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The effect of trifluoromethyl substitution on the B=N bond in trifluoromethyl-dimethylaminoboranes, $CF_3(R)BNMe_2$: crystal and molecular structure of $CF_3(Et)(NCCH_2)B \cdot NHMe_2$ ☆

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Abstract

Chloro-trifluoromethyl-dimethylaminoborane, $CF_3(Cl)BNMe_2$ (**I**), has been prepared from Cl_2BNMe_2 using the reagent combination $P(NEt_2)_3$–CF_3Br in sulpholane. Compound **I** undergoes [2 + 2] cycloaddition reactions with ^tBuNCO and Cl_2BNMe_2 to yield the four-membered heterocycles $CF_3(Cl)B\text{-}NMe_2\text{-}C(O)\text{-}N^tBu$ (**II**) and $CF_3(Cl)B\text{-}NMe_2\text{-}BCl_2\text{-}NMe_2$ (**III**). Addition of HCl to **I** formed $CF_3(Cl_2)B \cdot NHMe_2$ (**IV**). The Cl atom in **I** has been substituted by RMgX (R = Et or ^iPr) to yield the respective aminoboranes $CF_3(Et)BNMe_2$ (**V**) and $CF_3(^iPr)BNMe_2$ (**VI**). Compounds **V** and **VI** react slowly with CH_3CN in an ene-type reaction to form the amine-boranes $CF_3(Et)(NCCH_2)B \cdot NHMe_2$ (**VII**) and $CF_3(^iPr)(NCCH_2)B \cdot NHMe_2$ (**VIII**). The novel boron compounds have been characterized by multinuclear NMR, IR and mass spectra. The structure of **VII** has been determined by single-crystal X-ray diffraction.

Keywords: Boron; Trifluoromethyl; Crystal structure

1. Introduction

The reactivity of the B=N double bond in dimethylamino-dialkylboranes is greatly enhanced when both boron-bonded alkyls are replaced by CF_3 substituents. A common feature of the wide variety of reactions which are known for $(CF_3)_2BNMe_2$ (**A**) (cf. Scheme 1 of [1]) is the four-coordination of the boron atoms achieved in the corresponding products. Apparently, the strong electron-withdrawing power of the CF_3 groups makes the boron site much more susceptible to nucleophilic attack. Thus the inductive depletion of the electron density of the boron atom in **A** appears to expedite reactions which raise the boron coordination number.

Although the chemistry of **A** is now well established and documented, almost nothing is known about aminoboranes, $CF_3(R)BNMe_2$, which have just one CF_3 group attached to boron, the substituent R being an alkyl or halogen. Of such compounds, only $CF_3(Cl)BNEt_2$ and $CF_3(Br)BNEt_2$ have been described. These were obtained as byproducts in the trifluoromethylation of Cl_2BNEt_2 and Br_2BNEt_2 respectively, with the trifluoromethylating agent $P(NEt_2)_3$–CF_3Br in CH_2Cl_2 [2]. The addition of HCl and HBr across their B=N bonds has been studied. In order to investigate the effect of successive CF_3 substitution on the reactivity and chemical properties of aminoboranes, we first focused our efforts on the synthesis of $CF_3(Cl)BNMe_2$ and the related species $CF_3(R)BNMe_2$. More complex dialkylamino groups as in $CF_3(R)BNEt_2$ seemed to be currently of minor interest, since comparative experiments with $(CF_3)_2BNEt_2$ and $(CF_3)_2BNMe_2$ had shown that the latter more readily underwent [2 + 4] cycloaddition reactions [3]. Here we report our observations.

2. Results

2.1. Synthesis of trifluoromethyl-dimethylaminoboranes

Aminoboranes with two different groups R^1, R^2 attached to boron can be obtained by a ligand scrambling reaction, e.g.

$$Me_2BNMe_2 + Ph_2BNMe_2 \rightarrow 2MePhBNMe_2 \qquad (1)$$

☆ Dedicated to Professor P. Paetzold on the occasion of his 60th birthday.

