Halogenation of $(CF_3)_3B{\cdot}NH_3$: *N*,*N*-Dihaloamino- and Halo-tris(trifluoromethyl)borates $[(CF_3)_3B{-}NX_2]^-$ and $[(CF_3)_3B{-}X]^-$, X = F, Cl, Br

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$(CF_3)_3B{\cdot}NH_3$ (**1**) reacts with cesium hypochlorite or hypobromite to form the respective *N*,*N*-dichloroamino- or *N*,*N*-dibromoamino-tris(trifluoromethyl)borates $Cs[(CF_3)_3B{-}NCl_2]$ (**2**) or $Cs[(CF_3)_3B{-}NBr_2]$ (**3**). Fluorination of **2** or **3** in CH_3CN yields $Cs[(CF_3)_3B{-}NF_2]$ (**4**) and $Cs[(CF_3)_3B{-}F]$ (**5**). The fluorination reactions produce numerous byproducts; one of these, $Cs[(CF_3)_3B{-}NH{-}COCBr_3]$ (**6**), has been isolated from the reaction of **3**. Compound **5** was also formed when **2** or **3** was treated with AgF_2. Pyrolysis of **2** at 190 °C and **3** at 140 °C yielded the haloborates $Cs[(CF_3)_3B{-}Cl]$ (**7**) and $Cs[(CF_3)_3B{-}Br]$ (**8**), respectively. The constitution of the novel borates has been deduced from multinuclear NMR, IR, Raman, and mass spectra. The structures of **6**, **7**, **8**, and $Cs[(CF_3)_3B{-}NH_2{\times}(CF_3)_3B{-}NH_3]$ (**1a**) have been investigated by single-crystal X-ray diffraction. **1a**: $C_6H_5B_2CsF_{18}N_2$, monoclinic, $C2/c$, $a = 22.802(5)$ Å, $b = 7.0965(13)$ Å, $c = 11.000(2)$ Å, $\beta = 102.79(2)°$, $Z = 4$, R1 = 0.0374, wR2 = 0.0945. **6**: $C_5HBBr_3CsF_9NO$, monoclinic, $C2/c$, $a = 20.121(4)$ Å, $b = 16.765(3)$ Å, $c = 10.005(2)$ Å, $\beta = 118.416(12)°$, $Z = 8$, R1 = 0.0680, wR2 = 0.1766. **7**: $C_3BClCsF_9$, cubic, $P2_13$, $a = 9.8059(9)$ Å, $Z = 4$, R1 = 0.0252, wR2 = 0.0639. **8**: $C_3BBrCsF_9$, cubic, $P2_13$, $a = 9.9001(14)$ Å, $Z = 4$, R1 = 0.0631, wR2 = 0.1490.

Introduction

The free Lewis acid $(CF_3)_3B$ is still an elusive molecule that needs stabilization by a base, typically NH_3 or amines.[1] In these acid−base adducts the B−N bond is quite resistant to chemical attack. In order to weaken and eventually cleave this bond we have investigated oxidation reactions of amine−boranes and aminoborates, and in a preceding paper we reported on the electrochemical and ozone oxidations of $(CF_3)_3B{\cdot}NH_3$ (**1**).[2] In alkaline solution, first the nitrogen of **1** is deprotonated to form the aminoborate $[(CF_3)_3B{-}NH_2]^-$ anion, which is then oxidized to yield the nitroborate $[(CF_3)_3B{-}NO_2]^-$, the azodioxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3B{-}N(O){=}N(O){-}B(CF_3)_3]^{2-}$, and the azoxy-bis-tris(trifluoromethyl)borate $[(CF_3)_3B{-}N{=}N(O){-}B(CF_3)_3]^{2-}$. Thus $[(CF_3)_3B{-}NH_2]^-$ behaves like a primary amine, the oxidation of which furnishes the corresponding derivatives. As far as the activation of the B−N bond in these oxidation products is concerned, enhanced reactivity of this linkage was observed only in $[(CF_3)_3B{-}N(O){=}N(O){-}B(CF_3)_3]^{2-}$, the B−N bonds of which are easily hydrolyzed to give the hydroxyborate $[(CF_3)_3B{-}OH]^-$. The other derivatives were found to be quite unreactive.

Replacement of hydrogen in $[(CF_3)_3B{-}NH_2]^-$ by halogen (Br, Cl, F) should decrease the donor ability of the nitrogen atom and thus weaken the B−N bond. Therefore we have investigated N-halogenation of **1** using hypochlorite or hypobromite, and the substitution of hydrogen by fluorine. Here we report on our observations.

Experimental Section

Equipment. NMR: Bruker ARX 400 (400 MHz, 100.6 and 376.5 MHz, for ^1H, ^{13}C, and ^{19}F respectively), Bruker AC 250 (79.8 MHz for ^{11}B). [D$_3$]Acetonitrile as solvent and internal standard; ^1H, $\delta_H = 1.95$; ^{13}C, $\delta_C = 1.30$; ^{19}F, external standard $CFCl_3$; ^{11}B, external standard $BF_3{\cdot}OEt_2$. IR: Bruker IFS 25. Raman: Cary 82, Kr$^+$ 647.1 nm. MS: Varian MAT 311 (70 eV). Thermogravimetry: Mettler TA4000.

