

Polyfluoroaromatic Derivatives of Metal Carbonyls. Part V.¹ Further Reactions of the Anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with Substituted Polyfluoroaromatic Compounds

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Reactions of the anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with $\text{C}_6\text{F}_5\text{X}$ ($\text{X} = \text{Me}$, CH_2CH_2 , $\text{CH}_2\text{CH}(\text{CH}_3)$, and OMe) have given the complexes $p\text{-XC}_6\text{F}_4\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$. Isomers have been found in the products where $\text{X} = \text{CH}_2\text{CH}(\text{CH}_3)$ and OMe , and their structures and possible mode of formation are discussed. The reactions of the ethers $p\text{-HC}_6\text{F}_4\text{OR}$ ($\text{R} = \text{Me}$, Et , $\text{CH}_2\text{CH}(\text{CH}_3)$, and $\text{CH}_2\text{C}(\text{CH}_3)_2$) with the same anion have given the complexes $\text{RFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, and comparable products are formed in the reactions with $p\text{-(MeO)}_2\text{C}_6\text{F}_4$ and with $(p\text{-MeOC}_6\text{F}_4)_2$. The results are compared with other oxygen-alkyl fission reactions in the polyfluoro- and polychloro-aromatic series.

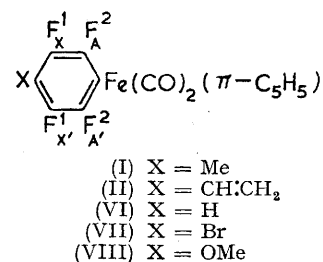
PREVIOUS papers^{2,3} in this series have described the reactions of carbonylmetal anions, particularly those of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$, with a variety of polyfluoroaromatic compounds containing functional groups. These reactions have been summarised elsewhere.⁴ This paper reports the extension of these investigations to include further types of functional group, and describes a novel carbon-oxygen fission promoted by a carbonylmetal anion.

Studies of reactions with polyfluorobenzenes substituted with groups which are not strongly electron-withdrawing (e.g., CN , CO_2Et) showed that substitution occurred *para* to a substituent other than fluorine, as found in similar reactions with more conventional nucleophiles.⁵ The substitution pattern found with compounds which contained electron-donating groups in reactions with e.g. methoxide varies; it is *para* (>90%) with methyl- and ethyl-pentafluorobenzenes,⁶ and *para* (52%), *meta* (32%), and *ortho* (16%) with pentafluoroanisole.⁶ We have now studied the reactions of these compounds, and also of those which contain alkenyl groups, with the anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$.

RESULTS AND DISCUSSION

The reaction between $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ and pentafluorotoluene gives a yellow-orange solid which was

1) contains only two bands. One is at low field, showing the characteristic deshielding effect of the transition-metal bonded to the aromatic ring on fluorines *ortho* to the metal. The fine structure of both resonances was of the expected AA'XX' pattern, with the signal at high field showing further splitting of each line into a quartet by the methyl group. Together with the analytical, i.r. [two characteristic ν_{CO} bands arising from the $\pi\text{-(C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ group], and mass spectrometric data, the n.m.r. results make the assignment of structure (I) to this complex unequivocal.



A similar reaction with pentafluorostyrene gave the *para*-vinyl-substituted complex, $p\text{-CH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{F}_4\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (II), identified in the usual way. In particular, the ^{19}F n.m.r. spectrum exhibited two resonances with an AA'XX' pattern. During the course of the reaction, a large amount of gelatinous material separated, which made filtration of the reaction mixture even more difficult than usual. This may have been a form of poly(pentafluorostyrene), but no further investigations of this material were made.

