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Amine adducts of bis(trifluoromethyl)borane, $(CF_3)_2BH$, crystal and molecular structure of $(CF_3)_2BH \cdot NMe_2CH_2Ph$

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Abstract

Trialkylstannanes R_3SnH (R = Me, Bu) and 9-BBN add to the B=N double bond in dimethylaminobis(trifluoromethyl)borane $(CF_3)_2B{=}NMe_2$ (**A**) to yield $(CF_3)_2BH \cdot NMe_2SnR_3$ and $(CF_3)_2BH \cdot NMe_2$-9-BBN respectively. Both hydrolyse to yield the dimethylamine adduct of bis(trifluoromethyl)borane $(CF_3)_2BH \cdot NHMe_2$ (**I**). Treatment of **I** with KOH in ether gave the salt $K[(CF_3)_2BHNMe_2]$ (**Ia**). The nitrogen in **Ia** has been alkylated with CH_3I, $ClCH_2Ph$, $ClCH_2CH{=}CH_2$ and $BrCH_2C{\equiv}CH$ to yield the respective amine boranes $(CF_3)_2BH \cdot NMe_3$ (**II**), $(CF_3)_2BH \cdot NMe_2CH_2Ph$ (**III**), $(CF_3)_2BH \cdot NMe_2CH_2CH{=}CH_2$ (**IV**) and $(CF_3)_2BH \cdot NMe_2CH_2C{\equiv}CH$ (**V**), whereas ring opening of 2-phenyloxirane led to $(CF_3)_2BH \cdot NMe_2CH_2CH(OH)C_6H_5$ (**VI**). **I–VI** have been characterised by elemental analyses, mass, IR and multinuclear NMR spectroscopy, and the crystal structure of **III** has been determined by X-ray methods.

Keywords: Adducts; Bis(trifluoromethyl)borane; X-ray

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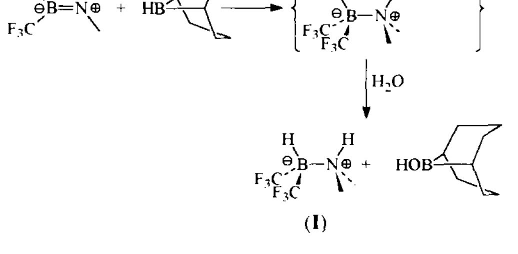
1. Introduction

Because of the strong electron withdrawing power of CF_3 groups, the chemistry of the B=N double bond in $(CF_3)_2B{=}NMe_2$ (**A**) more closely resembles that of a polar C=C bond than a B=N bond in aminodialkylboranes. Reactions of **A** which are unique in aminoborane chemistry are displayed in Scheme 1. Not only does **A** add H_2O, HF, HCl, and HBr [1] across the B=N double bond but it also undergoes [2,4] cycloaddition reactions with dienes [2] and ene type reactions with nitriles and carbonyl compounds [3]. Primary alkynes combine with **A** via a hydride transfer reaction [4] whereas addition of a third CF_3 group opens the way to derivatives of tris(trifluoromethyl)borane [5]. Diazoalkanes react with **A** under loss of N_2 to yield hitherto unknown azoniaboratacyclopropanes [6].

Hydroboration is a fundamental reaction of alkenes in which a B–H linkage adds across the double bond. In the course of our investigations into the chemical properties of amino-trifluoromethylboranes, the question arose of whether the B=N double bond in **A** could be hydroborated in a similar fashion. Hydrostannation is a related reaction, and in the following we report on hydroboration and hydrostannation reactions of **A** as well as on the reactivity of the resulting products.

2. Results

When **A** was added dropwise to a hexane solution of 9-BBN, the immediate formation of another species was indicated by the resonance of signal at −58.5 ppm in the ^{19}F NMR spectrum of the reaction mixture. We assume that this species is the product of an addition of 9-BBN to the B=N bond of **A**, as shown in Eq. (1).



(I)

(1)

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The N–B bond to the bicyclononane residue is readily cleaved upon contact with water. Separation of **I** from HO-9-BBN, however, proved to be difficult because these compounds possess not only similar volatility but also similar solubility in various solvents. In order to circumvent this problem, attempts were made to replace the hydroboration reagent with $BH_3 \cdot NMe_3$ and catecholborane. Whereas the former did not react, use of catecholborane led to attack on the CF_3 groups.

