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Perfluoroalkyl borates: congeners of perfluoroalkanes

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Abstract

This review describes the synthesis and properties of borates that carry CF_3 (or more generally, perfluoroalkyl R_f) groups bonded to boron. Some novel amine-boranes $R(CF_3)_2B{\cdot}NHMe_2$ with $R = CF_3$, C_2F_5, C_4F_9, C_6F_5, $F_2C{=}CF$, $CF_3{-}FC{=}CF$ that are precursor molecules for the borates are reported; cleavage of their BN bond by $NEt_3 \times 3HF$ furnishes fluoroborates $[R(CF_3)_2BF]^-$. Cyanomethylborates $[R(CF_3)_2BCH_2CN]^-$ with $R =$ *t*-Bu, C_6H_5, $F_2C{=}CF$, CH_2CN result from reaction of $NCCH_2(CF_3)_2B{\cdot}NMe_3$ with RLi. The well-known aminoborate $[(CF_3)_3BNH_2]^-$ reacts with OCl^- and OBr^- to yield *N*,*N*-dihalogenoaminoborates $[(CF_3)_3BNX_2]^-$ ($X = Cl$ and Br), which can be fluorinated to form the *N*,*N*-difluoroborate anion $[(CF_3)_3BNF_2]^-$. Condensation of $[(CF_3)_3BNH_2]^-$ with ONR_f yields diazenidoborates $[(CF_3)_3BN{=}NR_f]^-$. The fluoroborate $[(CF_3)_3BF]^-$ is obtained by fluorination of $[(CF_3)_3BNF_2]^-$ or by pyrolysis of $[(CF_3)_3BN{=}NR_f]^-$, whereas $[(CF_3)_3BX]^-$ ($X = Cl$ and Br) are formed when dihalogenoaminoborates $[(CF_3)_3BNX_2]^-$ are pyrolyzed. Nitroborates $[R_f(CF_3)_2BNO_2]^-$ and $[(C_2F_5)_3BNO_2]^-$ are accessible by ozone oxidation of the corresponding dimethylamine-boranes. Anodic oxidation of $[(CF_3)_3BNH_2]^-$ furnishes $[(CF_3)_3BNO_2]^-$ and azodioxy-$[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$ and azoxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3BN{=}N(O)B(CF_3)_3]^{2-}$ dianions. The BN bonds of $[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$, $[(CF_3)_3BN{=}NCF_3]^-$, and $[(CF_3)_3BNO_2]^-$ are hydrolyzed to yield the hydroxyborate $[(CF_3)_3BOH]^-$. The NMR spectral and vibrational data of the novel borates are discussed and potential applications are suggested.

Keywords: Perfluoroalkyl borates; NMR studies; CF_3 group

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1. Introduction

The isovalency relation of BN- with CC-systems has been a fruitful concept in boron–nitrogen chemistry, amine-boranes $X_3B{-}NR_3$ (formal charges will be generally omitted) corresponding to alkanes $X_3C{-}CR_3$, aminoboranes $X_2B{=}NR_2$ to alkenes $X_2C{=}CR_2$, iminoboranes $XB{\equiv}NR$ to alkynes $XC{\equiv}CR$, and BN to graphite and diamond. This formal analogy, however, cannot always be substantiated by experiment although the resemblance of polar olefins by amino-bis(trifluoromethyl)boranes $(CF_3)_2B{=}NR_2$ ($R = CH_3$, C_2H_5,…) is a favorable example for this analogy. A preceding review entitled “Trifluoromethyl-substituted aminoboranes and amine-boranes revealing alkene and alkane chemistry” [1] was mainly concerned with this chemical analogy (cycloaddition reactions, ene-type reactions,…) and moreover with the relation of amine-tris(trifluoromethyl)boranes to alkanes.

A similar analogy is that of a neutral carbon atom with B^-, which relates alkanes and their derivatives to negatively charged borates, e.g. X_3C–Hal to $[X_3B\text{–Hal}]^-$, and likewise ammonium salts $[X_3C\text{–}NR_3]^+$ to amine-boranes $X_3B\text{–}NR_3$. The present review picks up this concept and deals with borates that carry CF_3 (or more generally, perfluoroalkyl R_f) groups bonded to boron and which are negatively charged, thus corresponding to alkanes substituted by perfluoroalkyl groups. These will be themselves perfluoroalkyl derivatives, e.g. $(CF_3)_3CX$, when corresponding to a tris(trifluoromethyl)borate $[(CF_3)_3BX]^-$.

The scope of the present contribution is thus narrower than that of Ref. [1] and, above all, reviews the synthesis of such perfluoroalkyl borates of the general formula $[R(CF_3)_2BX]^-$ (R = alkyl, alkenyl, alkynyl, R_f,...; X = F, OH, NH_2, $NHal_2$,...) in which at least two perfluoroalkyl groups (in most cases CF_3 groups) are attached to boron. We will also report on their chemical, spectroscopic, and structural properties, and suggest potential applications.

Precursors for these species are in general amine-boranes. Whenever novel amine-boranes are concerned, which have not been quoted in Ref. [1], these will be described in greater detail in the present progress report. Moreover we will not discuss species like the $[(C_6F_5)_4B]^-$ anion. Pentafluorophenyl boranes and borates have been known since the early 1960s but were only regarded as laboratory curiosities for long time [2]. However, recently salts like $[Ph_3C][(C_6F_5)_4B]$ were found to be efficient co-catalysts for the polymerization of ethylene and propylene [3], and they certainly deserve a dedicated treatment that, on purpose, will not be given here. A fascinating novel species is the dodecakistrifluoromethylcarba-*closo*-dodecaborate anion $[CB_{11}(CF_3)_{12}]^-$ which has been recently described by King and Michl [4].

In contrast to any of the donor-free tris(perfluoroalkyl)boranes, $(R_f)_3B$, which still remain illusory species, perfluoroalkyl derivatives with tetracoordinated boron (amine-boranes $(R_f)_3B{\cdot}L$ (L = NH_3, NH_2R, NHR_2, NR_3), or borates like $[CF_3BF_3]^-$, $[(CF_3)_2BF_2]^-$) are remarkably stable. This was already discovered by Chambers et al. in 1960 [5] who were the first to prepare and characterize several salts with the $[CF_3BF_3]^-$ anion. In such tetracoordinated species the elimination of difluorocarbene according to Eq. (1).

$$[CF_3BF_3]^- \rightarrow [BF_4]^- + CF_2 \qquad (1)$$

is thermodynamically less favored than in tricoordinated trifluoromethyl boron compounds [6]. Carbene elimination from tetracoordinated perfluoroalkyl boron species is also kinetically hindered. The boron–carbon bonds are well protected by a sphere of fluorine atoms. Therefore oxidative cleavage of the B–C bond hardly occurs, and in result perfluoroalkyl borates are stable to air and to water. In this respect these borates differ sharply from their non-fluorinated alkyl borate congeners. In spite of the numerous examples and favorable properties that will be presented in the following, the synthesis of perfluoroalkylborates is still a challenge because generally used methods to form a B–C bond are not applicable.

The present review is organized as follows. In Section 2 we will report on the synthesis of novel uncharged amine-tris(fluoroorgano)boranes of the general formula $(R_f)_2XB{\cdot}NHR_2$, with R_f either CF_3 or C_2F_5. Substituent X is a fluoroorgano group, and R is usually (but not necessarily) CH_3. These compounds serve as precursors for the borates. Section 3 deals with perfluoroalkyl borates with one or two R_f groups bonded to boron. It is subdivided according to the nature of the further ligands, which can be halogen atoms, organo groups, or combinations thereof. In Section 4 we will discuss the synthesis of tris(perfluoroalkyl)borates with nitrogen derivatives, halogen, or OH acting as fourth substituent. Section 5 will describe NMR spectra of these fluoroalkyl borates, NMR spectroscopy being the most powerful method for their identification and characterization. In Section 6 vibrational spectra and group frequencies typical for trifluoromethylborates will be given. An outlook for potential applications of perfluoroalkylborates will conclude the contribution.

2. Synthesis of precursors: amine-perfluoroalkylboranes

2.1. *Amine-tris(perfluoroalkyl)boranes* $(R_f)_3B{\cdot}NHEt_2$ *and* $(R_f)_3B{\cdot}NHMe_2$

The amine-boranes, $(CF_3)_3B{\cdot}NHEt_2$ (**H1**) or alternatively $(CF_3)_3B{\cdot}NHMe_2$ (**H2**), and the aminoborane $(CF_3)_2BNMe_2$ (**3**), which are precursors for the borates, are accessible in quantities up to 100 g using standard laboratory equipment and commercially available chemicals. Thus, the tris(trifluoromethyl) derivatives **1** and analogously **2** are synthesized in methylene chloride according to Eq. (2) [1].

$$3P(NEt_2)_3 + Cl_2BNEt_2 + 3CF_3Br \rightarrow \underset{(\mathbf{1})}{[(CF_3)_3BNEt_2]^-} + 3[BrP(NEt_2)_3]^+ + 2Cl^- \qquad (2)$$

A different route uses, in combination with CF_3I, tetrakis(dimethylamino)ethylene $[(Me_2N)_2C]_2$ (TDAE) instead of $P(NEt_2)_3$ as reducing agent according to Eq. (3).

$$\begin{aligned} &3[(Me_2N)_2C]_2 + Cl_2BNEt_2 + 3CF_3I \\ &\rightarrow \underset{(\mathbf{1})}{[(CF_3)_3BNEt_2]^-} + 3[[(Me_2N)_2C]_2]^{2+} 2Cl^- + 3I^- \end{aligned} \qquad (3)$$

Reversible protonation of the borates using conc. HCl furnishes the amine-boranes [1]. Yields of **1** and **2** when prepared according to Eqs. (2) or (3) are typically 60%.

