to lithiate ferrocene gave a much higher yield of compound (VI). A mixture of (V) and (VI) could also be obtained by arylation of ferricinium salts, by the method of Beckwith and Leydon,[9] with pentafluorophenylhydrazine and silver oxide in glacial acetic acid.[10]

A second product (VII) was isolated in small yield from the reaction between dilithioferrocene (from n-BuLi–TMED and ferrocene) and hexafluorobenzene, as a relatively insoluble bright orange-red solid, m.p. 178—180°. The spectrum of this compound showed an intense parent ion at *m*/*e* 850, and an accurate mass determination indicated the molecular formula $C_{38}H_{16}F_{14}Fe_2$. The ^1H n.m.r. spectrum showed resonances at τ 5·24br (5H, m), 5·51 (6H, m) and 5·92 (5H, sharp s). The two multiplets each appeared to consist of overlapping resonances. The ^{19}F n.m.r. spectrum had absorptions at 140·0br (d), 141·8 (complex), 159·1 (t), and 164·4 (complex) p.p.m., with relative intensities *ca.* 2 : 2 : 1 : 2. However, a saturated solution in acetone was still too weak to allow full resolution of the signals; the absorptions at 141·8 and 164·4 p.p.m., appeared to be four- and ten-line resonances, respectively.



(VIIa)



(VIIb)

The molecular formula indicates that (VII) contains two ferrocene nuclei, and the singlet at τ 5·92 can be assigned to a single unsubstituted cyclopentadienyl group. In the fluorine n.m.r. spectrum the triplet suggests the *para*-fluorine of a C_6F_5 group, and the high-field resonance is reminiscent of two overlapping AA'XX' systems. The data are consistent with a molecule containing two ferrocene nuclei, two C_6F_5 groups, and a C_6F_4 group. A structure in which the C_6F_4 group bridges two ferrocene nuclei (VIIa) would be expected to show three lines in its ^{19}F n.m.r. spectrum, at about 140·5, 159·5, and 164·0 p.p.m., with relative intensities 4 : 1 : 2; the fluorines of the C_6F_4 group would be perhaps slightly separated from the *ortho*-fluorines of the C_6F_5 groups. This is consistent with the observed spectrum, but the formation of this complex is difficult to understand, since the most logical route is by attack of a 1-lithio-2(or 3)-pentafluorophenylferrocene on one of the *para*-fluorines of (VI), and to our knowledge, no instances of homoannular dimetallation under these conditions have been reported.

An alternative structure, (VIIb), can be entertained for this compound, and contains a biferrocenyl group bearing pentafluorophenyl and nonafluorobiphenyl sub-

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[6] M. D. Rausch and D. J. Ciappenelli, *J. Organometallic Chem.*, 1967, **10**, 127.

[7] E. B. Sokolova, G. P. Chalykh, and A. P. Suslov, *Zhur. obshchei. Khim.*, 1968, **38**, 537.

[8] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.

[9] A. L. J. Beckwith and R. J. Leydon, *Austral. J. Chem.*, 1966, **19**, 1381.

[10] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 1962, 4966.

stituents (either $R^1 = C_6F_5$, $R^2 = C_6F_4{\cdot}C_6F_5$ or $R^1 = C_6F_4{\cdot}C_6F_5$, $R^2 = C_6F_5$), but we are unable to distinguish between these possibilities, nor to determine the position of substitution relative to the biferrocenyl link.

The calculated n.m.r. spectra for (VIIb) shows absorptions at 137·6, 137·9, 140·5, 148·7, 159·4, 161·0, and 163·9 p.p.m., with relative intensities 2 : 4 : 2 : 1 : 1 : 2 : 2, which, with the exception of the fourth band, and allowing for solvent effects, is in fair agreement with the observed spectrum. The formation of a compound of this type parallels previous observations on the isolation of biferrocenyls from reactions involving lithioferrocenes, *e.g.* with trialkylbromosilanes,[11] and also the recently reported [12] formation of polynuclear fluoroaromatic derivatives in reactions of pentafluorophenyl-lithium with iodotrifluoroethylene, if the possibility of transmetalation to the fluoroaromatic ring is allowed. Unfortunately the mass spectrum did not allow a distinction to be drawn between the various possibilities.

