REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS

V. PERFLUOROARYL DERIVATIVES OF IRON PREPARED BY REACTION BETWEEN $NaFe(CO)_2C_5H_5$ AND CERTAIN AROMATIC FLUOROCARBONS*

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INTRODUCTION

Within the last few years hexafluorobenzene and other highly fluorinated aromatic hydrocarbons have become more readily available and their chemistry has been investigated in considerable detail**. One of the characteristic reactions of highly fluorinated aromatic hydrocarbons is the facile nucleophilic substitution of fluorine with other groups. For example, hexafluorobenzene reacts readily with sodium methoxide to form pentafluorophenyl methyl ether[3].

Recently we have been investigating the chemistry of various metal carbonyl anions[1,4]. It seemed likely that these rather nucleophilic anions might react with various highly fluorinated aromatic hydrocarbons to form new perfluoroaryl derivatives of transition metals.

When we began this work (July, 1963), no perfluoroaryl derivatives of transition metals had been reported. Shortly after our initial positive results we learned from two independent research groups[5,6] of the syntheses of several perfluoroaryl derivatives of transition metals such as $(C_5H_5)_2Ti(C_6F_5)_2$ (refs. 5 and 6), $C_6F_5Mn(CO)_5$ (refs. 5 and 6) and $C_6F_5Fe(CO)_2C_5H_5$ (ref. 6). Both groups of workers used the reactions between various complex transition metal halides and pentafluorophenyl derivatives of magnesium or lithium. Neither research group reported the preparation of transition metal derivatives of perfluoroaryl groups other than the pentafluorophenyl group.

This paper describes in detail the nucleophilic substitution of fluorine in several highly fluorinated aromatic hydrocarbons by the anion $[Fe(CO)_2C_5H_5]^-$.

EXPERIMENTAL

Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the

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* For Part IV of this series see ref. 1.
** For a summary of the chemistry of aromatic fluorine compounds see ref. 2.

TABLE 1

COMPOUNDS DESCRIBED IN THIS PAPER

Compound	*Color*	*M.p.*	*Preparation*	*Yield*	*Analyses*				
						C	*H*	*F*	*Fe*
1) $C_6F_5Fe(CO)_2C_5H_5$*	yellow-orange	142–143°*	$NaFe(CO)_2C_5H_5$ + C_6F_6	49%	Calcd.	45.4	1.4	27.6	16.3
					Found	46.1	1.4	27.9	16.2
2) $C_6F_4HFe(CO)_2C_5H_5$	yellow-orange	128–130°	$NaFe(CO)_2C_5H_5$ + C_6F_5H	39%	Calcd.	47.9	1.8	23.3	17.2
					Found	48.3	1.7	23.2	16.4
3) $C_6F_3H_2Fe(CO)_2C_5H_5$	yellow-orange	73–75°	$NaFe(CO)_2C_5H_5$ + 1,2,3,4-$C_6F_4H_2$	29%	Calcd.	50.7	2.3	18.5	
					Found	50.8	2.2	18.6	
4) $CF_3C_6F_4Fe(CO)_2C_5H_5$	yellow-orange	119–120°	$NaFe(CO)_2C_5H_5$ + $CF_3C_6F_5$	48%	Calcd.	42.6	1.3	33.7	14.2
					Found	42.4	1.4	33.8	13.7

* Lit.[5] m.p., 144.5–145°.

carbonyl regions of the infrared spectra were investigated in greater detail in Halocarbon oil mulls on a Beckman IR-9 spectrometer with grating optics. Ultraviolet spectra were taken in cyclohexane solution and recorded on a Cary model 14 spectrometer. The proton NMR spectra were taken in chloroform, carbon disulfide, or acetone solutions with hexamethyldisiloxane (9.95 τ) as an internal standard and recorded on a Varian A-60 spectrometer. The ^{19}F NMR spectra were taken in chloroform solutions with 1,2-difluoro-1,1,2,2-tetrachloroethane (Freon 112) (67.8 ϕ) as an internal standard and recorded at 56.4 Mc. on a Varian DP-60 spectrometer.

