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# The first alkyl bismuthates: tris(trifluoromethyl)fluoro- and tetrakis(trifluoromethyl)-bismuthate

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**Tris(trifluoromethyl)bismuth reacts with fluoride ions and intermediately generated trifluoromethyl anions to form the first representatives of hitherto unknown fluoroalkylbismuthates: tris(trifluoromethyl)fluoro- and tetrakis(trifluoromethyl)-bismuthates.**

Hypervalent bismuthate(III) anions with five electron pairs in the bismuth valence shell are important models for the transition states in nucleophilic substitution reactions at bismuth(III) centers. Therefore, such compounds are of considerable interest. To date some stable bismuthates have been isolated,[1–4] but to our knowledge there is no indication in the literature on the synthesis of acyclic hypervalent alkylbismuthate(III) species bearing at least one alkyl group on bismuth. Meanwhile such species have not only theoretical interest, but could be potentially used as precursors to prepare unknown tetra- and pentaalkyl derivatives of Bi(V), which are not available *via* reactions of trialkylbismuth dihalides with organometallic compounds. The only example of a tetramethylbismuth compound is $[Bi(CH_3)_4]OSO_2CF_3$ as the product of the reaction of $Bi(CH_3)_3$ and $CH_3OSO_2CF_3$.[5] Some of us have developed a convenient procedure to synthesize perfluorinated trialkyl bismuthanes.[6a,b]

We suppose that introduction of trifluoromethyl groups to bismuth(III) increases the Lewis acidity of the bismuth compounds which as a result should enhance the interaction of such fluorinated bismuthanes with nucleophiles, stabilizing hypervalent anionic four-coordinated bismuthates and increasing their ability for $CF_3$ group transfer. Successful fluoride induced $C_6F_5$ group transfer reactions presumably involving tris(pentafluorophenyl)fluorobismuthates, $[Bi(C_6F_5)_3F]^-$, have been established in the literature for several years.[7a,b]

The stabilising influence of fluorine and trifluoromethyl groups on phosphoranes is well documented. There are also two reports on stabilisation by fluorine atoms and $CF_3$ groups of phosphites, which can be regarded as the conjugate bases of phosphoranes.[8,9]

The reaction of $Bi(CF_3)_3$ with the fluoride ion proceeds in THF, glyme ($H_3COCH_2CH_2OCH_3$) or diethyl ether. As sources of $F^-$ we used $[\{N(C_2H_5)_2\}_3S]^+F^-$, $[N(PPh_3)_2]^+F^-$, $[N(CH_3)_4]^+F^-$ or $[N(C_2H_5)_2]_3PF_2$, as shown in eqn. (1), where

$$Bi(CF_3)_3 + A^+F^- \longrightarrow A^+\,\underset{\mathbf{1}}{[Bi(CF_3)_3F]^-} \qquad (1)$$

$A^+ = [\{N(C_2H_5)_2\}_3S]^+, [N(PPh_3)_2]^+, [N(CH_3)_4]^+$ or $[\{N(C_2H_5)_2\}_3PF]^+$.

The stability of hypervalent bismuthates formed depends on the counter ions and the nature of the fluoride ion source. The most stable solid bismuthate, $[N(CH_3)_4]^+[Bi(CF_3)_3F]^-$ **1**,† was prepared using $[N(CH_3)_4]^+F^-$ as a source of the fluoride ion. Surprisingly, tetramethylammonium fluoride was a better fluoride ion source than $[\{N(C_2H_5)_2\}_3S]F$. Covalent tris(diethylamino)difluorophosphorane, a mild donor of fluoride ion, reacts reversibly with $Bi(CF_3)_3$. The tris(diethylamino)fluorophosphonium cation formed in the course of this reaction is electrophilic enough to react reversibly with $[Bi(CF_3)_3F]^-$ to form $[N(C_2H_5)_2]_3PF_2$. This behaviour can be interpreted as a first hint of the fluorinating properties of $[Bi(CF_3)_3F]^-$, eqn. (2).

$$Bi(CF_3)_3 + [N(C_2H_5)_2]_3PF_2 \rightleftharpoons [\{N(C_2H_5)_2\}_3PF]^+ + [Bi(CF_3)_3F]^- \qquad (2)$$

Tris(trifluoromethyl)bismuth reacts with the intermediately formed $CF_3$ anions (generated from $(CH_3)_3SiCF_3$ and $[N(CH_3)_4]^+F^-$) in diethyl ether, THF or glyme to form tetrakis(trifluoromethyl)bismuthate $[N(CH_3)_4]^+[Bi(CF_3)_4]^-$ **2**,‡ eqn. (3). The reaction proceeds at −70 to −50 °C. An increase in temperature causes the formation of $[N(CH_3)_4]^+[Bi(CF_3)_3F]^-$ **1** as a by-product. The formation of **1** in reactions above −50 °C in the presence of $(CH_3)_3SiCF_3$ indicates that at lower temperatures primarily $[(CH_3)_3Si(CF_3)F]^-$ is formed which undergoes a replacement reaction with $Bi(CF_3)_3$ below −50 °C. At elevated temperatures (>−50 °C) $Bi(CF_3)_3$ appears to be a harder Lewis acid than $(CH_3)_3SiCF_3$ and reacts preferably with the fluoride ion. Therefore, temperature constancy (−70 to −50 °C) is necessary for the preparation of $[Bi(CF_3)_4]^-$.

$$Bi(CF_3)_3 + (CH_3)_3SiCF_3 + [N(CH_3)_4]^+F^- \longrightarrow \underset{\mathbf{2}}{[(CH_3)_4N]^+[Bi(CF_3)_4]^-} + (CH_3)_3SiF \qquad (3)$$

Hypervalent anionic bismuth species **1**,**2** are solids, which are stable in a dry nitrogen atmosphere at ambient temperature for some days and can be stored without decomposition in a refrigerator. $CF_3$-containing bismuthates are extremely reactive towards all common aprotic and especially protic solvents. Trifluoromethane formation in THF is observed even at −70 °C.