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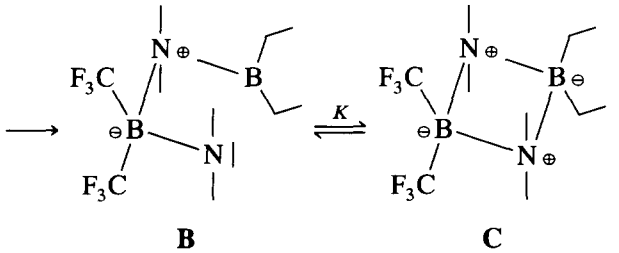
[4]. However, the temperature of 150°C which is required to initiate this reaction, lies far above the decomposition temperature of **A**, which already begins to decompose at 80°C. Therefore ligand scrambling according to

$$R_2BNMe_2 + (CF_3)_2BNMe_2 \nrightarrow 2CF_3(R)BNMe_2 \ (R = \text{alkyl}) \quad (2)$$

is not useful for the synthesis of the target molecules. While $^iPr_2BNMe_2$ does not react with **A**, Et_2BNMe_2 (and also Me_2BNMe_2) and **A** heterodimerize spontaneously at room temperature to form the head-to-tail dimer **B**. This is in equilibrium with the four-membered heterocycle **C** according to

$$Et_2BNMe_2 + (CF_3)_2BNMe_2$$

A



B **C**

(3)

The equilibrium constant $K = [\mathbf{B}]/[\mathbf{C}]$ has been determined in $CDCl_3$ solution by ^{19}F NMR spectroscopy in the temperature range 293–320 K. From the equations $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$, ΔH and ΔS were calculated: $\Delta H = 78 \pm 10$ kJ mol^{-1} and $\Delta S = 260 \pm 20$ J K^{-1} mol^{-1}.

Although solutions of **C** in C_6D_6 are stable at room temperature, addition of CH_3CN to such solutions led to the formation of $(NCCH_2)(CF_3)_2B \cdot NHMe_2$ [5]. This indicates that **C** is not only in equilibrium with **B** but both are in equilibrium with **A**. Since a simple ligand scrambling reaction involving **A** and appropriate dialkylaminoboranes failed, other pathways to species such as $CF_3(R)BNMe_2$ (R = alkyl) had to be found. Two approaches seemed promising either successive attachment of one CF_3 group and then of an alkyl group, i.e. pathway a

$$Cl_2BNMe_2 \rightarrow CF_3(Cl)BNMe_2 \rightarrow CF_3(R)BNMe_2$$

or pathway b

$$RB(NMe_2)_2 + RBBr_2 \rightarrow (R)BrBNMe_2 \rightarrow CF_3(R)BNMe_2$$

Both ways have their advantages and drawbacks, and it is not in general obvious which is the better way to start. We preferred pathway a for two reasons. First, since the trifluoromethylation of Cl_2BNMe_2 with two equivalents of $P(NEt_2)_3$–CF_3Br in sulpholane is known to furnish $(CF_3)_2BNMe_2$ with yields as high as 50–60% [6], we expected reasonable yields for a mono-trifluoromethylation reaction, too. Second, we knew that introduction of an alkyl group via a Grignard reaction would not affect the trifluoromethyl group.

The trifluoromethylation of Cl_2BNMe_2 with 1.1 equivalents of the reagent combination $P(NEt_2)_3$–CF_3Br follows roughly the stoichiometry indicated in

$$Cl_2BNMe_2 + 1.1P(NEt_2)_3\text{–}CF_3BR \rightarrow 1.1[BrP(NEt_2)_3]^{\oplus}Cl^{\ominus} + 0.3Cl_2BNMe_2 + 0.3CF_3(Cl)BNMe_2 + 0.4(CF_3)_2BNMe_2 \quad (4)$$

Experiments with different ratios of reactants showed that the maximum formation of $CF_3(Cl)BNMe_2$ (**I**) never exceeded 30% because also considerable amounts of the starting material Cl_2BNMe_2 as well as **A** were present in the reaction mixture. Separation of these three species turned out to be more difficult than expected. Although **A** could be separated by distillation over a slit-tube column under reduced pressure, Cl_2BNMe_2 and **I** possess similar volatilities; therefore the purity of **I** never exceeded 96% even after repeated distillation. Since each distillation is also accompanied by a considerable loss of material, the overall yield of **I** was only about 10–12%. The replacement of the chlorine by alkyl groups using Grignard reagents was straightforward and is described in the next section.

Pathway b was also tested, but the results were disappointing. The trifluoromethylation of $(Et)BrBNMe_2$ with one equivalent of $P(NEt_2)_3$–CF_3Br in sulpholane gave not only the desired product $CF_3(Et)BNMe_2$ (**V**) but also a bis-trifluoromethylated byproduct $[(CF_3)_2(Et)BNMe_2]^{\ominus}[BrP(NEt_2)_3]^{\oplus}$. Because the reaction mixture contained unreacted starting material, distillation over a slit-tube column was required for purification. Taking into account that the synthesis of $(Et)BrBNMe_2$ involves more steps than that of Cl_2BNMe_2, there is no advantage of pathway b over a; both are laborious and give unsatisfactory overall yields.