Boron compounds to which three R_f groups are attached are not restricted to $R_f = CF_3$. Reacting C_2F_5I instead of CF_3I with Br_2BNMe_2 and TDAE, $[(C_2F_5)_3BNMe_2]^-$ (**4**) was obtained in analogy to Eq. (3). Protonation of **4** gave the dimethylamine-borane $(C_2F_5)_3B{\cdot}NHMe_2$ (**H4**) [7]. The yield, however, is much lower than for **H2**, only 12% on average. Obviously the greater bulkiness of the three C_2F_5 groups compared with that of the CF_3 groups is responsible for hindrance of the perfluoroalkylation reaction. Compared with **H2**, which is a solid at room temperature, **H4** is a liquid, and surprisingly more volatile despite its higher molecular weight.

2.2. Dimethylamine-perfluoroorgano-bis(trifluoromethyl)boranes $R_f(CF_3)_2B{\cdot}NHMe_2$

The aminoborane **3** is a versatile precursor for the synthesis of dimethylamine-boranes $R_f(CF_3)_2B{\cdot}NHMe_2$. The former is most conveniently prepared in yields of 70% from Br_2BNMe_2 or Cl_2BNMe_2 in sulfolane solution using the reagent combination $CF_3Br/P(NEt_2)_3$ according to Eq. (4) [1].

$$2P(NEt_2)_3 + Br_2BNMe_2 + 2CF_3Br \rightarrow \underset{\mathbf{(3)}}{(CF_3)_2BNMe_2} + 2[BrP(NEt_2)_3]Br \qquad (4)$$

A perfluoroalkyl group R_f can be attached to boron by reacting **3** with the corresponding perfluoroalkyl iodide $F_3C(CF_2)_nI$ and TDAE, Eq. (5) [7].

$$(CF_3)_2BNMe_2 + F_3C(CF_2)_nI \xrightarrow[2.\ HCl-H_2O]{1.\ TDAE-CH_2Cl_2} F_3C(CF_2)_n(CF_3)_2B{\cdot}NHMe_2 \qquad (5)$$

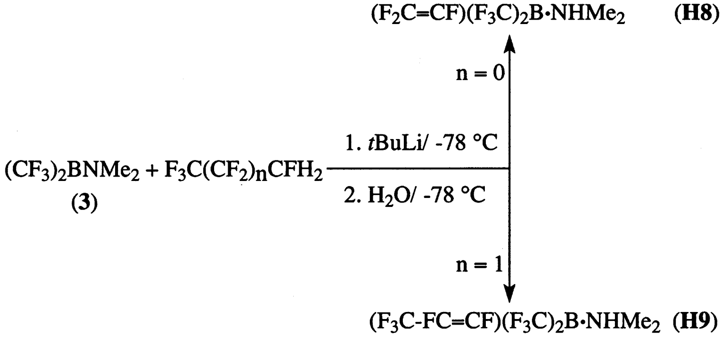
$n = 1$: **(H5)**
$n = 3$: **(H6)**

Both a perfluoroethyl or a perfluoro-*n*-butyl group can be bonded to boron, yields of 80% being obtained. While **H5** is liquid at room temperature, **H6** is a low-melting solid. The thermal stabilities of these amine-boranes are similar to that of **H2**.

Attachment of a C_6F_5 group to **3** is achieved analogously (Eq. (5)) using C_6F_5I and TDAE in CH_2Cl_2 solution. In this case the reaction temperature has to be raised to 35–40°C, whereas for C_2F_5 and C_4F_9 groups reaction (5) proceeds smoothly already at −5°C. Protonation of the borate with conc. HCl provides the dimethylamine-borane $C_6F_5(CF_3)_2B{\cdot}NHMe_2$ (**H7**) in almost quantitative yield as a volatile solid [8].

2.3. Dimethylamine-(trifluoroethenyl)- and (pentafluoropropenyl)-bis(trifluoromethyl)boranes $F_2C{=}CF(CF_3)_2B{\cdot}NHMe_2$ and $CF_3{-}FC{=}CF(CF_3)_2B{\cdot}NHMe_2$

Perfluoroalkenyl iodides are expensive ($F_2C{=}CFI$) or, to our knowledge, not commercially available, (e.g. $F_3CFC{=}CFI$). Therefore we have generated the required respective lithium reagents $F_2C{=}CFLi$ or $CF_3{-}FC{=}CFLi$ to be then reacted with **3** in situ from 1,1,1,2-tetrafluoroethane or 1,1,1,2,2,3-hexafluoropropane at −78°C using *t*-BuLi in ether, Eq. (6) [8,9].



(6)

Both $F_2C{=}CF(CF_3)_2B{\cdot}NHMe_2$ (**H8**) and $CF_3{-}FC{=}CF(CF_3)_2B{\cdot}NHMe_2$ (**H9**) were obtained in quantitative yield as solids which are resistant to air and water under ambient conditions. The perfluoropropenyl derivative **H9** afforded a 75:25 mixture of the *cis*/*trans* isomers [8]. The assignment to the two possible isomers, *cis* or *trans*, is based on the ^3J(FF) coupling constants. Assuming the generally accepted relation $|^3J(FF)_{trans}| \gg |^3J(FF)_{cis}|$ [10], the side product which shows a $^3J(\mathrm{FF})_{trans}$ coupling constant of -135.8 Hz is likely to be the *trans* isomer. The crystal and molecular structure of **H8** has been determined by X-ray diffraction [9].

3. Mono- and bis(perfluoromethyl)borates

3.1. *Trifluoromethyl-trifluoroborate* $[CF_3BF_3]^-$

The trifluoromethyl-trifluoroborate anion $[CF_3BF_3]^-$ (**10**) was the first species with a trifluoromethyl group attached to boron that could be fully characterized. It was obtained by Chambers et al. [5] via the reaction of Me_3SnCF_3 with BF_3 in CCl_4 solution according to Eq. (7).

$$Me_3SnCF_3 + BF_3 \rightarrow [Me_3Sn][CF_3BF_3] \qquad (7)$$

The potassium salt $K[CF_3BF_3]$ (**K10**) was prepared from $[Me_3Sn][CF_3BF_3]$ using KF/H_2O, the structure of which has been determined by X-ray diffraction [1]. The anion **10** is also formed, together with $[(CF_3)_2BF_2]^-$ (**11**), when BCl_3 or BBr_3 are reacted between -70 and -40°C with a large excess of Me_3SnCF_3 [1]. Species **10** and **11** are often observed as side products when borates carrying two or three trifluoromethyl groups decompose with concomitant elimination of CF_2 (vide infra).

3.2. *Bis(trifluoromethyl)borates* $[(CF_3)_2BF_2]^-$, $[(CF_3)_2B(OH)_2]^-$, $[(CF_3)_2BF(OH)]^-$

The bis(trifluoromethyl)difluoroborate anion **11** was first obtained, together with **10**, when a large excess of Me_3SnCF_3 was reacted with BF_3 at 60°C, or with BCl_3 (respectively BBr_3) at -70°C [1]. The structure of $Cs[(CF_3)_2BF_2]$ (**Cs11**) has been investigated by X-ray diffraction.

The dihydroxyborate $[(CF_3)_2B(OH)_2]^-$ (**12**) was obtained from $(CF_3)_2BNR_2$ ($R = Me$ (**3**) and Et) in a two-step process (Eq. (8)). In the first step, H_2O adds across the BN bond to yield $(CF_3)_2(HO)B{\cdot}NHR_2$. Then, second, the amine-hydroxyborane $(CF_3)_2(HO)B{\cdot}NHR_2$ eliminates the amine ligand upon treatment with aqueous KOH.

$$(CF_3)_2BNR_2 + H_2O \rightarrow (CF_3)_2(HO)B{\cdot}NHR_2$$

$$(CF_3)_2(HO)B{\cdot}NHR_2 + KOH \rightarrow \underset{\textbf{(K12)}}{K[(CF_3)_2B(OH)_2]} + HNR_2 \qquad (8)$$

The potassium salt $K[(CF_3)_2B(OH)_2]$ (**K12**) is stable at 20°C but may explode when heated to >72°C [1].