Reaction of the carbonylmetal anion with allylpentafluorobenzene (III) gave a similar yellow-orange product, which showed four lines in its ^{19}F n.m.r. spectrum, each having the AA'XX' pattern, and which evidently contained two isomers. One of these was isolated in a pure state by crystallisation, and was shown to be the expected complex $p\text{-CH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{F}_4\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (IV). The mother liquors gave a mixture which contained an increased amount of the second complex. Analytical and mass spectrometric data did not differ

TABLE 1

^{19}F N.m.r. data for some iron complexes

Complex	Chemical Shift *		Coupling constants (Hz)			
	ϕ_A	ϕ_X	$J_{AA'}$, $J_{XX'}$	$\pm J_{AX'}$	$\pm J_{A'X}$	
(I)	109.3	145.9	0, 4.1	28.65	11.9	
(II)	108.6	145.6	3.25, 3.25	27.35	12.6	
(IV)	108.8	146.9	1.6, 4.2	29.0	13.6	
(V)	109.4	146.5	2.35, 4.3	27.35	11.8	
(VII)	105.2	134.0	6.4, 6.4	32.2	14.8	
(calc.)	(108.4)	(133.2)				
(VIII)	108.3	158.15	1.0, 5.9	29.35	9.55	
(calc.)	(108.6)	(159.8)				

* In p.p.m. upfield from internal CFCl_3 (0.0 p.p.m.) reference, obtained with ca. 40% tetrahydrofuran solutions.

identified as the *para*-substituted complex, $p\text{-MeC}_6\text{F}_4\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (I). Thus the ^{19}F n.m.r. spectrum (Table

¹ Part IV, M. I. Bruce and C. H. Davies, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 675.

² M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. (A)*, 1966, 1837.

³ M. I. Bruce, *J. Organometallic Chem.*, 1967, **10**, 495.

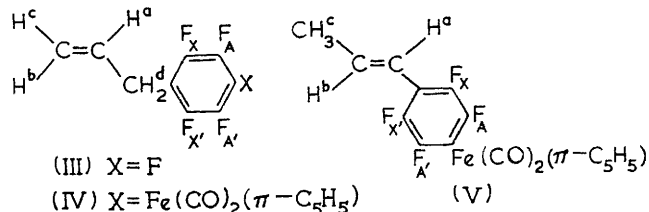
⁴ M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, 1968, **80**, 835 (*Angew. Chem. Internat. Edn.*, 1968, **7**, 747).

⁵ J. C. Tatlow, *Endeavour*, 1962, **22**, 89.

⁶ J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 5152.

significantly from those of complex (IV), and the two isomers were distinguished by their ^1H n.m.r. spectra, which allowed formulation of the second complex as $p\text{-MeCH:CH}\cdot\text{C}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (V).

The ^1H n.m.r. spectrum of allylpentafluorobenzene shows signals at τ 4.22 (m, relative intensity 1), 4.92 (s, 1), 5.06 (d, 1), and 6.62 (d, 2). With higher resolution, each



component of the doublets at τ 5.06 and 6.62 is further split into a triplet. By comparison with the spectrum of allyl bromide,⁷ these resonances may readily be assigned thus: H^a , τ 4.22; H^b , 4.92; H^c , 5.06; H^d , 6.62. The spectrum of complex (IV) has signals at τ 4.26br (m, 1), 4.98 (d, 1), 5.12 (s, 6), and 6.66 (d, 2). These may be assigned similarly to (III): H^a , τ 4.26; H^b , 4.98; H^d , 6.66. The resonance for H^c probably lies in the somewhat broadened base of the singlet at τ 5.12, which arises from the cyclopentadienyl protons.

The spectrum of the mixture of complexes (IV) and (V) contains, in addition to the peaks noted above for complex (IV), smaller resonances at τ 3.75br (s, 1), *ca.* 6.0br (1), and 8.10 (d, 3). The high-field signal can be assigned to the methyl group in complex (V), and is not sharp; this suggests the *trans*-stereochemistry shown. The other two resonances are assigned to H^a (τ 3.75) and H^b (τ *ca.* 6.0), respectively.

