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POLYFLUOROAROMATIC DERIVATIVES OF METAL CARBONYLS VI*. NUCLEOPHILIC SUBSTITUTION REACTIONS INVOLVING POLYNUCLEAR AROMATIC FLUOROCARBONS

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SUMMARY

The reactions of the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with decafluorobiphenyl, octafluoronaphthalene and octafluorobiphenylene have been shown to give products containing ring–metal σ-bonds, but which are often inseparable mixtures with similar complexes formed by fluorine–hydrogen exchange. The reactivity of the biphenylene is high, especially in the exchange reaction. Structures have been assigned to the complexes by a combination of mass and ^{19}F NMR spectrometry. Substitution occurs in accord with the previously determined tendency of the nucleophile to react *para* to a substituent other than fluorine. The complex $C_{12}F_8\text{-}4,4'\text{-}[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ is described, and evidence is presented for the formation of complexes containing two metal atoms on one ring, and a π-allyl group, in reactions with decafluorobiphenyl, and 4,4′-dimethyloctafluorobiphenyl, respectively.

INTRODUCTION

The readily availability of polyfluoroaromatic compounds has resulted in many investigations of their reactions, and after it became evident that these compounds were predominantly susceptible to nucleophilic substitution reactions, it was a natural corollary to investigate their reactions with carbonylmetal anions. From these studies have resulted a large number of complexes containing a transition metal σ-bonded to a ring carbon atom. These reactions have recently been summarised[2], and since that time, further publications describing reactions with other polyfluoroaromatic[1] and polyfluoroheterocyclic[3] compounds have appeared.

However, there have been relatively few investigations of the chemistry of fluorocarbons containing two aromatic rings, either joined together, as in decafluorobiphenyl, or fused together, as in octafluoronaphthalene.

The reaction of 2-bromononafluorobiphenyl with the anion $[Mn(CO)_5]^-$ is reported[4] to give σ-(2-nonafluorobiphenyl)manganese pentacarbonyl (I), identical with a product prepared by the reaction between 2-lithiononafluorobiphenyl and

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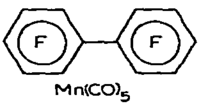
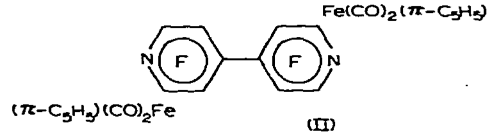
* For Part V see ref. 1.

$Mn(CO)_5Br$. However, no complexes could be isolated from the reaction of the anion $[Mn(CO)_5]^-$ and decafluorobiphenyl. The methyl compound π-$C_5H_5Fe(CO)_2CH_3$ was formed by cleavage of the O–CH_3 bond in 4,4'-dimethoxyoctafluorobiphenyl by the anion $[\pi$-$C_5H_5Fe(CO)_2]^-$; no ring-substituted product was formed[1].



(I)



(II)

In the heterocyclic field, investigations of the reactions of the anions $[\pi$-$C_5H_5Fe(CO)_2]^-$ and $[Re(CO)_5]^-$ have demonstrated the possibility of disubstitution in 4,4'-octafluorobipyridyl, which occurs with the iron anion to give (II), although only the monosubstituted complex is formed with $[Re(CO)_5]^-$. Substitution occurs in the pentafluorophenyl ring only with 4-(pentafluorophenyl)tetrafluoropyridine; other 4-substituents in the fluorinated pyridine, such as amino- or phenyl-, direct the entering anion to the 2-position.

This paper describes the reactions of the anion $[\pi$-$C_5H_5Fe(CO)_2]^-$, chosen as before on account of its high reactivity, and for the ease of chromatographic separation of any products, with decafluorobiphenyl and the 4,4'-dimethyl substituted compound, and with octafluoronaphthalene and octafluorobiphenylene. Although the latter compound has been described in several places, no account of any part of its chemistry has hitherto appeared*.

Accounts of reactions between decafluorobiphenyl with more conventional nucleophiles, such as methoxide or hydrazine, suggest that monosubstitution should occur in the 4-position, and that the second substituent should enter in the 4'-position. With octafluoronaphthalene, the 2-substituted compounds are formed in reactions with nucleophiles such as hydride, hydroxide, methoxide, hydrazine or methyllithium[5]. Preliminary experiments with octafluorobiphenylene have suggested that this molecule is very reactive, polysubstitution occurring readily; initially attack occurs predominantly at the 2-position[6].