Bis(trifluoromethyl)fluorohydroxyborate $[(CF_3)_2BF(OH)]^-$ (**13**) has been prepared from **12** in a one-step reaction. When **K12** is dissolved in ether/HCl, an etheral adduct $(CF_3)_2BOH \times OEt_2$ is formed, which reacts with KHF_2 to give the fluorohydroxyborate **13** (Eq. (9)). The potassium salt $K[(CF_3)_2BF(OH)]$ (**K13**) is thermally stable up to its melting point at 172°C [1].

$$\underset{\mathbf{(K12)}}{K[(CF_3)_2B(OH)_2]} \xrightarrow{HCl-OEt_2} \{(CF_3)_2BOH \times OEt_2\} \xrightarrow{KHF_2} \underset{\mathbf{(K13)}}{K[(CF_3)_2BF(OH)]} \qquad (9)$$

3.3. *Organo-bis(trifluoromethyl)fluoroborates $[R(CF_3)_2BF]^-$ with $R = C_6F_5$, $F_2C{=}CF$, $CF_3{-}FC{=}CF$, C_2H_5, $C_6H_5CH_2$, C_6H_5, $H_2C{=}CH$, $HC{\equiv}C$*

The relative base strength of amines towards trialkylboranes has been studied by Brown [11]. In adducts formed from these partners the strength of the BN bond depends predominantly on steric strain, and the order of strength $NH_3 < (CH_3)_3N$ valid for $B(CH_3)_3$ is reversed for $B(C_2H_5)_3$ and $B(t\text{-}Bu)_3$. For the latter borane the relative strength of the BN bond increases in the order $(CH_3)_3N < (CH_3)_2NH < NH_3 < CH_3NH_2$.

The steric demand of a CF_3 group can be compared with that of an *i*-Pr group. Hence in the above-mentioned dimethylamine-boranes $R_f(CF_3)_2B{\cdot}NHMe_2$ the boron atom is more efficiently shielded than, e.g. in $B(C_2H_5)_3$. However, as a result of the strong electron withdrawing power of at least two CF_3 groups, which is further reinforced by the additional R_f substituent, the BN bond is much stronger in these amine-boranes than in non-fluorinated analogues. The dimethylamine ligand cannot be replaced easily by any other group. Moreover, due to the putative instability of the free perfluoroalkylboranes $R_f(CF_3)_2B$, the determination of equilibrium constants for complex formation was not possible. Nevertheless the findings of Brown [11] should also hold for $R_f(CF_3)_2B$. Accordingly, adducts of $R_f(CF_3)_2B$ with trimethylamine should have weaker BN bonds than complexes with dimethylamine. Trimethylamine-boranes are therefore better candidates for BN cleavage reactions than dimethylamine derivatives.

Dimethylamine-bis(trifluoromethyl)boranes, $R(CF_3)_2B{\cdot}NHMe_2$, which result from the addition of a nucleophile R^- to **3** [1], and also those species which were mentioned in Sections 2.1, 2.2 and 2.3, can be alkylated with CH_3I/KOH in etheral solution to yield the corresponding trimethylamine-bis(trifluoromethyl)boranes, $R(CF_3)_2B{\cdot}NMe_3$, according to Eq. (10).

$$R(CF_3)_2B{\cdot}NHMe_2 + KOH + CH_3I \rightarrow R(CF_3)_2B{\cdot}NMe_3 + H_2O + KI \qquad (10)$$

The BN bond in these trimethylamine-boranes is cleaved by $NEt_3 \times 3HF$ at elevated temperature to form the corresponding fluoroborate anions $[R(CF_3)_2BF]^-$ according to Eq. (11). Depending on R the temperature for the displacement of the trimethylamine ligand by F^- varies significantly (Table 1). While a temperature of 155°C is sufficient for $R = C_2H_5$, heating to 195°C is required when $R = F_2C{=}CF$ [8,9].

$$R(CF_3)_2B{\cdot}NMe_3 \xrightarrow[-NMe_3/+F^-]{NEt_3 \times 3HF} \underset{\mathbf{(14-21)}}{[R(CF_3)_2BF]^-} \qquad (11)$$

Table 1
Temperature for the thermal replacement of trimethylamine by fluoride in $R(CF_3)_2B\cdot NMe_3$ with formation of $[R(CF_3)_2BF]^-$ (**14**–**21**)

R	Temperature (°C)	R	Temperature (°C)
C_2H_5 (**14**)	155	C_6F_5 (**18**)	165
$C_6H_5CH_2$ (**15**)	160	HC≡C (**19**)	170
C_6H_5 (**16**)	160	$F_2C{=}CF$ (**20**)	195
$H_2C{=}CH$ (**17**)	165	$F_3C{-}FC{=}CF$ (**21**)	195

Whereas no side reactions were observed for $R = C_6H_5CH_2$, C_6H_5, C_6F_5, $F_2C{=}CF$, and $F_3C{-}FC{=}CF$, for $R = C_2H_5$, $H_2C{=}CH$ and HC ≡ C the displacement of NMe_3 is accompanied by formation of a considerable amount (10–15%) of **10** and some (5%) of **11**. For the rate of the B–N bond cleavage both the electronegativity (− I effect) of R and the capability of R for back-donation (+ M effect) are important. The more electron withdrawing the ligand R is, the stronger will be the BN bond and the higher the temperature for the displacement reaction (CF_3 + 80°C compared to $C_6H_5CH_2$). Fluorination of the benzene ring has only little influence on the temperature for the displacement reaction (C_6F_5 + 5°C compared to C_6H_5) whereas the effect of fluorination is stronger for the ethenyl ligands ($F_2C{=}CF$ + 30°C compared to $H_2C{=}CH$). The latter two ligands are capable of back donation and might thus stabilize a tricoordinated boron atom.

A side reaction with loss of the ligand R and degradation of CF_3 groups has been observed for $R = C_2H_5$, $H_2C{=}CH$, and HC≡C despite the different reaction temperatures. We suppose that these species undergo to some extent a dehydroboration reaction in the transition state. Species with a BH function like $H(CF_3)_2B\cdot NMe_3$ decompose rapidly at and above 150°C in an acidic medium like $NEt_3 \times 3HF$. It should be further noted that the BN bond in $(CF_3)_3B\cdot NMe_3$ cannot be thermally cleaved at all to form $[(CF_3)_3BF]^-$ (vide infra). Indeed reactions conducted above 235°C for 7 h gave **10** and **11** in low yield, together with ca. 80% of unreacted material.

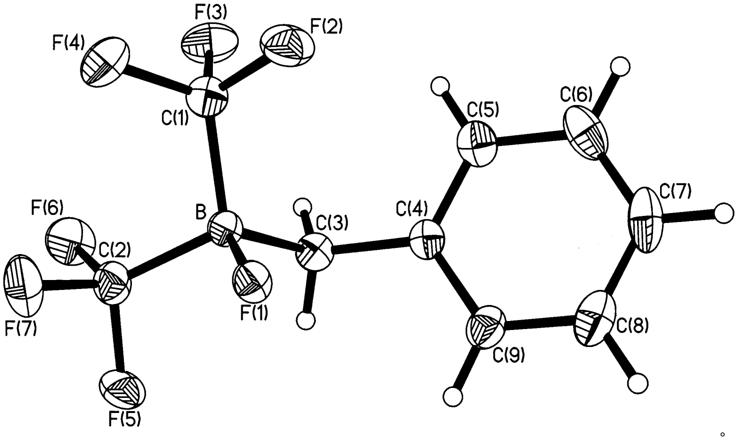


Fig. 1. The structure of $[C_6H_5CH_2(CF_3)_2BF]^-$ anion **K15** exhibits a B–F bond of 1.446(3) Å, and the B–CF_3 bond lengths, 1.617(4) Å, are not significantly longer than in the $C_6H_5CH_2$–B attachment, 1.609(4) Å.

Treatment of the reaction mixtures containing the triethylammonium salts of **14–21** with K_2CO_3 or Cs_2CO_3 in acetone converts these into the corresponding alkali salts. The structures of $K[C_6H_5(CF_3)_2BF]$ (**K16**) and $K[C_6H_5CH_2(CF_3)_2BF]$ (**K15**) have been investigated by X-ray diffraction [8] and the constitution of **15** is displayed in Fig. 1.

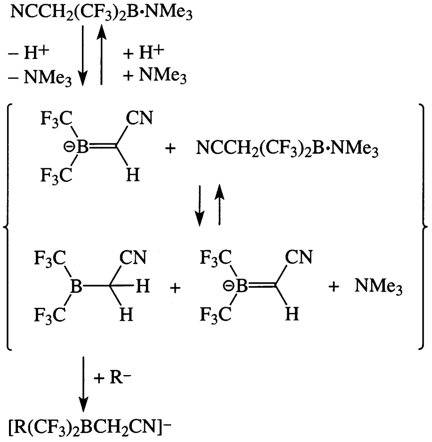
3.4. Organo-bis(trifluoromethyl)cyanomethylborates $[R(CF_3)_2BCH_2CN]^-$ with $R = t\text{-}Bu$, C_6H_5, $F_2C{=}CF$, CH_2CN

The reactivity of the BN bond in amine-bis(trifluoromethyl)boranes $R'(CF_3)_2B{\cdot}NMe_3$ is strongly dependent on the nature of the substituent R′. If R′ is an alkyl, phenyl, or F_3C group, the BN bond is stable to acids as well as resistant to bases. However, when the R′ group possesses a hydrogen atom on the carbon α to boron that is sufficiently acidic to be easily deprotonated by bases, the BN bond is readily cleaved. Such a group R′ with acidic hydrogen atoms is the cyanomethyl group $NCCH_2$. Accordingly the BN bond in $NCCH_2(CF_3)_2B{\cdot}NMe_3$ (**22**) is readily cleaved by organolithium reagents RLi. With concomitant elimination of trimethylamine, organo-bis(trifluoromethyl)cyanomethylborates of the general formula $[R(CF_3)_2BCH_2CN]^-$ are formed at $-60°C$ in ether according to Eq. (12) [12].