Reagents

Tetrahydrofuran was always freshly redistilled over lithium aluminum hydride. The fluorinated aromatic hydrocarbons were purchased from Pierce Chemical Co., Rockford, Illinois. The sodium salt $NaFe(CO)_2C_5H_5$ was prepared under nitrogen from $[C_5H_5Fe(CO)_2]_2$ and an ~ 30% excess of ~ 1% sodium amalgam in tetrahydrofuran solution as described in previous papers[1-4].

General procedure for the reactions between $NaFe(CO)_2C_5H_5$ and aromatic fluorocarbons

A mixture of 10 mmoles of $NaFe(CO)_2C_5H_5$ and 10 mmoles of the aromatic fluorocarbon in 60 ml of tetrahydrofuran was refluxed 12–18 h under nitrogen with stirring. After cooling to room temperature, solvent was removed at ~ 30 mm. Nitrogen was admitted and the residue extracted with three 50 ml portions of dichloromethane. After gravity filtration, solvent was removed from the filtrate at ~ 30 mm.

The resulting brownish residue was dissolved in 50–100 ml of benzene and the filtered benzene solution chromatographed on a 2 × 50 cm alumina column. The chromatogram was developed with benzene. A yellow band of the perfluoroaryl-$Fe(CO)_2C_5H_5$ derivative appeared followed by a red-brown band of $[C_5H_5Fe(CO)_2]_2$. In most cases the red-brown band of $[C_5H_5Fe(CO)_2]_2$ was not further investigated. The yellow band of the perfluoroaryl-$Fe(CO)_2C_5H_5$ derivative was eluted with benzene. The yellow-orange eluate was filtered by gravity collecting the filtrate under nitrogen. Removal of benzene at ~ 30 mm from this filtrate left yellow-orange crystals. These were purified by extracting with a minimum of pentane at room temperature and cooling the filtered solution to —78° to reprecipitate the product. The analytical samples were finally purified by sublimation at ~ 80°/0.1 mm.

The perfluoroaryl-$Fe(CO)_2C_5H_5$ compounds melting above 100° (Table 1) were rather sparingly soluble in pentane. Therefore, significant additional amounts of these materials were obtained by sublimation of the insoluble material remaining after the pentane extraction.

In the case of the preparation of $C_6F_5Fe(CO)_2C_5H_5$ from $NaFe(CO)_2C_5H_5$ and hexafluorobenzene, the original dichloromethane extract appeared to contain no $[C_5H_5Fe(CO)_2]_2$. Therefore, in this preparation chromatography was omitted, the product being isolated from the residue remaining from the dichloromethane extract by pentane crystallization and vacuum sublimation.

Tables 1, 2, and 3 give the analytical data, infrared spectra, and NMR spectra, respectively, of the new compounds.

TABLE 2

INFRARED SPECTRA OF THE COMPOUNDS DESCRIBED IN THIS PAPER (cm^{-1})