Polyfluoroaromatic compounds are characterised by their susceptibility to nucleophilic substitution, *e.g.* by methoxide. Studies on transition-metal derivatives containing σ-bonded C_6F_5 groups have indicated [13] that the fluoroaromatic ring in these compounds is deactivated towards further substitution. Overlap of filled metal *d* orbirals with π* orbitals of the ring offers a means for back donation of electron density to the ring, with consequent resistance to nucleophilic attack. In ferrocene derivatives, some interaction of metal orbitals with substituents has been postulated, *e.g.* in the stabilisation of metallocene carbonium ions.[14] We examined the reaction of sodium methoxide with (V) and (VI) to determine whether the reactivity of polyfluoroaromatic ferrocene derivatives was subject to any similar effects.

Inasmuch as no substituted product could be isolated from the reaction between sodium methoxide and pentafluorophenylferrocene in refluxing methanol for 15 hr., ferrocene must react more slowly than hexafluorobenzene, which forms pentafluoroanisole in 72% yield in similar conditions.[15] However, prolonged reaction gave the expected methoxy-derivatives, which were isolated and characterised by conventional means. The mono- and 1,1′-bis-(*p*-methoxytetrafluorophenyl) derivatives (VII) and (VIII) were made, but no evidence for the formation of a mixed C_6F_5–C_6F_4OMe compound was obtained. No kinetic studies were made, nor were the reactions of other nucleophiles studied, but there is little doubt that many derivatives can be prepared by similar reactions. Qualitatively, the ferrocenyl group appears to have some deactivating effect on the reactivity of the fluoroaromatic nucleus.

Infrared Spectra.—The i.r. spectra (Table 1) show many of the usual features which have been noted previously in the spectra both of ferrocene derivatives and of polyfluoroaromatic compounds. However, the spectra are notable in that *all* compounds exhibit two strong bands in the 1100 and 1000 cm.$^{-1}$ regions. These compounds must therefore be added to the number of ferrocene derivatives which violate the '9—10 μ' rule, *i.e.*, the disubstituted compounds exhibit bands which have been used to characterise mono- and homoannularly substituted ferrocenes.[16] This is not surprising, since it is well known that fluorocarbons exhibit strong bands in the 1400—950 cm.$^{-1}$ region. The presence of these bands contributed to the difficulty of separating compounds (V) and (VI).

TABLE 1

Partial i.r. spectra of some substituted ferrocenes (2000—800 cm.$^{-1}$)

(I)	1658vs, 1516m, 1497sh, 1492vs, 1447s, 1408m, 1373m, 1337m, 1316s, 1258m, 1119s, 1104w, 1051w, 1026w, 995s, 977m, 897w, 826m
(II)	1666vs, 1517s, 1494vs, 1447s, 1403m, 1370m, 1342m, 1315s, 1256s, 1123s, 1052m, 1026w, 995s, 981s, 896w, 877vw, 837w, 814w
(III)	1657s, 1497vs,br, 1398w, 1357s, 1314s, 1164m, 1119vs, 1105s, 1038m, 1024s, 1000vs,sh, 990vs, 966vs,sh, 960vs, 901s
(IV)	1656m, 1500vs, 1484s, 1420w, 1377w, 1310m, 1248m, 1166m, 1119s, 1095m, 1038m, 1024m, 1005s, 992s, 985sh, 967s, 967s, 959s, 920w, 900m, 830m, 814m
$Fc(C_6F_5)C{:}C(C_6F_5)Fc$	1652m, 1489vs,br, 1401w, 1323w, 1300m, 1116vs, 1105s, 1030w, 1000s,sh, 981vs, 963s
(V)	1651m, 1613w, 1482vs,br, 1391m, 1380m, 1133w, 1105s, 1083vs, 1061m, 1031vs, 983vs, 919w, 863w
(VI)	1651w, 1612w, 1525m,sh, 1488s,br, 1396m, 1381w, 1330w, 1315m, 1135w, 1088s, 1065m, 1036s, 984vs
(VII)	1652w, 1615w, 1516w,sh, 1494vs,sh, 1479vs,br, 1392m, 1315w, 1305m, 1156m, 1104m, 1086s, 1064m, 1037s, 982vs, 970vs, 861w
(VIII)	1651m, 1478s,br, 1433m,br, 1393m, 1324w, 1306w, 1099vs,br, 1061m, 1040s, 999s,sh, 982vs,br, 958m,sh, 911w, 864w
(IX)	1653m, 1489vs,br, 1433m,br, 1395m, 1330w, 1307w, 1102vs, 1067m, 1046s, 987vs, 958w