2.2. Reactions of trifluoromethyl-dimethylaminoboranes

We found that the reactivity of **I** was notably lower than that of **A**. For example, **I** did not form a [2 + 4] cycloaddition product with 2,3-dimethylbutadiene, nor did it undergo ene-type reactions with various carbonyl compounds, nitriles or alkenes tested. On the contrary, **I** reacted with ^{t}BuNCO to form a four-membered ring **II** according to

$$CF_3(Cl)BNMe_2 + {}^t\text{BuNCO} \rightarrow CF_3(Cl)\overline{B\text{–}NMe_2\text{–}C(O)\text{–}N}{}^t\text{Bu} \ (\mathbf{II}) \quad (5)$$

in analogy to a reaction of **A** [7]. Although dimerization of **I** was not observed, it combined with Cl_2BNMe_2 to form the four-membered heterocycle (**III**) according to

$$CF_3(Cl)BNMe_2 + Cl_2BNMe_2 \rightarrow CF_3(Cl)\overline{B{-}NMe_2{-}BCl_2{-}NMe_2}\ (\mathbf{III}) \quad (6)$$

Compound **I** added HCl readily across the B=N bond according to

$$CF_3(Cl)BNMe_2 + HCl\text{–ether} \rightarrow CF_3(Cl)_2B \cdot NHMe_2\ (\mathbf{IV}) \quad (7)$$

to yield the dimethylamine adduct of dichloro-trifluoromethylborane (**IV**). The chlorine in **I** has been substituted by an ethyl and isopropyl group using Grignard reagents in ether at −30°C according to

$$CF_3(Cl)BNMe_2 + RMgBr \rightarrow CF_3(R)BNMe_2 + MgClBr$$

$$R = Et\ (\mathbf{V})\ \text{or}\ {}^{i}Pr\ (\mathbf{VI}) \quad (8)$$

Because **I** could not be obtained free of Cl_2BNMe_2, **V** and **VI** thus obtained were also contaminated with Et_2BNMe_2 and $^{i}Pr_2BNMe_2$ respectively; therefore distillation at reduced pressure over a slit-tube column with about 30 theoretical plates was again necessary to obtain fairly pure material. Although $CF_3(Et)BNMe_2$ was carefully distilled, it sometimes contained considerable amounts of Et_2BNMe_2 according to NMR spectra. In the analogous reaction of **I** with PhMgBr, $CF_3(Ph)BNMe_2$ was formed and identified by NMR spectroscopy (^{1}H NMR: $\delta(N(CH_3)_2) = 2.98, 3.26$ ppm; $\delta(C_6H_5) = 7.6$ ppm; ^{13}C NMR: $\delta(N(CH_3)_2) = 39.8, 41.8$ ppm; $\delta(C_6H_5) = 127.6, 128.6, 131.9$ ppm; ^{19}F NMR: $\delta(CF_3) = -61.0$ ppm; ^{11}B NMR: $\delta(B) = 37.2$ ppm). Owing to its low thermal stability and poor volatility, accompanying traces of biphenyl and bromobenzene could not be removed.

Different types of reactions which **A** readily undergoes have been tested with **V** and **VI**. We have found that only the ene-type reaction with CH_3CN took place smoothly and led to isolable products with high yields according to

$$CF_3(R)BNMe_2 + CH_3CN \rightarrow CF_3(R)(NCCH_2)B \cdot NHMe_2$$

$$R = Et\ (\mathbf{VII})\ \text{or}\ {}^{i}Pr\ (\mathbf{VIII}) \quad (9)$$

While **A** underwent this type of reaction rapidly also with long-chain nitriles [4], **V** and **VI** reacted only with acetonitrile, the reaction time being days rather than minutes as found in the case of **A**.

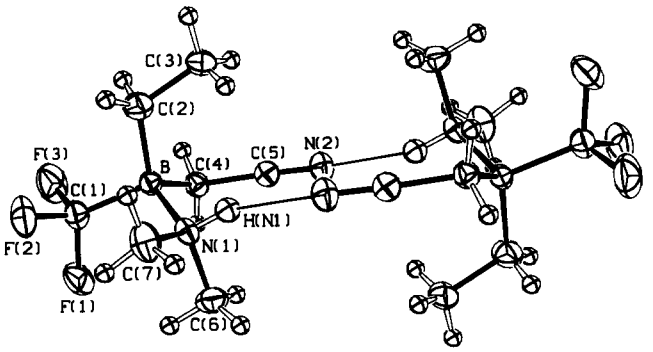


Fig. 1. A perspective drawing of a hydrogen-bonded dimer of **VII** with 20% probability thermal ellipsoids for the non-idealized atoms.