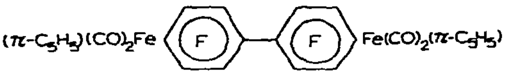
In general, attack of fluorocarbons by nucleophilic reagents occurs at positions which have, either in the unperturbed state, or under the influence of the reagent, the greatest deficiency in electron density. Both the fused ring systems described can be considered to be *ortho*-disubstituted tetrafluorobenzenes, and thus it would be expected that initial substitution should occur in the 2-position. However, the effect of the central four-membered ring in the biphenylene cannot be accurately estimated.

RESULTS AND DISCUSSION

Decafluorobiphenyl

As with all the reactions described in this paper, that with decafluorobiphenyl is quite sensitive to the conditions, inasmuch as several reactions gave several products in varying proportions, and the optimum conditions have been determined only in one case. Thus, if a mixture of the two reactants was refluxed in tetrahydrofuran for 18 h, the only product isolated apart from recovered fluorocarbon and $[\pi$-$C_5H_5Fe(CO)_2]_2$, was the disubstituted complex, $C_{12}F_8$-4,4'-$[Fe(CO)_2(\pi$-$C_5H_5)]_2$ (III).

Note added in proof. A recent paper describes the synthesis and some reactions of octafluorobiphenylene in some detail (see ref. 6).



(III)

The identity of complex (III) was established by conventional methods. Analysis and the mass spectrum (Table 1) gave the molecular formula, and the fluorine-19 NMR spectrum (Table 2) showed only two peaks, which confirmed the 4,4′-disubstitution. The IR spectrum showed only two ν(CO) bands, which suggested a similar environment for the two iron carbonyl groups. The mass spectrum also showed the presence of very small amounts of complexes with molecular weights of 808 and 966, which correspond to $C_{12}F_7[Fe(CO)_2(\pi\text{-}C_5H_5)]_3$ and $C_{12}F_6[Fe(CO)_2(\pi\text{-}C_5H_5)]_4$. The relative intensities of the ions associated with these two complexes were less than 1% of those for complex (III), and these novel polynuclear complexes could not be isolated pure, nor was their presence detected in the NMR spectrum of complex (III). Nevertheless, their formation is the first reported example of complexes containing two transition metals attached to the same polyfluoroaromatic ring.

TABLE 1

PARTIAL MASS SPECTRA OF POLYNUCLEAR FLUORINATED BIPHENYL COMPLEXES

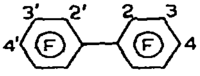
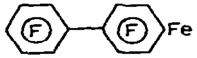
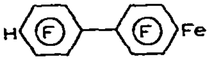
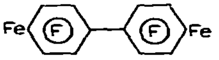
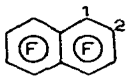
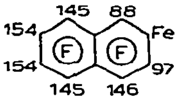
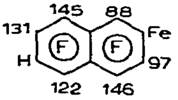
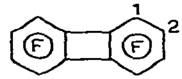
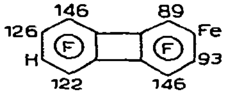
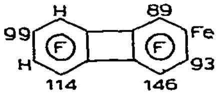
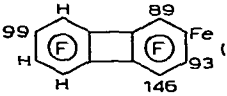
Ion	Relative abundances		
	(III)[a] $R_f=C_{12}F_8$	(IIIa)[a] $R_f=C_{12}F_7$	(IIIb)[a] $R_f=C_{12}F_6$
$C_3H_3^+$	190		
Fe^+	200		
$C_5H_5^+$	140		
FeF^+	110		
$C_5H_5Fe^+$	280		
$C_5H_5FeF^+$	130		
$(C_5H_5)_2Fe^+$	430		
$[M\text{-}4CO\text{-}FeF_2]^+$	9.5	1.1	0.8
$[M\text{-}2CO\text{-}FeF_2]^+$	0.5	0.33	0.02
$[M\text{-}8CO]^+$			0.25
$[M\text{-}7CO]^+$			0.02
$[M\text{-}6CO]^+$		0.14	
$[M\text{-}5CO]^+$		0.8	0.02
$[M\text{-}4CO]^+$	100	0.28	0.06
$[M\text{-}3CO]^+$	21	0.06	0.28
$[M\text{-}2CO]^+$	29	0.02	0.15
$[M\text{-}CO]^+$	24	0.8	0.15
M^+	13	0.02	0.15

[a] (III)=$C_{12}F_8[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$; (IIIa)=$C_{12}F_7[Fe(CO)_2(\pi\text{-}C_5H_5)]_3$; (IIIb)=$C_{12}F_6[Fe(CO)_2\text{-}(\pi\text{-}C_5H_5)]_4$.