Absorptions characteristic of polyfluoroaromatic compounds occurred as medium intensity absorptions at 1650—1660 cm.$^{-1}$, and as very strong bands at *ca.* 1500 cm.$^{-1}$. The latter were broad absorptions, and often contained medium to strong shoulders, probably because of overlap of C–F and ring C–C stretching modes. Most compounds showed a weak to medium intensity band between 1400 and 1420 cm.$^{-1}$, which is probably

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[11] S. I. Goldberg, D. W. Mayo, and J. A. Alford, *J. Org. Chem.*, 1963, **28**, 1708.

[12] C. Tamborski, E. J. Soloski, and R. J. de Pasquale, *J. Organometallic Chem.*, 1968, **15**, 494.

[13] D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5275.

[14] M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[15] E. J. Forbes, R. D. Richardson, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1959, 2019.

[16] M. Rosenblum and R. B. Woodward, *J. Amer. Chem. Soc.*, 1958, **80**, 5443; P. T. Kan, C. T. Lenk, and R. L. Schaaf, *J. Org. Chem.*, 1961, **26**, 4038.

a substituent-sensitive C–C stretching mode in the ferrocene nucleus.

A very strong band at *ca.* 1660 cm.$^{-1}$ in the spectra of compounds (I) and (II), is assigned to the acyl ν_{CO} frequency, and overlaps the fluorinated ring vibration mentioned above.

Nuclear Magnetic Resonance Spectra.—^{1}H N.m.r. spectra (Table 2) were used to confirm monosubstitution: the C_5H_5 ring protons appeared as a sharp singlet at τ *ca.* 5·9, and also to indicate that disubstitution occurred heteroannularly. Substituted ring protons gave two resonances with apparent triplet or quintuplet structure, but we were unable to resolve these spectra sufficiently to obtain coupling constant data. As found for other ferrocene derivatives containing electron-withdrawing groups, the resonance of the 2- and 5-protons occurs at higher field than that of the 3- and 4-protons, and both were down-field from the resonance of the unsubstituted ring. The methoxy-protons in compounds (VIII) and (IX) appeared as a triplet at τ *ca.* 6·0, due to coupling with the fluorine atoms *ortho* to the methoxy-group.

TABLE 2

N.m.r. data for some ferrocene derivatives

(*a*) ^{1}H n.m.r. spectra

		Chemical shifts (τ)			
	Solvent	3- and 4-H	2- and 5-H	C_5H_5	Others
(I)	CCl_4	5·44(m)	5·55(t)	5·90(s)	
(II)	$(CD_3)_2CO$	5·10(s)	5·19(d)		
(V)	$CDCl_3$	5·30(quintet)	5·66(t)	5·94(s)	
(VI)	$CDCl_3$	5·32(quintet)	5·66(t)		
(VIII)	$(CD_3)_2CO$	5·34(quintet)	5·69(t)	5·97(s)	6·02(t, OMe)
(IX)	$(CD_3)_2CO$	5·26(quintet)	5·56 (quintet)		5·98(t, OMe)

(*b*) ^{19}F n.m.r. spectra [a]