The relative amounts of complexes (IV) and (V) in the original reaction product were determined as 7:1 from both the ^{19}F and ^1H n.m.r. spectra. Formation of complex (V) involves a suprafacial 1,3-sigmatropic hydrogen shift which is forbidden in the parent allylpentafluorobenzene. This suggests involvement of the metal in some way, and the most plausible mechanism is an interaction of the excess carbonyl anion with the allylic group and intermediate formation of a metal-hydrogen link. Return of this hydrogen to the symmetrical carbanion so formed would give either complex (IV) or (V). Such an involvement of the metal has been mentioned previously in connection with the cobalt-catalysed isomerisation of allylbenzene to β -methylstyrene.⁸

There is an apparent difficulty in the attachment of two transition metals to the same fluoroaromatic ring, although there seems to be no obstacle to the formation of derivatives in which two metal moieties are σ -bonded to different rings. Examples of these which can be

cited are the biphenyl derivative 4,4'- $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-C}_{12}\text{F}_8$,⁹ and the bipyridyl complex 2,2'- $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{-4,4'-C}_{10}\text{F}_6\text{N}_2$.¹⁰ In the non-fluorinated system, complexes analogous to those which we wished to prepare, *e.g.*, $(\text{CO})_5\text{ReC}_6\text{H}_4\text{Re}(\text{CO})_5$, have been made by the ready decarbonylation of the diacyl complexes.¹¹

The reaction between p -dibromotetrafluorobenzene and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ was examined, as a possible route to the complex $p\text{-}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{C}_6\text{F}_4$. Under the usual conditions, this reaction produced a volatile yellow solid, similar in properties to many of the other complexes reported herein. The ^{19}F n.m.r. spectrum showed four resonances, each with the AA'XX' pattern, which indicated that the required complex had not been prepared. Two of the resonances were readily assigned to the known¹² complex $p\text{-HC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (VI). The other complex might reasonably be expected to be the corresponding bromo-complex (VII), and calculations with substituent shielding parameters previously obtained¹³ with similar systems indicated that the chemical shifts found for the second complex were in reasonable agreement with those expected for complex (VII) (Table I). The mass spectrum of the mixture gave support to this idea, with peaks at m/e 326, 298, and 270, which were attributed to the ions M^+ , $(M - \text{CO})^+$, and $(M - 2\text{CO})^+$, respectively, formed from complex (VI), and pairs of ions at m/e 404/406, 376/378, and 348/350, assigned to similar ions from the bromo-compound (VII) (which contained ^{79}Br and ^{81}Br , respectively).

The ^{19}F n.m.r. spectrum indicated that complexes (VI) and (VII) were present in the ratio of 3:2, with which the analytical data were in agreement. The formation of complex (VI) in this reaction may be compared with similar reactions with $\text{C}_6\text{F}_5\cdot\text{X}$ ($\text{X} = \text{F}$, Cl, Br, or I), in which mixtures of $\text{C}_6\text{F}_5\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ and complex (VI) were obtained.² The reluctance of the fluoroaromatic ring to undergo further substitution has been attributed¹⁴ to back-bonding between the metal d -electrons and the antibonding orbitals of the ring, which makes the fluoroaromatic group less susceptible to nucleophilic attack.

Reactions with substrates in which the *para*-position is blocked by a substituent other than fluorine (or other halogen) give much lower yields of isolated complex, and the complexes themselves seem to be of lower stability than those in which the metal is not *para* to a fluorine atom. We have attempted two further reactions of this type, namely with $p\text{-C}_6\text{F}_4(\text{CO}_2\text{Et})_2$ and with $p\text{-C}_6\text{F}_4(\text{CN})_2$, but in each case, only i.r. evidence for a possible ring-substituted product was obtained, and no pure complexes were obtained. These results may be compared with the corresponding reactions of $p\text{-C}_6\text{F}_4\text{H}_2$, which gave

⁷ N. S. Bhacca, L. R. Johnson, and J. N. Shoolery, 'N.m.r. Spectra Catalog,' Varian Associates, 1962, spectrum no. 24.

⁸ L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 5502; F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

⁹ M. I. Bruce, unpublished results.

¹⁰ M. Green, A. Taunton-Rigby, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2762.

¹¹ A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Johansson, *Dokl. Akad. Nauk S.S.S.R.*, 1967, **175**, 358.

¹² M. B. Bisnette and R. B. King, *J. Organometallic Chem.*, 1964, **2**, 38.