Preparation of Compounds. Cesium Dichloroamino-tris(trifluoromethyl)borate (2) and Cesium Dibromoamino-tris(trifluoromethyl)borate (3). At 10 °C, Cl_2 was bubbled through a stirred solution of 4.3 g (14 mmol) of $(CF_3)_3B{\cdot}NH_3{\times}4H_2O$ and 7.5 mL of 50% CsOH in 20 mL of water, until the starting material had disappeared in the ^{19}F NMR spectra. Water was completely removed in vacuo at 20 °C, and the residue was stirred in dry acetone. The slurry was filtered, and the filtrate was taken to dryness in vacuo. The residue was dissolved in water, and crystals of **2** were grown by slow evaporation in the dark. Yield: 65%. IR (KBr)/Raman: ν = 1270/1271, 1140−1100/1140−1100, 1055/1053 (CF), −/676, 670/− (NCl_2). Calcd for $C_3BCl_2CsF_9N$ (435.65): C, 8.27; N, 3.22; Cl, 16.28. Found: C, 8.3; N, 3.2; Cl, 16.8.

At 10 °C 1.5 mL (30 mmol) of Br_2 was added to a stirred solution of 3.0 g (10 mmol) of $(CF_3)_3B{\cdot}NH_3{\times}4H_2O$ and 7.5 mL of $CsOH{\times}H_2O$ in 20 mL of water. Most of the $CsBrO_3$ and some **3** crystallized upon cooling of the mixture to 2−4 °C. The solution was filtered, and the filtrate was evaporated in vacuo. Crystallization from water was repeated four times, and finally crystals of **3** were grown in the dark by slow evaporation. Yield: 60%. IR (KBr)/Raman: ν = 1265/1260, 1130−1090/1130−1090, 1053/1050 (CF), 632/635, 613/605 (NBr_2). Calcd for $C_3BBr_2CsF_9N$ (524.55): C, 6.87; N, 2.67. Found: C, 7.6; N, 2.8.

Cesium Difluoroamino-tris(trifluoromethyl)borate (4) and Cesium Fluoro-tris(trifluoromethyl)borate (5). All fluorination experiments were carried out in Teflon PFA reaction vessels using a Teflon PFA/stainless steel vacuum line. The progress of the fluorination was monitored by recording ^{19}F NMR spectra of the reaction mixture.

Fluorination of 2 in Acetonitrile. After 2.0 g (4.5 mmol) of **2** had been dried at 50 °C in a Teflon PFA reaction tube connected to the vacuum line, the solid was dissolved in 10 mL of acetonitrile which

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(2) Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Eur. J. Inorg. Chem.* **1999**, 247−253.

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had been distilled over P_4O_{10}. The solution was stirred at −30 °C while a gentle flow of F_2/He (1/15) was bubbled through the solution using a 3.5 mm inlet tube. The fluorination was stopped immediately upon disappearance of the greenish color of the reaction mixture. Volatile material was removed in vacuo, and the residue was stirred in fresh acetonitrile. The slurry was filtered and the filtrate taken to dryness. Crystals of **4** were obtained after repeated crystallizations from aqueous solution. Yield: 5−10%. When F_2/He was passed through the solution for 20−30 min, **5** and $(CF_3)_3B\cdot NCCH_3$ were the main reaction products. However, if **5** is the desired product, fluorination of **2** should be preferentially carried out in anhydrous HF (AHF).

Fluorination of 2 (3) in AHF. **2** (2.0 g, 4.5 mmol) was dissolved in 7 mL of AHF, and a gentle flow of 5% F_2 in He was passed through the solution at −50 °C until the color of **2** had disappeared. All volatile material was removed in vacuo, and the residue was stirred in ether/water. The side products, $Cs[(CF_3)_2BF_2]$ and $Cs[CF_3BF_3]$, accumulate in the organic phase, whereas $Cs[(CF_3)_3BF]$ remains in the aqueous phase. Extraction of $Cs[(CF_3)_2BF_2]$ and $Cs[CF_3BF_3]$ with ether was repeated four to five times. Crystals of **5** were grown from aqueous solution. Yield: ca. 50%. Fluorination of **3** was carried out analogously and was stopped when the intense blue color of the reaction mixture had disappeared.

Fluorination of 2 with AgF_2. Finely powdered **2** (2.0 g, 4.5 mmol) was stirred for 2 days with 3.3 g (22.5 mmol) of AgF_2 (Aldrich) under dry nitrogen in the dark. The solution was filtered after the addition of 2−3 mL of dilute HCl. The filtrate was evaporated to dryness, and workup, as described above, yielded ca. 60% of **5**. IR (KBr)/Raman: ν = 1295/1300, 1110/− (CF), 792/− (BF). Calcd for C_3BCsF_{10} (369.73): C, 9.75. Found: C, 10.2.

Cesium Chloro-tris(trifluoromethyl)borate (7) and Cesium Bromo-tris(trifluoromethyl)borate (8). After drying of 1.0 g (2.29 mmol) of finely powdered **2** for 2 h at 50 °C and 10^{-3} mbar, the temperature was slowly raised and held for 10 h at 190 °C, while the solid material was agitated with a magnetic stirring bar. The solid residue was stirred in 5 mL of acetonitrile and filtered off. The collected filtrates from four pyrolysis runs were evaporated to dryness, and the residue was dissolved in hot water. Colorless crystals of **7** were obtained upon cooling with an ice bath. Single crystals were grown by slowly evaporating the aqueous solution at room temperature. Yield: ca. 55%. IR (KBr)/Raman: ν = 1295/−, 1280/1280, 1100/1100 (CF), −/360 (BCl). Calcd for $C_3BClCsF_9$ (386.19): C, 9.33; Cl, 9.18; F, 44.28. Found: C, 9.4; Cl, 10.5; F, 44.4. Compound **8** was obtained analogously in ca. 40% yield from **3**, the pyrolysis being carried out at 140 °C. IR (KBr)/Raman: ν = 1295/−, 1275/1272, 1120/1100 (CF), −/266 (BBr). Calcd for $C_3BBrCsF_9$ (430.64): C, 8.37; F, 39.71. Found: C, 9.0; F, 39.2. **WARNING:** Pyrolysis experiments should not be performed on a larger scale! Sometimes violent decomposition was observed when the starting material contained traces of $CsClO_3$ or $CsBrO_3$.