	Chemical shifts (p.p.m.) [b]			Coupling constants (Hz)				
	2- and 6-F	3- and 5-F	4-F	$\pm J_{2,3}$	$\lvert J_{2,4}\rvert$	$\mp J_{2,5;3,6}$	$\lvert J_{2,6}\rvert$, $\lvert J_{3,5}\rvert$	$\pm J_{3,4}$
(I)	141·2	161·9	154·2	21·96	0	8·36	0,4·2	20·4
(II)	141·1	161·4	153·2	22·63	2·75	8·54	0,4·8	19·85
(V)	140·5	163·9	159·4	21·67	0	7·07	2·25, 2·25	20·3
(VI)	140·6	164·3	159·6	21·8	0	7·5	2·6, 2·6	24·0
(VIII)	142·0	159·6		Not determined				
(IX)	140·9	159·6		Not determined				

[a] In tetrahydrofuran. [b] Upfield from internal $CFCl_3$.

The ^{19}F n.m.r. spectra of compounds containing C_6F_5 groups showed the expected three resonances, of relative intensities 2 : 1 : 2, which are assigned to the fluorines *ortho*, *para*, and *meta* to the ferrocenyl group, respectively. The substituent effects of the Fc and FcCO groups are: *ortho*, 23·4, 22·7; *meta*, 0·0, 2·0; and *para*, 4·5 and 9·7 p.p.m. There is little effect of the substituents in one ring on the chemical shifts of a C_6F_5 group attached to the second ring.

The spectra of compounds (VII) and (VIII) showed two fluorine resonances, confirming that the methoxy-group had replaced the fluorine atom *para* to the ferrocenyl group. The resonances were not well resolved, and coupling constant data were not obtained.

Little or no coupling was found between the cyclopentadienyl ring protons and the aromatic ring fluorines *ortho* to the ring–ring bond. Except in complex (II), there was also no coupling between the *ortho*- and *para*-fluorines. Other coupling constants lie in the ranges already determined for J_{FF} (*ortho*), J_{FF} (*meta*), and J_{FF} (*para*).

EXPERIMENTAL

I.r. spectra were recorded for solutions in chloroform with a Perkin-Elmer 257 double grating spectrophotometer. ^{1}H N.m.r. spectra were obtained with a Varian HA100 spectrometer at 100 MHz; ^{19}F spectra were recorded with this instrument at 94·1 MHz, or with a Perkin-Elmer R10 permanent magnet spectrometer, at 56·4 MHz. Mass spectra were obtained with an AEI MS9 double-focussing mass spectrometer, operating with 70 ev ionising energy. Samples were introduced on a ceramic probe *via* a direct insertion lock, with an ion chamber temperature of *ca.* 110—130°.

All reactions were carried out under nitrogen, but during work-up no particular precautions were taken to exclude oxygen. Chromatography was performed on columns packed with Florisil or with alumina (B.D.H. chromatography grade). Light petroleum refers to a fraction b.p. 40—60°. n-Butyl-lithium in hexane was obtained from the Foote Mineral Company; polyfluoroaromatic compounds were supplied by the Imperial Smelting Corporation.

Analytical data and m.p.s are collected in Table 3.

Reactions of Ferrocene with Pentafluorobenzoyl Chloride.—

TABLE 3

Analytical data for some ferrocene derivatives

			Found			Calc.		
	Formula	M.p.	C(%)	H(%)	*M* *	C(%)	H(%)	*M*
(I)	$C_{17}H_9F_5FeO$	81—82°	54·3	2·4	380	53·7	2·35	380
(II)	$C_{24}H_8F_{10}FeO_2$	188—189	50·25	1·5	574	50·2	1·4	574
(III)	$C_{17}H_{11}F_5Fe$	96—98	55·9	3·25	366	55·75	3·0	366
(IV)	$C_{24}H_{12}F_{10}Fe$	140	52·8	2·45	546	52·25	2·2	546
$Fc(C_6F_5)C{:}C(C_6F_5)Fc$	$C_{34}H_{18}F_{10}Fe_2$	244 (decomp.)			728			728
(V)	$C_{16}H_9F_5Fe$	98—99	54·65	2·9	352	54·55	2·55	352
(VI)	$C_{22}H_8F_{10}Fe$	183—186	51·0	1·55	518	50·85	1·45	518
(VII)	$C_{38}H_{16}F_{14}Fe_2$ †	178—180	55·85	2·45	850	53·65	1·9	850
(VIII)	$C_{17}H_{12}F_4FeO$	84—85	56·15	3·15	364	56·05	3·3	364
(IX)	$C_{24}H_{14}F_8FeO_2$	131—132	53·25	2·35	542	53·1	2·6	542

* By mass spectrometry (^{56}Fe). † Found: Fe, 15·6. Required: Fe, 13·2%.