The reactivity of both bismuthate anions was studied in reactions with some organic and inorganic electrophilic reagents. To date, only reactions accompanied by a cleavage of the Bi–F or one Bi–$CF_3$ bond have been found.

Compound **1** reacts as a fluorinating agent. The interaction of this compound with trimethylchlorosilane and trichlorofluoromethane leads to chlorine exchange affording $(CH_3)_3SiF$ and $CCl_2F_2$, respectively, and $Bi(CF_3)_3$.

We have found, despite the high reactivity with aprotic solvents, that **2** is an excellent source of the trifluoromethyl anion even at −78 °C. Successful trifluoromethylations with this hypervalent bismuthate were carried out with pentafluoropyridine, $(CH_3)_3SnCl$ and $SO_2Cl_2$ to give the trifluoromethylated compounds 4-(trifluoromethyl)tetrafluoropyridine, trimethyl(trifluoromethyl)tin and trifluoromethylsulfurylchloride, respectively.

The bismuthates **1**,**2** are unambiguously identified by a combination of NMR techniques supported by a satisfactory elemental analysis for all elements. In the $^{19}F$ NMR spectrum (−58 °C, THF-$d_8$) of the $[Bi(CF_3)_3F]^-$ anion the $CF_3$ group resonance is detected as a broad singlet at $\delta$ −39.84, remarkably shifted to higher field in comparison with the parent molecule $Bi(CF_3)_3$ $\delta$ −33.40, and the fluorine atom as a singlet at $\delta$ −106.33. The $^{13}C$ NMR resonance of the $CF_3$ groups is detected as a quartet at $\delta$ 183.16 ($^{1}J_{CF} = 395.0$ Hz). The $^{19}F$ NMR resonance of the trifluoromethyl groups in $[Bi(CF_3)_4]^-$ is located at higher field ($\delta$ −41.21). The quartet of the trifluoromethyl groups in the $^{13}C$ NMR spectrum is detected at $\delta$ 167.37 ($^{1}J_{CF} = 405$ Hz).

According to VSEPR theory, both salts should show resonances of two different types of $CF_3$ groups in the $^{19}F$ NMR spectrum. The fact that only one resonance is observed may be explained by a fast exchange of axial and equatorial $CF_3$ groups in solution (even at low temperature), which is not detectable on the NMR time scale.

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## Notes and references

† Preparation of **1**: tetramethylammonium fluoride (1 mmol) was gradually added under argon to a solution of tris(trifluoromethyl)bismuth (1 mmol) in 5 ml diethyl ether at −50 °C and the reaction mixture was stirred for 2 h at −40 °C. The solvent was removed *in vacuo* below −20 °C and the remaining product was washed twice with diethyl ether at −30 °C and finally dried *in vacuo*. The salt was obtained in nearly quantitative yield and was stable at −30 °C under argon for two weeks. $^{19}F$ NMR (282.35 MHz, THF-$d_8$, −58 °C, ppm) $\delta$ −39.84 ($CF_3$, 9F), −106.33 (F, 1F); $^{13}C$ NMR (75.48 MHz, THF-$d_8$, −58 °C, ppm) $\delta$ 183.16 ($CF_3$, q, $^{1}J_{CF}$ 395), 53.28 ($CH_3$, q, $^{1}J_{CH}$ 146 Hz) (Found: C, 16.88; H, 2.64; Bi, 40.68; F, 37.20; N, 2.41. $C_7H_{12}BiF_{10}N$ requires C, 16.51; H, 2.38; Bi, 41.05; F, 37,31; N, 2.75%).

‡ Preparation of **2**: to a solution of tris(trifluoromethyl)bismuth (1 mmol) in 5 ml diethyl ether at −70 °C trifluoromethyltrimethylsilane (3 mmol) and tetramethylammonium fluoride (1 mmol) were added. The mixture was stirred at −60 to −65 °C for 1 h. All volatile products were removed *in vacuo* at −30 °C, the remaining product was washed twice with diethyl ether at −30 °C and dried *in vacuo*. The salt was obtained in nearly quantitative yield and was stable at −30 °C under argon for 2–3 days. $^{19}F$ NMR (282.35 MHz, THF-$d_8$; −58 °C, ppm) $\delta$ −41.21 ($CF_3$); $^{13}C$ NMR (75.48 MHz, THF-$d_8$, −58 °C, ppm) $\delta$ 167.37 ($CF_3$, q, $^{1}J_{CF}$ 405), 55.10 ($CH_3$, q, $^{1}J_{CH}$ 146 Hz) (Found: C, 16.81; H, 2.45; Bi, 37.72; F, 39.43; N, 2.09. $C_8H_{12}BiF_{12}N$ requires C, 17.18; H, 2.16; Bi, 37.37; F, 40.77; N, 2.51%).

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