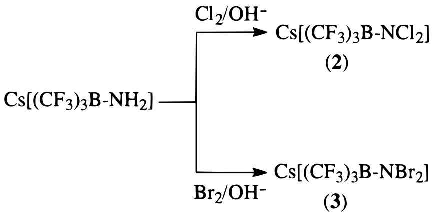
Crystallography. X-ray data on **1a**, **6**, **7**, and **8** were measured at room temperature with a Siemens P3 diffractometer employing graphite-monochromated radiation. The intensities were corrected for absorption by integration, ψ-scan data being used to hand-optimize the interfacial distances. A Patterson search technique was used to locate the cesium and seven fluorine atoms of **1a**, and the remaining atoms were found by difference Fourier syntheses. The ammine hydrogens appeared as two maxima of 0.55 e/Å^3 and a third of 0.37 e/Å^3 which was just 0.49 Å from an inversion center. Since an unconstrained refinement of the hydrogen coordinates gave N−H bond lengths with large standard deviations (0.09 Å), the hydrogen positions were idealized (N−H 0.90 Å, H−N−H 109.5°), and only the torsional orientation of the NH_3 group about the B−N bond and the isotropic temperature factors of the hydrogen atoms were varied. Direct methods led to the coordinates of the cesium and bromine atoms in **6**, the identification of the latter being based on their relative electron density, the lengths of the Br···Br contacts, and chemical plausibility. The amide hydrogen was placed geometrically, and only its isotropic temperature factor was refined. Direct methods yielded the positions of all atoms of **7**, which is isomorphous with **8**. Refinements were made on F^2 using all unique data with non-hydrogen atoms assigned anisotropic temperature factors. Extinction corrections were applied for **1a**, **6**, and **7**. Crystal data are summarized in Table 1. Structural solution, refinement and graphical display were all made with a SHELXTL[3] program package.

Table 1. Crystallographic Data

	1a	**6**	**7**	**8**
formula	$C_6H_5B_2CsF_{18}N_2$	$C_5HBBr_3CsF_9N$	$C_3BClCsF_9$	$C_3BBrCsF_9$
fw	601.65	645.52	386.20	430.66
a (Å)	22.802(5)	20.121(4)	9.8059(9)	9.9001(14)
b (Å)	7.0965(13)	16.765(3)	9.8059(9)	9.9001(14)
c (Å)	11.000(2)	10.005(2)	9.8059(9)	9.9001(14)
α (deg)	90	90	90	90
β (deg)	102.79(2)	118.416(12)	90	90
γ (deg)	90	90	90	90
V (Å^3)	1735.7(6)	2968.4(9)	942.9(1)	970.3(2)
Z	4	8	4	4
space group	$C2/c$	$C2/c$	$P2_13$	$P2_13$
T (°C)	293(2)	294(2)	294(2)	294(2)
λ (Å)	0.710 73	1.541 84	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	2.302	2.889	2.721	2.948
μ (mm^{-1})	2.312	29.875	4.311	8.032
$R(F)^a$ (all data)	0.0374	0.0680	0.0252	0.0631
$R_w(F^2)^b$ (all data)	0.0945	0.1766	0.0639	0.1490

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Scheme 1



(1)

Results

Ammine tris(trifluoromethyl)borane (**1**), which is highly soluble in water, is a weak acid with a pK_a value of 5 and behaves like an alkylammonium cation, with which it is isoelectronic.[1] Upon raising the pH of the aqueous solution to about 10, **1** is deprotonated to form the stable amino-tris(trifluoromethyl)borate anion $[(CF_3)_3B{-}NH_2]^-$, which is the analogue of a primary amine. The structures of **1** and of its tetrahydrate $(CF_3)_3B\cdot NH_3\times 4H_2O$ have been determined.[4] Attempts to obtain single crystals of $Cs[(CF_3)_3B{-}NH_2]$ furnished incidentally crystalline material which turned out to be the double salt $Cs[(CF_3)_3B{-}NH_2\times(CF_3)_3B{-}NH_3]$ (**1a**), the structure of which has now been determined.

When chlorine or bromine is added to an alkaline solution of **1**, rapid chlorination or bromination at nitrogen occurs to yield the *N*,*N*-dichloroamino-tris(trifluoromethyl)borate $[(CF_3)_3B{-}NCl_2]^-$ anion or the *N*,*N*-dibromoamino-tris(trifluoromethyl)borate $[(CF_3)_3B{-}NBr_2]^-$ anion. Both form stable, crystalline cesium salts (**2** and **3**) (Scheme 1).