$$NCCH_2(CF_3)_2B{\cdot}NMe_3 + RLi \xrightarrow{-60°C} Li[R(CF_3)_2BCH_2CN] + NMe_3$$

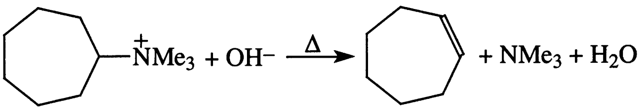
$$R = t\text{-Bu}\ (\mathbf{Li23}),\ C_6H_5\ (\mathbf{Li24}),\ F_2C = CF\ (\mathbf{Li25}),\ CH_2CN\ (\mathbf{Li26}) \qquad (12)$$

The displacement of trimethylamine in **22** is initiated by deprotonation of the cyanomethyl group with intermediate formation of an alkylideneborate $[NCCH{=}B(CF_3)_2]^-$. We believe that this intermediate is in equilibrium with further trimethylamine-borane **22** and thus small quantities of donor-free bis(trifluoromethyl)cyanomethylborane are generated which will react rapidly and irreversibly with R^- to form the cyanomethylborate $[R(CF_3)_2BCH_2CN]^-$ **23–26** (Scheme 1).



Scheme 1. Replacement of NMe_3 by R^- via an intermediate alkylidene borate.

The trimethylamine-borane **22** behaves like a quaternary ammonium salt. Such salts are known to generally eliminate an alkene when heated with strong bases like KOH. This reaction is named *Hofmann elimination*, and cycloheptene for example is obtained from the corresponding ammonium salt according to Eq. (13).



(13)

Thus the reaction of **22** with organolithium reagents may be regarded as a boron version of the *Hofmann elimination* taking place at low temperature.

4. Tris(perfluoroalkyl)borates $[R_f(CF_3)_2BY]^-$

4.1. *Amino-tris(trifluoromethyl)borate* $[(CF_3)_3BNH_2]^-$

Amino-tris(trifluoromethyl)borate $[(CF_3)_3BNH_2]^-$ (**27**) is the prototype and most useful starting material for other borates. As mentioned earlier, the ammine-borane $(CF_3)_3B{\cdot}NH_3$ (**H27**) behaves like a protonated primary amine. On raising the pH value to 8–9, the nitrogen atom is deprotonated to form **27**. The structures of **H27** [1] and of its tetrahydrate $(CF_3)_3B{\cdot}NH_3 \times 4H_2O$ (**28**) [13] have been determined. Attempts to obtain single crystals of $Cs[(CF_3)_3BNH_2]$ (**Cs27**) incidentally furnished crystalline material which turned out to be a 1:1 ammine-borane–aminoborate complex $Cs[(CF_3)_3B{\cdot}NH_3 \times (CF_3)_3BNH_2]$ (**H27** × **27**). The structure as determined by single-crystal X-ray diffraction is characterized by a hydrogen bridge connecting the two halves (Fig. 2) [14].

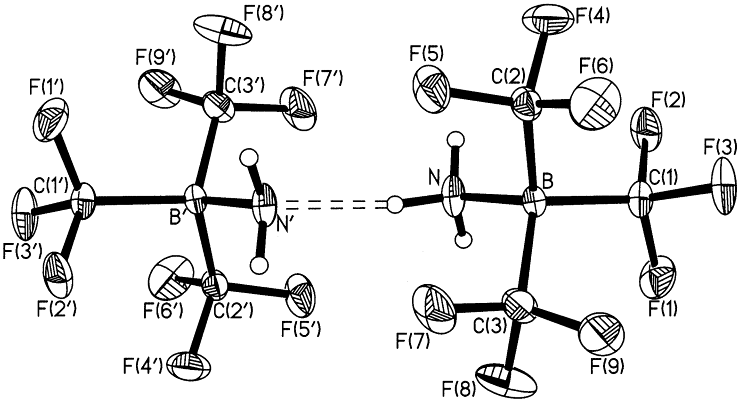


Fig. 2. In the structure of $[(CF_3)_3BNH_2 \times (CF_3)_3B{\cdot}NH_3]^-$ hydrogen bonding couples the ammine-borane and the aminoborate in the solid state.

4.2. *N*,*N*-Dihalogenoaminoborates $[(CF_3)_3BNX_2]^-$ ($X = F$, Cl, Br)

Compound **27** is a versatile starting material for oxidation reactions in which the $(CF_3)_3B$ moiety is not generally attacked even by strong oxidizing agents. Thus, **Cs27** reacts with hypochlorite OCl^- or hypobromite OBr^- to form the respective *N*,*N*-dichloroamino- or *N*,*N*-dibromoamino-tris(trifluoromethyl)borates $[(CF_3)_3BNCl_2]^-$ (**29**) and $[(CF_3)_3BNBr_2]^-$ (**30**) [14] Eq. (14).

$$\underset{\mathbf{27}}{[(CF_3)_3BNH_2]^-} + 2OX^- \rightarrow \underset{X = Cl,\ \mathbf{29};\ X = Br,\ \mathbf{30}}{[(CF_3)_3BNX_2]^-} + 2OH^- \tag{14}$$

Both salts, the yellow Cs salt **Cs29** and the brown Cs salt **Cs30**, are thermally stable up to 180 and 140°C, respectively. In solution both salts are sensitive to light and act as chlorinating and brominating agents, respectively. Fluorination of both of them in CH_3CN solution with $3\%F_2/He$ yields $[(CF_3)_3BNF_2]^-$ (**31**). Upon treatment with fluorine **31** reacts further to form, among other side products (vide infra), the fluoroborate $[(CF_3)_3BF]^-$ (**32**) [14].

4.3. Diazenidoborates $[(CF_3)_3BN{=}NR_f]^-$ ($R_f = CF_3$, C_2F_5)

The reaction of amines with electron deficient nitroso compounds is a standard method to form diazenes with an N=N double bond. Transferring this concept to aminoborates, **27** was reacted with CF_3NO or C_2F_5NO in THF solution. Orange–yellow fluoroalkyldiazenido-tris(trifluoromethyl)borates $[(CF_3)_3BN{=}NCF_3]^-$ (**33**) and $[(CF_3)_3BN{=}NC_2F_5]^-$ (**34**), respectively, were obtained in high yield according to Eq. (15).

$$\underset{\mathbf{27}}{[(CF_3)_3BNH_2]^-} + ON(CF_2)_nF \rightarrow \underset{(n = 1\ (\mathbf{33}),\ n = 2\ (\mathbf{34}))}{[(CF_3)_3BN = N(CF_2)_nF]^-} + H_2O \tag{15}$$

The constitution and *trans* arrangement of the diazene unit were established for $Cs[(CF_3)_3BN{=}NCF_3]$ (**Cs33**) by a single-crystal X-ray investigation [15]. The structure of **33** is depicted in Fig. 3. Moreover, a Raman line characteristic of the N=N bridge was observed at 1586 and 1575 cm^{-1}, respectively, for **33** and **34**. The Cs salts **Cs33** and **Cs34** are stable up to ca 150°C. Above this temperature they decompose to form quantitatively **Cs32** according to Eq. (16).

$$\underset{(n = 1,2)\ \mathbf{Cs33},\ \mathbf{Cs34}}{Cs[CF_3)_3BN = N(CF_2)_nF]} \xrightarrow{\Delta(160°C)} \underset{(\mathbf{Cs32})}{Cs[(CF_3)_3BF]} + N_2 + \{(CF_2)_n\} \tag{16}$$

Both borates **33** and **34** are stable to hydrolysis. Upon irradiation, however, of an aqueous solution with the 254 nm line of a mercury lamp, the BN bond is cleaved – $[(CF_3)_3BOH]^-$ (**35**) (vide infra) being the major reaction product (Eq. (17)).

$$\underset{(n = 1,2)\ \mathbf{33},\ \mathbf{34}}{[CF_3)_3BN = N(CF_2)_nF]^-} \xrightarrow{h\nu/H_2O} \underset{(\mathbf{35})}{[(CF_3)_3BOH]^-} + N_2 + H(CF_2)_nF \tag{17}$$

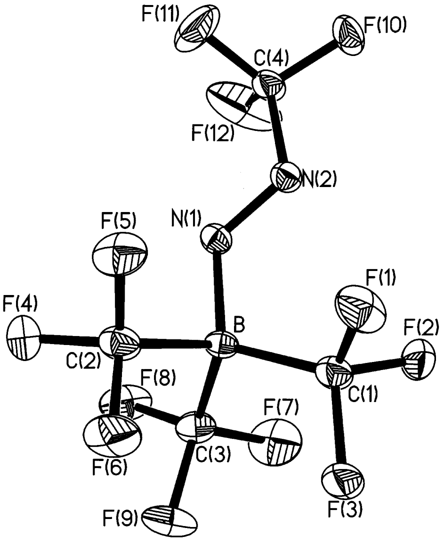


Fig. 3. The structure of $[(CF_3)_3BN{=}NCF_3]^-$ in **Cs33** showing the *trans* configuration at the N=N bond.

