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# TRANSITION METAL COMPLEXES WITH σ-BONDED FLUORINE-CONTAINING GROUPS

## III *. REACTIONS OF PERFLUOR-n-PROPYLIRON TETRACARBONYL IODIDE WITH MERCURY COMPOUNDS

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## Summary

We have studied the reactions of perfluoropropyliron tetracarbonyl iodide with fluorine-containing mercury compounds. The symmetrical complex $(C_3F_7)_2Fe(CO)_4$ is formed as a result of treating $Hg[N(CF_3)_2]_2$ with $C_3F_7Fe(CO)_4I$ and also by pyrolysis of $C_3F_7Fe(CO)_4OCOCF_3$ obtained by means of iodine atom exchange with $Hg(OCOCF_3)_2$ in carbonyliodide. By the interaction of $C_3F_7Fe(CO)_4I$ with $HgF_2$, $Hg_2F_2$ and PhHgF, the symmetrical complex is formed in low yield while the major reaction products are mercury-containing carbonyliron complexes $[C_3F_7Fe(CO)_4]_2Hg$ and $C_3F_7Fe(CO)_4HgC_3F_7$. It is shown that metallic mercury is inserted into the Fe–I bond of $C_3F_7Fe(CO)_4I$ resulting in unstable $C_3F_7Fe(CO)_4HgI$. The structure of the compounds obtained is established based on the analysis of $^{19}F$ NMR spectra.

## Introduction

In our previous studies we have found a symmetrization reaction of carbonyliron complexes: disproportionation of perfluoroalkyliron tetracarbonyl iodides with AgF into bis(perfluoroalkyl)iron tetracarbonyls [1,2].

$$2R_FFe(CO)_4I + 4\,AgF \rightarrow (R_F)_2Fe(CO)_4 + FeF_2 + 4\,CO + 2\,AgI \cdot AgF$$

$$R_F = CF_3, C_3F_7, C_4F_9, C_6F_{13}, C_6F_5, (CF_3)_2CH \qquad (1)$$

The fluorinated radical shift probably occurs during the formation of the unstable perfluoroalkyliron tetracarbonyl fluoride dimer containing bridging fluorine atoms [3].

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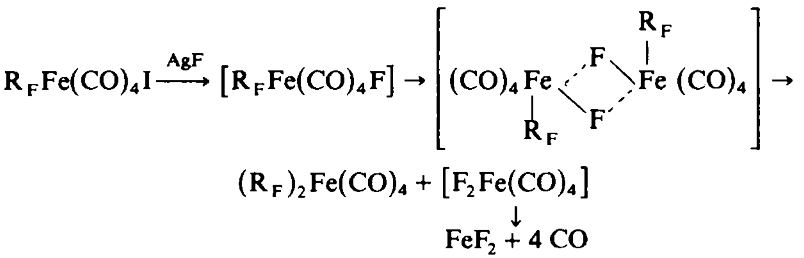
* For part II see ref. [1].



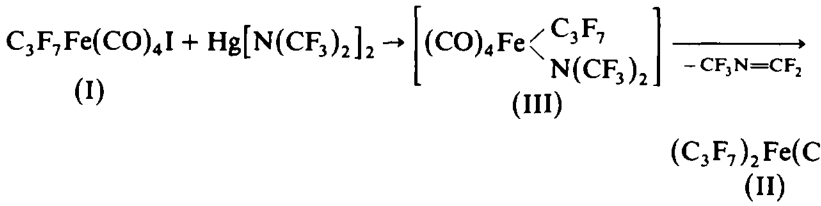
(2)

It may be assumed that substitution of the iodine atom by another bidentate ligand, reducing the stability of the carbonyliron complex, would promote symmetrization reaction.

As shown in our previous studies, other fluorinating agents such as HF, KF, CsF, $ZnF_2$, $CuF_2$, $SbF_3$ do not cause the formation of symmetrical bis(perfluoroalkyl)iron tetracarbonyls from the corresponding carbonyliodides. Some fluorine-containing mercurials were found to be suitable for the transformation of $R_FFe(CO)_4I$ complexes into the symmetrical $(R_F)_2Fe(CO)_4$ complexes.