Table 1
Selected bond distances (Å) and angles (°) in $CF_3(Et)(NCCH_2)B{-}NHMe_2$

Bond lengths			
B–N(1)	1.616(4)	C(1)–F(1)	1.357(4)
B–C(1)	1.628(4)	C(1)–F(2)	1.336(4)
B–C(2)	1.604(5)	C(1)–F(3)	1.346(4)
B–C(4)	1.628(4)	C(2)–C(3)	1.476(5)
N(1)–C(6)	1.493(4)	C(2)–C(3A)	1.32(4)
N(1)–C(7)	1.488(4)	C(4)–C(5)	1.449(4)
N(1)–H(N1)	0.88(3)	C(5)–N(2)	1.128(4)
N(1)–N(2′) [a]	2.993(4)	N(2)–H(N1′)	2.20(3)
Bond angles			
N(1)–B–C(1)	109.6(2)	B–C(2)–C(3)	117.9(3)
N(1)–B–C(2)	110.9(3)	B–C(2)–C(3A)	124(2)
N(1)–B–C(4)	108.9(2)	B–C(4)–C(5)	114.6(2)
C(1)–B–C(2)	108.2(3)	C(4)–C(5)–N(2)	176.5(3)
C(1)–B–C(4)	106.2(2)	B–N(1)–C(6)	117.8(2)
C(2)–B–C(4)	112.8(3)	B–N(1)–C(7)	115.9(3)
B–C(1)–F(1)	115.3(3)	B–N(1)–H(N1)	105(2)
B–C(1)–F(2)	117.0(3)	C(6)–N(1)–C(7)	108.2(3)
B–C(1)–F(3)	112.7(3)	C(6)–N(1)–H(N1)	102(2)
F(1)–C(1)–F(2)	102.2(3)	C(7)–N(1)–H(N1)	107(2)
F(1)–C(1)–F(3)	103.0(3)	C(5)–N(2)–H(N1′)	153.4(8)
F(2)–C(1)–F(3)	105.1(3)	N(1)–H(N1)–N(2′)	149(3)

[a] $x', y', z' = 1-x, 2-y, 1-z$.

3. Description of the structure of $CF_3(Et)(NCCH_2)B \cdot NHMe_2$

The lability of the B–N bond in amine borane adducts is dependent on the nature of the other boron substituents. In particular, replacement of simple alkyl groups on boron by trifluoromethyl substituents greatly

Table 2
Comparison of bond distances (Å) in $CF_3(X)(NCCH_2)B \cdot NHMe_2$

	X = CF_3	X = C_2H_5
B–CF_3	1.627(3)	1.628(4)
B–CH_2CN	1.629(4)	1.628(4)
B–N	1.600(3)	1.616(4)
C–CN	1.454(4)	1.449(4)
C–N	1.124(5)	1.128(4)
N–CH_3	1.496(3)	1.490(4)

stabilizes the B–N linkage. Since the structure of $NCCH_2(CF_3)_2B \cdot NHMe_2$ (**D**) is known [5], we have determined the structure of **VII** in order to investigate the effect of CF_3/Et substitution on the B–N bond length.

Molecules of **VII** dimerize in the solid state by interaction of the amine hydrogen and cyano nitrogen atoms across inversion centres, 12-membered rings being formed (Fig. 1). In accord with this mode of hydrogen bonding, the N(1)–B–C(4)–C(5) fragment exhibits a *syn*-clinal conformation (torsion angle, −47.6(6)°). Interestingly, the corresponding fragment in **D** possesses an antiperiplanar conformation, hydrogen bonding linking those molecules into infinite chains. Despite these differences, very similar distances are found between the hydrogen donor and acceptor nitrogen atoms, 2.993(4) and 2.968(4) Å in **VII** and **D** respectively.

Three different types of alkyl group are attached to the boron atom in **VII**; therefore its structural parameters (Table 1) illustrate the effects of fluoro and cyano substitution on B–C bond lengths. The $B–CF_3$ bond is 0.024(6) Å longer than the $B–CH_2CH_3$ bond. This fluorination effect is not significantly smaller than that found in the cyclic adduct $(CF_3)_2B–CH_2–C(Me)=C(Me)–NMe_2$, 0.039(4) Å [3]. The equality of the $B–CF_3$ and $B–CH_2CN$ bond distances in **VII** attest to the surprisingly similar degree of B–C bond lengthening caused by either one cyano group or three fluorine substituents. Essentially equal values for the $B–CF_3$ and $B–CH_2CN$ bond lengths were also reported for **D**.