The UV–vis spectra of both diazenido derivatives in water show a broad absorption at λ_{max} 440–450 nm (ε ca. $10 \times cm^{-1}\ mol^{-1}$).

4.4. Halogeno-tris(trifluoromethyl)borates $[(CF_3)_3BX]^-$ ($X = F$, Cl, Br)

The fluoroborate anion $[(CF_3)_3BF]^-$ **32** is obtained quantitatively by thermal decomposition of the cesium diazenido borates **Cs33** and **Cs34** above 150°C (see Section 4.3) [15]. It is also formed in high yield when **Cs29** or **Cs30** are fluorinated in anhydrous HF with 3% F_2/He, or are reacted with AgF_2 [14] (see Section 4.2). The anion **32** was also identified as a side product in the reaction of $[(CF_3)_3BNO_2]^-$ (**36**) with $NEt_3 \times 3HF$ at 230°C [7] according to Eq. (18).

$$3[(CF_3)_3BNO_2]^- \xrightarrow{NEt_3 \times 3HF\ (230°C)} \underset{\mathbf{(32)}}{[(CF_3)_3BF]^-} + 2\underset{\mathbf{(35)}}{[(CF_3)_3BOH]^-} \qquad (18)$$

The Cs salt $Cs[(CF_3)_3BF]$ (**Cs32**) is thermally stable up to ca. 300°C, above which temperature it decomposes under elimination of CF_2.

The Cs salts **Cs37** and **Cs38** of the borates $[(CF_3)_3BCl]^-$ (**37**) and $[(CF_3)_3BBr]^-$ (**38**) were obtained in moderate yields by thermal decomposition of the corresponding cesium *N*,*N*-dihalogenoaminoborates **Cs29** and **Cs30**, respectively, [14]. Ideally this decomposition can be represented by Eq. (19).

$$\underset{\mathbf{(Cs29,\ Cs30)}}{2Cs[(CF_3)_3BNX_2]} \xrightarrow{X = \substack{Cl180-190°C \\ Br140-150°C}} \underset{\mathbf{(Cs37,\ Cs38)}}{2Cs[(CF_3)_3BX]} + N_2 + X_2 \qquad (19)$$

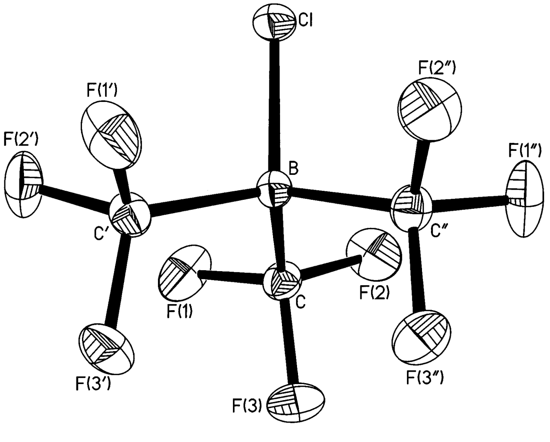


Fig. 4. The structure of $[(CF_3)_3BCl]^-$ in **Cs37** with B–C and B–Cl bond lengths of 1.627(4) and 1.861(6) Å, respectively, deviates slightly from C_{3v} symmetry.

Though this decomposition stoichiometry is supported by thermogravimetric analyses, formation of CF_3Cl and CF_3Br, respectively, and of **10** and **11** is observed as well. These products prove that the cleavage of BC bonds takes place concomitantly. The structures of the Cs salts **Cs37** and **Cs38** have been investigated by X-ray diffraction [14]. That of the anion of **Cs37** is illustrated in Fig. 4.

The thermal and hydrolytic stabilities of the cesium chloro- and bromo-borates **Cs37** and **Cs38** deserve a comment. Corresponding derivatives of trimethylborane $[(CH_3)_3BX]^-$ ($X = Cl$ and Br) are unknown whereas ring-substituted triarylhalogenoborates $[Ar_3BX]^-$ ($X = F$ and Cl) have been described [16]. Unlike BF_4^-, the tetrahalogenoborates BCl_4^- and BBr_4^- are only moderately stable, but they may be prepared using large counterions such as Cs^+, tetraalkylammonium and tropylium. Both anions are rapidly hydrolyzed by water. Since properties of CF_3 groups are often compared with those of chlorine and bromine because of apparent similarities like electronegativity and size, also the BCl bond in **37** and the BBr bond in **38** might be expected to undergo hydrolytic cleavage. However, it was noted that both **37** and **38** are resistant to water.

The Lewis acidity of $(CF_3)_3B$ towards chloride or bromide is expected to be higher than that of BCl_3 or BBr_3. First the CF_3 group has strong electron withdrawing character but second, unlike the halides, is not capable of p–π back-donation into orbitals of tricoordinate boron. So, if one of the B–Cl bonds in the tetrahedral BCl_4^- anion is lengthened and Cl^- eventually removed, the remaining three chlorine atoms can donate additional electron density to boron via p–π interaction as the BCl_3 skeleton flattens. An analogous carbon → boron electron transfer from the three CF_3 groups in **37** cannot occur, hence the barrier for dissociation into $(CF_3)_3B$ and Cl^- should be much higher than for dissociation of BCl_4^- into BCl_3 and Cl^-.

4.5. Tris(trifluoromethyl)hydroxyborate $[(CF_3)_3BOH]^-$

According to the preceding section tris(trifluoromethyl)hydroxyborate $[(CF_3)_3BOH]^-$ **35** cannot be obtained by hydrolysis of any of the halogenoborates, respectively, or the aminoborate **27**. However, when the oxidation number of a nitrogen atom linked to the $(CF_3)_3B$ moiety is raised the readiness to hydrolytic cleavage of the BN bond with formation of the hydroxyborate increases significantly. Thus the hydroxyborate **35** is the main product of the reaction of the nitroborate **36** with $NEt_3 \times 3HF$ [7]. It is also formed quantitatively when aqueous solutions of **33** or **34** [15] (Eq. (17)) or **36** [7] are irradiated with the 254 nm line of a mercury lamp (Eq. (20)).

$$\underset{\mathbf{(36)}}{[(CF_3)_3BNO_2]^-} + H_2O \xrightarrow{h\nu} \underset{\mathbf{(35)}}{[(CF_3)_3BOH]^-} + HNO_2 \tag{20}$$

Furthermore **35** is quantitatively formed by hydrolysis of azodioxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$ (**39**) [17]. This dianion slowly reacts already at room temperature with water according to Eq. (21).

$$\underset{\mathbf{(39)}}{[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}} + H_2O \rightarrow 2\underset{\mathbf{(35)}}{[(CF_3)_3BOH]^-} + N_2O \tag{21}$$

The elimination of N_2O was confirmed by IR spectroscopy. The Cs hydroxyborate (**Cs35**) is thermally stable and can be protonated by HCl in ether to form a volatile etherate $(CF_3)_3B{\cdot}OH_2 \times Et_2O$. On contact with moist air the ether molecule is replaced by five molecules of water. The pentahydrate $(CF_3)_3B{\cdot}OH_2 \times 5H_2O$ behaves as an acid, with a pK_a value of 1.6, and it is thermally stable up to 70°C. The structure of **Cs35** has been examined by X-ray diffraction [17].

4.6. Nitroborates $[R_f(CF_3)_2BNO_2]^-$ ($R_f = CF_3, C_2F_5, C_4F_9$) and $[(C_2F_5)_3BNO_2]^-$

Aminoborates with an oxidation number of the nitrogen atom of -3 are the genuine precursors not only of species with oxidation numbers -1 like in the diazenidoborates (Section 4.3) and with $-1/+1$ (depending on the halogen) of the dihalogenoaminoborates (Section 4.2) but also for higher oxidation states that may be reached, i.e. $+3$ in nitroborates. Expectedly their syntheses require very strong oxidizing agents like ozone or anodic oxidation.

Tris(perfluoroalkyl)nitroborates $[R_f(CF_3)_2BNO_2]^-$, ($R_f = CF_3$ (**36**), C_2F_5 (**40**), C_4F_9 (**41**)), and $[(C_2F_5)_3BNO_2]^-$ (**42**) are obtained straightforwardly from the respective dimethylamine-boranes **1** or **2**, **5**, **6**, and **4**, by oxidation with ozone in CsOH solution [7,17]. Compound **36** is also the main product of the electrochemical oxidation of **Cs27** using a platinum anode and a potential of 4.5 V at a pH of 8.5 [17]. The Cs salts **Cs36** and **Cs40**–**Cs42** are only moderately soluble in water but are exceedingly soluble in organic solvents like acetone or acetonitrile. They are thermally stable up to ca. 260°C. The melting points of **Cs40** and **Cs41**, ca. 65–70°C, and **Cs42**, 165–170°C, are rather low compared with that of **Cs36** which does not melt before the decomposition occurs. The structures of **Cs36** [17] and **Cs42** [18] have been examined by X-ray diffraction and are depicted in Figs. 5 and 6.

