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NOTE

# POLYFLUOROAROMATIC DERIVATIVES OF METAL CARBONYLS III*. THE NATURE OF TWO BY-PRODUCTS OBTAINED FROM REACTIONS BETWEEN $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ AND POLYFLUOROAROMATIC COMPOUNDS

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The reaction of the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with monosubstituted perfluoroaromatic compounds has been shown to give a series of complexes of the type $p\text{-}XC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$ ($X = H$[2], $CF_3$[2], $CO_2Et$[3], etc.). In general, these reactions proceed to give a single complex, but the reactions of this anion with $C_6F_5X$ ($X = F$, Cl, Br, or I) gave mixtures of $C_6F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ and $p\text{-}HC_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$[3]. In addition to these two complexes, the reaction with iodopentafluorobenzene gave a third product in ~30% yield, which was not identified[3].

This compound has now been identified as bis(pentafluorophenyl)mercury from its analysis and NMR and mass spectra. The source of the mercury is undoubtedly the small particles of mercury left after the preparation of the anion by reaction between $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and sodium amalgam. The mercury compound has been made by reaction of lithium amalgam with bromopentafluorobenzene[4], and the formation of this compound in 75% yield has been reported[5] in the thermal reaction between iodopentafluorobenzene and mercury at 300°. The isolation of mercury salts of metal carbonyls from various reactions of the corresponding sodium derivatives, prepared by the sodium amalgam method, has been noted previously[6]. It is notable that $Hg(C_6F_5)_2$ does not appear to be formed in the reactions of $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ with hexafluorobenzene or chloro- or bromopentafluorobenzenes.

It is suggested that formation of $Hg(C_6F_5)_2$ may involve a radical reaction after abstraction of iodine, either by the mercury, or alternatively, by traces of amalgam not completely removed by the usual rinsing with more fresh mercury. The formation of decafluorobiphenyl, among other products, in the reaction between nickel carbonyl and $C_6F_5I$, suggests the easy formation of $C_6F_5$ radicals from this fluorocarbon[7].

The mass spectrum of $Hg(C_6F_5)_2$ (see *Experimental* for full details) shows major peaks corresponding to $C_3F_3^+$, $C_5F_2^+$, $C_5F_3^+$, $C_6F_4^+$, $C_6F_5^+$ (base peak), $C_6F_5Hg^+$ and $(C_6F_5)_2Hg^+$. The appropriate metastable peaks indicate that the main processes are fission of a $C_6F_5$ group from the parent ion, and the elimination of mercury to give $C_6F_5^+$. Subsequent fragmentation of this ion suggests that it has a similar structure to those formed from compounds such as $C_6F_5X$ ($X =$ halogen).

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* For Part II see ref. 1.

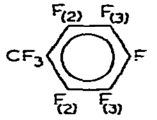
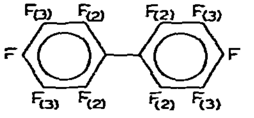
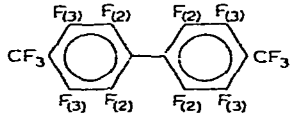
This is in contrast to the various breakdown patterns shown by transition metal complexes containing $C_6F_5$ groups[8]. The low abundance of an ion at *m/e* 386 ($C_6F_5HgF^+$, 0.2%) indicates that the formation of ions with metal–fluorine bonds does not occur to any appreciable extent. Loss of one fluorine atom from the parent ion, to give $C_{12}F_9Hg^+$, also occurs to a small extent. There is no evidence for the formation of either $HgF^+$ or $HgF_2^+$.

There were relatively strong doubly-charged ions which could be assigned to $Hg^{2+}$, $C_{12}F_9Hg^{2+}$ and $C_{12}F_{10}Hg^{2+}$; the appearance of these ions seems to be characteristic of compounds containing elements of high atomic number.

