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The preparations and properties of tris(perfluoroorgano)bismuth compounds $Bi(R_f)_3$ ($R_f = CF_3$, C_2F_5, n-C_3F_7, n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}, C_6F_5)

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Abstract

Tris(perfluoroorgano)bismuth compounds $Bi(R_f)_3$ ($R_f = CF_3$, C_2F_5, n-C_3F_7, n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}, C_6F_5) are easily prepared in high yields from the reactions of perfluoroorganocadmium complexes with $BiCl_3$ or $BiBr_3$ in aprotic solvents. The perfluoroorganobismuth halides intermediates in these reactions have been detected by NMR spectroscopy.

Introduction

Although many non-fluorinated organobismuth compounds are known, only a few perfluoroorganobismuth compounds have been reported. Reactions of CF_3 radicals with elemental bismuth carried out by Bell, Pullman and West [1] provided the first evidence for the existence of $Bi(CF_3)_3$. In 1977 Lagow and Morrison [2] obtained $Bi(CF_3)_3$ in 32% yield from the reaction of BiI_3 with CF_3 radicals. In a method described by Juhlke et al. [3], $Bi(CF_3)_3$ was obtained in 31% yield in about 100 h from the reaction of CF_3 radicals with Bi vapour.

$Bi(C_6F_5)_3$ was synthesized by Royo and Uson in 1969 [4] and by Deacon and Johnson in 1972 [5]:

$$3\ C_6F_5MgBr + BiCl_3 \rightarrow Bi(C_6F_5)_3 + 3\ MgBrCl$$

In recent years perfluoroorganocadmium complexes have been shown to be excellent perfluoroorganylation reagents. Three different methods for the syntheses of these complexes have been described [6,7,8]. References to preparations of CF_3 element compounds from $Cd(CF_3)_2$ complexes are listed in Table 1.

The table indicates that perfluoroorganocadmium complexes are excellent reagents for the syntheses of many new or otherwise not readily available perfluoroorganoelement compounds. In the present paper we show that a complete series of tris(perfluoroorgano)bismuth compounds can be obtained in high yields from the

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Table 1

Trifluoromethylelement compounds prepared from element halides or trifluoroacetates and $Cd(CF_3)_2$ complexes

Product	Starting material	Ref.
$P(CF_3)_xI_{3-x}$	PI_3	6
$Sn(CF_3)_xBr_{4-x}$	$SnBr_4$	6
$Ge(CF_3)_xI_{4-x}$	GeI_4	6
$(CH_3)_3SnCF_3$ [a]	$(CH_3)_3SnOCOCF_3$	9
$(CH_3)_3PbCF_3$ [a]	$(CH_3)_3PbOCOCF_3$	9
$Te(CF_3)_4$	$Te(CF_3)_2Cl_2$	10
$Sb(CF_3)_3$	$SbCl_3$, $SbBr_3$, SbI_3	11
$Bi(CF_3)_3$ [a]	$BiCl_3$, $BiBr_3$	this work
$Ag[Ag(CF_3)_4]$	$AgNO_3$	12
$Fe(CF_3)_2(CO)_4$	$Fe(CO)_4X_2$ (X = Cl, Br, I)	13
$Co(CF_3)_2(CO)cp$	$Co(CO)cpI_2$	14
$\langle CuCF_3 \rangle$	CuCl	15
$M(CF_3)_2(PR_3)_2$ (M = Ni, Pd, Pt)	$MX_2(PR_3)_2$ (X = Br, I)	17

[a] C_2F_5, $C_3F_7 \ldots C_6F_5$ derivatives also described.

reactions of bis(perfluoroorgano)cadmium complexes with bismuth trihalides in polar solvents.

Results and discussion

Perfluoroorganocadmium complexes react with bismuth trihalides in a large number of solvents to form tris(perfluoroorgano)bismuth compounds; the best results were obtained using acetonitrile solutions. $BiBr_3$ is the most suitable starting material for high yield syntheses. The reactions proceed in a stepwise manner. As for other recently investigated perfluoroalkylations of elements, the reaction rates depend on the dissociation of the bismuth trihalides and the partially perfluoroalkylated bismuth halides $Bi(R_f)_{3-n}X_n$. In the case of the trifluoromethyl compounds, for example, all the intermediates have been identified by ^{19}F NMR spectroscopy (Fig. 1). The ^{19}F chemical shifts depend on the bismuth trihalides used (CH_3CN; external standard CCl_3F):

X	$Bi(CF_3)X_2$ [a]	$Bi(CF_3)_2X$	$Bi(CF_3)_3$
Cl	−40.2 ± 2	−37.8	−33.4
Br	−39.3 ± 2	−36.8	−33.4
I	−38.4 ± 2	−35.5	−33.2

[a] Concentration-dependent.