The use of shorter reaction times or lower temperatures results in inseparable mixtures being obtained, containing two complexes which have been identified as $C_{12}F_9Fe(CO)_2(\pi\text{-}C_5H_5)$ (IV) and $HC_{12}F_8Fe(CO)_2(\pi\text{-}C_5H_5)$ (V). The empirical and molecular formulae of these complexes were established by analysis and mass

TABLE 2

^{19}F NMR SPECTRA

Compound[a]	Chemical shift[b]
Decafluorobiphenyl	
	$F_{2,2'}$, 137.9(2); $F_{3,3'}$, 160.0(2); $F_{4,4'}$, 148.7(1)
 (IV)	$F_{2,2'}$, 139.2(2); F_3, 106.4(1); $F_{3'}$, 162.9(1); $F_{4'}$, 153.9(1)
 (V)	$F_{2,2'}$, 139.4(8); F_3, 106.6(4); $F_{3'}$, 142.1(4)
 (III)	$F_{2,2'}$, 141.9(1); $F_{3,3'}$, 107.5(1)
Octafluoronaphthalene	
	F_1, 145.7(1); F_2, 154.5(1)
 (X)	83.4(2), 99.4(2), 146.5(2), 149.4(2), 152.8(2), 160.9(3.5)
 (XI)	83.2(1), 101.6(1), 119.7(1), 123.5(1), 139.8(1), 153.0(1)
Octafluorobiphenylene	
	F_1, 146.2(1); F_2, 150.2(1)[c]
 (XIV)	90.1(1.5), 92.9(1.5), 123.7(1.5), 129.2(1.5), 148.2(2), 154.9(2)
 (XV)	88.9(3), 94.3(2.5), 124.0(3), 145.4(5)
 (XVI)	88.8(1), 93.1(1), 95.6(1), 144.2(1)

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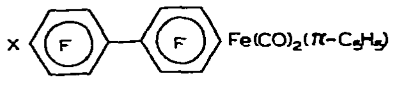
[a] Numbers indicate the positions or the approximate calculated chemical shifts. The relative positions of substituents in one ring may be reversed with respect to the other in fused ring complexes, *e.g.* complex (XI) may be 2,6- or 2,7-disubstituted. Fe$=$Fe(CO)$_2$(π-C$_5$H$_5$). [b] Chemical shift in ppm above CFCl$_3$ internal reference, tetrahydrofuran solution. Numbers in brackets indicate approximate relative intensities. Other bands with less than unit intensity were observed at 127.3, 128.4 and 143.0 ppm in the spectrum of the mixed biphenylene complexes. [c] Ref. 6 gives 139.6, 150.1 (calc. using $C_6F_6 = 162.9$ ppm).



(IV) X = F
(V) X = H

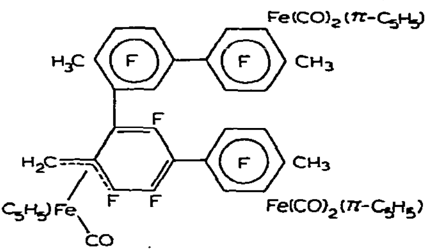
spectrometry (Table 3). The latter indicated one particular mixture to contain complexes (IV) and (V) in a ratio of about 1/4, and this was confirmed by the analytical results. The ^{19}F NMR spectrum was complex, as expected, but examination of the spectra of different mixtures enabled the various related resonances to be assigned. The results are consistent with the presence of the 4-mono- and 4,4′-disubstituted complexes as shown, the number and observed chemical shifts being in fair agreement with those calculated for complexes (IV) and (V). The low solubility of these complexes, even in tetrahydrofuran, has precluded any determinations of coupling constants.

The mass spectrum of the mixture also showed peaks due to a small amount of a third complex $H_2C_{12}F_7Fe(CO)_2(\pi\text{-}C_5H_5)$ (VI); the intensities of the ions associated with this compound were less than 6% of those of complex (V).