## Results and discussion

In the course of the interaction of perfluoropropyliron tetracarbonyl iodide (I) with di[bis(trifluoromethyl)amino]mercury we have isolated bis(perfluoropropyl)iron tetracarbonyl (II) as the only reaction product.



$$\underset{(I)}{C_3F_7Fe(CO)_4I} + Hg[N(CF_3)_2]_2 \rightarrow \underset{(III)}{\left[(CO)_4Fe\begin{smallmatrix}C_3F_7\\N(CF_3)_2\end{smallmatrix}\right]} \xrightarrow[-CF_3N{=}CF_2]{} \underset{(II)}{(C_3F_7)_2Fe(CO)_4} \qquad (3)$$

The intermediate complex (III) contains an $N(CF_3)_2$ group which is able, when acting as a bridging ligand, to cause the dimerization and subsequent disproportionation of complex III. Complex II can also be formed in the course of the decomposition of the $N(CF_3)_2$ group of complex III with elimination of perfluoroazopropene, which leads to perfluoropropyliron tetracarbonyl fluoride and further as in eq. 2.

We have prepared the symmetrical complex II by pyrolysis of perfluoropropyliron tetracarbonyltrifluoroacetate (IV).

$$\underset{(IV)}{C_3F_7Fe(CO)_4OCOCF_3} \xrightarrow{100°C} \underset{(II)}{(C_3F_7)_2Fe(CO)_4} + Fe(OCOCF_3)_2 + 4\,CO \qquad (4)$$

The pyrolysis was carried out both in boiling heptane and in the absence of solvent. The yield complex II was 20–25%, which accounts for extreme reaction conditions that cause elimination of the fluorinated residue. So, in the IR spectrum of the gas evolved in reaction 4 the C–F bond absorption bands were found. The probable scheme of the pyrolysis of complex IV is similar to eq. 2, since the trifluoroacetate group is also a bidentate ligand and can cause complex IV to dimerize with subsequent disproportionation. The trifluoroacetate IV is synthesized from the interaction of $Hg(OCOCF_3)_2$ with iodide I in ether in 70% yield, unlike the procedure using $AgOCOCF_3$ (30% product yield) outlined in the previous studies [2].

Unlike the case of AgF, from the interaction of fluorides $Hg^{I}$ and $Hg^{II}$ with iodide I, the symmetrization product $(C_3F_7)_2Fe(CO)_4$ (II) is obtained in a low yield of 7–8%. The major reaction products are mercury-containing tetracarbonyliron complexes: bis(perfluoropropyl-iron tetracarbonyl)mercury (V) and perfluoropropyl-(perfluoropropyl-iron tetracarbonyl)mercury (VI).

$$\underset{(I)}{C_3F_7Fe(CO)_4I} + XHgF \rightarrow \underset{(II)}{(C_3F_7)_2Fe(CO)_4} + \underset{(V)}{[C_3F_7Fe(CO)_4]_2Hg} + \underset{(VI)}{C_3F_7Fe(CO)_4HgC_3F_7} \qquad (5)$$

X = F, Ph, HgF

The products of reaction 5 were separated by means of column chromatography using anhydrous silica gel and freon 113 as eluent. Complex V is a pink crystalline substance stable in the air and decomposing in daylight in solution. Earlier, the synthesis of a compound which was assigned the structure of complex V from the reaction of $Hg(CN)_2$ with $C_3F_7Fe(CO)_4^-Na^+$ was reported [4]. However, the structure of the product obtained was confirmed on the basis of its mass spectrum only, and no other physical constants were cited. Complex VI is a white crystalline substance readily soluble in most organic solvents, very volatile, with a strong smell.

We have also synthesized the symmetrical complex V by the reaction of metallic mercury with iodide I.

$$\underset{(I)}{C_3F_7Fe(CO)_4I} + Hg \xrightarrow{20\text{–}30\ h} \underset{(VII)}{C_3F_7Fe(CO)_4HgI} \xrightarrow{250\ h} \rightarrow \underset{(V)}{[C_3F_7Fe(CO)_4]_2Hg} + HgI_2 \qquad (6)$$

Perfluoropropyliron tetracarbonylmercury iodide (VII) is formed in this reaction as an intermediate as a result of insertion of a mercury atom into the Fe–I bond. A similar insertion was observed in the reaction of mercury with $CpFe(CO)_2Hlg$, however, the reaction ceased at the stage of formation of $CpFe(CO)_2HgHlg$, which failed to symmetrize [5]. Complex VII is an unstable yellow substance which is difficult to isolate in the pure state.