Etheral HCl protonates **36** and forms an etherate of the composition $(CF_3)_3B{\cdot}NO_2H \times Et_2O$ that can be sublimed in vacuo. This etherate is converted by moist air into what analyzes to be a pentahydrate $(CF_3)_3B{\cdot}NO_2H \times 5H_2O$. Titration of the latter revealed a pK_a value of ca. 1.9 and a molecular weight of 359 g mol^{-1}. This hydrate is stable at room temperature but according to thermogravimetric experiments decomposes at 75°C without leaving any residue.

The anion **36** is reduced in aqueous KOH by zinc to form **27** (Eq. (22)).

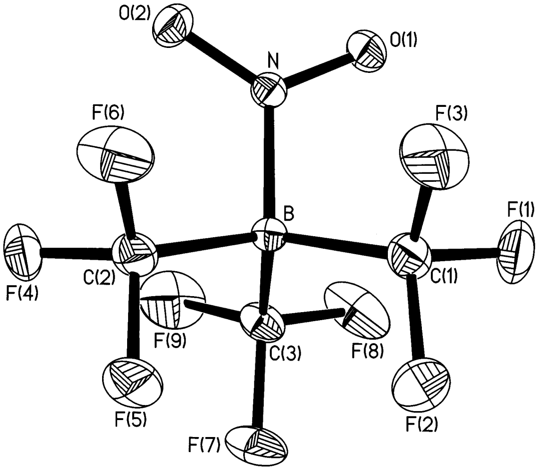


Fig. 5. The structure of the $[(CF_3)_3BNO_2]^-$ anion in **Cs36**. The r(B–N) (1.606(4) Å) and r(B–C) (1.618(10) Å) bonds describe a slightly distorted tetrahedron.

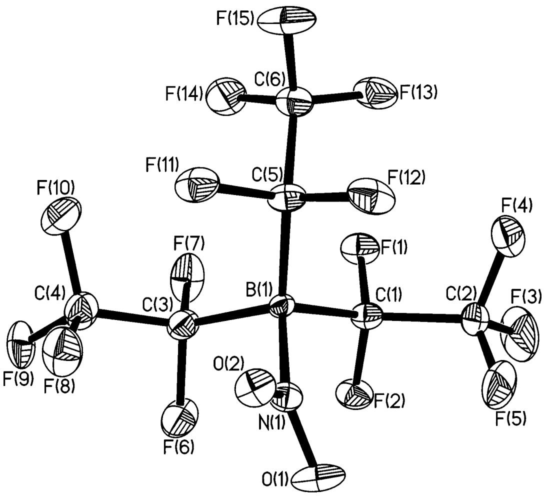
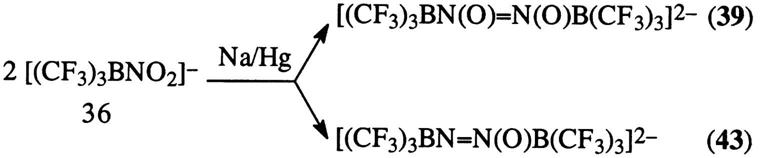


Fig. 6. The structure of the $[(C_2F_5)_3BNO_2]^-$ anion deviates slightly from C_s symmetry with average B–C and B–N bond lengths of 1.65(2) and 1.63(2) Å, respectively.

$$\underset{\mathbf{(36)}}{[(CF_3)_3BNO_2]^-} \xrightarrow{Zn/KOH/H_2O} \underset{\mathbf{(27)}}{[(CF_3)_3BNH_2]^-} \qquad (22)$$

Reduction of **36** with sodium amalgam in ether forms, according to ^{19}F-NMR spectra, a mixture of $[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$ (**39**) and $[(CF_3)_3BN{=}N(O)B(CF_3)_3]^{2-}$ (**43**) (Eq. (23)) [17]. These are borates in which the nitrogen atom has the intermediate oxidation states +1 and −1, respectively.



(23)

Nitroborates are stable to hydrolysis both in basic and acidic aqueous solutions. However, as mentioned above, irradiation of an aqueous solution of **36** with the 254 nm line of a mercury lamp furnishes quantitatively **35** [7]. The replacement reaction of NO_2^- is presumably initiated by a photochemical rearrangement of the nitroborate into the isomeric nitritoborate $[(CF_3)_3BONO]^-$. Hydrolysis of the latter yields the hydroxyborate **35**, Eq. (20). Though there is no conclusive experimental evidence for the intermediacy of a nitrito derivative, such a behavior is typical, for e.g. nitromethane, the photochemical rearrangement reaction of which has been studied by Brown and Pimentel [19].

The overall stability of the BN bond in these perfluoroalkyl nitroborates towards cleavage should be pointed out. The related $[F_3BNO_2]^-$ anion, whose formation in solution has been reported [20], has been characterized only by its ^{19}F-NMR spectrum and was found to readily undergo disproportionation into $[BF_4]^-$ and $[F_2B(NO_2)_2]^-$.

4.7. Azodioxy-$[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$ and azoxy-bis-tris(trifluoromethyl)borates $[(CF_3)_3BN{=}N(O)B(CF_3)_3]^{2-}$

Cesium salts both of azodioxy-bis-tris(trifluoromethyl)borate, $Cs_2[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]$ (**Cs39**), and of azoxy-bis-tris(trifluoromethyl)borate, $Cs_2[(CF_3)_3BN{=}N(O)B(CF_3)_3]$ (**Cs43**), were obtained when **Cs27** was oxidized using a platinum anode at a pH value of 8.5 and a potential of 4.5 V (vide supra) [17]. Both salts being almost insoluble in water, they accumulated on the anode and on the bottom of the electrolysis cell. While **Cs43** is thermally stable up to 190°C, **Cs39** decomposes violently at 80°C. The sodium salt of **39** seems to be even less stable: attempts to crystallize material obtained by reduction of **Cs36** with sodium amalgam (vide supra) repeatedly led to explosive decomposition.

The anion **39** can be regarded either as a borane complex of the hyponitrite anion $[N_2O_2]^{2-}$, or a dinitroso compound. It is well known that some organic dinitroso derivatives are in a thermal equilibrium with their monomers. However, no evidence for an analogous equilibrium according to Eq. (24) was found for the boron derivative.

$$[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-} \not\rightleftharpoons 2\,[(CF_3)_3BN{=}O]^{-} \qquad (24)$$

39

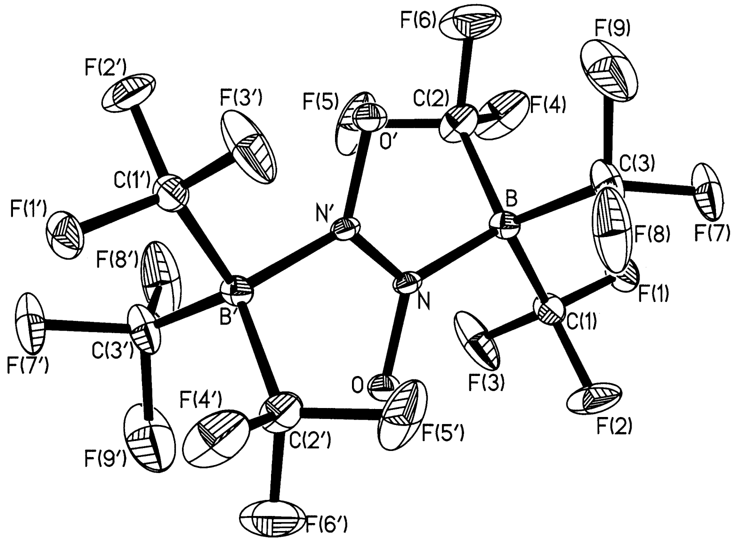


Fig. 7. The structure of the dianion $[(CF_3)_3BN(O){=}N(O)B(CF_3)_3]^{2-}$ in **Cs39**. The anion possesses crystallographic C_i symmetry with N–N and N–O bonds lengths of 1.30(2) and 1.30(1) Å, respectively.

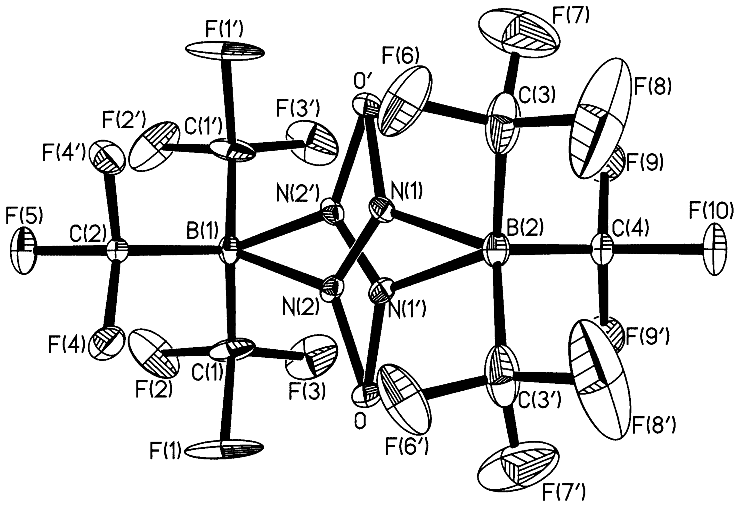


Fig. 8. The structure of $[(CF_3)_3BN{=}N(O)B(CF_3)_3]^{2-}$ in **Cs43**. While the N–N–O entity is disordered over a mirror plane, the study shows that it is bonded to the boron atoms via B–N bonds.