The splittings of the ^{13}C satellites allow the assignments of the $BiBr_n(CF_3)_{3-n}$ intermediates: $BiBr_2(CF_3)$ singlet, $BiBr(CF_3)_2$ quartet, $Bi(CF_3)_3$ septet. Other NMR data for these three compounds are:

	$BiBr_2CF_3$	$BiBr(CF_3)_2$	$Bi(CF_3)_3$
$^1J(F, C)$ (Hz)	395.2	389.0	390.5
$^4J(F, F)$ (Hz)	–	4.7	4.7
$\Delta\delta$(ppm) [a]	0.141	0.139	0.139
$\Delta_{1/2}$ (Hz)	17	7	5

[a] Compare Ref. 18.

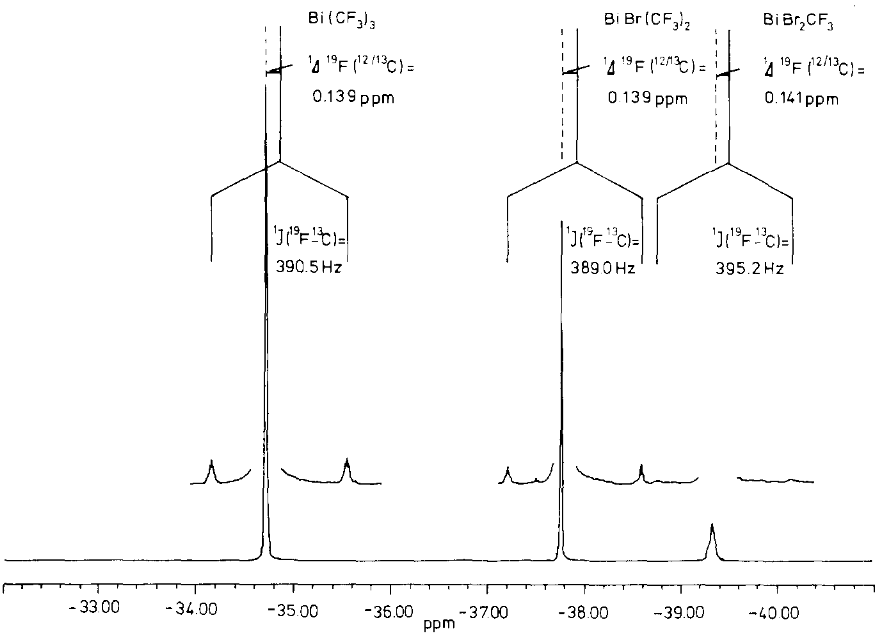

Fig. 1. ^{19}F NMR spectrum of $BiBr_n(CF_3)_{3-n}$ ($n = 0$–2) (CH_3CN; standard CCl_3F, ext.).

These data lead us to propose the following reaction sequence (the complexing solvent molecules are omitted):

$$\begin{array}{lll}
2\,BiX_3 & \rightleftarrows BiX_2^+ & +\,BiX_4^- \\
BiX_2^+ + Cd(CF_3)_2 + X^- & \rightarrow BiCF_3X_2 & +\,Cd(CF_3)X \\
BiCF_3X_2 & \rightleftarrows BiCF_3X^+ & +\,X^- \\
BiCF_3X^+ + Cd(CF_3)_2 + X^- & \rightarrow Bi(CF_3)_2X & +\,Cd(CF_3)X \\
Bi(CF_3)_2X & \rightleftarrows Bi(CF_3)_2^+ & +\,X^- \\
Bi(CF_3)_2^+ + Cd(CF_3)_2 + X^- & \rightarrow Bi(CF_3)_3 & +\,Cd(CF_3)X
\end{array}$$

$Cd(CF_3)X$ similarly also undergoes trifluoromethylation reactions, e.g.:

$$Bi(CF_3)_2X + Cd(CF_3)X \rightarrow Bi(CF_3)_3 + CdX_2$$

The formation of the higher perfluoroalkyl- and of the perfluorophenyl-bismuth compounds involves analogous sequences. The tris(perfluoroorgano)bismuth compounds can be isolated readily after the solvent is distilled off. $Bi(CF_3)_3$ and $Bi(C_2F_5)_3$ are purified by vacuum distillation, and the other perfluoroorganobismuth compounds by vacuum sublimation. The compounds, which are mainly new, were identified by their ^{19}F NMR and mass spectra.