In another study, the known[2] complex $p$-$CF_3C_6F_4Fe(CO)_2(\pi$-$C_5H_5)$ was required, and was prepared by the reaction of the anion $[\pi$-$C_5H_5Fe(CO)_2]^-$ with octafluorotoluene. A second product was isolated in small yield from this reaction, which showed a parent ion at *m/e* 434 ($C_{14}F_{14}^+$) in its mass spectrum, together with many other peaks which could all be assigned to other fluorocarbon fragments. In particular, the peak at *m/e* 217 ($C_7F_7^+$) was very weak (relative intensity, 5%) suggesting that the compound did not readily form this ion. This fact, together with the $^{19}F$ NMR spectrum, rule out a formulation $C_6F_5CF_2CF_2C_6F_5$.

The three resonances in the $^{19}F$ NMR spectrum occur at 56.1, 135.2 and 138.4 ppm (relative intensities, 3/2/2). The first, a triplet, can be assigned to the $CF_3$ group coupled to *ortho*-aromatic fluorines. The other two signals may be assigned to the ring fluorines in a *para*-disubstituted tetrafluorophenyl group. The only compound which is consistent with these data is 4,4'-bis(trifluoromethyl)octafluorobiphenyl.

The observed chemical shifts may be compared to those calculated for this compound on the basis of substituent shielding parameters obtained from $C_6F_6$, $CF_3C_6F_5$, and decafluorobiphenyl[9], as shown below. Unfortunately, the fine structure of the aromatic fluorine resonances could not be resolved adequately for the determination of the appropriate coupling constants.

| |  |  |  |
|---|---|---|---|
| $CF_3$ | 56.6 | | 56.1 ppm |
| $F_{(2)}$ | 140.2 | 137.9 | 135.2 (calcd. 135.5) |
| $F_{(3)}$ | 160.5 | 160.0 | 138.4 (calcd. 137.3) |
| $J(CF_3$–$F_{(2)})$ | 22.75 | | 22.6 Hz |

The formation of this compound can be explained by the dimerisation of heptafluorotolyl radicals. Their abstraction of hydrogen from solvent to form $p$-$CF_3C_6F_4H$ may also occur, but the lower reactivity of this compound towards the anion makes unlikely the formation of any complex*. Heptafluorotoluene was not looked for, and may have been present.

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* It was postulated[3] that formation of $p$-$HC_6F_4Fe(CO)_2(\pi$-$C_5H_5)$ in the reactions involving $C_6F_5X$ (X = F, Cl, Br or I) occurs via reaction of the anion with pentafluorobenzene formed by a similar hydrogen-abstraction process.

## EXPERIMENTAL

General experimental details were similar to those described before[3].

Mass spectra were obtained with an AEI MS9 double-focussing mass spectrometer, operating with 70 eV ionising energy, 8 kV accelerating voltage, and 100 $\mu$A trap current. Samples were admitted via the direct insertion lock, with an ion chamber temperature of $\sim 130°$.

The $^{19}$F NMR spectrum of the substituted biphenyl was obtained with a Varian Associates HA100 instrument, operating at 94.1 MHz, using the microcell attachment.

### *Identification of bis(pentafluorophenyl)mercury*

The reaction between iodopentafluorobenzene and the anion $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ has been described previously[3]. The white crystals which were present in the reaction product were separated by fractional crystallisation from pentane, followed by fractional sublimations, to give a solid which still contained some iron complex. This was removed by air oxidation of a pentane solution, and sublimation of the evaporated solution gave the pure white $Hg(C_6F_5)_2$, m.p. 136° (lit.[10] m.p. 142.3°). (Found: C, 27.54; H, 0.41; F, 33.35; I, 0.0; mol. wt. by mass spectrometry, 536. $C_{12}F_{10}{}^{202}Hg$ calcd.: C, 26.87; H, 0.0; F, 35.45; I, 0.0%; mol.wt., 536.) Infrared spectrum (cyclohexane): 1640 w, 1512 s, 1509 s(sh), 1481 vs, 1376 m, 1286 w, 1089 m(sh), 1083 m(sh), 1078 m, 1070 m(sh), 1055 w(sh), 970 vs, 960 m, 811 m, 772 w cm$^{-1}$.

The $^{19}$F NMR spectrum (in tetrahydrofuran solution) showed three resonances at 121.2, 151.8 and 160.6 ppm, relative intensity 2/1/2 (lit.[11] 119.7, 150.6, 159.0 ppm, solvent not given).