Hydrostannation of **A** was therefore attempted with R_3SnH (R = Me, Bu). We found that both stannanes add quantitatively across the B=N double bond according to Eqn. (2).

$$(CF_3)_2B{=}NMe_2 + R_3SnH \rightarrow (CF_3)_2BH \cdot NMe_2SnR_3$$
$$(R = Me, Bu) \qquad (2)$$

The covalent character of these addition compounds is suggested by the facts that both are oily liquids and that the ^{19}F NMR spectra are quite different for R = Me (−67.0 ppm) and R = Bu (−57.3 ppm). The Sn–N bond is rapidly cleaved upon contact with water to yield **I** as well (Eqn. 3).

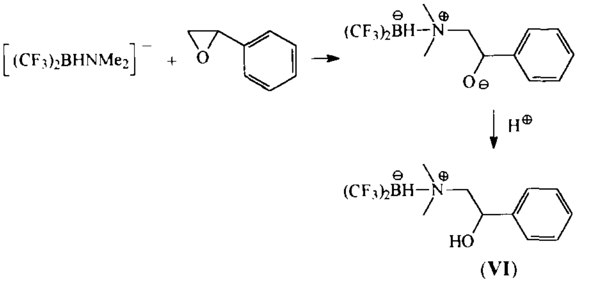
$$(CF_3)_2BH \cdot NMe_2SnR_3 + H_2O$$
$$\rightarrow (CF_3)_2BH \cdot NHMe_2 + HOSnR_3$$
$$(R = Me, Bu) \qquad (3)$$

Separation of **I** from Bu_3SnOH was greatly facilitated by their near immiscibility; Bu_3SnH is therefore the reagent of choice for the synthesis of **I**. The analogous diethylamine derivative $(CF_3)_2BH \cdot NHEt_2$ (**VII**), however, is only accessible using Me_3SnH [7].

The nitrogen in **I** is smoothly deprotonated by KOH in ether to give etheral solutions of the potassium salt (**Ia**). The salt reacts with methyl iodide, benzyl chloride, allyl chloride and propargyl bromide according to Eqn. (4) to yield the respective bis(trifluoromethyl)-borane adducts of tertiary amines (**II–V**).

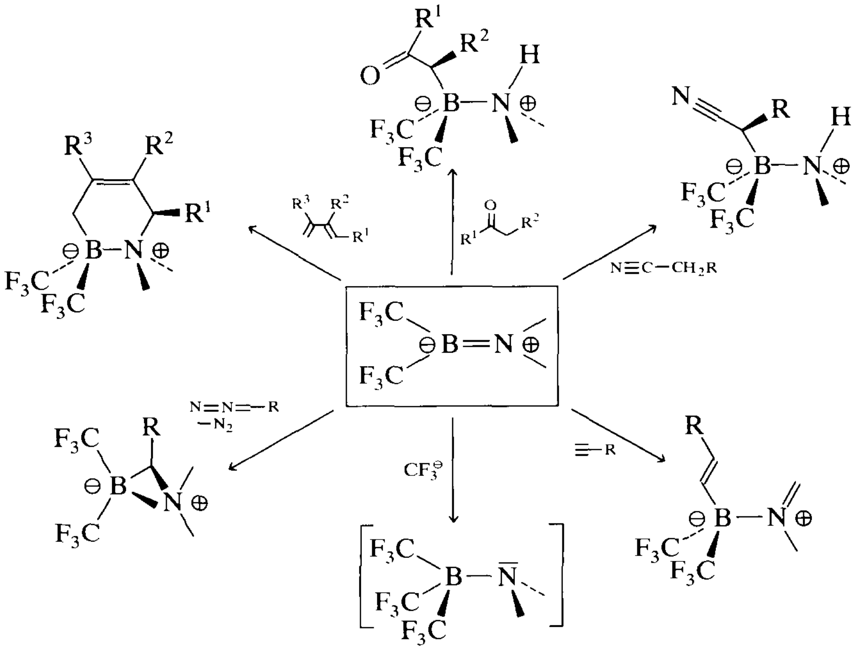
$$[(CF_3)_2BH\text{-}NMe_2]^- + R\text{–}X$$
$$\rightarrow (CF_3)_2BH \cdot NMe_2R + X^- \qquad (4)$$
$$X = I,\ R = CH_3(\mathbf{II});\ X = Cl,\ R = C_6H_5CH_2,\ (\mathbf{III});$$
$$CH_2{=}CHCH_2\ (\mathbf{IV});\ X = Br,\ R = HC{\equiv}CCH_2\ (\mathbf{V})$$