$Bi(CF_3)_3$ (b.p. 50 °C/1 torr) and $Bi(C_2F_5)_3$ (b.p. 65 °C/1 torr) are volatile colourless liquids, the other $Bi(R_f)_3$ are white to pale yellow solids. $Bi(C_nF_{2n+1})_3$ ($n = 1,2,3$) compounds are somewhat unstable, but can be stored in solvents like CH_3CN or C_2H_5CN for several days, while the other solid perfluoroorganobismuth compounds are, when pure, stable for several weeks. All these compounds smell like chlorine. On exposure to the air they all rapidly decompose. They react slowly with water or alcohols to form R_fH, which can be identified from their ^{19}F NMR spectra.

In order to investigate the trifluoromethylation properties of $Bi(CF_3)_3$ we chose the reactions with iodobenzene, silver nitrate and iodine monochloride as examples. No reaction took place with iodobenzene. Reaction with $AgNO_3$ forms the same products as those from $Cd(CF_3)_2$ complexes [12]: $Ag[Ag(CF_3)_4]$, $[Ag(CF_3)_2]^-$ and CF_3NO were identified from their NMR spectra. The reaction with ICl yields CF_3I as the only CF_3-containing product. These results demonstrate that $Bi(CF_3)_3$ enters into polar rather than radical trifluoromethylation reactions, and that its chemical properties are comparable with those of the Cd-CF_3 complexes.

Experimental

Chemicals. $Cd(R_f)_2$ complexes were prepared as previously described [7]. $BiCl_3$(Fa. Fluka, Buchs) was dried in vacuum. $BiBr_3$ was prepared by a standard method [16]. CH_3CN(Fa. Merck, Darmstadt) was dried over P_4O_{10}.

NMR spectra. Bruker FT NMR spectrometer AM 300: ^{19}F NMR: H_0 282.41 MHz; ^{13}C NMR: H_0 75.47 MHz; Standards: CCl_3F (ext., ^{19}F), TMS (ext., ^{13}C). Mass spectra: Finnigan MAT 8230, (70 eV). Raman spectra: Coderg Modell PHO and exciter Spectra Physics (Kr Laser: λ_0 488 nm).

All reactions were carried out under dry nitrogen.

General procedure for the preparations of tris(perfluoroalkyl)bismuth compounds

To a suspension of the bismuth trihalide in acetonitrile at $-40\,°C$ is added a small molar excess of solid $Cd(R_f)_2 \cdot 2CH_3CN$. The mixture is stirred for several hours, and ^{19}F NMR spectroscopy used to find when the reaction is complete. Details are summarized in Table 2.

Preparation of $Bi(C_6F_5)_3$. 1.84 g (4.11 mmol) $BiBr_3$ and 3.83 g (6.60 mmol) $Cd(C_6F_5)_2$ diglyme were dissolved in 10 ml CH_3CN and the solution is heated to $50\,°C$ for 12 h. The solvent and traces of diglyme and C_6F_5H are distilled off. The grey solid residue is sublimed twice at $60\,°C/2 \times 10^{-3}$ torr, to give 2.07 g (2.92 mmol; 71%) of pure $Bi(C_6F_5)_3$.

Spectral data for tris(perfluoroorgano)bismuth compounds

$Bi(CF_3)_3$: ^{19}F NMR, 1 *M* solution in CH_3CN (CCl_3F, int.): δ -33.72 ppm, singlet; $^1J(F, C)$ 390.5 Hz, splitting of the ^{13}C satellites into septets, $^4J(F, F)$ 4.7 Hz, $\Delta\delta$ 0.139 ppm, $\Delta_{1/2}$ 5 Hz. ^{13}C NMR, $Bi(CF_3)_3$ neat: δ 189.8 ppm, quartet of broad multiplets $^1J(F, C)$ 391 Hz. Solvent dependence of $\delta(^{19}F)$ (ppm): pure -33.1; DMF -32.2; CH_2Cl_2 -32.73; diglyme -33.46; CH_3CN -33.72; pyridine -33.82; glyme -33.95; DMSO -35.8.

Vibrational spectra: IR identical to [2]; Raman spectrum (cm^{-1}): 205vs, 515w, 720s, 1080s,br, 1150m, 1445w. Mass spectrum identical to [2].

The ^{19}F NMR spectra of the other compounds are summarized in Table 3.