To ferrocene (5·0 g., 27 mmoles) in dichloromethane (40 ml.) was added dropwise, at room temperature, a mixture of freshly sublimed aluminium chloride (3·6 g., 27 mmoles) and pentafluorobenzoyl chloride (6·2 g., 26 mmoles) in the same solvent (130 ml.). The mixture was refluxed for 24 hr., and then poured on a mixture of conc. hydrochloric acid (20 ml.) and ice (200 g.). The organic layer was separated, and the aqueous layer was treated with tin(II) chloride (*ca.* 1 g.), and extracted further with dichloromethane (2 × 5 ml.). The combined organic layers were washed with water, dried ($\mathrm{MgSO_4}$), and evaporated. Chromatography (alumina) of the residue gave recovered ferrocene (2·1 g., 42%), eluted with light petroleum, and a red band, eluted with 1 : 1 ether–light petroleum. Evaporation and recrystallisation from light petroleum gave red-purple needles of *pentafluorobenzoylferrocene* (I) (2·2 g., 37%). No disubstituted derivative was obtained.

A similar experiment, with carbon disulphide as solvent, gave recovered ferrocene (3·4 g., 68%), pentafluorobenzoylferrocene (0·33 g., 5·5%) and 1,1′-bis(pentafluorobenzoyl)-ferrocene (0·19 g., 3·8%), eluted with ether.

An experiment with ferrocene (2·5 g., 13·5 mmoles), aluminium chloride (5·4 g., 40 mmoles) and pentafluorobenzoyl chloride (9·6 g., 42 mmoles) in dichloromethane, for 4 days under reflux, gave recovered ferrocene (0·6 g., 24%), pentafluorobenzoylferrocene (0·4 g., 5·6%), and the disubstituted product (0·5 g., 8·4%).

The monosubstituted product was best purified by slowly cooling to room temperature a solution in light petroleum. Viscous oils were obtained on evaporation of solutions in a variety of solvents, or from low temperature recrystallisations; attempted sublimation gave only oily sublimates or varnish-like films on the probe.

Metalation of Ferrocene with n-Butyl-lithium–TMED Reagent.—n-Butyl-lithium (35 ml. of 20% hexane solution, 0·11 mole) was added to TMED (11·1 ml., 0·1 mole) in hexane (10 ml.) at 0°. After 10 min., a solution of ferrocene (5·6 g., 0·03 mole) in hexane (250 ml.) was added dropwise (1 hr.), and the mixture was stirred for 6 hr., after which time a suspension of fine orange crystals had formed.

Reactions of Lithiated Ferrocene.—(a) *With pentafluorobenzoyl chloride.* Ferrocene (5·6 g., 30 mmoles) was metalated as described, and pentafluorobenzoyl chloride (14·8 g., 64 mmoles) in hexane (10 ml.) was added dropwise to the suspension. The mixture was refluxed for 3 hr., and left at room temperature overnight. After removal of approximately half the solvent, the remainder of the mixture was poured on ice (150 g.). The organic layer was separated, washed with water, and dried ($\mathrm{MgSO_4}$), and the volume of solvent was reduced sufficiently to allow chromatography (Florisil). Light petroleum eluted ferrocene (1·8 g., 32%). Ether then eluted a dark red band, from which fine purple-red needles of 1,1′-*bis(pentafluorobenzoyl)ferrocene* (II) (2·5 g., 21%) were obtained on evaporation and recrystallisation from dichloromethane–light petroleum. The compound is not volatile below 140° (0·1 mm.).