Important structural parameters of **VII** and **D** are compared in Table 2. The only significant difference involves the B–N bond lengths, which is 0.015(5) Å shorter in **D**. The tightening of this bond is the trend expected upon replacement of a simple alkyl substituent on the boron atom by a trifluoromethyl group.

Selected bond distances and angles are given in Table 1.

Table 3
NMR spectral data for **I–VII**, and **B** and **C** [a]

	I	II	III	IV	V	VI	VII	VIII	C	B
^1H										
δ (BC*H*) (ppm)						2.02		0.9		
δ (BCH_2CN) (ppm)							1.41	1.43		
							1.56	1.47		
δ ($NH(CH_3)_2$) (ppm)				2.68			2.52	2.56		
							2.57	2.62		
δ (N*H*) (ppm)				5.2			4.9	4.8		
							0.37			
δ ($CH_2–CH_3$) (ppm)					0.97		0.58		0.65	0.92
δ ($CH(CH_3)_2$) (ppm)						1.50		0.9		
δ ($N(CH_3)_2$) (ppm)	2.99	2.81	2.75		2.89	2.87			2.36	2.61
						3.36				2.67
δ ($CH_2–CH_3$) (ppm)					0.97		0.84		0.85	1.02
δ ($C(CH_3)_3$) (ppm)		1.36								
^{19}F										
δ (CF_3) (ppm)	−64.3	−67.2	−63.3	−71.0	−64.0	−59.4	−63.5	−62.4	−58.0	−62.7
^{11}B										
δ (*B*) (ppm)	31.6	1.8	4.9	2.8	37.0	38.3	−5.2	−4.1	−6.5	22.7
			11.6						7.7	43.2
^{13}C										
δ (BCH) (ppm)						15.0		14.0		
δ (BCH_2CN) (ppm)							≈ 5	1.9		
δ ($C(CH_3)_3$) (ppm)		52.8								
δ ($C(CH_3)_3$) (ppm)		27.9								
				39.4				38.8		
δ ($NH(CH_3)_2$) (ppm)								39.3		
δ ($CH(CH_3)_2$) (ppm)						17.3		19.2		
								19.7		
δ ($CH_2–CH_3$) (ppm)					14.6		8		9.9	9.8
δ ($CH_2–CH_3$) (ppm)					7.4		8.8		9.8	9.0
	39.3	40.7	45.1		39.9	40.2	38.6		44.3	41.0
δ ($N(CH_3)_2$) (ppm)	40.7	43.2	48.0			40.4	38.9			38.8
δ (C≡N) (ppm)							123.5	123.9		
δ (C=O) (ppm)		152.3								

[a] **I, II** and **IV–VII** in $CDCl_3$, **III** in CD_3CN, **B, C** in C_6D_6 (308 K). ^1H: 250.13 MHz, internal standard $CHCl_3$, 7.27 ppm, CD_2HCN, 1.95 ppm. ^{13}C: 62.9 MHz, internal standard $CDCl_3$, 77.0 ppm, CD_3CN, 1.30 ppm, C_6D_6, 128.0 ppm. ^{19}F: 84.67 and 235.37 MHz, internal standard $CFCl_3$. ^{11}B: 25.52 and 79.79 MHz, external standard $BF_3.OEt_2$.

4. Properties and spectra

Compounds **II**, **III**, **IV**, **VII** and **VIII** are colourless solids. Their melting points are given in Section 6. They are not sensitive towards air and moisture and are soluble in polar organic solvents such as CH_2Cl_2 and CH_3CN. The chemical stability of **IV** is surprising. In CH_2Cl_2 solution **IV** is stable to HCl even at 100°C and decomposes at 20°C only slowly upon contact with BCl_3 under formation of $FBCl_2$. The aminoboranes **I**, **V** and **VI** are volatile liquids, which are sensitive to moist air. Compound **C** is a volatile solid, which is slowly hydrolysed upon contact with water.

The ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **I–VII**, **B** and **C** were recorded. The shift data, which are set out in Table 3, are consistent with the proposed structures, and only a few comments will be necessary. As usual, the resonances of the CF_3 groups were not found in the ^{13}C NMR spectra due to quadrupole broadening by the boron nucleus. The structure of adduct **B** is derived from NMR spectra (Table 3), particularly from the ^{11}B shift data. The ^{11}B shifts in **B**($\delta^{11}B$ ($B(CF_3)_2$) = 22.7 ppm and $\delta^{11}B$ (BEt_2) = 43.2 ppm) are different from those in **A**($\delta^{11}B$ = 31 ppm) and Et_2BNMe_2 ($\delta^{11}B$ = 45.7 ppm) [8]. The fact that the BEt_2 resonance in **B** is closer to that in Et_2BNMe_2 than the $B(CF_3)_2$ resonance to that in **A** suggests a fourfold coordination for the boron of the $B(CF_3)_2$ moiety and reflects also the higher lability of the Et_2B–N bonds in the four-membered ring **C**.