Passing diluted fluorine gas through an alkaline aqueous solution of **1** failed to synthesize the homologous *N*,*N*-difluoroamino-tris(trifluoromethyl)borate $[(CF_3)_3B{-}NF_2]^-$, the nitroborate $[(CF_3)_3B{-}NO_2]^-$ being isolated instead.[2] Therefore the replacement of chlorine in **2** or bromine in **3** by fluorine was investigated. When a mixture of 5% fluorine in 95% helium was passed through a solution of **2** in dry acetonitrile at −30

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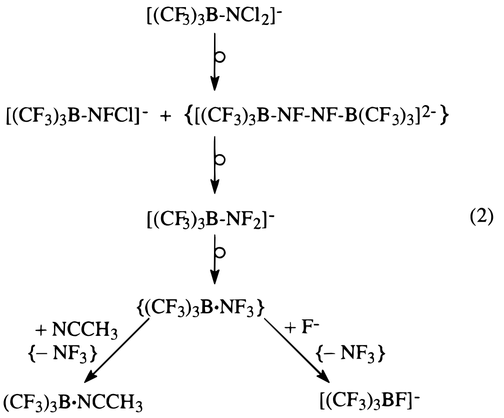
(3) Sheldrick, G. M. *SHELXTL PC Version 5.03: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(4) (a) Ansorge, A.; Brauer, D. J.; Bürger, H.; Krumm, B.; Pawelke, G. *J. Organomet. Chem.* **1993**, *446*, 25−35. (b) Meyer, C.; Dahlems, T.; Mootz, D. *Z. Kristallogr.*−*New Cryst. Struct.* **1998**, *231*, 201−202.

Scheme 2



°C, ^{19}F NMR spectra revealed that chlorine is successively replaced by fluorine. Altogether six ^{19}F NMR signals were assigned to the novel *N*-haloborates $[(CF_3)_3B{-}NClF]^-$, $[(CF_3)_3B{-}NF_2]^-$, and presumably $[(CF_3)_3B{-}NF{-}NF{-}B[(CF_3)_3]^{2-}$, the assignment being based on characteristic BF and FF coupling patterns. The CF_3 resonance of $[(CF_3)_3B{-}NClF]^-$ at −62.7 ppm is split by the ^{11}B nucleus into a quartet (^2J(BF) = 26.0 Hz), which is further split into doublets by ^4J(FF) coupling (9.1 Hz) with the NF fluorine atom, which give rise to a resonance at −35.7 ppm. Analogously the CF_3 resonance of $[(CF_3)_3B{-}NF_2]^-$ at −62.9 ppm appears as a quartet due to coupling with boron (^2J(BF) = 26.1 Hz), each line being split into a triplet (^4J(FF) = 7.6 Hz) by the NF_2 group having δ ^{19}F at 0.0 ppm. A CF_3 resonance at −65.0 ppm and a broad NF ^{19}F resonance at −24.9 ppm were tentatively assigned to the binuclear anion $[(CF_3)_3B{-}NF{-}NF{-}B[(CF_3)_3]^{2-}$. The CF_3 signal of the latter is split into a quartet of doublets by coupling to boron (^2J(BF) = 27.7 Hz) and the NF fluorine atom (^4J(FF) = 8.2 Hz). To the best of our knowledge ^{19}F NMR data on species containing an −NF−NF− unit like, e.g., the putative $CF_3{-}NF{-}NF{-}CF_3$ are not available in the literature.

Upon further treatment with fluorine, several additional ^{19}F resonances belonging to CF_3 groups appeared even before all of the starting material, **2** or **3**, had been consumed and the signals assigned to the NF-containing species had completely disappeared. One of the main products which was identified is the acetonitrile adduct $(CF_3)_3B{\cdot}NCCH_3$, the synthesis of which has already been described.[4a] A further species was identified as the fluoroborate $[(CF_3)_3BF]^-$.

The progress of the fluorination and the formation of products is depicted in Scheme 2.

The replacement of chlorine by fluorine is a smooth reaction up to the formation of $[(CF_3)_3B{-}NF_2]^-$. In the next step fluorine is expected to react according to:

$$[(CF_3)_3B{-}NF_2]^- + F_2 \rightarrow \{(CF_3)_3B{\cdot}NF_3\} + F^-$$

However, an NF_3 adduct is expected to be unstable, because $B(CF_3)_3$ should not behave much differently from BF_3, which shows no interaction with NF_3.[5] If NF_3 is indeed formed, then the B−N bond rapidly dissociates, the $(CF_3)_3B$ thus eliminated immediately reacting either with the solvent acetonitrile or with fluoride ion.

Fluorination of **3** proceeds analogously except that no experimental evidence for an intermediate $[(CF_3)_3B{-}NFBr]^-$ anion could be gathered. The signals tentatively assigned to $[(CF_3)_3B{-}NF{-}NF{-}B(CF_3)_3]^{2-}$ appeared with higher relative intensity than in fluorination experiments with **2**. Attempts to isolate $[(CF_3)_3B{-}NF_2]^-$ and $[(CF_3)_3BF]^-$ as cesium salts (**4** and **5**) proved tedious owing to their specific solubilities, and they could be isolated only in low yields.

In the course of these operations some crystalline material was isolated from a fluorination experiment performed with **3**. This was identified as $Cs[(CF_3)_3B{-}NH{-}COCBr_3]$ (**6**) with the help of an X-ray investigation. This species obviously arises from $(CF_3)_3B{\cdot}NCCH_3$, the hydrogens of which are replaced by bromine. Addition of OH^- across the NC bond during workup leads to formation of **6**. We assume that compound **6** belongs to a series of unidentified intermediates of the general formula $Cs[(CF_3)_3B{-}NH{-}COCH_nX_{(3-n)}]$ ($n = 0-3$; X = Cl, Br).

