Synthesis of phenyl(perfluoroorgano)mercury derivatives $C_6H_5Hg(R_f)$ $[R_f = C_nF_{2n+1}$ ($n = 1$–4 or 6) or $C_6F_5]$ by the reactions of bis(perfluoroorgano)cadmium compounds with phenylmercury chloride

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Abstract

The mixed phenyl(perfluoroorgano)mercury derivatives $C_6H_5Hg(R_f)$ $[R_f = C_nF_{2n+1}$ ($n = 1$–4 or 6), $C_6F_5]$ have been prepared by reactions of C_6H_5HgCl with $Cd(R_f)_2$ compounds, and their ^{19}F NMR, ^{199}Hg and (in some cases) ^{13}C NMR spectra and mass spectra recorded.
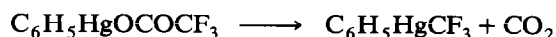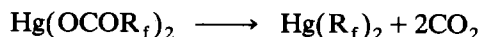
Introduction

Although organomercury compounds have been known since 1853 [1] and perfluoroorganomercury derivatives since 1949 [2] there have been few reports of the synthesis and properties of mixed phenyl(perfluoroorgano)mercury derivatives, although $C_6H_5HgCF_3$, $3\text{-}FC_6H_4HgCF_3$, $4\text{-}FC_6H_4HgCF_3$ [3–5], $C_6H_5HgC_6F_5$ [6,7] and $C_6H_5HgC_8F_{17}$ have been made [8].

Several methods for the preparation of perfluoroorganomercury compounds have been described in the literature. Compounds of the type $Hg(R_f)_2$ and HgR_fI can be obtained by the thermal or electrochemical reaction of the corresponding perfluoroiodoalkane with elemental mercury or amalgams [2,9–12].

$$Hg + R_fI \longrightarrow Hg(R_f)I + Hg(R_f)_2 + HgI_2$$
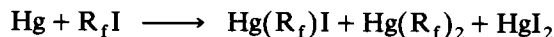
Thermal decarboxylation of the corresponding perfluorocarboxylates yields $Hg(R_f)_2$ [13–15], $C_6H_5HgCF_3$ [15] and $RHgC_6F_5$ ($R = CH_3$, C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$) [14].

$$Hg(OCOR_f)_2 \longrightarrow Hg(R_f)_2 + 2CO_2$$

$$C_6H_5HgOCOCF_3 \longrightarrow C_6H_5HgCF_3 + CO_2$$

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Addition of HgF_2 to perfluoroolefins also yields bis(perfluoroalkyl)mercury derivatives [16], *e.g.*

$$HgF_2 + 2CF_2\text{=}CFCF_3 \longrightarrow Hg[CF(CF_3)_2]_2$$
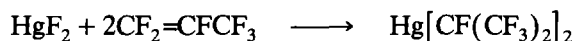
There is disagreement about the results of direct fluorination of dimethylmercury: Liu and Lagow [17] reported the preparation of $Hg(CF_3)_2$ by reaction of $Hg(CH_3)_2$ with elemental fluorine whereas Naumann and Lange [18] obtained only CH_3HgF and CH_3F under similar conditions. $C_6H_5HgCF_3$ can also be made by treatment of $C_6H_5HgCBr_3$ with C_6H_5HgF [19].

The plasmachemical reactions of elemental mercury or mercury dihalides with trifluoromethyl radicals yield bis(trifluoromethyl)mercury and trifluoromethylmercury halides [20,21]. For the preparation of aryl(perfluoroorgano)mercury derivatives several routes based on ligand exchange reactions have been reported. The reactions of $HgAr_2$ with $Hg(CF_3)I$ gave the corresponding $ArHgCF_3$ derivative in *ca.* 70% yield [3–5].

In the same manner the series $Hg(R_f)X$ ($R_f = $ n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}; $X = R_f$, Cl, Br, I, NO_3, $OCOCH_3$, $OCOCF_3$) was obtained by reactions of mercury salts with $Mg(R_f)I$, the mixed organo(perfluoroorgano)mercury derivatives $C_6H_5HgC_8F_{17}$, $C_2H_5HgC_8F_{17}$ and $C_2H_5HgC_4F_9$ were also produced [8].