4,4′-Dimethyloctafluorobiphenyl

In previous studies of tetrafluorobenzenes[7], it was found that a *para*-disubstituted compound was relatively unreactive, and that low yields of complex were obtained. 4,4′-Dimethyloctafluorobiphenyl also shows this behaviour, and in reactions of this fluorocarbon with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$, only milligram amounts of an orange product were obtained. As shown in Table 3, the mass spectrum shows ions consistent with the composition $(CH_3)_2C_{12}F_7Fe(CO)_2(\pi\text{-}C_5H_5)$ (VII), and containing a small amount (~10%) of the hydrogen-substituted complex $(CH_3)_2C_{12}F_6HFe(CO)_2(\pi\text{-}C_5H_5)$(VIII). There was not sufficient for the NMR spectrum, so that the position of substitution could not be determined.

A second product could be obtained if the reaction was prolonged, as deep purple-black needle crystals. These showed three ν(CO) bands, two of equal intensity, and in the region characteristic of $\pi\text{-}C_5H_5Fe(CO)_2$ bands. Again, the low yield only enabled a mass spectrometric study of the product to be made. The highest ion was at *m/e* 1079±2. This corresponds to two fluorocarbon units and three iron carbonyl units, $[(CH_3)_2C_{12}F_6]_2Fe_3(CO)_5(\pi\text{-}C_5H_5)_3$ (calcd. *m/e* 1078). Other ions in the mass spectrum lend support to the presence of a dimeric fluorocarbon unit, and it is suggested that the third metal atom is bonded to the ring and methyl carbons by a π-allyl–iron bond, as in the recently described π-benzyl complexes of molybdenum[8,9]. A structure



which satisfies the IR and mass spectral requirements is (IX), but variations in substitution position are obviously possible. The crystals of the complex were unfortunately unsuitable for detailed X-ray examination[10].

TABLE 3

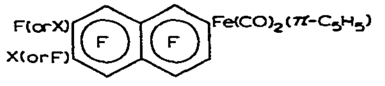
PARTIAL MASS SPECTRA

Ion	Relative abundances															
	(IV) R_f= $C_{12}F_9$	(V) R_f= $HC_{12}F_8$	(VI) R_f= $H_2C_{12}F_7$	(VII) R_f= $Me_2C_{12}F_7$	(VIII) R_f= $Me_2C_{12}F_6H$	(X) R_f= $C_{10}F_7$	(XI) R_f= $HC_{10}F_6$	(XII) R_f= $H_2C_{10}F_5$	(XIII)^b R_f= $C_{12}F_7$		(XIV)^b R_f= $HC_{12}F_6$		(XV)^b R_f= $H_2C_{12}F_5$		(XVI)^b R_f= $H_3C_{12}F_4$	
									(a)	(b)						
$C_3H_3^+$	64			7		80			14	20						
Fe^+	30			7		33			8	15						
$C_5H_5^+$	60			10		59			16	18						
FeF^+	69			10		71			13.5	22						
$C_5H_5Fe^+$	26			8		11			7.5	11						
$C_5H_5FeF^+$	110			31.5		100			18	26						
$(C_5H_5)_2Fe^+$	15			9		12			8	7.5						
									(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
R_fH^+	11	36	18	22	6	26	13	6	9		16	1.1	10	20		9
$R_fC_5H_5^+$	5	15	1.5	1.5	^{a}	15	1	5	16		^{a}	21	^{a}	^{a}		^{a}
$[M-2CO-FeF_2]^+$	22	87	^{a}	90	12	50	33	12	14		29	42	18.5	53		25
$[M-2CO]^+$	17	66	^{a}	29	15	30	17	5	14		27	39	21.5	77		42
$[M-CO]^+$	14	57	1	31	2.5	20	9	0.5	7.5		12.5	17	11	39		11
M^+	4	20	<1	13	2	26	12	2	9.5		18	28	11.5	42		19

[a] Ions coincident with contributions from other products present. [b] (*a*) Spectrum of mixture of (XIII), (XIV) and (XV) only; (*b*) spectrum of mixture containing (XIV), (XV) and (XVI) only.

Octafluoronaphthalene

The volatile yellow product from the reaction between $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and octafluoronaphthalene was shown by analysis and mass spectrometry to be an approximately 2/1 mixture of $C_{10}F_7Fe(CO)_2(\pi\text{-}C_5H_5)$ (X) and $HC_{10}F_6Fe(CO)_2(\pi\text{-}C_5H_5)$ (XI). About 2% of $H_2C_{10}F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ (XII) was also present, but since no resonances due to this complex were observed in the NMR spectrum, nothing else can be said concerning it. No evidence for any complex containing more than one iron atom was obtained.