The problems encountered in the isolation of **5** from the complex reaction mixture stimulated us to look for other solvents for the fluorination of **2** and **3**. Anhydrous HF was tested and the fluorination proceeded smoothly to yield **5**, no **4** being formed at all. Similar results were obtained when finely powdered **2** or **3** was treated with F_2/He in the absence of any solvent, or when the *N*-haloborates were stirred with powdered AgF_2.

The thermal decompositions of **2** and **3** have been studied by thermogravimetric methods. That of **2** starts smoothly at 180−190 °C and accelerates at 220−250 °C until a total weight loss of 45% is reached. The decomposition of **3** proceeds in two distinct steps. In the first step, between 140 and 200 °C, a weight loss of 29% is found. The second step begins at 280 °C and is brought to completion at 300 °C. We suppose that the first step of the decomposition of **3** corresponds to the equation

$$Cs[(CF_3)_3BNBr_2] \rightarrow Cs[(CF_3)_3BBr] + {}^1/_2N_2 + {}^1/_2Br_2$$

which would imply a weight loss of 17%. To get more insight into this step, finely powdered **3** was slowly heated in a dynamic vacuum to 140 °C for 6 h, and the volatile decomposition products were collected in a −196 °C trap. In addition to the expected Br_2, a considerable amount of CF_3Br was found in the trap. The solid residue was mainly $Cs[(CF_3)_3BBr]$, contaminated with $Cs[(CF_3)_3BF]$ and $Cs[(CF_3)_2BF_2]$.

Analogously, $Cs[(CF_3)_3BCl]$ was prepared from **2** at 190 °C. The success of the pyrolysis reactions depends on the accurate temperature chosen and on the purity of **2** and **3**. **CAUTION:** When samples contaminated with $CsBrO_3$ or $CsClO_3$ were heated, explosions occurred, or formation of the nitroborate $Cs[(CF_3)_3BNO_2]$ was observed. Therefore such experiments should be carried out on a small scale with appropriate safety precautions.

Spectra and Properties

The NMR chemical shifts and coupling constants of **2**−**8** are gathered in Table 2 and are consistent with the proposed structures. $[(CF_3)_3BF]^-$ is the missing member of the series of trifluoromethyl-fluoroborates $[(CF_3)_{4-n}BF_n]^-$ ($n = 1-3$). In the ^{19}F NMR spectrum it shows a ^3J(FF) coupling of 4.8 Hz, which facilitates its identification. No such coupling has been observed for the related species $[(CF_3)_2BF_2]^-$ and $[CF_3BF_3]^-$ as is evident from a comparison of NMR data[6] given in Table 3. The ^{19}F chemical shift of the boron-bonded fluorine atom in **5** occurs at unusually high field, δ −230.0 ppm. This shift is larger than

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(5) Craig, A. D. *Inorg. Chem.* **1964**, *3*, 1628−1633.

(6) Pawelke, G.; Heyder, F.; Bürger, H. *J. Organomet. Chem.* **1979**, *178*, 1−4.

Table 2. NMR Spectral Data for **2**−**8**

	2	**3**	**4**	**5**	**6**	**7**	**8**
^{1}H NMR							
$\delta(NH)$					6.1		
^{19}F NMR							
$\delta(CF_3)$	−62.0	−61.8	−62.9	−69.0	−66.3	−65.8	−64.3
$^2J(BF)$	25.7	25.6	26.1	28.5	26.6	27.4	30.2
$^4J(FF)$			7.6				
$^3J(FF)$				4.8			
$\delta(NF)$			0.0				
$\delta(BF)$				−230.0			
$^1J(BF)$				59.0			
^{11}B NMR							
$\delta(B)$	−9.0	−8.2	−11.4	−7.3		−12.7	−14.9
$^2J(BF)$	25.7	25.6	26.0	28.5		30.2	30.1
$^2J(BF)$			4.0				
^{13}C NMR							
$\delta(CF_3)$	132.4	132.0	131.6	132.6	133.4	134.2	131.8
$^1J(BC)$	77.0	77.1	78.4	80.0	76.4	77.0	83.0
$^1J(CF)$	307.2	309.1	304.5	309.4	305.0	308.0	302.7
$\delta(CBr_3)$					42.9		
$\delta(CO)$					164.9		

Table 3. ^{19}F and ^{11}B NMR Spectral Data of Trifluoromethyl-fluoroborates $[(CF_3)_{4-n}BF_n]^-$ ($n = 1-3$)

$[CF_3BF_3]^-$	$[(CF_3)_2BF_2]^-$	$[(CF_3)_3BF]^-$
$\delta(CF_3) = -75.3$ (ppm)	$\delta(CF_3) = -73.9$ (ppm)	$\delta(CF_3) = -69.0$ (ppm)
$^2J(BF) = 33.6$ (Hz)	$^2J(BF) = 30.6$ (Hz)	$^2J(BF) = 28.5$ (Hz)
		$^3J(FF) = 4.8$ (Hz)
$\delta(BF) = -155.5$ (ppm)	$\delta(BF) = -180.5$ (ppm)	$\delta(BF) = -230.0$ (ppm)
$^1J(BF) = 39.7$ (Hz)	$^1J(BF) = 57.2$ (Hz)	$^1J(BF) = 59.0$ (Hz)
$\delta(B) = -1.7$ (ppm)	$\delta(B) = -2.2$ (ppm)	$\delta(B) = -7.3$ (ppm)

that registered for $(CF_3)_2BF-CF{=}NMe_2$ (δ −220.9 ppm),[7] which was previously believed to be the upper limit for a fluorine bonded directly to boron.