Compound	*Metal Carbonyl Bands*[a]	*C–H Bands*[b]	*Other Bands*[b]
1) $C_6F_5Fe(CO)_2C_5H_5$	2045 (s) 1997 (s) 1958 (m)	3100 (w)	1620 (w), 1595 (w), 1490 (s), 1450 (s), 1435 (sh), 1360 (m), 1352 (sh), 1262 (w), 1246 (vw), 1111 (w), 1062 (sh), 1055 (s), 1050 (sh), 1045 (sh), 1019 (sh), 1014 (w), 1003 (w), 962 (s), 955 (s), 854 (s), 842 (sh), 768 (s), 738 (w), 713 (vw)
2) $C_6F_4HFe(CO)_2C_5H_5$	2033 (s) 1980 (vs) 1973 (vw) 1946 (w)	3100 (w) 3075 (w)	1626 (m), 1590 (m), 1580 (m), 1450 (vs), 1443 (vs), 1425 (m), 1415 (m), 1400 (m), 1355 (w), 1334 (w), 1272 (vw), 1242 (w), 1228 (w), 1178 (s), 1160 (s), 1085 (m), 1013 (w), 1003 (m), 983 (w), 945 (w), 888 (vs), 856 (m), 842 (s), 823 (s), 800 (s), 703 (s), 698 (s)
3) $C_6F_3H_2Fe(CO)_2C_5H_5$	2041 (s) 1992 (s) 1957 (m) 1933 (w)	3020 (w)	1548 (w), 1430 (s), 1400 (m), 1373 (m), 1265 (m), 1255 (w), 1198 (m), 1140 (m), 955 (s), 835 (m), 823 (s), 795 (m), 792 (sh), 725 (m), 710 (w)
4) $CF_3C_6F_4Fe(CO)_2C_5H_5$	2054 (s) 2003 (s) 1968 (w)	3100 (w)	1630 (m), 1615 (sh), 1570 (m), 1565 (m), 1450 (vs), 1435 (vs), 1425 (vs), 1400 (m), 1318 (vs), 1305 (vs), 1188 (s), 1160 (s), 1115 (vs), 1062 (w), 1014 (w), 1002 (w), 960 (vs), 940 (sh), 907 (m), 852 (s), 766 (s), 742 (m), 710 (s)

[a] Halocarbon Oil mull, Beckman IR-9 spectrometer.
[b] KBr pellet, Perkin-Elmer 21 spectrometer.

The visible spectrum of $C_6F_5Fe(CO)_2C_5H_5$ exhibited no maxima, the absorption decreasing gradually from 400 to ~ 580 mμ.

Ultraviolet spectra

A. $C_6F_5Fe(CO)_2C_5H_5$. Maximum at 356 mμ ($\varepsilon = 942$).
B. $CF_3C_6F_4Fe(CO)_2C_5H_5$. Maximum at 356 mμ ($\varepsilon = 926$).

TABLE 3

NMR SPECTRA[a] OF PERFLUOROARYL IRON COMPLEXES[b]

Compound	^{19}F Chemical Shifts, o				^{1}H Chemical Shifts, τ	
	ortho	meta	para	CF_3	C_5H_5	Other
$C_6F_5Fe(CO)_2C_5H_5$	107.3 (2)[c]	163.6 (2)[d]	160.3 (1)[d]	—	5.02	—
$C_6F_5Mn(CO)_5$[e]	104.3 (2)	161.2 (2)	157.5 (1)	—	—	—
$C_6F_4HFe(CO)_2C_5H_5$	108.9 (2)[f]	141.5 (2)[g]	—	—	5.03 4.80[h]	3.34[i] 3.12[h,i]
$C_6F_3H_2Fe(CO)_2C_5H_5$	85.5 (1)[j] 102.6 (1)[j]	144.4 (1)[k]	—	—	5.07 4.85[h]	~ 3.4[j] ~ 3.3[h,j]
$CF_3C_6F_4Fe(CO)_2C_5H_5$	106.5 (2)[k]	144.5 (2)[k]	—	56.9 (3)[l]	4.99	—

[a] Relative intensities given in parentheses.
[b] Chloroform solution unless otherwise indicated.
[c] Doublet, $J = 21$ c.p.s.
[d] Triplet, $J = 21$ c.p.s.
[e] Data from ref. 7.
[f] Double doublet, $J_1 = 7$ c.p.s., $J_2 = 15$ c.p.s.
[g] Double doublet, $J_1 = 10$ c.p.s., $J_2 = 15$ c.p.s
[h] Acetone solution.
[i] Triple triplet, $J_1 = 7$ c.p.s., $J_2 = 10$ c.p.s.
[j] Complex multiplet.
[k] Fine structure not clear.
[l] Triplet, $J = 20$ c.p.s.