(b) *With hexafluorobenzene.* Ferrocene (5·6 g., 30 mmoles) was metalated as described, and treated with a solution of hexafluorobenzene (11·2 g., 60 mmoles) in hexane (50 ml.) at room temperature. The mixture was stirred for 2 days. The resulting dark brown mixture was hydrolysed with 5% hydrochloric acid at 0°, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried ($\mathrm{MgSO_4}$). Removal of solvent gave a dark brown solid, which was chromatographed (Florisil). Three main fractions were successively eluted with light petroleum–benzene mixtures (A), light petroleum–ether mixtures (B), and ether (C).

Sublimation of fraction A below 60° (0·01 mm.) gave an orange-red solid (1·96 g.), which was a mixture of ferrocene and *pentafluorophenylferrocene* (V); above 60°, the darker orange solid (1·84 g.) which sublimed consisted mainly of 1,1′-*bis(pentafluorophenyl)ferrocene* (VI). Pure samples of these compounds were obtained as large orange brown plates, and dark orange crystals, respectively, by extensive chromatography, fractional sublimations, and several recrystallisations from light petroleum at −10°. The progress of these purifications could be followed by the relative intensities of i.r. absorptions at *ca.* 1500 cm.$^{-1}$ (for the C_6F_5 compounds), and those due to ferrocene at *ca.* 1100, 1000, and 840 cm.$^{-1}$ (see later).

The i.r. spectra of fractions B and C were similar, so these were combined and sublimed to remove compound (VII); the orange-red residue (155 mg.) was recrystallised from ether–acetone to give a bright red solid, tentatively identified as the (pentafluorophenyl)(nonafluorobiphenyl)biferrocenyl (VII), *m/e* (M^+) 847·9737, 849·9642, and 850·9711 (calc. for $C_{38}H_{16}F_{14}Fe_2$: 847·9774, 849·9727, and 850·9732).

Reaction of Ferrocenyl-lithium with Bromopentafluorobenzene.—A mixture of ferrocene (2·0 g., 10·8 mmoles) in ether (30 ml.) with n-butyl-lithium (3·5 ml. of a 20% hexane solution, 10·9 mmoles) in ether (10 ml.) gave an orange precipitate, which gradually dissolved on refluxing the mixture for 22 hr. After removal of solvent, chromatography of the residue gave a major fraction, eluted with 10% ether–light petroleum, and a second red band eluted with ether. The latter gave only a small amount of solid material, and was not further investigated. The major fraction was sublimed to give an orange solid, shown to be a mixture of ferrocene [i.r. bands at 1412, 1109, 1003, and 820 cm.$^{-1}$, *m/e* (M^+) 186] and bromoferrocene [i.r. bands at 1508, 1481, 1050, 993 cm'$^{-1}$, *m/e* (M^+) 264 and 266].

Reaction of Ferrocene with Pentafluorophenylhydrazine and Silver Oxide.—Silver oxide (5 g., 21·5 mmoles) was added in small portions to ferrocene (1·4 g., 7·5 mmoles) in glacial acetic acid (50 ml.) at room temperature. The mixture rapidly became dark blue. Pentafluorophenylhydrazine (5 g., 25 mmoles) in glacial acetic acid (35 ml.) was then added during *ca.* 30 min. As the addition progressed, the colour changed to greenish-black, and finally to yellow-brown. After 1 hr. the mixture was filtered through a small bed of Florisil, which was then washed with glacial acetic acid (2 × 5 ml.). The combined filtrates were then poured into water (400 ml.), and the resulting emulsion was immediately extracted with ether (200 ml.). The ether layer was separated and washed successively with water, 10% hydrochloric acid, water, saturated potassium hydrogen carbonate, solution, and finally water, and dried ($\mathrm{Na_2SO_4}$). Removal of solvent and chromatography (Florisil) gave a mixture of ferrocene and pentafluorophenylferrocenes (1·34 g.), eluted with light petroleum. Other coloured bands were eluted with benzene and with ether, but no tractable materials were isolated.