Infrared and Raman spectra of **2**, **3**, **5**, **7**, and **8** have been recorded. All of these novel borates possess the $(CF_3)_3B$ group, the typical vibrations of which have been discussed in ref 2. The two N−Cl stretching vibrations of compound **2** almost coincide and are assigned to a strong Raman line at 670 cm^{-1} and a strong infrared band at 676 cm^{-1}. In compound **3** the symmetric and antisymmetric N−Br stretches are separated from each other and associated with Raman lines and infrared bands near 632 and 610 cm^{-1}. The two stretching modes of the NF_2 group in **5** fall into the range of the skeletal vibrations of the $(CF_3)_3B$ group between 1000 and 800 cm^{-1}. They are ascribed to Raman lines/IR bands at 938/927 cm^{-1} and 847/845 cm^{-1}. Of particular interest are the B−X stretching vibrations in $[(CF_3)_3B-X]^-$ (**5**, **7**, and **8**). Just as in the isoelectronic species $(CF_3)_3C-X$ (X = F, Cl, Br), these vibrations should be strongly coupled with the stretching and bending vibrations of the BC_3 skeleton.[8] For the heavier homologues with X = Cl or Br, these vibrations are expected to be associated with strong Raman lines below 500 cm^{-1}. On the basis of this assumption, the B−Cl stretching vibration of **7** was assigned to a strong line at 360 cm^{-1}. In **8** the corresponding B−Br mode appears at 266 cm^{-1}. The B−F stretching vibration in **5** is expected at 800 cm^{-1} and should be associated with a weak Raman line and a more intense infrared absorption. Therefore an IR band of medium intensity at 792 cm^{-1} with a shoulder at high frequency (^{10}B) is assigned to the B−F stretch.

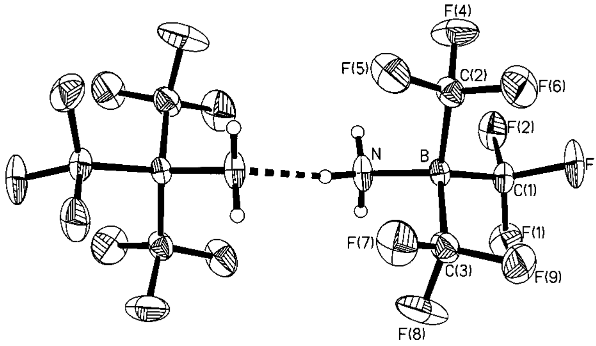

Figure 1. Perspective drawing of the anion of **1a** with 20% probability thermal ellipsoids for the non-hydrogen atoms. The bridging hydrogen atom is disordered over an inversion center, and only one of the two sites is shown.

Compound **2** was also investigated by electrospray mass spectrometry (ESI/negative spectrum, CH_3CN + 10% H_2O). This method has been successfully applied to the analysis of hydridoborates ($Cs[B_3H_8]$, $Cs_2[B_{10}H_{10}]$, ...).[9] Peaks of the anions with $m/e = 267$ $[(CF_3)_3B-NCl]^-$ (100%), $m/e = 302$ $[(CF_3)_3B-NCl_2]^-$ (75%), and $m/e = 198$ $[(CF_3)_2B-NCl]^-$ (50%), showing the correct isotopic patterns, confirm the constitution of **2**.

Compounds **2** and **3** are yellow and red-brown solids, respectively, which should be stored in the dark. They are soluble both in water and in polar organic solvents such as acetonitrile or acetone. However, depending on the temperature, these two *N*-haloborates act in these solvents as halogenating agents, $(CF_3)_3B{\cdot}NH_3$ being formed. While acetone is relatively stable toward **2** at 20 °C, it reacts readily with **3**; therefore separation from $CsBrO_3$ and purification are more difficult for **3** than for **2** (see Experimental Section).

Description of the Crystal Structures. The anions of **1a**, **6**, **7**, and **8** are widely separated in the solid state with no interanionic contacts which are markedly shorter than the sum of the corresponding van der Waals radii.[10] With B−C bond distances between 1.617(5) and 1.657(11) Å, tetrahedrally bonded boron atoms, and roughly staggered orientations for the trifluoromethyl groups, the geometries of the $B(CF_3)_3$ fragments of these compounds are not unusual.

In crystals of **1a**, inversion-related pairs of $[B(CF_3)_3NH_2]^-$ entities are linked by hydrogen bonding (Figure 1). Since the hydrogen bonding is markedly asymmetric, the anionic dimer might well be described as an ammine−amide which is disordered in the solid state; accordingly, the observed B−N bond should be a superposition of a $B-NH_3$ and a $B-NH_2^-$ interaction. In fact the distance found, 1.536(4) Å, falls between the values reported for **1**, 1.595(8) Å,[4a] and four-coordinate boron bonded to an amide with a localized nitrogen lone pair such as in the ylide adduct $B(CF_3)_2(NMe_2)CH_2PPh_3$, 1.500(4) Å.[11]

A view of the anion of **6** is given in Figure 2. Its constitution as a tribromoacetamido derivative is further substantiated by the reasonable agreement between the observed average C−Br bond length, 1.932(20) Å, and the average value found for such bonds in organic compounds, 1.966(29) Å.[12] Except for the 0.05(1) Å longer C(4)−C(5) bond (1.55(1) Å) in **6**, the dimensions of this acetamido group conform within experimental error with the values found for that in $B(CF_3)_2[CH(SiMe_3)_3$-