Some electron impact mass spectral data are listed in Table 4. Compounds **VII** and **VIII** show the same base peak m/e = 115 and give a $[M + H]^+$ fragment as well as ions with $m/e > [M]^+$. This indicates association in the vapour phase.

5. Discussion

The experiments carried out with $CF_3(Cl)BNMe_2$ show that the substitution of one Cl in Cl_2BNMe_2 by CF_3 has little effect on the reactivity of the B=N bond except that the trifluoromethylated species shows no tendency to dimerize. Perhaps steric interactions involving the relatively bulky CF_3 groups effectively destabilize a cyclic dimer of **I**. The substitution of an alkyl group R (Et or ^{i}Pr) in R_2BNMe_2 by a CF_3 group significantly enhances the susceptibility of the B=N bond towards addition reactions. Although its reactivity in **V** and **VI** is much inferior than that in **A**, the ability of **V** and **VI** to undergo an ene-type reaction with acetonitrile is indicative of the enhanced bond polarity. Since the steric demand of an ^{i}Pr group is close to that of the CF_3 ligand, the increased reactivity of the B=N bond in the following series of molecules is dominated by electronic substitution effects:

$$^iPr_2BNMe_2 < (CF_3)(^iPr)BNMe_2 \ll (CF_3)_2BNMe_2$$

The failure of **VI** to undergo most of the reactions known for **A** suggests that at least two CF_3 groups have to be placed on boron in order to make it sufficiently electronically poor. This electronic imbalance of the boron can be relieved by increasing its coordination number.

6. Experimental section

6.1. Chloro-trifluoromethyl-dimethylaminoborane (I)

A stirred solution containing 40 g (0.320 mol) of Cl_2BNMe_2 in 500 ml of dry sulpholane was saturated with CF_3Br at 4°C, and a stream of CF_3Br was passed through as 87 g (0.352 mol) of $P(NEt_2)_3$ were added dropwise. When no further CF_3Br was being consumed, the reaction vessel was connected to a vacuum line and evacuated. Crude **I** was collected in a trap held at dry ice temperature when the reaction mixture was slowly heated to 85°C. The content of the dry-ice trap was subjected to an isothermal fractionated distillation at 15°C over a slit-tube column (Fischer; 30 theoretical plates). Two fractions were taken. The first fraction was a mixture of Cl_2BNMe_2 and **I**; the second was pure

Table 4
Electron impact mass spectral data in the order of decreasing intensity for **II–IV**, **VII** and **VIII**

Compound	m/e (relative intensity (%)) [fragment]$^+$
II	57 (100) $[C(CH_3)_3]^+$, 72 (90) $[OCN(CH_3)_2]^+$, 84 (25) $[OCNC(CH_3)_2]^+$, 193 (6) $[M - CF_2 - CH_3]^+$, 177 (3) $[M - CFCl - CH_3]^+$, 189 (2) $[M - CF_3]^+$, 243 (1) $[M - CH_3]^+$
III	125 (100) $[FCl_2B_2N]^+$, 90 (30) $[ClBN(CH_3)_2]^+$, 108 (25) $[FClBNCH_2CH_3]^+$, 99 (20) $[B(N(CH_3)_2)_2]^+$, 74 (10) $[FBN(CH_3)_2]^+$, 215 (8) $[M - CF_3]^+$, 165 (6) $[Cl_2B_2N_2(CH_3)]^+$, 140 (5) $[FCl_2B_2NCH_3]^+$, 199 (1) $[M - Cl_2 - CH_3]^+$
IV	94 (100) $[(F_2BNH(CH_3)_2]^+$, 110 (72) $[M - CF_2 - Cl]^+$, 74 (25) $[FBN(CH_3)_2]^+$, 126 (7) $[M - CF_3]^+$
VII	115 (100) $[FBCH_2CNHN(CH_3)_2]^+$, 74 (68) $[FBN(CH_3)_2]^+$, 94 (65) $[(F_2BNH(CH_3)_2]^+$, 104 (62) $[M - CF_2 - CH_2CN]^+$, 125 (18) $[M - CF_3]^+$, 195 (2) $[M + H]^+$
VIII	115 (100) $[FBCH_2CNHN(CH_3)_2]^+$, 74 (53) $[(FBN(CH_3)_2]^+$, 94 (35) $[(F_2BNH(CH_3)_2]^+$, 118 (16) $[M - CF_2 - CH_2CN]^+$, 139 (4) $[M - CF_3]^+$, 164 (4) $[M - C_3H_8]^+$, 209 (1) $[M + H]^+$

$(CF_3)_2BNMe_2$. The first fraction was again distilled similarly. Thus 5.1 g of **I** of 96% purity were obtained.