¹³ M. I. Bruce, *J. Chem. Soc. (A)*, 1968, 1459.

¹⁴ M. I. Bruce and F. G. A. Stone, *Prep. Inorg. React.*, 1968, **4**, 229.

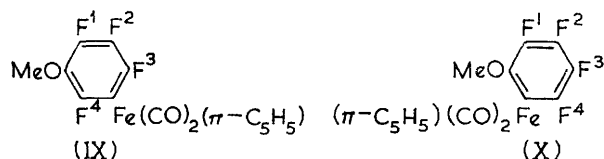
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a lower yield of complex than either the *ortho*- or *meta*-isomers, and of $o\text{-C}_6\text{F}_4(\text{CO}_2\text{Et})_2$ and of $o\text{-C}_6\text{F}_4(\text{CN})_2$, which gave the analogous complexes in 32 and 25% yield, respectively.²

The majority of functional groups used in these studies have been *para*-directing. The exceptions have either given no isolated complex ($\text{C}_6\text{F}_5\cdot\text{NH}_2$ or $\text{C}_6\text{F}_5\cdot\text{NO}_2$), or a complex which did not retain the original substituent ($\text{C}_6\text{F}_5\cdot\text{NH}\cdot\text{NH}_2$). As mentioned above, reaction between pentafluoroanisole and methoxide gives appreciable amounts of all three isomers of $\text{C}_6\text{F}_4(\text{OMe})_2$. We therefore examined the behaviour of this fluorocarbon with the nucleophile $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$.

The ^{19}F n.m.r. spectrum of the product obtained from this reaction showed six peaks, two of which were of greater relative intensity than the other four. These were readily assigned to the complex $p\text{-MeOC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (VIII) by calculations of chemical shifts as for the bromo-complex, and confirmed by the mass spectrum. The AA'XX' structures of the resonances also supported this assignment.

The remaining four lines, at 99.7, 107.4, 156.3, and 165.5 p.p.m., were of equal relative intensity, and were evidently due to one of the other isomers of the complex, (IX) or (X). The presence of two signals at low field



suggested that the metal group was *ortho* to two different fluorines, and indicated that the *meta*-isomer (IX) was present. The chemical shifts calculated for (IX) and (X) are compared with the observed values in Table 2, and confirm the assignment.

TABLE 2
Calculated and observed chemical shifts

Complex	Chemical shifts							
	Calculated				Observed *			
	F ¹	F ²	F ³	F ⁴	F ¹	F ²	F ³	F ⁴
(VIII)	159.8	108.6			158.15	108.3		
(IX)	170.6	166.2	104.8	111.2	165.5	156.3	99.7	107.4
(X)	168.0	163.6	161.6	104.8				
(XI)	158.8	138.5	83.5		160.5	142.7	79.3	
(XII)	156.2	141.1	101.2					

* In p.p.m. upfield from internal CFCl_3 (0.0 p.p.m.) reference, obtained with *ca.* 40% tetrahydrofuran solutions.

Complexes (VIII) and (IX) were present in the ratio of *ca.* 4 : 1, and this result can be compared to the 52 : 32 *para* : *meta*-ratio found in the reaction between pentafluoroanisole with methoxide.⁶ We could find no n.m.r. spectral evidence for the presence of complex (X) in the product, so that, if present, it was formed to the extent of <10% of complex (IX).

The complexes described so far are yellow or yellow-orange crystalline solids, which can be sublimed *in vacuo*, and which are air-stable in the solid state, al-

though solutions decompose more or less rapidly in the presence of oxygen. Their ^{19}F n.m.r. spectra are given in Tables 1 and 2, and Table 3 records some i.r. data.