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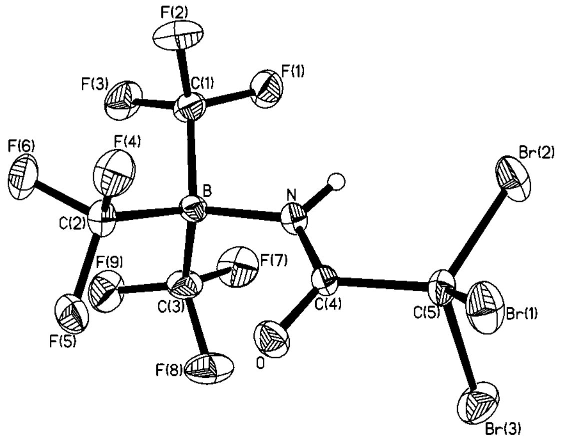

Figure 2. Perspective drawing of the anion of **6** with 20% probability thermal ellipsoids for all atoms except the hydrogen.

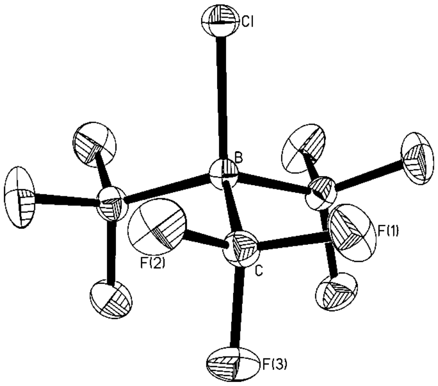

Figure 3. Perspective drawing of the anion of **7** with 20% probability thermal ellipsoids.

NHMe$_2$]NHC(O)Me.[13] In particular, the B−N bond lengths in the latter and **6** (1.558(4) and 1.547(10) Å, respectively) agree well. The variation of the N−B−C bond angles attests to appreciable steric interactions between the acetamido and a trifluoromethyl group; thus, the angle N−B−C(2), 113.8(6)°, is markedly larger than the average of the N−B−C(1) and N−B−C(3) angles, 107.0(11)°, the O···F(5) approach (2.79(1) Å) being particularly short.

Crystals of **7** and **8** are isomorphous with the cesium, boron, chlorine, and bromine atoms lying on crystallographic 3-fold axes. A view of the anion of **7** is given in Figure 3. The respective B−Cl and B−Br bond lengths, 1.861(6) and 2.029(17) Å, are not significantly longer than the average values tabulated for such bonds to four-coordinate boron, 1.833(13) and 2.017(31) Å, respectively.[12] In **7** the C−B−C′ bond angles, 110.8(2)°, are slightly but significantly larger than the Cl−B−C angle, 108.2(2)°. A similar trend is found in **8**, but the angles, 110.2(6) and 108.7(7)°, do not differ significantly.

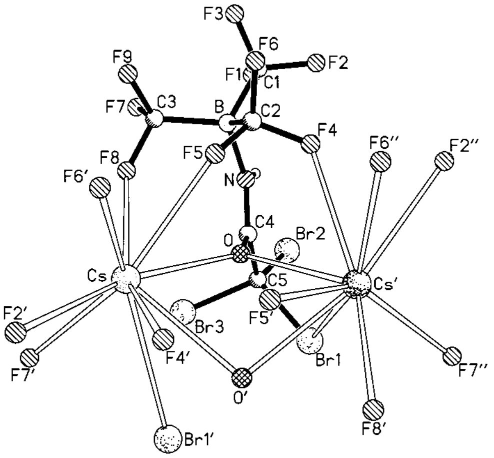

Figure 4. Bridging of a 2-fold related pair of cesium cations. Of the eight anions coordinated to the two cations, only one is displayed completely.

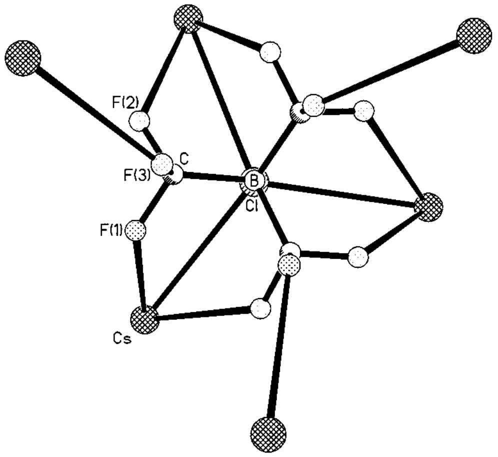

Figure 5. View along the C_3 axis of the anion of **7** showing the locations of the six closest cesium cations.

Because of the electrostatic nature of the attractive forces in the above-mentioned crystals, the contacts between the cesium cations and the anions are of interest. In **1a**, the cesium cation, which lies on a crystallographic C_2 axis, is surrounded solely by trifluoromethyl groups, and the 12 shortest Cs−F separations lie in the 3.129(4)−3.464(4) Å range.[14] With two Cs−O contacts of 3.056(8) and 3.164(8) Å, six Cs−F interactions in the 3.115(7)−3.339(8) Å range,[15] and a long Cs−Br(1) contact of 3.910(1) Å, the cation of **6** achieves an irregular nonacoordination. As shown in Figure 4, the anion coordinates in a tridentate fashion to two cations which are related by a crystallographic C_2 axis. The complex bridging interaction results in the shortest Cs−Cs′ distance (4.742(1) Å) of all of the presently reported structures. In **7** the cation forms nine contacts to fluorine in the 3.189(3)−3.366(4) Å range[16] and makes three Cs−Cl approaches of 3.713(1) Å. The Cs−Br contacts in **8** are somewhat longer, 3.760(1) Å, and the nine shortest Cs−F distances[17] are on the average 0.05 Å longer than in **7**. The expansion of the cation coordination sphere caused by replacement of chlorine by bromine is much less than the difference in the interionic distances in CsCl (3.56 Å) and CsBr (3.72 Å),[18] a fact which emphasizes the importance of the Cs−F interactions for determining the interionic separations. Of the six cations which surround each anion, three form short contacts to just one fluorine atom while the other three cations form short interactions with one chlorine and two fluorine atoms (Figure 5). This bridging leaves the cations widely spread, the shortest Cs−Cs′ distance in the two crystals being 6.375(1) Å. The hydrogen-bridged anion of **1a** also forms its Cs−F contacts with six widely separated cations (Cs−Cs′ ≥ 6.022(1) Å) whereas the anion of **6** makes contacts with five cations.