IR: ν(BN) 1545 s; $\nu(CF_3)$ 1135, 1085 vs; $\delta_s(CF_3)$ 710 s cm^{-1}.

6.2. *1-Chloro-1-trifluoromethyl-2,2-dimethyl-4-t-butyl-borata-2-azonia-4-azacyclobutan-3-one (II)*

tert-Butylisocyanate (2 g, 20 mmol) was added dropwise to a stirred ice-cold solution of 3.2 g (20 mmol) of $CF_3(Cl)BNMe_2$ in 20 ml of dry pentane. The reaction mixture was warmed to room temperature and stirred for 30 min; the solvent removed in vacuo and the solid residue sublimed (30°C(10^{-2} mbar)) (yield 4.4 g (85%); melting point (m.p.), 96°C).

IR: ν(C=O) 1815 vsb; $\nu(CF_3)$ 1110, 1090, 1080 vs; ν(BCl) 850 s cm^{-1}.

6.3. *1,3,3-Trichloro-1-trifluoromethyl-1,3-diborata-2,4-diazonia-cyclobutane (III)*

Cl_2BNMe_2 (0.138 g, 1.1 mmol) and **I** (0.340 g, 2.1 mmol) were sealed in a small ampoule and kept for 5 days at 20°C. The ampoule was opened, all unreacted material pumped off and the residue sublimed (yield, 0.167 g (53%); m.p., 133°C).

IR: $\nu(CF_3)$ 1085 vsb, 1030 vs, $\rho(CH_3)$ 940, 920 vs; ν(BCl) 820 vsb cm^{-1}.

6.4. *Dimethylamine-dichloro(trifluoromethyl)borane (IV)*

To a stirred solution of anhydrous HCl in 50 ml of ether, 1.9 g (12 mmol) of **I** were added dropwise at −78°C. The reaction mixture was warmed to room temperature, all volatile material removed in vacuo, and the solid residue sublimed (yield, 1.95 g (83%); m.p.; 94°C).

IR: ν(NH) 3190 s; $\nu(CF_3)$ 1105, 1090, 1075 vs; ν(BCl) 785 sb; $\delta_s(CF_3)$ 685 s cm^{-1}.

6.5. *Ethyl-trifluoromethyl-dimethylamino-borane (V) and trifluoromethyl-dimethylamino-isopropyl-borane (VI)*

(a) To a stirred solution of 63 mmol EtMgI in 100 ml of ether, 10 g (63 mmol) of **I** were added dropwise at −30°C. The reaction mixture was warmed to room temperature, the reaction vessel connected to a vacuum line and the crude **V** collected in a trap held at dry-ice temperature. Isothermal distillation at 15°C (about 8 mbar) over a slit-tube column yielded 1–1.5 of g **V** (10–16%).

(b) A stirred solution containing 25 g (0.15 mol) of $(Et)BrBNMe_2$ in 250 ml of dry sulpholane was saturated with CF_3Br at 4°C, and a stream of CF_3Br was passed through as 41 g (0.165 mol) of $P(NEt_2)_3$ were added dropwise. When consumption of CF_3Br ceased, the reaction vessel was connected to a vacuum line and evacuated; crude **V** collected in a trap held at dry-ice temperature while the vessel was slowly heated to 60°C. The content of the dry-ice trap was subjected to an isothermal fractionated distillation at 15°C(about 8 mbar) over a slit-tube column (yield, 2.8 g **V** (12%)).

Compound **VI** has been obtained analogously according to (a) with a 11% yield.

V: IR: ν(BN) 1560 m; $\nu(CF_3)$ 1110, 1080 vs 1065 sh; $\delta_s(CF_3)$ 716 s cm^{-1}.

VI: IR: ν(BN) 1538 s; $\nu(CF_3)$ 1106, 1076 vs; $\delta_s(CF_3)$ 715 s cm^{-1}.