The structures proposed by us for complexes V, VI and VII are based on elemental analysis data, molecular weight determination by ebullioscopy (for compound VI) and $^{19}F$ NMR spectra (Table 1). The mercury atoms in the compounds obtained cause satellites of the signals of the fluorine nuclei to appear in $^{19}F$ NMR spectra as a result of magnetic interaction of $^{199}Hg$(spin − 1/2) and $^{19}F$ nuclei. Spectra of compounds V and VII containing the $CF_3CF_2CF_2FeHg$ fragment are of first order and consist of three signals from the $\alpha CF_2$, $\beta CF_2$ and $CF_3$ groups ($\delta \approx 50$, 115 and 78 ppm). The coupling constants $J$(Hg–F) for the $\alpha$- and $\beta$-$CF_2$ groups differ only slightly for $C_3F_7Fe(CO)_4HgI$ (VII) and $[C_3F_7Fe(CO)_4]_2Hg$ (V), viz. 150 and 135 Hz for $\alpha$-$CF_2$ and 89 and 52 Hz for $\beta$-$CF_2$. Complex VI has two distinct $C_3F_7$ groups bonded to the Fe and Hg atoms; therefore six signals are observed in

TABLE 1

$^{19}$F NMR AND IR SPECTRA OF COMPLEXES V–VII

| Complex | Molecule fragment | $^{19}$F NMR spectral data [a] | | | | | | $\nu$(CO) (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | $\alpha$CF$_2$ group | | $\beta$CF$_2$ group | | CF$_3$ group | | |
| | | $\delta$ (ppm) | $J$(Hg–F$_\alpha$) (Hz) | $\delta$ (ppm) | $J$(Hg–F$_\beta$) (Hz) | $\delta$ (ppm) | $J$(F$_\alpha$–F$_\gamma$) (Hz) | |
| V | HgFeCF$_2$CF$_2$CF$_3$<br>$\alpha$ $\beta$ $\gamma$ | 53.4 | 135 | 115.15 | 89 | 78.5 | 11.0 | 2120w, 2097vs, 2060m<br>2045vs, 2020vw, 2003vw |
| VI | HgFeCF$_2$CF$_2$CF$_3$ | 52.8 | 120 | 114.6 | 72 | 78.4 | 11.8 | 2118s, 2098vw, 2069s |
| | FeHgCF$_2$CF$_2$CF$_3$ | 105.4 | 730 | 123.64 | 103 | 80.2 | 9 | 2048vs, 2015vw, 2005vw |
| VII | HgFeCF$_2$CF$_2$CF$_3$ | 49.0 | 150 | 114.4 | 52 | 78.25 | 11.0 | |
| | CF$_3$CF$_2$HgCF$_2$CF$_3$ [6] | 110.3 | 770 | | | 84.5<br>[$J$(Hg–F$_\beta$)71 Hz] | | |

[a] Complexes V and VII in CDCl$_3$ solution, complex VI in CH$_2$Cl$_2$ + (CD$_3$)$_2$CO mixture.

the spectrum, three of them of the $CF_3CF_2CF_2FeHg$ fragment have parameters ($\delta$ and $J$(Hg–F)) similar to those in complexes V and VII. The other three signals can be assigned from their chemical shifts (absence of group low-field shift of the $\alpha$-$CF_2$ signal under the influence of the Fe atom) and coupling constants to the $CF_3CF_2CF_2Hg$ fragment by analogy with $(C_2F_5)_2Hg$ [6].

The IR spectral data of complexes V and VI in hexane solution in the $\nu$(CO) region (2200–1900 $cm^{-1}$) indicate *cis*-configuration for these compounds (Table 1) [7].

In the reaction of mercury fluorides with iodide I, three reaction products are generated simultaneously as we have established by thin layer chromatography. This is indicative of the reaction proceeding in several directions. The formation of the symmetrical complex II in low yield testifies to the fact that mercury fluorides as well as AgF can cause symmetrization of iodide I as in eq. 2. Complex V is probably formed by symmetrization of the $C_3F_7Fe(CO)_4HgX$ intermediate (VIII) where X = F or I. This can occur only if iodide I reacts with mercurials capable of being oxidized, e.g. $Hg_2F_2$.

$$\underset{(I)}{C_3F_7Fe(CO)_4I} + Hg_2F_2 \rightarrow \underset{(VIII)}{C_3F_7Fe(CO)_4HgX} + HgFY \qquad (7)$$
$$X = F, Y = I$$
$$X = I, Y = F$$

Among the reaction products only $HgI_2$ was isolated and no $Hg_2I_2$ was found.