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(14) One further Cs−F approach < 4 Å: 3.838(4) Å.

(15) Three further Cs−F approaches < 4 Å: 3.659(10), 3.799(9), 3.989(8) Å.

(16) Three further Cs−F approaches < 4 Å: each 3.848(3) Å.

(17) Three further Cs−F approaches < 4 Å: each 3.846(9) Å.

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Discussion

N-Chlorination and N-bromination reactions of NH_3 attached to strong inorganic Lewis acids are rare. One example is sulfamic acid, which has in the solid state the structure of an ammine complex of SO_3 ($H_3N{\cdot}SO_3$). Its reactions with hypochlorite and hypobromite were studied as early as 1918 by Traube et al.[19] They showed that the replacement of one hydrogen by chlorine or bromine led to the formation of the stable salts $K[HNCl-SO_3]$ and $K[HNBr-SO_3]$. *N*,*N*-Dichlorosulfamate $[Cl_2N-SO_3]^-$, however, exists only in aqueous solution. Stable *N*,*N*-difluorosulfamic acid forms when SO_3 is reacted with HNF_2.[20]

The N-halogenation reactions of **1** leading to the *N*,*N*-dihaloborates **2** and **3** are indicative of the remarkable stability of the B−N bond; thus the deprotonated ammine complex behaves like a primary amine. *N*,*N*-Dihaloamines, RNX_2 (X = F, Cl, Br), with various groups R (R = Me, *t*-Bu, CF_3, C_2F_5, ...) are known. Their thermal stability depends, on one hand, on the group R and, on the other hand, on the halogen X. The stability of compounds bearing the same substituent R decreases from fluorine to bromine. The exothermic elimination of HX according to

$$R^1R^2CH-NX_2 \rightarrow R^1R^2C{=}NX + HX$$

is typical of species bearing a hydrogen on the α carbon atom. This reaction proceeds further to yield nitriles when R^1 or R^2 or both are also hydrogen atoms. Consequently, the RNX_2 compounds are particularly stable when the α carbon atom carries no hydrogen substituent (e.g., R = *t*-Bu[21] or C_nF_{2n+1}[22]). The $(CF_3)_3B^-$ anion, which is isoelectronic with the perfluoro-*tert*-butyl group, also fulfills this criterion, and this analogy offers a rationale for the extraordinary stability of **2** to **4**, of which **3** may well be the most stable $RNBr_2$ derivative prepared so far.

To our knowledge **2**−**4** are the first species with a N(halogen)$_2$ group attached to boron that have been isolated and characterized. In the reaction between trialkylboranes and NCl_3 discovered by H. C. Brown et al.,[23] the formation of R_2BNCl_2, $RB(NCl_2)_2$, and $B(NCl_2)_3$ has been postulated. However, no evidence has been offered to establish the constitution of the products which contain boron and nitrogen.

The thermal and hydrolytic stability of the three cesium haloborates **5**, **7**, and **8** deserves comment. The corresponding derivatives of trimethylborane $[(H_3C)_3BX]^-$ (X = F, Cl, Br) are unknown whereas ring-substituted triarylhaloborates $[Ar_3BX]^-$ (X = F, Cl) have been described.[24] Unlike BF_4^-, the tetrahaloborates BCl_4^- and BBr_4^- are only moderately stable, but they may be prepared using large counterions such as Cs^+, tetraalkylammonium, tropylium, etc. Both anions are rapidly hydrolyzed by water. Because the properties of the CF_3 group are often compared with those of chlorine and bromine, the B−Cl bond in $[(CF_3)_3BCl]^-$ and the B−Br bond in $[(CF_3)_3BBr]^-$ might also be expected to undergo hydrolytic cleavage. However, they are stable to water. The Lewis acidity of $(CF_3)_3B$ toward chloride or bromide is expected to be higher than that of Cl_3B or Br_3B because the CF_3 group has good withdrawing properties but, unlike the halides, is not capable of forming a pπ back-bond to tricoordinate boron. Thus, if one of the B−Cl bonds in the tetrahedral BCl_4^- anion is lengthened, the remaining three chlorine atoms can provide additional electron density by a pπ interaction as the BCl_3 skeleton is flattened. Since an analogous electron transfer from the three CF_3 groups in **7** cannot occur, the barrier for dissociation of $[(CF_3)_3BCl]^-$ into $(CF_3)_3B$ and Cl^- is much higher than for dissociation of BCl_4^- into Cl_3B and Cl^-. Although only cesium salts of **5**, **7**, and **8** were prepared, conversion into lithium salts using a cation exchange resin is possible. Due to the small countercation these 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.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1a** and **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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