The rather rapid alkylation of **Ia**, which is faster than that of $[(CF_3)_3BNMe_2]^-$ [5], may be explained by the smaller steric requirement of the $(CF_3)_2BH$ fragment. The nucleophilicity of **Ia** is also demonstrated by a ring opening reaction of 2-phenyloxirane which yielded after treatment with HCl the β-hydroxy amine derivative (**VI**) according to Eq. (5).



(VI)

(5)



Scheme 1. Reactions of $(CF_3)_2B{=}NMe_2$.

Table 1
NMR spectral data for **I–VII** (δ in ppm) [a]

	I	Ia	II	III	IV	V	VI	VII [7]
^1H								
$\delta\ (\mathrm{CC}H_3)$								1.36
$\delta\ (\mathrm{NC}H_3)$	2.78	2.32	2.87	2.71	2.75	2.92	3.03 3.07	
$\delta\ (\mathrm{NC}H_2)$				4.28	3.66	3.93	3.16 3.41	3.01 3.31
$\delta\ (\mathrm{B}H)$	1.95	1.67	2.00	2.01	2.05	2.01	~ 2	~ 2
$\delta\ (\mathrm{N}H)(\mathrm{O}H)$	4.46						2.14	~ 3.2
$\delta\ (=\mathrm{C}H\mathrm{CH}_2)$					5.98			
$\delta\ (\mathrm{C}H\mathrm{OH})$							5.37	
$\delta\ (=\mathrm{C}H_2)$					5.49 5.58			
$\delta\ (\equiv\mathrm{C}H)$						2.66		
$\delta\ (\mathrm{C_6}H_5)$				7.39 7.50			7.38 7.39	
^{19}F								
$\delta\ (\mathrm{C}F_3)$	−60.4	−59.2	−58.0	−57.3	−58.0	−58.3	−58.1	−61.6
^{11}B								
$\delta\ (B)$	−10.0	−11.2	−8.0	−8.2	−8.2	−9.0	−8.0	−12.6
^{13}C								
$\delta\ (\mathrm{C}C\mathrm{H_3})$								12.7
$\delta\ (\mathrm{N}C\mathrm{H_3})$	41.8	44.0	53.0	47.8	48.4	48.4	49.5 51.3	
$\delta\ (\mathrm{N}C\mathrm{H_2})$				65.3	65.5	52.3	68.7	47.3
$\delta\ (C\mathrm{HOH})$							70.0	
$\delta\ (\mathrm{C}{=}C\mathrm{H_2})$					126.7			
$\delta\ (C{=}\mathrm{CH_2})$					126.2			
$\delta\ (C\equiv\mathrm{CH})$						79.6		
$\delta\ (\mathrm{C}\equiv C\mathrm{H})$						72.1		
$\delta\ (C_6\mathrm{H_5})$				128.2 128.9 130.1 132.9			125.3 128.9 129.1 140.8	

[a] **I**, **II–VII** in $CDCl_3$ **Ia** in CD_3CN. ^1H: 250.13 MHz. int. std. $CHCl_3$ = 7.27 ppm/CD_2HCN = 1.95 ppm. ^{13}C: 62.9 MHz. int. std. $CDCl_3$ = 77.0 ppm/CD_3CN = 1.30 ppm. ^{19}F: 84.67 MHz. int. std. $CFCl_3$. ^{11}B: 25.52 MHz. ext. std. BF_3-OEt_2.