When using $HgF_2$ and PhHgF, no mercurials capable of being oxidized are present and, therefore, univalent mercury must be formed. $Fe^{II}$ ions are probably acting as reducing agents to reduce $Hg^{II} \rightarrow Hg^{I}$, which is confirmed by the $Fe^{III}$ found in the reaction products.

When PhHgF was treated with the iodide, apart from complexes II, V and VI, diphenylmercury was identified, which may be formed by the symmetrization $PhHgF \rightarrow Ph_2Hg + HgF_2$. $HgF_2$ probably reacts with I. However, the $^{19}F$ NMR spectrum of the reaction mixture is indicative of another compound containing a $C_3F_7$ group on a mercury atom [$\delta$ 110.5($\alpha CF_2$), 123.6 ($\beta CF_2$), 80.2 ($CF_3$) ppm, satellites of the $\alpha CF_2$ group signal $J$(Hg–F) 625 Hz], which we failed to isolate.

Complex VI is probably generated from complex V. This is confirmed by the fact that after 1.5 h irradiation by the sunlight of a solution of $[C_3F_7Fe(CO)_4]_2Hg$ (V) in freon 113 at 20°C only complex VI was observed in solution. CO evolution was also observed, and a precipitate was formed which was a complex mixture of decomposition products. Transformation of complex V into VI was also found when solutions of complex V were stirred with $Hg_2F_2$ in the dark, whereas neither Hg, $HgF_2$ nor PhHgF cause this reaction under the above-mentioned conditions.

## Experimental

Iodide I was obtained using the procedure outlined previously [8]. PhHgF was obtained from the reaction of KF with an aqueous solution of $PhHgOCOCF_3$ [9]. $HgF_2$ and $Hg_2F_2$ were obtained from the reaction between $SF_4$ and the corresponding mercury acetates in a rotating autoclave [10].

The $^{19}F$ NMR spectra were registered on a Bruker WP-200 spectrometer operating at 188.28 MHz, all signals being at high field relative to an internal $CCl_3F$ standard. The IR spectra were registered on UR-20 spectrometer in hexane. The molecular weight was determined using an EP-68 ebulliometer.

All operations for solvent evaporation were carried out at reduced pressure (10–15 mmHg) using a water-jet pump. Silica gel used in column chromatography was dried for 4 h under 0.05 mmHg vacuum at 50°C.

### *Reaction of $C_3F_7Fe(CO)_4I$ (I) with $Hg[N(CF_3)_2]_2$*

A solution of 0.15 g of di[bis(trifluoromethyl)amino] mercury in 5 ml of freon 113 was added to a solution of 0.27 g of iodide I in 5 ml of freon 113 at −30°C under argon. The mixture was allowed to warm up to 20°C, stirred for 6 h and allowed to stand for two days until it lost its colour. The mixture was filtered, the precipitate washed with freon 113, the latter was evaporated and the residue crystallized from hexane. Yield: $(C_3F_7)_2Fe(CO)_4$ (II) 0.06 g (40.7%), m.p. 92°C [2].

### *Perfluoropropyliron tetracarbonyl trifluoroacetate (IV)*

A solution of 0.9 g of $Hg(OCOCF_3)_2$ in 10 ml of ether was added within 5 min dropwise to a solution of 1 g of iodide I in 15 ml of anhydrous diethyl ether at 0°C. The mixture was then stirred for 30 min and the ether was evaporated at 0°C. The residue was dissolved in warm freon 113, the latter was evaporated and the residue was recrystallized from a 1/1 hexane/freon 113 mixture. Yield: IV 0.7 g (70%), m.p. 102°C [2].

### *Pyrolysis of $C_3F_7Fe(CO)_4OCOCF_3$(IV)*

0.43 g of trifluoroacetate (IV) was heated at 105–110°C until gas evolution ceased (10–20 min). The residue was chromatographed on a 25 × 1.5 cm silica gel (μ 100/160) column, freon 113 eluent. Yield: $(C_3F_7)_2Fe(CO)_4$ (II) 0.05 g (21%), m.p. 91–92°C (from hexane).

### *Reaction of iodide I with mercury fluorides*

A solution of iodide I in freon 113 was added to a mercury fluoride suspension in freon 113 at 20°C. The mixture was stirred until the solution colour turned from red to yellow. The reaction was monitored by thin layer chromatography on Silufol UV-254 plates, freon 113 eluent. Upon completion of the reaction, the precipitate was separated, washed with freon 113, and the latter was evaporated off. The residue was chromatographed on a 30 × 1.5 cm silica gel (μ 100/160) column, freon 113 eluent. Reagent quantities, reaction times and product yields are shown in Table 2.