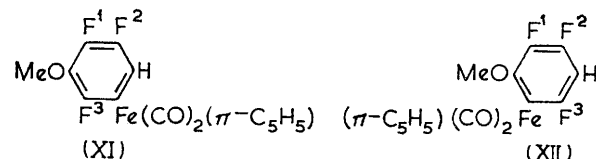
TABLE 3
I.r. spectra of some iron complexes (cm^{-1})*

Complex	ν_{CO}	Other bands
(I)	2038vs, 1993vs	1635w, 1580w, 1432m, 1376w, 1233m, 1102m, 1048m, 1000w, 894s, 836m (C_6H_5), 768s
(II)	2040vs, 1995vs	1633m, 1625w(sh), 1557w, 1409s, 1239m, 1108w, 986m, 963m, 932vs, 919s, 832s (C_6H_5), 764s, 740w, 675w
(IV)	2040vs, 1995vs	1640w, 1427s, 1228m, 1119w, 982m, 963s, 916s, 873s, 837s (C_6H_5), 776m, 744m
(V)	2026vs, 1976vs	
(VII)	2043vs, 1999vs	
(VIII)	2038vs, 1994vs	1628w, 1487s, 1420s, 1090s, 1046m, 1010m, 957s(br), 836s (C_6H_5), 771s
(IX)	2032vs, 1987vs	
(XI)	2032vs, 1983vs	

* In cyclohexane solution.

The mass spectra of the complexes are characterised by the presence of ions which correspond to M^+ , $(M - \text{CO})^+$, and $(M - 2\text{CO})^+$; in some cases, the loss of a neutral FeF_2 fragment from $(M - 2\text{CO})^+$ occurs.

Extension of these reactions to 2,3,5,6-tetrafluoroanisole was expected to result in either (a) some reaction with the methoxy-group, caused by the blocking of the *para*-position by the hydrogen atom, or (b) the formation of a mixture of products, the relative proportions of which might reflect the relative *meta*-directing effects of the H and OMe groups. In fact, both types of reaction were found.* Two products were isolated, and their mass spectra indicated empirical formulae which corresponded to $\text{H}(\text{MeO})\text{C}_6\text{F}_3\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ and $\text{Me}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$. Thus the former, of which only 14 mg. were isolated, showed peaks at m/e 338, 310, and 282, which arose from the ions M^+ , $(M - \text{CO})^+$, $(M - 2\text{CO})^+$, as already mentioned. This complex was further characterised by its ^{19}F n.m.r. spectrum (Table 2) as the isomer (XI). The absence of detectable amounts

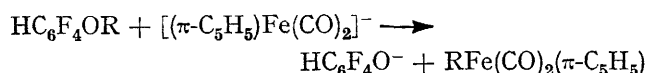


of isomer (XII) may be the result of steric factors which arise from the relatively large metal group being *ortho* to the methoxy-group.

The second product, $\text{Me}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, initially identified from its mass spectrum [M^+ , $(M - \text{CO})^+$, and $(M - 2\text{CO})^+$ at m/e 192, 164, and 136], was further characterised by analysis and by its i.r. spectrum. This complex must be formed by fission of the alkyl-oxygen bond of the methoxy-group. This reaction produces tetrafluorophenoxide as the other product, and is undoubtedly promoted by the stability of this anion.

* For a preliminary communication, see ref. 1.

Similar reactions have been observed in the polychloroaromatic series,¹⁵ though with more conventional nucleophiles, and also in the reactions of pentafluoroanisole with methoxide,⁶ to give pentafluorophenoxide (isolated as the phenol), and with hydrazine, when hydrazinium pentafluorophenoxide was isolated.¹⁶ In the case of the allyl ether, we have isolated both the σ -allyl iron complex, and the parent phenol, and we believe this is the first time for the polyfluoroaromatic series that both reaction products have been successfully identified.



We have investigated the reactions of a number of other tetrafluorophenyl ethers with $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$, and the results are summarised in Table 4. In no other

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 double grating spectrophotometer. ^1H N.m.r. spectra were obtained with a Varian HA 100 spectrometer, operating at 100 MHz, and ^{19}F n.m.r. spectra were obtained either with a Perkin-Elmer R10 spectrometer at 56.4 MHz, or with the Varian HA 100 spectrometer at 94.1 MHz. Mass spectra were obtained with an A.E.I. MS9 double focussing mass spectrometer.