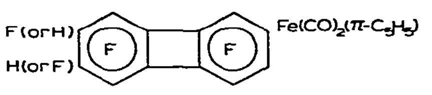
(X) X=F
(XI) X=H

The fluorine-19 NMR spectrum showed most of the thirteen resonances expected for a mixture of (X) and (XI), and the relative intensities of the peaks agreed fairly well with the proportions determined above. Although substituent parameters for the naphthalene system are not yet available, the strong deshielding caused by the transition metal group enabled the *ortho* fluorines to be assigned, and the presence of two low-field signals indicated that 2-substitution had occurred, as expected, and complex (X) is assigned the structure shown.

The second complex is not so readily identified, but making the reasonable assumptions (*i*) that the $\pi\text{-}C_5H_5Fe(CO)_2$ group is similarly in the 2-position, and (*ii*) that the hydrogen atom is introduced into ring B, the observed chemical shifts compare favourably with those expected for the 2,6- or 2,7-isomers. As before, full analysis of the spectrum was not possible because of its complexity and low intensity.

Octafluorobiphenylene

Even under the mildest conditions examined, *i.e.* reaction of the carbonylmetal anion with the fluorocarbon for about 3 h at room temperature, a mixture of complexes was formed. The mass spectrum showed the presence of $C_{12}F_7Fe(CO)_2(\pi\text{-}C_5H_5)$ (XIII), $HC_{12}F_6Fe(CO)_2(\pi\text{-}C_5H_5)$ (XIV) and $H_2C_{12}F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ (XV). When the reaction mixture was refluxed overnight, no simple substitution product (XIII) was present, and mass spectrometry indicated that a fourth complex, $H_3C_{12}F_4Fe(CO)_2(\pi\text{-}C_5H_5)$ (XVI) was also formed. No evidence was found to indicate the formation of complexes containing more than one metal atom. In spite of the apparent ready substitution of fluorine atoms, the yield of isolated complex was not high, and never exceeded ~1%.



(XIII)

(XV)

The assignment of the ^{19}F NMR spectrum followed the usual procedures, and was made with a mixture that contained no (XIII). The observed resonances correlated reasonably well with the illustrated structures, although the results are more tentative than the others mentioned here. Again, 2-substitution is found, but the introduction of the third and fourth substituents into the 1-positions indicates that the reactivity of these positions is higher than in the fluorinated naphthalenes*.

Mass spectra

The use of mass and ^{19}F NMR spectrometry to resolve the identities of inseparable mixtures has been described previously[11], and must depend on comparable volatilities of the complexes concerned. In view of the similarities in physical properties between the fluorocarbons discussed here and the analogous hydrocarbons, it is reasonable to assume similar volatilities for the complexes containing one or two fluorine atoms replaced by hydrogen, and this is borne out in the agreement found in the analytical and spectrometric results. With these assumptions in mind, the analysis of the spectra will be described.

Two recent investigations [12,13] have indicated that the mass spectra of polyfluoroaromatic derivatives of transition metals are characterised by ions which depend on the nature of the metal. For cyclopentadienyliron dicarbonyl complexes, such ions may be formed by the loss of neutral groups such as CO, HF or FeF_2, and also include ions such as $C_5H_5FeF^+$, R_fH^+ and $R_fC_5H_5^+$ (R_f=fluorocarbon radical). Table 3 lists the *m/e* values and relative intensities of these ions which were used to confirm the molecular formulae of the complexes described.

^{19}F NMR spectra

The use of ^{19}F NMR spectra in the assignment of the structures of the complexes described above also depends on certain assumptions. In particular, the extrapolation of substituent constants from the benzene series[11] to the naphthalene and biphenylene nuclei is probably the most suspect, in the absence of any confirmatory data for simpler derivatives of these systems. For simplicity, the formation of only one isomer of each complex was assumed. In calculating the chemical shifts expected in these polynuclear systems, it has also been assumed that the deshielding influence of a substituent in one ring is only of the order of a few ppm at most in the other fused ring. The values for all isomers of the complexes described were calculated, and only those which resembled the observed chemical shifts are shown in Table 2. The agreement between observed and calculated values, whilst not exact, is sufficiently favourable to justify at least in part, the assumptions made above, although unassigned resonances occur in the spectrum of the biphenylene derivatives. Methoxide gives approximately 1/4 mixtures of the 1- and 2-methoxyheptafluorobiphenylenes[6], and similar 1- and 2-substitution may have occurred in our product.