Mass spectra (only Bi containing fragments; m/e). $Bi(C_2F_5)_3$ (T $30\,°C$): 446 ($Bi(C_2F_5)_2^+$, 16%), 347 ($Bi(C_2F_5)F^+$, 56%), 328 ($BiC_2F_5^+$, 6%), 247 (BiF_2^+, 37%), 228 (BiF^+, 35%), 209 (Bi^+, 100%). $Bi(n\text{-}C_3F_7)_3$ (T $30\,°C$): 547 ($Bi(C_3F_7)_2^+$, 11%), 459 ($BiC_5F_{10}^+$, 44%), 457 (BiC_8F_8, 40%), 397 ($BiC_3F_8^+$, 10%), 378 ($BiC_3F_7^+$, 4%),

Table 2

Reactions of bismuth trihalides with $Cd(R_f)_2 \cdot 2CH_3CN$

R_f	X	BiX_3		$(R_f)_2Cd \cdot 2CH_3CN$		CH_3CN (ml)	T (°C)	t (h)	Isolation [a]	Yield $(R_f)_3Bi$		
		mg	mmol	mg	mmol					mg	mmol	%
CF_3	Cl	1545	4.88	2466	7.42	12	r.t.	8	v.d. [b]	1606	3.86	79.1
	Br	4368	9.71	4940	14.86	20	r.t.	8	v.d. [b]	3719	8.94	92.1
C_2F_5	Cl	961	3.04	2036	4.71	15	r.t. 50	24 4	v.d. [c]	1019	1.80	59.2
	Br	1103	2.45	1946	4.50	12	r.t. 50	24 4	v.d. [c]	906	1.60	65.3
n-C_3F_7	Br	1446	3.21	2649	4.98	10	r.t.	3d	v.s. [d]	1597	2.23	61.5
n-C_4F_9	Br	1860	4.14	4210	6.63	12	60	24	v.s. [e]	2330	2.69	61.0
n-C_6F_{13}	Br	2920	6.50	9310	11.18	25	65	48	v.s. [c]	2240	1.92	29.6
n-C_8F_{17}	Br	3160	7.03	12390	12.00	25	65	48	v.s. [f]	3840	2.00	28.4

[a] v.d. vacuum distillation, v.s. vacuum sublimation. [b] 60 °C/10^{-3} Torr. [c] 85 °C/10^{-3} Torr. [d] 65 °C/10^{-3} Torr. [e] 80 °C/4×10^{-3} Torr; [f] 100 °C/2×10^{-3} Torr.

Table 3

^{19}F NMR spectra of tris(perfluoroorgano)bismuth compounds [a]

	$\delta(CF_3)$	$\delta(\alpha\text{-}CF_2)$	$(\beta\text{-}CF_2)$	Other
$Bi(C_2F_5)_3$	−81.71	−99.94	–	
$Bi(n\text{-}C_3F_7)_3$	−79.48	−98.61	−119.45	
$Bi(n\text{-}C_4F_9)_3$	−80.84	−97.46	−115.71	−125.60
$Bi(n\text{-}C_6F_{13})_3$	−82.19	−95.17	−115.50	−121.2; −123.8; −124.3.
$Bi(n\text{-}C_8F_{17})_3$	−81.69	−97.73	−118.9	−119.7; −122.2; −122.5; −123.1; −126.6.
	$\delta(F_o)$	$\delta(F_m)$	$\delta(F_p)$	
$Bi(C_6F_5)_3$	−117.52	−160.37	−152.39	
	−118.18	−158.55	−149.67	in C_6H_6 solution
	−118.4	−158.8	−149.7	Ref. 5

[a] Solvent CH_3CN; standard CCl_3F (ext.).

247 (BiF_2^+, 6%), 228 (BiF^+, 23%), 209 (Bi^+, 100%). $Bi(n\text{-}C_4F_9)_3$ (T 50 °C): 647 ($Bi(C_4F_9)_2^+$, 23.9%), 509 ($BiC_6F_{12}^+$, 57%), 507 ($BiC_9F_{10}^+$, 59%), 447 ($BiC_4F_{10}^+$, 8%), 309 ($BiC_2F_4^+$, 7%), 290 ($BiC_2F_3^+$, 40%), 247 (BiF_2^+, 15%), 228 (BiF^+, 21%), 209 (Bi^+, 100%). $Bi(C_6F_5)_3$ (T 115 °C): 710 ($Bi(C_6F_5)_3^+$, 22%), 543 ($Bi(C_6F_5)_2^+$, 62%), 395 ($BiC_6F_6^+$, 15%), 376 ($BiC_6F_5^+$, 100%), 247 (BiF_2^+, 8%), 228 (BiF^+, 12%), 209 (Bi^+, 80%).

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