Perfluoroorganomercury derivatives with secondary and tertiary perfluoroalkyl groups can also be obtained from the reactions of intermediately-generated perfluoroalkyl-potassium or -caesium compounds with mercury salts [22,23].

In continuation of our studies on polar perfluoroorgano group transfer reactions with bis(perfluoroorgano)cadmium compounds [24–26] we now report on our investigations of the system $C_6H_5HgCl/Cd(R_f)_2$.

Results and discussion

According to Pearson's HSAB concept [27] organomercury cations can be classified as soft Lewis acids. It has been shown that in polar perfluoroorgano group transfer reactions R_f groups react preferentially with soft Lewis acids and should therefore be classified as soft Lewis bases [24–26,28].

In terms of our view of the nature of the polar perfluoroorgano group transfer [28] it is advantageous when the species that is to be perfluoroorganylated forms a soft cation in solution, and so it is necessary to measure the molar conductivity in various aprotic organic solvents in advance. Ionic equilibria involving $Cd(R_f)_2$ complexes are known in many aprotic basic solvents such as CH_3CN and dimethylformamide (DMF) [26].

The chloride C_6H_5HgCl shows the greatest molar conductivity in pyridine (Table 1). In keeping with this, it reacts most rapidly with $Cd(R_f)_2$ complexes in pyridine:

$$2C_6H_5HgCl + Cd(R_f)_2 \cdot 2D \longrightarrow 2C_6H_5HgR_f + CdCl_2 + 2D$$
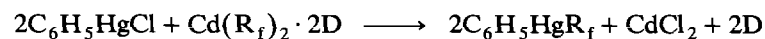
($R_f = C_nF_{2n+1}$ ($n = $ 1–4 or 6), C_6F_5; D = CH_3CN, DMF, none). These results clearly demonstrate that the existence of ionic equilibria in solution facilitates the exchange reaction.
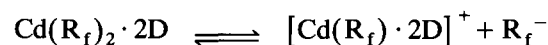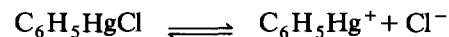
$$C_6H_5HgCl \rightleftharpoons C_6H_5Hg^+ + Cl^-$$

$$Cd(R_f)_2 \cdot 2D \rightleftharpoons [Cd(R_f) \cdot 2D]^+ + R_f^-$$

Table 1

Molar conductivity of C_6H_5HgCl in various solvents at 21°C

Solvent	Molar conductivity $(\Omega^{-1} cm^2 mol^{-1})$	Concentration $(mol\ l^{-1})$
Glyme	0.01	$1.25 \cdot 10^{-4}$
CH_2Cl_2	0.04	$1.45 \cdot 10^{-4}$
CH_3CN	0.05	$1.20 \cdot 10^{-4}$
THF	0.05	$1.30 \cdot 10^{-4}$
DMSO	0.16	$1.04 \cdot 10^{-4}$
Acetone	0.84	$1.17 \cdot 10^{-3}$
DMF	1.92	$9.90 \cdot 10^{-5}$
Pyridine	5.45	$1.10 \cdot 10^{-4}$

From the reaction mixtures in pyridine, $C_6H_5HgCF_3$, $C_6H_5HgC_2F_5$, $C_6H_5HgC_3F_7$ and $C_6H_5HgC_6F_5$ were isolated as colourless crystalline or waxy solids. Although the reactions in the case of higher perfluoroalkyl groups proceeded very selectively in pyridine it was impossible to isolate the pure higher phenyl(perfluoroalkyl)mercury derivatives from the reaction mixtures.