The structures of **Cs39** and **Cs43** have been determined by X-ray diffraction [17]. They are illustrated in Figs. 7 and 8.

5. NMR spectroscopic investigation

The $R_f(CF_3)B$ moiety, and moreover some of the further substituents, are amenable to ^{19}F-, ^{13}C-, ^{11}B- and, in part, also to ^{1}H-NMR spectroscopy. The huge body of NMR data that has been accumulated on the species, which are the subjects of this review, provides a powerful tool for the identification, constitution, and analysis of these species so that the NMR spectra deserve a dedicated treatment in this place.

5.1. ^{19}F-NMR spectra

In the ^{19}F-NMR spectra the resonance of the boron-bonded fluorines in fluoroalkylborates is of particular interest. All species $[R(CF_3)_2BF]^-$ with three boron–carbon bonds that have been mentioned in the preceding section show a B–*F* resonance between −220 ppm, $[HC{\equiv}C(CF_3)_2BF]^-$ **19**, and −230 ppm, $[(CF_3)_3BF]^-$ **32** (Table 2). The $^{1}J(BF)$ coupling constant determined from the splitting of the 1:1:1:1 quartets ($I\,(^{11}B) = 3/2$) range from 55 Hz ($R = HC{\equiv}C$) to 59 Hz ($R = CF_3$).

The B–CF_3 group reveals a 1:1:1:1 quartet near −70 ppm with a $^{2}J(BF)$ coupling constant of 25–29 Hz. In some cases this signal may be further split by $^{3}J(FF)$ coupling of ca. 4–5 Hz, e.g. in **32**.

The ^{19}F resonance of the B–CF_2–C group like in $[(C_2F_5)_3BNO_2]^-$ **42**, $[C_2F_5(CF_3)_2BNO_2]^-$ **40**, and $[C_4F_9(CF_3)_2BNO_2]^-$ **41** is found between −120 and −130 ppm, with a $^{2}J(BF)$ coupling constant of 17–18 Hz.

Table 2
^{11}B- and ^{19}F-NMR chemical shifts δ(B–*F*) (ppm) of the boron-bonded fluorine in $[R(CF_3)_2BF]^-$ derivatives

R	δ(B)	δ(B–F)
C_2H_5 (**14**)	−1.9	−221.8
$C_6H_5CH_2$ (**15**)	−3.3	−220.9
C_6H_5 (**16**)	−3.6	−224.1
$H_2C{=}CH$ (**17**)	−4.7	−226.9
C_6F_5 (**18**)	−3.8	−220.7
$HC{\equiv}C$ (**19**)	−8.7	−220.0
$F_2C{=}CF$ (**20**)	−6.3	−229.9
cis F_3C–$FC{=}CF$ (**21**)	−6.3	−225.2
trans F_3C–$FC{=}CF$ (**21**)	−6.3	−227.2
CF_3 (**32**)	−7.3	−230.0

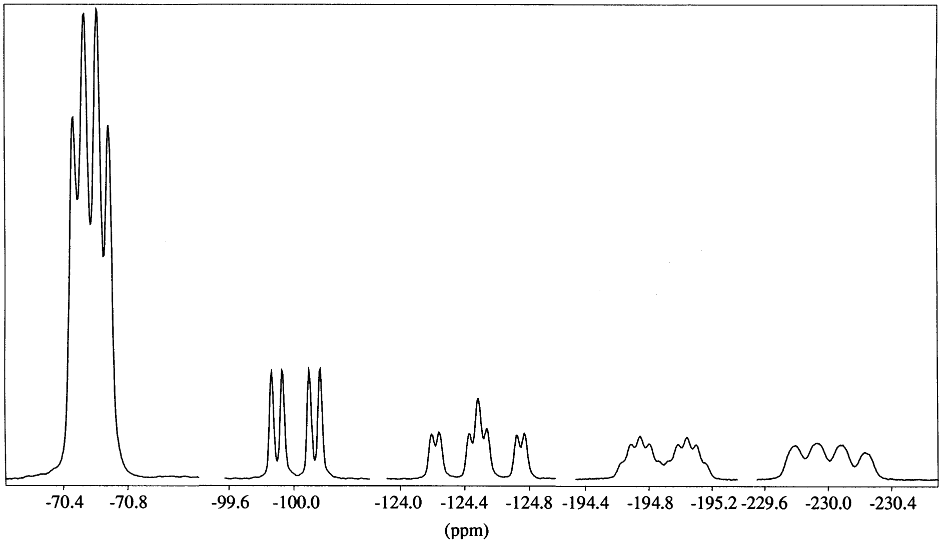


Fig. 9. ^{19}F-NMR spectrum of $[F_2C{=}CF(CF_3)_2BF]^-$.

The assignment of the three fluorine resonances of the trifluoroethenyl group in $[F_2C{=}CF(CF_3)_2BF]^-$ **20** (Fig. 9) at -100 ppm (F_2C=) (Z), -124.5 ppm (F_2C=) (E), and -195 ppm (=CFB) is based on the general assumption that $^2J(\mathrm{FF}) > 0$, $^3J(\mathrm{FF})_{trans} < 0$, $^3J(\mathrm{FF})_{cis} > 0$, and $|^3J(\mathrm{FF})_{trans}| > |^3J(\mathrm{FF})_{cis}|$ [10]. In trifluoroethenyl derivatives $F_2C{=}CFX$ the $^3J(\mathrm{FF})_{cis}$ coupling constant is sensitive to the electronegativity of X-varying from 58 Hz for X = Cl to 23 Hz for $X = B(CH_3)_2$ [10]. The $^3J(\mathrm{FF})_{cis}$ coupling constant of 25.5 Hz in **20** is herewith in reasonable agreement. Furthermore we note that in **20** the F_2C= signal at -124.3 ppm is further split by $^5J(\mathrm{FF})$ coupling of 4.6 Hz with the fluorine atoms of the $B(CF_3)_2$ group.

5.2. ^{11}B-NMR spectra

The ^{11}B resonances in halogeno-tris(trifluoromethyl)borates are observed between -7.3 ppm (**32**) and -14.9 ppm (**38**). The resonances of the anions $[R(CF_3)_2BF]^-$ ranging from -1.9 to -6.7 ppm are given in Table 2. The ^{11}B resonances of borates with four B–C bonds are observed between -15 ppm in **23** and -19 ppm in **25**.

5.3. ^{13}C-NMR spectra

The ^{13}C resonances of boron-bonded carbon atoms are in general broadened by the boron nucleus and provide only limited information on the ^{13}C^{11}B coupling. When fluorine atoms are also attached to such carbon atoms the ^{13}C signal is further split by CF coupling. In particularly unfavorable cases the signals of boron-bonded CF_3 groups may be 900 Hz broad, without any fine structure resolved and therefore difficult to detect.

However, in borates the relaxation of the tetracoordinated boron nucleus is rather slow, and in general signals are sharp. The carbon atoms of CF_3 groups attached to boron show resonances between 131 and 136 ppm, and the coupling constants are typically $^1J(BC) = 70–110$ Hz and $^1J(CF) = 300–310$ Hz and ^2J (CF) 70–30 Hz. The data for the three trifluoromethyl-fluoroborates $[(CF_3)_nBF_{(4-n)}]^-$ ($n = 1–3$) are collected in Table 3.

The ^{13}C resonances of B*C*F_2C groups are located near 123 ppm, with ^1J(CF) coupling constants between 285 and 300 Hz. The NMR parameters of the F_2C=CF group in $[F_2C{=}CF(CF_3)_2BCH_2CN]^-$ (**25**), which gives sharp resonance lines, are: (B–F*C*=CF_2) 136 ppm, ^1J(BC) 65 and ^1J(CF) 306 Hz; (B–FC=*C*F_2) 162 ppm, ^2J(BC) 8, ^1J(CF) 293 and 273 Hz, and ^2J(CF) 46 Hz.

Table 3
^{13}C-NMR data (δ in ppm, J in Hz) of the trifluoromethyl-fluoroborates $[(CF_3)_nBF_{(4-n)}]^-$ ($n = 1–3$)

	$[CF_3BF_3]^-$ (**10**)	$[(CF_3)_2BF_2]^-$ (**11**)	$[(CF_3)_3BF]^-$ (**32**)
$\delta(CF_3)$	131.9	132.0	132.6
^1J(BC)	109.9	91.0	80.0
^1J(CF)	309.6	309.4	309.4
^2J(CF)	66.6	42.0	30.5

6. Vibrational spectra

Besides NMR investigations, infrared and Raman spectra are a useful and frequently complementary tool for the identification of perfluoroalkylborates and the determination of their constitution. However, in most cases the borates under consideration have only low molecular symmetry, e.g. $[R(CF_3)_2BF]^-$ ($R \neq CF_3$), $[R(CF_3)_2BCH_2CN]^-$, and their vibrational spectra may be complicated. Then, as will be done in the following, only characteristic frequencies of functional groups are used for analytic purposes. In general, the typical group vibrations of the functional groups do not differ significantly in the perfluorinated borates from those in related organic compounds.