TABLE 2

| Mercury fluorides | Reagent quantities (g) | | Reaction time (h) | Product yield (g) (%) | | |
|---|---|---|---|---|---|---|
| | Iodide I | XHgF | | II | V | VI |
| $HgF_2$ | 1.0 | 1.05 | 6 | 0.045(8) | 0.18(19) | 0.30(39.5) |
| PhHgF | 1.0 | 2.0 | 8 | 0.04(7.5) | 0.2(21.2) | 0.36(47) |
| $Hg_2F_2$ [a] | 0.5 | 0.55 | 24 | 0.02(7) | 0.015(3) | 0.11(29) |

[a] Reaction in the dark.

### *Perfluoropropyliron tetracarbonyl mercury iodide (VII)*

A solution of 1 g of iodide I in 30 ml of freon 113 was mixed with 3 ml of metallic mercury at 20°C in the dark and stirred for 10–15 h. The mixture was filtered, freon was evaporated and the residue dissolved in hexane. The hexane solution on cooling to −10°C afforded a yellow crystalline product. Yield of VII: 0.2 g (14%), t.dec. 85–90°C. Found: I, 20.25, 20.45; Fe, 8.39, 8.36; Hg, 28.13, 29.99. $C_7F_7FeHgIO_4$ calcd.: I, 19.10; Fe, 8.41; Hg, 30.19%.

### *Bis(perfluoropropyliron tetracarbonyl)mercury (V)*

A solution of 0.6 g of iodide I in 10 ml of freon 113 was mixed with 3 ml of metallic mercury at 25°C in the dark and stirred for 3 days. The mixture was then allowed to stand for 10 days. The mixture was filtered off, the precipitate washed with freon 113, the latter evaporated and the residue crystallized from hexane at 0°C. Yield of V: 0.21 g (44.3%), m.p. 98°C. Found: C, 19.51, 19.50; Fe, 12.48, 12.37; Hg, 23.05, 22.88. $C_{14}F_{14}Fe_2HgO_8$ calcd.: C, 19.23, Fe, 12.77, Hg, 22.94%.

### *Perfluoropropyl(perfluoropropyliron tetracarbonyl)mercury (VI)*

A solution of 0.09 g of complex V in 10 ml of freon 113 was stirred in glass flask at 23°C in sunlight. Precipitation and CO evolution started immediately. After 1.5 h the gas evolution ceased and thin layer chromatography showed that only complex VI was present in the solution. The solution was filtered off and the freon was evaporated. Yield of VII: 0.01 g (14%), m.p. 50–52°C. By crystallization from small amounts of pentane at −10°C, we obtained colourless needle-shaped crystals with m.p. 58°C. The molecular weight determined by ebullioscopy was 712.9. Found: C, 16.93, 16.92; Fe, 6.40, 5.84; Hg, 28.90, 27.10. $C_{10}F_{14}FeHgO_4$ calcd.: C 17.00; Fe, 7.90; Hg, 28.39% Mol. wt. 706.5.

## References

1 I.I. Guerus, Yu. L. Yagupolskii and N.D. Volkov, Zh. Org. Khim., 18 (1982) 1186.
2 Yu.L. Yagupolskii, I.I. Guerus and L.M. Yagupolskii, Zh. Org. Khim., 17 (1981) 2512.
3 J. Reedijk and R.W.M. ten Hoedt, Recueil, 101 (1982) 49.
4 F. Seel and G.-V. Röschenthaler, Z. Anorg. Allg. Chem., 373 (1970) 182.
5 A.N. Nesmeyanov, L.G. Makarova and V.N. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 1984.
6 C.G. Krespan, J. Org. Chem., 25 (1960) 105.
7 K. Stanley and D. McBride, Can. J. Chem., 54 (1976) 1700.
8 R.B. King, S.L. Stafford, P.M. Treichel and F.G.A. Stone, J. Am. Chem. Soc., 83 (1961) 3604.
9 V.R. Polishchuk. Master's Thesis. Institute of Organo-element Compounds, Moscow, 1970.
10 V.P. Shendrik, O.D. Liakh and L.M. Yagupolskii, Ukr. Khim. Zh., in press.