Since all attempts to isolate $C_6H_5HgC_4F_9$ and $C_6H_5HgC_6F_{13}$ from reaction mixtures in pyridine, DMF and dimethyl sulphoxide (DMSO) failed, acetone was used as a low boiling solvent. In contrast to $Cd(C_nF_{2n+1})_2 \cdot 2D$ $(n = 1-3)$ the higher perfluoroalkylcadmium compounds do not decompose in acetone solution to give R_fH, and C_6H_5HgCl shows a significant molar conductivity in this solvent (Table 1). From reactions in acetone, $C_6H_5HgC_4F_9$ and $C_6H_5HgC_6F_{13}$ were isolated as yellow oils, which gave waxy white solids after repeated sublimation.

All the compounds were characterized by mass spectroscopy, ^{19}F, ^{199}Hg and (in some cases) ^{13}C NMR spectra, and by fluorine analysis.

The mass spectra of $C_6H_5HgR_f$

The mass spectra of all the compounds show a common fragmentation pattern (see Table 2). The spectra are dominated by the high intensity peaks of the

Table 2

Electron impact mass spectra of the compounds $C_6H_5Hg(R_f)$ (relative intensity in %; electron beam energy, EBE, in eV)

	R_f					
	CF_3	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}	C_6F_5
$Hg(R_f)_2^+$	–	–	–	–	–	5.0
$C_6H_5Hg(R_f)^+$	77.9	86.3	68.0	51.6	11.7	100.0
$(C_6H_5)_2Hg^+$	1.3	2.6	0.9	2.1	1.3	12.2
$C_6H_5Hg^+$	100.0	100.0	100.0	100.0	100.0	6.0
$Hg(R_f)^+$	–	–	–	0.5	1.1	–
Hg^+	–	13.4	7.0	4.9	2.6	6.0
$C_6H_5^+$	7.9	35.2	26.8	16.4	5.7	0.7
R_f^+	–	0.3	–	0.6	4.5	–
EBE	15	20	15	15	15	13
Temp.	45°C	50°C	30°C	30°C	30°C	85°C

Table 3

^{19}F NMR data for $C_6H_5HgC_nF_{2n+1}$ ($n = 1$–4 or 6) (CH_2Cl_2; external lock: acetone-d_6; δ in ppm; J in Hz)

| | C_nF_{2n+1} | | | | |
	CF$_3$	C$_2$F$_5$	C$_3$F$_7$	C$_4$F$_9$	C$_6$F$_{13}$
δ(CF$_3$)	-38.1	-84.0	-80.4	-81.2	-81.3
δ(α-CF$_2$)		-112.1	-110.6	-109.7	-109.6
δ(β-CF$_2$)			-123.9	-119.9	-119.3
δ(γ-CF$_2$)				-125.8	-122.2
δ(δ-CF$_2$)					-123.2
δ(ϵ-CF$_2$)					-126.6
$^2J(^{199}$Hg–^{19}F)	1006	640	631	628	626
$^3J(^{199}$Hg–^{19}F)		50	106	113	114

molecular ion, $C_6H_5Hg^+$ and $C_6H_5{}^+$. In all cases low intensity peaks of $(C_6H_5)_2Hg^+$ are also observed. We assume that diphenylmercury is formed during the evaporation in the mass spectrometer because all samples were analytically pure and the amount of formation of the $(C_6H_5)_2Hg$ seems to be temperature-dependent. Low-energy spectra recorded at various temperatures show a significant increase of the $(C_6H_5)_2Hg^+$ intensity with increasing temperature in the case of $C_6H_5HgCF_3$ studied as an example. Only in the spectra of the higher perfluoroalkylmercury compounds were $Hg(R_f)^+$, R_f^+ ions or fragments of the perfluoroorgano group detected. We thus assume that all the compounds undergo initial fragmentation by loss of the perfluoroorgano group.

The intensity of the molecular ions of the perfluoroalkyl derivative decreases with increasing chain length, and the intensities of the $Hg(R_f)^+$ and R_f^+ peaks correspondingly increase. This feature may be referred to the lower stability of the higher perfluoroalkyl derivatives.