DISCUSSION

The successful synthesis of $C_6F_5Fe(CO)_2C_5H_5$ from hexafluorobenzene and $NaFe(CO)_2C_5H_5$ led us to investigate the reactions between other metal carbonyl anions and hexafluorobenzene in order to prepare pentafluorophenyl derivatives of other transition metals. However, pentafluorophenyl–transition metal derivatives were not isolated in the reactions of hexafluorobenzene with the sodium salts $NaMn(CO)_5$, $NaCo(CO)_4$, $Na_2Fe(CO)_4$, or $NaMo(CO)_3C_5H_5$ in refluxing tetrahydrofuran. Thus present indications are that the nucleophilic substitution of hexafluorobenzene with metal carbonyl anions is limited to the preparation of $C_6F_5Fe(CO)_2C_5H_5$. It is possible, of course, that sufficient modification of the reaction conditions might eventually lead to successful nucleophilic substitution of hexafluorobenzene with some of these other anions.

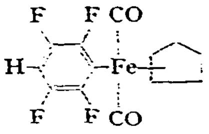
Despite this severe limitation, nucleophilic substitution of highly fluorinated aromatic hydrocarbons with $NaFe(CO)_2C_5H_5$ does appear to be a preferred synthetic method in some cases. For example, $C_6F_5Fe(CO)_2C_5H_5$, obtained in only ~ 7 % yield from pentafluorophenylmagnesium bromide and $C_5H_5Fe(CO)_2I$ with much formation of $[C_5H_5Fe(CO)_2]_2$ (ref 6), was obtained in ~ 49 % yield from hexafluorobenzene and $NaFe(CO)_2C_5H_5$ with little formation of $[C_5H_5Fe(CO)_2]_2$ as a by-product. Nucleophilic substitution of aromatic fluorocarbons other than hexafluorobenzene with $NaFe(CO)_2C_5H_5$ provided a route for the preparation of other perfluoroaryliron derivatives for which the bromo- or iodo-derivatives required for the preparation of the appropriate magnesium or lithium derivative may not be readily available. Besides hexafluorobenzene, the reactions of the aromatic fluorocarbons pentafluorobenzene, 1,2,3,4-tetrafluorobenzene, and octafluorotoluene with $NaFe(CO)_2C_5H_5$ were investigated and the corresponding perfluoroaryliron compounds prepared. Undoubtedly, many other highly fluorinated aromatic derivatives would also form similar perfluoroaryliron derivatives on treatment with $NaFe(CO)_2C_5H_5$; but the relatively high cost of most highly fluorinated aromatic compounds discouraged the preparation of an extended series of such perfluoroaryliron derivatives.

In reactions between $NaFe(CO)_2C_5H_5$ and aromatic fluorocarbons other than hexafluorobenzene, several products are possible in each case depending which one of two or more possible fluorine atoms is replaced with the $Fe(CO)_2C_5H_5$ group. Fortunately, ^{19}F NMR spectroscopy permitted an unequivocal structure assignment to each perfluoroaryliron compound prepared in this work.

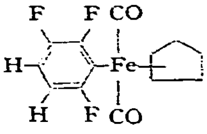
Thus the iron compound $C_6F_4HFe(CO)_2C_5H_5$ obtained from pentafluorobenzene and $NaFe(CO)_2C_5H_5$ was found to exhibit only *two* resonances of equal intensity in its ^{19}F NMR spectrum (Table 3). This clearly indicates structure (I) for this complex in which the hydrogen atom and the $Fe(CO)_2C_5H_5$ group are located in mutually *para*-positions. On the basis of similarity in positions to the corresponding resonances in $C_6F_5Fe(CO)_2C_5H_5$ and $C_6F_5Mn(CO)_5$, the double doublet at 108.9 ϕ may be assigned to the two fluorine atoms in *ortho*-positions relative to the iron atom and the double doublet at 141.5 ϕ to the two fluorine atoms in *meta*-positions relative to the iron atom. The double doublets arise from unequal coupling to the other type of fluorine atom and to the single proton. The single benzenoid aromatic proton in $C_6F_4HFe(CO)_2C_5H_5$ appears as a triple triplet at 3.34 τ in the proton NMR spectrum due to unequal coupling with the two different pairs of fluorine atoms.