All reactions which involved the anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ were performed under nitrogen. Light petroleum had b.p. 40–60°; tetrahydrofuran was dried by distillation over calcium hydride immediately before use. In general, reaction conditions were similar to those described in previous papers.^{2,3} Products were separated by chromatography of a dichloromethane extract of the evaporated reaction mixture on columns packed with 'Florisil', and finally purified by recrystallisation and sublimation.

The majority of the fluorocarbons were obtained from the

TABLE 4
Products from the reactions of $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with polyfluoroaromatic ethers

Substrate	Product *	ν_{CO} (obs.)	(Lit.)	Mass spectrum †
<i>p</i> -HC ₆ F ₄ OMe	[Fe]Me	2010, 1957	2010, 1955 ^a	192, 164, 136
<i>p</i> -HC ₆ F ₄ OEt	[Fe]Et	2010, 1955	2010, 1950 ^a	
<i>p</i> -HC ₆ F ₄ OCH ₂ CH ₂ CH ₂	[Fe]CH ₂ CH ₂ CH ₂	2009, 1950	2010, 1948 ^b	
<i>p</i> -HC ₆ F ₄ OCH ₂ C≡CH	[Fe]CH ₂ C≡CH ‡	2025, 1975	2032, 1980 ^c	216, 188, 260
		ν_{CH} 3303	3315	
<i>p</i> -C ₆ H ₄ (OMe) ₂	[Fe]Me	2012, 1957		
[<i>p</i> -MeOC ₆ F ₄] ₂	[Fe]Me	2011, 1957		

* [Fe] = $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$. † *m/e* values for $[M]^+$, $[M - \text{CO}]^+$, $[M - 2\text{CO}]^+$ in mass spectrum of the product. ‡ Also contains some [Fe]C≡CMe. ^a Ref. 18. ^b Ref. 19. ^c Ref. 17.

TABLE 5
Analytical data

Complex	Formula	M.p.	Found (%)			Required (%)		
			C	H	M *	C	H	M *
(I)	C ₁₄ H ₈ F ₄ FeO ₂	123–124°	49.3	2.42	340, 312, 284	49.4	2.35	340, 312, 284
(II) †	C ₁₅ H ₈ F ₄ FeO ₂	115–117	51.3	2.35	352, 324, 296	51.1	2.3	352, 324, 296
(IV)	C ₁₆ H ₁₀ F ₄ FeO ₂	108–111	52.5	2.8	366, 338, 310	52.4	2.73	366, 338, 310
(VIII)	C ₁₄ H ₈ F ₄ FeO ₃		47.8	2.53	356, 328, 300	47.2	2.25	356, 328, 300

* *m/e* Values for M^+ , $(M - \text{CO})^+$ and $(M - 2\text{CO})^+$ given. † Found: F, 21.5; required: F, 21.6%.

case were we able to isolate any ring-substituted product. In all cases, the alkyl-iron complex which was isolated corresponded to the alkyl group present in the ether. Thus, reactions with 1,4-dimethoxytetrafluorobenzene and 4,4'-dimethoxyoctafluorobiphenyl gave $\text{Me}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$; the corresponding allyl ether gave $\text{CH}_2\cdot\text{CHCH}_2\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$. None of the isomeric propenyl complex was detected. Only with the propargyl ether was any evidence found for rearrangement. The yellow product exhibited bands in its i.r. spectrum which indicated that it was a mixture of the complexes $\text{HC}\equiv\text{CCH}_2\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ and $\text{MeC}\equiv\text{C}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$. However, it is known that rearrangement of the propargyl ion complex to the propynyl compound occurs relatively easily.¹⁷

Imperial Smelting Corporation, Avonmouth, Bristol. The tetrafluorophenyl ethers were prepared by reaction of the corresponding sodium alkoxide with pentafluorobenzene, followed by purification in the usual manner. Diethyl tetrafluoroterephthalate was obtained by esterification of tetrafluoroterephthalic acid with ethanol and sulphuric acid in the normal way.

Analyses, m.p.'s, and some characteristic ions in the mass spectra of the complexes are listed in Table 5.