The NMR spectra of $C_6H_5HgR_f$

The ^{19}F NMR resonances of the derivatives $C_6H_5HgC_nF_{2n+1}$ ($n = 2$–4 or 6) lie between -80 ppm and -130 ppm upfield from external CCl_3F (see Table 3). The CF$_3$ group of the perfluoroalkyl chain gives a resonance at *ca.* -81 ppm and the α-CF$_2$ group at *ca.* -110 ppm. The signals of the α- and β-CF$_2$ groups have ^{199}Hg satellites with typical couplings, $^2J(^{199}$Hg–^{19}F), of *ca.* 630 Hz. The pentafluoroethyl derivative shows a $^3J(^{199}$Hg–^{19}F) coupling of 50 Hz, whereas for the longer-chain derivatives couplings of *ca.* 110 Hz are observed. All the data are in good agreement with those previously published [8,9,11].

The ^{199}Hg{^{1}H} NMR spectra show the expected splitting. The chemical shifts (see Table 4 and Fig. 1) show variations similar to those observed for the corresponding bis(perfluoroalkyl)cadmium complexes $Cd(R_f)_2 \cdot 2D$ [29].

Experimental

NMR spectra. Bruker FT NMR spectrometer AC 200; ^{19}F NMR: 188.3 MHz, ^{13}C NMR: 50.4 MHz. Bruker FT NMR spectrometer AMX 300; ^{199}Hg{^{1}H} NMR: 53.5 MHz. Standards: CCl_3F (ext., ^{19}F), $Si(CH_3)_4$ (ext., ^{13}C), $Hg(CH_3)_2$ neat (ext.,

Table 4

^{199}Hg{^{1}H} NMR data for $C_6H_5Hg(R_f)$ (CH_2Cl_2; external lock: acetone-d_6; δ in ppm; J in Hz)

	R_f					
	CF_3 [a]	C_2F_5	C_3F_7	C_4F_9	C_6F_{13}	C_6F_5 [b]
$\delta(^{199}Hg)$	−1140	−1124	−1131	−1142	−1153	−798
$^2J(^{199}Hg-^{19}F)$	1006	638	628	637	626	
$^3J(^{199}Hg-^{19}F)$		47	106	114	114	342
$^4J(^{199}Hg-^{19}F)$			78	54	35	59

[a] $\delta(^{199}Hg)$ −1160 ppm in $CDCl_3$ [30]. [b] $\delta(^{199}Hg)$ −829 ppm in CH_2Cl_2 [31].

^{199}Hg). A negative chemical shift denotes a resonance appearing to low frequency (high field) of the reference compound.

Mass spectra. Varian MAT CH 5 (modified). Ions containing Hg refer to ^{202}Hg (natural abundance 29.80%); conversion to monoisotopic relations by the coefficient 100/29.80.

Other measurements. Fluorine analysis was as described in ref. 32. Melting points were obtained with a HWS Mainz SG 2000 apparatus, open glass capillaries, and conductivity measurements with a Metrohm 660 Conductometer.

Preparations

All reactions were carried out under dry nitrogen in Schlenk tubes. Solvents were purified and dried by standard methods. $Cd(CF_3)_2 \cdot 2CH_3CN$, $Cd(C_2F_5)_2 \cdot 2CH_3CN$ and $Cd(C_6F_5)_2 \cdot 2$ DMF were prepared as described previously [26,33]. Uncomplexed $Cd(C_3F_7)_2$ and $Cd(C_4F_9)_2$ were prepared in the way described for $Cd(C_6F_{13})_2$ [26]; $Cd(CH_3)_2$ and CF_3I were prepared according to refs. 34 and 35 respectively. All other chemicals were used as supplied by Aldrich (C_6H_5HgCl, C_2F_5I, C_6F_5I), Merck-Schuchardt (C_4F_9I, $C_6F_{13}I$), and Fluorochem/ABCR (C_3F_7I).