The C=C stretching vibration in **20**, 1751 cm^{-1}, is higher than in the non-fluorinated analogue **17**, 1613 cm^{-1}. This high wavenumber results from the coupling of the C=C stretching vibration with the CF stretches in **20** and is typical for trifluoroethenyl derivatives.

The NO_2 stretching vibrations of **36** and **40**–**42** which are listed in Table 4 are useful for the identification of these species because ^{14}N or ^{15}N-NMR spectra of boron-bonded nitrogen atoms are difficult to obtain. The Raman spectrum of $[(CF_3)_3BNO_2]^-$ is displayed in Fig. 10. The symmetric stretch ν_sNO_2 appears at 1390 cm^{-1} as a weak IR absorption but gives rise to a strong Raman line. The

Table 4
Characteristic frequencies of the NO_2 group (cm^{-1})

	36	**40**	**41**	**42**
$\nu_{as}NO_2$	1481	1480	1478	1471
$\nu_{s}NO_2$	1398	1394	1391	1383

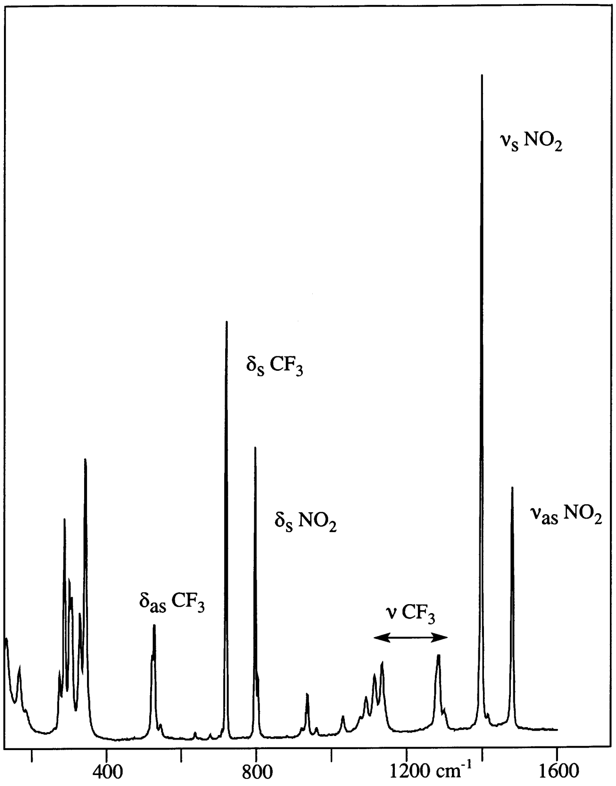


Fig. 10. Raman spectrum of $[(CF_3)_3BNO_2]^-$ in **Cs36**.

asymmetric stretch $\nu_{as}NO_2$ is located at 1480 cm^{-1} with high IR but lower Raman intensity.

Halogeno-tris(trifluoromethyl)borates $[(CF_3)_3BX]^-$ (X = F **32**, Cl **37**, Br **38**) have effective C_{3v} symmetry and their fundamental vibrations can here be assigned by comparison with the spectra of the perfluoroalkyl derivatives $(CF_3)_3CX$ [21]. Thus the analogy of perfluoroalkylborates and perfluoroalkane derivatives is also evident from the vibrational spectra. The Raman spectra of $(CF_3)_3CBr$ and **38** are displayed

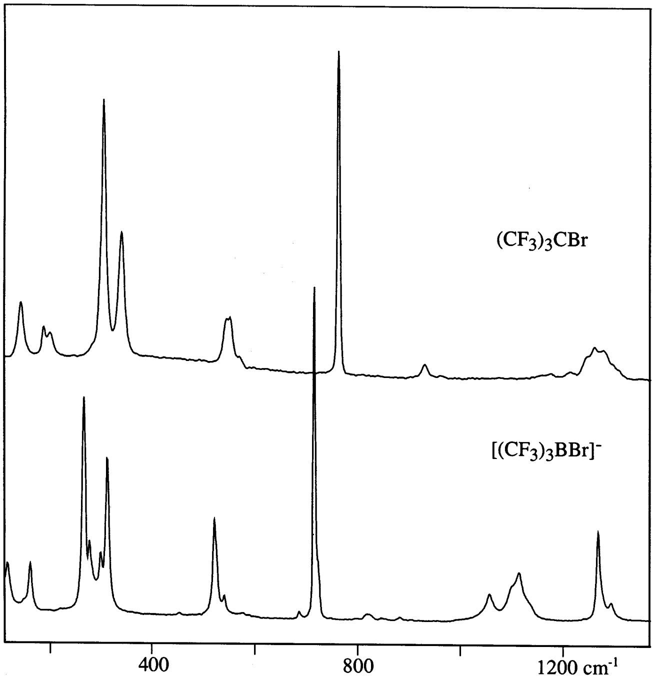


Fig. 11. Raman spectra of $(CF_3)_3CBr$ and $[(CF_3)_3BBr]^-$.

in Fig. 11, and the similarity of the two spectra is striking. In general all frequencies are lower for **38** than for $(CF_3)_3CBr$, indicating presumably weaker bonds. The bands in the range of 1300–1280 and 1140–1060 cm^{-1} are assigned to $\nu(CF_3)$ vibrations. These are associated with very strong infrared absorptions but medium to weak Raman lines. These vibrations are spread over a larger spectral region than in $(CF_3)_3CBr$. In the borates the $\delta_s(CF_3)$ modes are found at 715 and 686 cm^{-1}, the former appearing as a strong Raman line and the latter as a medium to strong infrared band. Features with medium infrared and Raman intensities occurring near 540 cm^{-1} are assigned to $\delta_{as}(CF_3)$ while $\rho(CF_3)$ is associated with weak infrared bands and medium to strong Raman lines at 340–280 cm^{-1}. The B–Br stretching vibration is strongly coupled with the C–C stretches and bendings of the skeleton and may be assigned to the strong Raman line at 266 cm^{-1}. The deformations of the C_3BBr skeleton are located below 200 cm^{-1}.

7. Conclusions and potential applications of perfluoroalkyl borates

Perfluoroalkyl groups alter dramatically the properties of boron compounds (aminoboranes, amine-boranes and borates) with regard to their non-fluorinated analogues. The CF_3 group, being strongly electron withdrawing so that it is often compared with chlorine, is however, incapable of back donation. On the other hand the CF_3 group is much larger than, e.g. a methyl group, and its effective steric demand is comparable with that of an isopropyl ligand. Perfluoroethyl or perfluorobutyl groups having similar electronic properties are even bulkier. Moreover R_f groups are poorer leaving groups than halides.

The yet unknown free $(CF_3)_3B$ molecule is presumably a "super" Lewis acid towards small, hard bases. This follows from the properties of its derivatives, e.g. ($[(CF_3)_3BX]^-$ (X = F, Cl, Br, NO_2, OH)). Due to the steric demand of perfluoroalkyl groups the B–C bonds are efficiently protected against oxidative cleavage, e.g. by halogens, by ozone, and electrochemically. This shielding would be even more efficient for tetrakis(perfluoroalkyl)borates $[(R_f)_4B]^-$. In such species the boron atom would be encapsulated by a sphere of fluorine atoms, and the negative charge spread over four ligands. Due to the bulkiness and the poor polarizability of fluorine atoms such species would be perfect *non* or *weakly coordinating anions*. They might resemble perfluoroalkanes which are known for their outstanding chemical inertness and might exceed the commonly used $[(C_6F_5)_4B]^-$ anion in this respect [2].

Potential applications for perfluoroalkyl borates are conceivable whenever non-coordinating stable anions are needed. They may be as useful co-catalysts as the above-mentioned tetrakis(pentafluorophenyl)borate. Compared to this species tetrakis(perfluoroalkyl)borates $[(R_f)_4B]^-$ are expected to be more stable against oxidation.

Our own work described in the present review is mostly focused on cesium salts of a selection of perfluoroalkyl borates because above all we were heading for crystalline material for intended X-ray investigations. In many cases these cesium salts were found to be exceedingly soluble both in water and organic solvents. Their conversion into lithium salts using a cation exchange resin is possible. Due to the smallness of the countercation the Li salts are expected to be hygroscopic and excellently soluble in organic solvents and thus are promising candidates for electrolytes in lithium-ion electric storage cells.

Moreover, perfluoroalkyl borates with functionalized (polymerizable) side chains like $[H_2C{=}CH–(C_6H_4)–(CF_3)_2BF]^-$ appear to be accessible by reactions similar to those presented in this review. Such a compound may be a useful monomer for polymers or oligomers with structures as shown in Fig. 12.

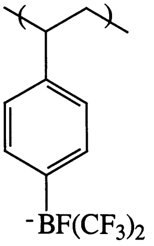


Fig. 12. Constitution of a poly(perfluoroalkylborate).

Altogether it is the aim of this contribution to point out the particular properties an arbitrarily chosen selection of borates can adopt when at the same time perfluoroorgano groups shield the boron atom and efficiently withdraw electron density from boron. We believe that such favorable properties will also apply to tris(perfluoroalkyl)boron derivatives of other groups and elements the synthesis of which has not yet been attempted. We note that the analogy of aminoboranes with polar olefins stressed in Ref. [1] is resembled by that of aminoborates with aminoalkanes and that of perfluoroalkylborates with perfluoroalkane derivatives.

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