CONCLUSIONS

The reactions of the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with the fluorocarbons described above have followed the expected course, but further exchange of fluorine by hydrogen occurs readily. The reactivity of octafluorobiphenylene, previously undescribed, is shown to be high, especially in fluorine–hydrogen exchange reactions. The high reactivity suggests that carbonylmetal anions which are weaker nucleophi-

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* A similar tendency for polysubstitution was noted recently in the reactions of octafluorobiphenylene with methoxide, together with the formation of 1- and 2-isomers (ref. 6).

les, such as $[Mn(CO)_5]^-$ or $[\pi\text{-}C_5H_5W(CO)_3]^-$ (ref. 14) may form complexes with this ring. The relatively small amount of this fluorocarbon which was available at the time of this investigation (1967) prevented a more detailed examination of its reactions.

EXPERIMENTAL

All reactions involving sodium derivatives of metal carbonyls were performed under nitrogen, but during the subsequent work-up, no particular care was taken to exclude air. Chromatography was performed on columns packed with Florisil, initially in light petroleum. Tetrahydrofuran was redistilled from calcium hydride immediately before use. Light petroleum refers to a fraction b.p. 40–60°. The fluorocarbons were obtained from the Imperial Smelting Corporation, Avonmouth, Bristol, except for octafluorobiphenylene, which was prepared by reduced pressure pyrolysis of tetrafluorophthalic anhydride[6].

IR spectra were recorded on a Perkin–Elmer 257 spectrophotometer. ^{19}F NMR spectra were obtained with a Perkin–Elmer R10 permanent magnet instrument at 56.46 MHz, or with a Varian HA100 instrument at 94.1 MHz. Mass spectra were obtained with an AEI MS9 double-focussing machine, operating with 70 eV ionising energy, 8 kV accelerating voltage and 100 μA trap current, with a source temperature of 130–150°.

The sodium derivative of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ was obtained by stirring a tetrahydrofuran solution of the dimer with $\sim 1\%$ sodium amalgam for about 2 h under nitrogen. Excess amalgam was removed from the flask by means of a tap in the base, and small pieces of amalgam remaining were removed by rinsing with a further 5 ml mercury. The fluorocarbon, also in tetrahydrofuran, was then added dropwise to the solution so obtained. Amounts used, and subsequent work-up procedures, are described in detail below.

Reactions with decafluorobiphenyl

(*a*). The reaction mixture from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.77 g, 5 mmoles) and decafluorobiphenyl (3.34 g, 10 mmoles) was left overnight under nitrogen. A large amount of brown solid material was then removed by filtration, and the filtrate was evaporated to a syrup, and dissolved in dichloromethane for chromatography. Light petroleum eluted a very pale yellow solution, which was evaporated to give recovered decafluorobiphenyl (1.14 g, 34%), which contained the usual small amount of ferrocene (IR spectrum). Benzene/light petroleum mixtures eluted a yellow band, followed by a purple band, from which $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (840 mg, 46.5%) was recovered. The yellow solution was evaporated, and the residue sublimed to give a yellow solid (290 mg), m.p. 161–161.5°, which was shown to be a mixture of complexes (IV), (V) and (VI). [Found: C, 48.13; H, 1.05; F, 34.52. $C_{19}H_5F_9FeO_2$ (IV) calcd.: C, 46.33; H, 1.02; F, 34.76; $C_{19}H_6F_8FeO_2$ (V) calcd.: C, 48.10; H, 1.27; F, 32.05; a 1/4 mixture of (IV) and (V) calcd.: C, 47.75; H, 1.21; F, 32.60%.] IR spectrum ($CHCl_3$): ν(CO) 2038 vs, 1988 vs cm^{-1}.