The combined product from three such reactions was purified as already described, to give pentafluorophenylferrocene and 1,1′-bis(pentafluorophenyl)ferrocene, identical with the products obtained before.

Clemmensen Reduction of Pentafluorobenzoylferrocenes.—(a) *Pentafluorobenzoylferrocene*. A mixture of zinc dust (3 g.), mercury(II) chloride (0·23 g.), water (3·75 ml.), and conc. hydrochloric acid (0·15 ml.) was heated on a boiling-water bath for 10 min. with stirring, after which the aqueous layer was decanted, and the resulting zinc amalgam was washed with a little water. A mixture of water (1·5 ml.), conc. hydrochloric acid (3·0 ml.), and toluene (5 ml.) was then added, and the whole was treated with pentafluorobenzoylferrocene (1·14 g., 3·3 mmoles). The mixture was refluxed for 44 hr. during which time two further additions of conc. hydrochloric acid (2·5 ml.) were made. The mixture was cooled and the organic layer was separated, washed with sodium hydrogen carbonate and water, and evaporated. The residue was extracted six times with light petroleum, and the concentrated extracts were chromatographed (alumina) to give a bright yellow band, eluted with light petroleum, and recovered pentafluorobenzoylferrocene (0·14 g., 12%), eluted with ether–light petroleum (1 : 4). Sublimation of the first product (90°/0·1 mm.) gave yellow *pentafluorobenzylferrocene* (III) (0·5 g., 47%).

The insoluble yellow material remaining after the light petroleum extraction showed a parent ion cluster centred on m/e 728, and is assumed to be 1,2-*diferrocenyl*-1,2-*bis*-(*pentafluorophenyl*)*ethylene*, m/e (M^+) 727·9986, 728·9985, 729·9929, and 730·9947 (Calc. for $C_{34}H_{18}F_{10}Fe_2$: 727·9948, 728·9952, 729·9933, and 730·9936).

(b) 1,1′-*Bis*(*pentafluorobenzoyl*)*ferrocene*. A similar reaction with amalgamated zinc (2 g.), toluene (10 ml.), conc. hydrochloric acid (7 ml. total) and the disubstituted ferrocene (0·54 g., 0·94 mmole) was stirred and refluxed for 88 hr. Work-up of the organic layer as in (a) gave bright yellow 1,1′-*bis*(*pentafluorobenzyl*)*ferrocene* (IV) (0·12 g., 23%), which sublimed at 110° (0·1 mm.). Both (III) and (IV) could be recrystallised from light petroleum.

Reaction of Pentafluorophenylferrocenes with Sodium Methoxide.—(a) *Pentafluorophenylferrocene*. Sodium (70 mg., 3 mg.-atom) in methanol (20 ml.) and pentafluorophenylferrocene (520 mg., 1·5 mmoles) were refluxed together overnight. Hydrolysis of the mixture with dilute hydrochloric acid at 0°, followed by extraction and chromatography (alumina) gave only starting material.

A similar experiment with sodium methoxide (500 mg., 9·3 mmoles) and the ferrocene (520 mg., 1·5 mmoles), under reflux for 18 hr., gave after the usual work-up and chromatography, recovered pentafluorophenylferrocene (31 mg., 6%) and orange 4-*methoxytetrafluorophenylferrocene* (VIII) (255 mg., 47·5%), eluted successively with light petroleum, and purified by sublimation (80—100°/0·1 mm.).

(b) 1,1′-*Bis*(*pentafluorophenyl*)*ferrocene*.—The ferrocene (200 mg., 0·39 mmole) and sodium methoxide (200 mg., 3·7 mmoles) in methanol–acetone (6 : 1) were refluxed overnight, set aside for 2 days at room temperature. Hydrolysis of the mixture with 5% hydrochloric acid at 0°, followed by the usual work-up, gave a solid, which was recrystallised from ether–light petroleum to give reddish-orange leaflets of 1,1′-*bis*-(4-*methoxytetrafluorophenyl*)*ferrocene* (IX) (110 mg., 52·5%).

[9/613 *Received, April* 14*th*, 1969]