Preparation of $C_6H_5Hg(R_f)$

To a solution of C_6H_5HgCl in the appropriate solvent at room temperature were added the solid $Cd(R_f)_2$ compounds. The mixtures were stirred for several

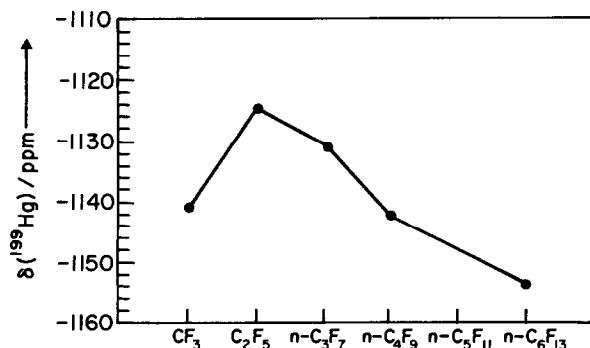Fig. 1. The dependence of the ^{199}Hg NMR chemical shifts of $C_6H_5Hg(C_nF_{2n+1})$ ($n = 1$–4 or 6) on the length of the perfluoroalkyl chain.

Table 5

Reactions of C_6H_5HgCl with $Cd(R_f)_2$ compounds

R_f	C_6H_5HgCl		$Cd(R_f)_2$		Solvent		t	Yield	Fluorine analysis	M.p.
	g	mmol	g	mmol		(ml)	(d)	(%)	(%) [a]	(°C)
CF_3	4.66	14.90	2.47	7.45	pyridine	40	4	94 [b]	16.2 (16.4)	142–143
C_2F_5	2.03	6.48	1.39	3.24	pyridine	10	4	81 [b]	24.7 (23.9)	138
C_3F_7	0.25	0.80	0.18	0.40	pyridine	5	2	39 [c]	29.3 (29.8)	74– 75
C_4F_9	0.99	3.18	0.87	1.59	acetone	15	3	43 [c]	34.9 (34.4)	71– 72
C_6F_{13}	1.59	5.10	1.91	2.55	acetone	15	3	40 [c]	41.6 (41.4)	51– 53
C_6F_5	1.74	5.56	1.64	2.78	pyridine	10	5	74 [b]		160–161 [d]

[a] The values in brackets are calculated. [b] Purified by extraction with n-hexane. [c] Purified by sublimation. [d] $C_6H_5HgC_6F_5$ contained $Hg(C_6F_5)_2$ as an impurity up to 5% (determined from the ^{19}F NMR spectra).

days and completion of the reaction established by ^{19}F NMR spectroscopy. The precipitate was filtered off and washed several times with the appropriate solvent. The filtrate and the washing liquors were combined. The solvent was distilled off at room temperature under reduced pressure and the residue purified by repeated extraction with n-hexane or by vacuum sublimation at 30–40°C. Experimental details, analytical data, and yields are summarized in Table 5; the ^{19}F NMR data for the perfluoroalkyl derivatives are listed in Table 3 and the ^{199}Hg$\{^1$H$\}$ NMR data in Table 4. Some mass spectral data are listed in Table 2.

^{13}C$\{^1$H$\}$ NMR spectrum of $C_6H_5HgCF_3$ (CDCl$_3$, 20°C) δ(CF$_3$) 174.3 ppm, q, $^1J(^{19}$F–^{13}C$) = 358.0$ Hz; $^1J(^{199}$Hg–^{13}C$) = 1930$ Hz; δ(1–C) 157.7 ppm, q, $^3J(^{19}$F–^{13}C$) = 15$ Hz; $^1J(^{199}$Hg–^{13}C$) = 1474$ Hz; δ(2, 6–C) 128.9 ppm, s, $^2J(^{199}$Hg–^{13}C$) = 125$ Hz; δ (3, 5–C) 137.3 ppm, s, $^3J(^{199}$Hg–^{13}C$) = 95$ Hz; δ(4–C) 129.4 ppm, s, $^4J(^{199}$Hg–^{13}C$) = 21$ Hz.

^{19}F NMR spectrum of $C_6H_5HgC_6F_5$ (CH$_2$Cl$_2$, 20°C) δ(2,6–F) -120.6 ppm, m, $^3J(^{199}$Hg–^{19}F$) = 342.2$ Hz; δ(3,5–F) -160.9 ppm, m; δ(4–F) -154.0 ppm, m.

Acknowledgments

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