(*b*). A similar experiment to (a), but refluxing overnight, gave on chromatography of the filtered reaction mixture, recovered decafluorobiphenyl (690 mg, 20%) and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. Benzene/ether (9/1) eluted two yellow bands, the first of which gave a mixture similar to that obtained in (a). The major product was in the second fraction, and recrystallisation of the involatile solid from a light petroleum/ether mixture gave a deep yellow solid, identified as the disubstituted complex $C_{12}F_8[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ (III) (462 mg, 9%), decompn. 230–240°. (Found: C, 48.81; H, 1.64; F, 23.45. $C_{26}H_{10}F_8Fe_2O_4$ calcd.: C, 48.00; H, 1.54; F, 23.38%.) IR spectrum ($CHCl_3$): ν(CO) 2039 vs, 1990 vs cm^{-1}. Other bands at 1627 m, 1576 vw, 1432 vs, 1378 vw, 1365 vw, 1193 m. 1007 w, 972 m, 940 s, 851 m, 766 w cm^{-1}.

Reaction with 4,4'-dimethyloctafluorobiphenyl

A reaction using the fluorocarbon (2.0 g, 6 mmoles) and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.8 g, 5 mmoles) gave on chromatography recovered fluorocarbon (880 mg, 44%), $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.04 g, 58%), and a pale yellow-brown eluate, eluting just in front of the purple $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ fraction. Recrystallisation gave a mixture, from which orange crystals (VII) and purple-back needles (IX) were separated by hand picking. The latter forms unstable solutions in light petroleum/dichloromethane mixtures. IR spectra ($CHCl_3$): complex (VII): ν(CO) 2028 vs, 1979 vs cm^{-1}; complex (IX): ν(CO) 2029 s, 2021 vs, 1979 s cm^{-1}.

Reactions with octafluoronaphthalene

(*a*). A mixture of octafluoronaphthalene (2.7 g, 10 mmoles) and the sodium salt from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.78 g, 5 mmoles) in tetrahydrofuran (60 ml) was refluxed overnight. Chromatography of a dichloromethane extract gave recovered $C_{10}F_8$ (1.06 g, 39%) and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.66 g, 37%), eluted with light petroleum and benzene, respectively. Between these two fractions, 15% benzene/light petroleum eluted a yellow band, which was evaporated and sublimed at 130–140°/0.1 mm to give a yellow solid, m.p. 180–182° (380 mg, 8.8%), shown to be a mixture of complexes (X), (XI) and (XII). IR spectrum ($CHCl_3$): ν(CO) 2038 vs, 1988 vs cm^{-1}.

(*b*). A second similar reaction gave recovered octafluoronaphthalene (630 mg, 23%) and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, and a yellow solid (425 mg, 10%), which was identified as a mixture of complexes (X) and (XI) in the approximate ratio of 2/1. [Found: C, 49.15; H, 1.25; F, 30.31. $C_{17}H_5F_7FeO_2$ (X) calcd.: C, 47.44; H, 1.16; F, 30.94; $C_{17}H_6F_6FeO_2$ (XI) calcd.: C, 49.50; H, 1.46; F, 27.68. A 2/1 mixture of (X) and (XI) calcd.: C, 48.22; H, 1.26; F, 29.88%.]

Reactions with octafluorobiphenylene

(*a*). The reaction mixture from octafluorobiphenylene (0.5 g, 1.25 mmoles) and the sodium salt from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (1.8 g, 5 mmoles) was refluxed overnight. Chromatography gave recovered $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.67 g, 37%), but no unreacted fluorocarbon could be found. A 15% benzene/light petroleum mixture eluted a yellow band, which was sublimed at ~140°/0.1 mm to give an orange solid (44 mg) which exhibited four ν(CO) bands, and proved to be a mixture of complexes (XIV), (XV) and (XVI) (44 mg). [Found: C, 53.47; H, 1.55; F, 24.48, $C_{19}H_6F_6FeO_2$ (XIV) calcd.: C, 52.30; H, 1.38; F, 26.15; $C_{19}H_7F_5FeO_2$ (XV) calcd.: C, 54.57; H, 1.67; F, 22.73%.] IR spectrum ($CHCl_3$): ν(CO) 2042 vs, 2036 m, 1997 vs, 1987 m.

(*b*). A similar reaction mixture from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.75 g, 2.0 mmoles) and $C_{12}F_8$ (0.4 g, 1.0 mmole) reacted for 3 h. A pale yellow solid was left at the top of the column on chromatography; light petroleum eluted a brown band from the column, and benzene gave a purple eluate. These fractions were combined and rechromatographed to give a yellow solid which was sublimed between 110–140°/0.1 mm to give a bright yellow solid mixture of complexes (XIII), (XIV) and (XV) (42 mg).

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