Reactions of the Anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with Polyfluoroaromatic Compounds.—The anion was prepared from $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (1.77 g., 5 mmoles) and sodium amalgam in tetrahydrofuran (30 ml.), and the solution was treated with the polyfluoroaromatic compound, also in tetrahydrofuran (20 ml.), and the mixture was worked up as described below.

¹⁷ P. W. Jolly and R. Pettit, *J. Organometallic Chem.*, 1968, **12**, 491.

¹⁸ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

¹⁹ M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189.

¹⁵ S. M. Shein and V. A. Ignatov, *Zhur. obshchei. Khim.*, 1963, **33**, 2645; T. de Crauw, *Rec. Trav. chim.*, 1931, **50**, 753.

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(a) *Pentafluorotoluene*. A mixture of the anion with pentafluorotoluene (1.82 g., 10 mmoles) was heated under reflux overnight. After the usual work-up, chromatography gave a yellow band eluted with light petroleum, followed by $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (380 mg., 21%), eluted with benzene. The first product was recrystallised from light petroleum to give yellow crystals of $p\text{-MeC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (I) (1.25 g., 46%).

(b) *Pentafluorostyrene*. The anion was allowed to react with pentafluorostyrene (1.94 g., 10 mmoles), and after the mixture had been stirred overnight at room temperature it contained much gelatinous material. Chromatography gave a yellow band, eluted with 20% benzene–light petroleum, and recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (690 mg., 39%), eluted with benzene. Evaporation of the first eluate, and recrystallisation (light petroleum), followed by sublimation, gave yellow crystals of $p\text{-CH}_2\text{:CHC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (II), (900 mg., 42%).

(c) *Allylpentafluorobenzene*. Chromatography of the product by use of allylpentafluorobenzene (2.08 g., 10 mmoles) gave a yellow product, eluted with 10% benzene–light petroleum. This was recrystallised (light petroleum) to give yellow crystals (700 mg., 24%) of a mixture of $p\text{-CH}_2\text{:CHCH}_2\text{C}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (IV) and $p\text{-MeCH:CHC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (V). Further recrystallisations gave pure complex (IV), but a pure sample of complex (V) could not be obtained from the mother liquors. The complex $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (390 mg., 22%) was recovered by elution with benzene.

(d) *p-Dibromotetrafluorobenzene*. A mixture of the fluorocarbon (3.08 g., 10 mmoles) and the anion was heated under reflux overnight. Chromatography gave two fractions eluted with benzene–light petroleum mixtures, and recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (500 mg., 28%) eluted with benzene. The first fraction contained recovered $p\text{-C}_6\text{F}_4\text{Br}_2$ (800 mg., 26%). The yellow-brown solid obtained from the second eluate was recrystallised (light petroleum) to give a yellow crystalline product (160 mg., 5.5%), which was shown to be a 3 : 2 mixture of $p\text{-HC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (VI) and $p\text{-BrC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (VII) by its ^{19}F spectrum and analysis [Calc. for a 3 : 2 mixture of (VI) and (VII): C, 44.1; H, 1.62. Found: C, 43.6; H, 1.64%].

(e) *Pentafluoroanisole*. Reaction of the anion with pentafluoroanisole (1.98 g., 10 mmoles), followed by chromatography gave a yellow band, eluted with 10% benzene–light petroleum, and recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (400 mg., 23%), eluted with benzene. The yellow product was purified by sublimation (90°/0.1 mm.) to give a mixture of two isomers of $\text{MeOC}_6\text{F}_4\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (VIII and IX) (930 mg., 33%).

(f) *Tetrafluoroterephthalodinitrile*. A similar reaction between the anion and the dinitrile (2.0 g., 10 mmoles) gave, on chromatography, recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (350 mg., 20%) eluted with benzene, and a small amount of an unstable brown material, which showed ν_{CN} at 2251 cm^{-1} and ν_{CO} at 2040 and 1992 cm^{-1} (CHCl_3), which decomposed on attempted purification.