Mass spectrum (*m/e**, relative intensity, assignment): 69, 0.7, $CF_3^+$; 79, 5.4, $C_5F^+$; 85, 2.2, –; 86, 1.3, $C_4F_2^+$; 93, 9.0, $C_3F_3^+$; 98, 8.6, $C_5F_2^+$; 101, 0.3, $Hg^{2+}$; 110, 1.7, $C_6F_2^+$; 117, 38, $C_5F_3^+$; 129, 2.5, $C_6F_3^+$; 136, 0.6, $C_5F_4^+$; 148, 5.6, $C_6F_4^+$; 155, 0.2, $C_5F_5^+$; 167, 100, $C_6F_5^+$; 202, 4, $Hg^+$; 245, 0.1, $HgC_2F^+$; 258.5, 0.1, $C_{12}F_9Hg^{2+}$; 268, 1.7, $C_{12}F_{10}Hg^{2+}$; 369, 17, $C_6F_5Hg^+$; 386, 0.2, $C_6F_5HgF^+$; 498, 0.1, $C_{12}F_8Hg^+$; 517, 0.9, $C_{12}F_9Hg^+$; 536, 21, $C_{12}F_{10}Hg^+$. There were relatively strong metastable peaks at *m/e* ~254 (536→369), 82.0 (167→117 and 117→98) and 75.6 (369→167). The peak at *m/e* 254 is considerably broadened because of the presence of the multi-isotopic mercury.

### *Formation of 4,4'-bis(trifluoromethyl)octafluorobiphenyl*

The reaction between the sodium salt from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (3.54 g) and octafluorotoluene (4.7 g) gave the previously reported complex $p\text{-}CF_3C_6F_4Fe(CO)_2(\pi\text{-}C_5H_5)$ (1.87 g, 24%), isolated by sublimation. A more volatile compound, which formed square white crystals further up the cooled probe, was separated and re-sublimed to give 4,4'-bis(trifluoromethyl)octafluorobiphenyl (7 mg), mol.wt., 433.9765 (calcd. for $C_{14}F_{14}$ 433.9776).

Other ions in the mass spectrum were at (*m/e*, intensity relative to *m/e* 434 = 100, assignment): 69, 8, $CF_3^+$; 93, 4, $C_3F_3^+$; 117, 2.5, $C_5F_3^+$; 141, 2, $C_7F_3^+$; 148, 2, $C_6F_4^+$;

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* Based on $^{202}$Hg (29.8%). The identification of this compound was first suggested by the presence of the characteristic seven-line mercury isotope pattern in the parent ion.

165, 2, $C_9F_3^+$; 189, 2, $C_{11}F_3^+$;196, 2, $C_{10}F_4^+$; 203, 2, $C_9F_5^+$; 208, 2, $C_{11}F_4^+$; 217, 5, $C_7F_7^+$; 227, 7, $C_{11}F_5^+$; 234, 2, $C_{10}F_6^+$; 241, 4, $C_9F_7^+$; 246, 5, $C_{11}F_6^+$; 258, 6, $C_{12}F_6^+$; 265, 9, $C_{11}F_7^+$; 272, 2, $C_{10}F_8^+$; 277, 6, $C_{12}F_7^+$; 284, 2, $C_{11}F_8^+$; 289, 2, $C_{13}F_7^+$; 291, 2, $C_{10}F_9^+$; 296, 17, $C_{12}F_8^+$; 315, 12, $C_{12}F_9^+$; 327, 13, $C_{13}F_9^+$; 334, 6, $C_{12}F_{10}^+$; 346, 13, $C_{13}F_{10}^+$; 365, 8, $C_{13}F_{11}^+$; 377, 3, $C_{14}F_{11}^+$; 379, 2, $C_{11}F_{13}^+$?; 384, 47, $C_{13}F_{12}^+$; 398, 4, $C_{11}F_{14}^+$?; 415, 56, $C_{14}F_{13}^+$. Infrared spectrum (cyclohexane): 1660 w, 1599 w, 1503 s, 1484 vs, 1400 vw, 1332 vs(sh), 1325 vs, 1197 m, 1177 m(sh), 1163 vs, 1052 vw, 1003 m, 982 vs, 902 w, 708 vs $cm^{-1}$.

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