6.6. *Dimethylamine-cyanomethyl-ethyl-trifluoromethyl-borane (VII) and dimethylamine-cyanomethyl-trifluoromethyl-isopropyl-borane (VIII)*

After condensing 73 mmol of dry CH_3CN onto 9 mmol of **V**, the reaction mixture was kept for 5 days at 20°C. The excess of CH_3CN was pumped off in vacuo, and sublimation of the residue gave **VII** with about 80% yield (m.p., 68°C). Similarly, **VIII** was obtained from **VI** and acetonitrile with about 77% yield. (m.p., 75°C).

VII: IR: ν(NH) 3161 s; ν(C≡N) 2235 s; $\nu(CF_3)$ 1066, 1045, 1030 vs cm^{-1}.

VIII: IR: ν(NH) 3180 s; ν(C≡N) 2240 s; $\nu(CF_3)$ 1070, 1050, 1032 vs cm^{-1}.

For elemental analyses see Table 5.

6.7 *Structure determination of $CF_3(Et)(NCCH_2)B-NHMe_2$ (VII)*

Crystal data on **VII** were obtained with a Siemens AED-1 diffractometer at 20°C employing Zr-filtered Mo Kα ($\lambda = 0.710\ 73$ Å) radiation and a crystal of dimensions $0.37 \times 0.37 \times 0.72$ mm. The compound crystallizes in the space group $P2_1/c$ with $a = 6.684(1)$, $b = 13.941(4)$, $c = 11.240(2)$ Å, $\beta = 102.50(2)°$, $Z = 4$ and $D_c = 1.260$ g cm^{-3}. Of the 3387 reflections measured ($5° \leqslant 2\Theta \leqslant 50°$), 1792 were unique, and 1225 were deemed observed ($F_0 \geqslant 4\sigma(F_0)$). The structure was solved by direct methods using SHELXS-86 [9] and refined by least-squares methods using SHELX-76 [10].

Table 5
Elemental analyses

Compound	Formula	Analy.: (Found; Calc) (%)		
		C	H	N
II	$C_8H_{15}BClF_3N_2O$	35.7; 37.17	6.1; 5.85	10.7; 10.84
III	$C_5H_{12}B_2Cl_3F_3N_2$	21.1; 21.06	4.4; 4.24	9.7; 9.82
IV	$C_3H_7BCl_2F_3N$	18.5; 18.40	3.6; 3.60	7.2; 7.15
VI	$C_6H_{13}BF_3N$	44.3; 43.16	8.3; 7.85	8.8; 8.39
VII	$C_7H_{14}BF_3N_2$	42.7; 43.34	7.4; 7.27	13.4; 14.44

Table 6
Atomic coordinates and thermal parameters of the non-idealized atoms of **VII**

Atom	x	y	z	U [a]
F(1)	−0.0972(3)	0.9206(2)	0.1082(2)	0.113(1)
F(2)	0.1119(4)	0.8357(2)	0.0407(2)	0.119(1)
F(3)	−0.0736(4)	0.7728(2)	0.1517(2)	0.132(1)
N(1)	0.3258(4)	0.9720(2)	0.2550(2)	0.0579(9)
N(2)	0.3011(4)	0.9542(2)	0.5720(2)	0.077(1)
C(1)	0.0432(6)	0.8500(3)	0.1424(3)	0.076(1)
C(2)	0.3762(7)	0.7843(3)	0.2864(3)	0.088(2)
C(3)	0.5353(6)	0.7827(3)	0.4002(4)	0.084(2)
C(3A)	0.392(6)	0.720(3)	0.373(3)	0.09(1)
C(4)	0.0893(4)	0.8785(2)	0.3758(3)	0.061(1)
C(5)	0.2055(5)	0.9196(2)	0.4880(3)	0.059(1)
C(6)	0.2036(6)	1.0615(2)	0.2561(4)	0.085(2)
C(7)	0.4365(6)	0.9793(3)	0.1539(3)	0.094(2)
B	0.2141(5)	0.8707(2)	0.2668(3)	0.056(1)
H(N1)	0.419(4)	0.978(2)	0.324(3)	0.053(8)

[a] $U = U_{iso}$ for C(3A) and H(N1); otherwise $U = \frac{1}{3}\Sigma_i\Sigma_j \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$.

The methyl carbon of the ethyl group is disordered over a major (C(3)) and minor site (C(3A)) of occupancies 0.88(1) and 0.12(1) respectively. While the coordinates of the H(N1) atom were not constrained, the methyl and methylene hydrogen atoms were refined as rigid groups (C–H, 0.95 Å). The refinement of the 147 parameters converged with $R = 0.062$ and $R_w = 0.081$. Residual density in the final difference Fourier synthesis varied between 0.26 and −0.15 electrons $Å^{-1}$. Coordinates of the non-idealized atoms are given in Table 6 [11].

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