(g) *Diethyl tetrafluoroterephthalate*. Although an exothermic reaction occurred on addition of the diester (2.94 g., 10 mmoles) to a solution of the anion, chromatography gave recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (410 mg., 23%) as the sole tractable product. Elution with ether gave a yellow

solution, which rapidly turned brown, and a brown solid, which showed ν_{CO} at 2032 and 1982, and ν_{acylCO} at 1730 cm^{-1} (CHCl_3). However, no purification could be effected without decomposition of the complex.

Reaction of the Anion $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with Tetrafluorophenyl Ethers.—(a) *2,3,5,6-Tetrafluoroanisole*. The anion was prepared as described above, and allowed to react with tetrafluoroanisole (1.80 g., 10 mmoles) overnight. Chromatography gave two yellow bands eluted with 10% (A) and 30% benzene–light petroleum (B), together with recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (310 mg., 17.5%), eluted with benzene. Band A was unstable especially in solution, but could be sublimed to give an orange-brown waxy solid (100 mg., 6%), identified as $\text{MeFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ by its i.r. (Table 4), and mass spectra [ions M^+ , $(M - \text{CO})^+$, and $(M - 2\text{CO})^+$ at m/e 192, 164, and 136]. Band B was sublimed (85°/0.1 mm.) to give a yellow solid (14 mg., 0.5%), identified as complex (XI) by its ^{19}F n.m.r. spectrum (Table 2) and mass spectrum [ions M^+ , $(M - \text{CO})^+$, and $(M - 2\text{CO})^+$ at m/e 338, 310, and 282].

(b) *1,4-Dimethoxytetrafluorobenzene*. A similar reaction between the anion and the diether (1.05 g., 5 mmoles) gave $\text{MeFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (150 mg., 9.5%), identified spectroscopically, and recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (300 mg., 17%).

(c) *4,4'-Dimethoxyoctafluorobiphenyl*. The reaction between the anion and the fluorocarbon (3.58 g., 10 mmoles) gave, after the usual work-up, $\text{MeFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (350 mg., 10%), identified by its i.r. spectrum, and recovered $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (260 mg., 15%).

(d) *2,3,5,6-Tetrafluorophenetole*. From the reaction with tetrafluorophenetole (1.94 g., 10 mmoles), the very unstable $\text{EtFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ was isolated and identified from its i.r. spectrum (Table 4).

(e) *2,3,5,6-Tetrafluorophenyl allyl ether*. A similar reaction with the allyl ether (2.06 g., 10 mmoles) gave $\text{CH}_2\text{:CHCH}_2\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ as a yellow oil, identified by its i.r. and mass spectra (Table 4). After separation of the σ -allyl complex, the dark-coloured residue was treated briefly with 10% aqueous hydrochloric acid, dried, and resublimed. A small amount of a pale brown semi-solid collected on the probe, and was identified as 2,3,5,6-tetrafluorophenol from its i.r. spectrum [comparison with an authentic sample, characteristic bands at 3580s (ν_{OH}) 1658s, 1314m, 1230m, 1167s, 1123m, 1073s, 923s, 821s, 720s, 685w, and 671w cm^{-1}].

(f) *2,3,5,6-Tetrafluorophenyl prop-2-ynyl ether*. The iron complex isolated from the reaction between the anion and the prop-2-ynyl ether (2.04 g., 10 mmoles) was a mixture of $\text{HC}\equiv\text{CCH}_2\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ (major component) and $\text{MeC}\equiv\text{C}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, as shown by its i.r. spectrum. This contained bands at 3303 (ν_{CH}), 2026vs, and 1977vs cm^{-1} (ν_{CO}), and weaker absorptions at 2126 ($\nu_{\text{C}\equiv\text{C}}$), 2039, and 1994 cm^{-1} (ν_{CO}) [lit.¹⁷ values: $\text{HC}\equiv\text{CCH}_2\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, 3315w (ν_{CH}), 2032vs cm^{-1} (ν_{CO}); $\text{MeC}\equiv\text{C}\cdot\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, 2140m ($\nu_{\text{C}\equiv\text{C}}$), 2048vs, 1999vs cm^{-1} (ν_{CO})].

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