The compound $C_6F_3H_2Fe(CO)_2C_5H_5$ obtained from 1,2,3,4-tetrafluorobenzene and $NaFe(CO)_2C_5H_5$ was found to exhibit three resonances of equal intensity in its ^{19}F NMR spectrum (Table 3). This fact alone does not distinguish between the two possible structures (II) and (III). However, fluorine atoms in both *meta*- and *para*-positions relative to transition metal atoms appear in the range 141–164 ϕ (Table 3). Only one of the three fluorine resonances in $C_6F_3H_2Fe(CO)_2C_5H_5$ appears in this range indicating the presence of only one *meta*- or *para*-fluorine atom relative to the iron atom. The other two resonances which appear at 85.5 ϕ and 102.6 ϕ, chemical shifts characteristic of fluorine atoms in *ortho*-positions relative to transition metals, may be assigned to two different types of *ortho*-fluorine atoms. Thus the chemical shifts of the ^{19}F NMR resonances in $C_6F_3H_2Fe(CO)_2C_5H_5$ clearly indicate structure (II) rather than structure (III) for this compound. The relatively low symmetry of the substituted benzene ring in $C_6F_3H_2Fe(CO)_2C_5H_5$ has prevented interpretation of the fine structures of both the ^{19}F and proton NMR resonances.

The reaction between the rather expensive octafluorotoluene and $NaFe(CO)_2C_5H_5$ was carried out in order to ascertain whether the benzylic fluorine atoms of the CF_3 group or the aromatic fluorine atoms of the C_6F_5 group would be substituted preferentially with $Fe(CO)_2C_5H_5$ groups. The ^{19}F NMR spectrum of the resulting $C_7F_7Fe(CO)_2C_5H_5$ clearly indicated structure (IV), substitution of the aromatic fluorine atoms in a *para*-position relative to the CF_3 group having occurred in preference to substitution of either the *ortho*- or *meta*-fluorine atoms of the aromatic ring or the benzylic fluorine atoms of the CF_3 groups. Only three resonances were observed in this ^{19}F NMR spectrum of relative intensities 3:2:2. The triplet of relative intensity 3 at 56.9 ϕ may clearly be assigned to the three fluorine atoms of the CF_3 group being split by the two equivalent aromatic fluorine atoms in an *ortho*-position relative to the CF_3 group. The remaining two resonances of equal intensity at 106.5 ϕ and 144.5 ϕ may be assigned to the two fluorine atoms in *ortho*-positions relative to the iron atom and the two fluorine atoms in *meta*-positions relative to the iron atom, respectively. The chemical shifts of these fluorine atoms are very similar to the chemical shifts of the corresponding fluorine atoms in $C_6F_4HFe(CO)_2C_5H_5$ confirming this assignment.



(I)



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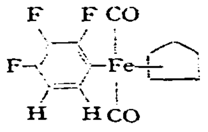

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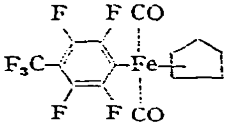

(IV)

From the reactions of aromatic fluorocarbons with $NaFe(CO)_2C_5H_5$ discussed in this paper, the following general conclusions may be drawn regarding the position of nucleophilic substitution of fluorine atoms with $Fe(CO)_2C_5H_5$ groups:

(1) Substitution occurs in a *para*-position relative to a substituent other than fluorine.

(2) Substitution in an aromatic nucleus occurs in preference to substitution in a side chain.

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SUMMARY

The sodium salt $NaFe(CO)_2C_5H_5$ reacts with hexafluorobenzene, pentafluorobenzene, and 1,2,3,4-tetrafluorobenzene in tetrahydrofuran to form the yellow-orange derivatives $C_6F_5Fe(CO)_2C_5H_5$, $(p\text{-}C_6F_4H)Fe(CO)_2C_5H_5$, and $(2,3,6\text{-}C_6F_3H_2)Fe(CO)_2C_5H_5$, respectively. Octafluorotoluene reacts with $NaFe(CO)_2C_5H_5$ in tetrahydrofuran to form yellow-orange $(p\text{-}CF_3C_6F_4)Fe(CO)_2C_5H_5$ rather than a heptafluorobenzyl derivative.

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