3. Properties and spectra

The compounds **I–VI** are colourless volatile oily liquids or low melting solids, the melting points of which are given in the Experimental section. They are not sensitive towards air and moisture, and they are soluble in polar organic solvents like $CHCl_3$, CH_2Cl_2 and CH_3CN. They are remarkably thermally stable; for example, no decomposition was observed for IV even after prolonged heating to 160°C.

The ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **I–VI** were recorded. The shift data (Table 1) are consistent with the proposed structures, and only a few comments will be necessary. Except for **Ia** the BH resonance is hardly

Table 2
EI-mass spectral data for **I–VII** (m/e(%)[fragment]$^+$/)

I	76(100)[M − C_2F_5]$^+$/94(95)[M − C_2F_4H]$^+$/60(63)[$FBHNCH_3$]$^+$/106(34)[CF_3BNC]$^+$/126(10)[M − CF_3]$^+$/92(8)[$F_2BN{=}CH_2CH_3$]$^+$
II	108(100)[M − C_2F_4H]$^+$/90(91)[M − C_2F_5]$^+$/58(82)[$(CH_3)_2N{=}CH_2$]$^+$/74(41)[$FBHN{=}CH_2CH_3$]$^+$/ 92(19)[$F_2BN{=}CH_2CH_3$]$^+$/140(7)[M − CF_3]$^+$
III	91(100)[C_7H_7]$^+$/92(59)[$F_2BN{=}CH_2CH_3$]$^+$/65(55)[C_5H_5]$^+$/58(37)[$(CH_3)_2N{=}CH_2$]$^+$/ 135(12)[$FBHN{=}CHC_6H_5$]$^+$/166(1)[M − C_2F_5]$^+$
IV	74(100)[$FBHN{=}CH_2CH_3$]$^+$/73(85)[$(CH_3)_2NC_2H_5$]$^+$/58(47)[$(CH_3)_2N{=}CH_2$]$^+$/92(32)[$F_2BN{=}CH_2CH_3$]$^+$/ 134(14)[M − C_2F_4H]$^+$/116(10)[M − C_2F_5]$^+$/106(9)[CF_3BNC]$^+$
V	58(100)[$(CH_3)_2N{=}CH_2$]$^+$/74(70)[$FBHN{=}CH_2CH_3$]$^+$/82(34)[$FBHNCCCH$]$^+$/92(28)[$F_2BN{=}CH_2CH_3$]$^+$/ 132(13)[M − C_2F_4H]$^+$/114(9)[M − C_2F_5]$^+$
VI	58(100)[$(CH_3)_2N{=}CH_2$]$^+$/148(48)[$C_6H_5CHCHNH(CH_3)_2$]$^+$/105(36)[C_6H_5CO]$^+$/107(33)[C_6H_5CHOH]$^+$/ 77(33)[C_6H_5]$^+$/120(25)[$C_6H_5C_2H_3O$]$^+$/91(18)[C_7H_7]$^+$/133(16)[$C_6H_5CHCHNHCH_3$]$^+$/315(2)[M]$^+$
VII [7]	122(100)[M − C_2F_4H]$^+$/104(78)[M − C_2F_5]$^+$/106(46)[CF_3BNC]$^+$/92(22)[$F_2BN{=}CH_2CH_3$]$^+$/154(11)[M − CF_3]$^+$

detectable in the ^1H NMR spectra because of extreme line broadening. Reliable coupling constants could therefore only be obtained for **Ia**: ^1J BH = 90.0, ^3J HF = 11.9, ^2J BF = 25.3 Hz. In all other species the presence of a hydrogen directly bonded to boron gives rise to extremely broadened ^{11}B resonances. The ^{11}B chemical shifts fall into a narrow range between −9 and −12 ppm. As usual, the CF_3 groups were not found in the ^{13}C NMR spectra due to quadrupole broadening by the boron nucleus.

EI mass spectra of **I–VI** were recorded, and selected fragments and their relative intensities are set out in Table 2. Except for **VI**, molecular ions are very weak; the fragments $[M - C_2F_5]^+$ and $[M - C_2F_4H]^+$ are therefore taken as an indicator for the molecular weight. The latter ion, which was previously not observed for bis(trifluoromethyl)boron derivatives, is further proof of the presence of a B–H bond. Fragments of the aromatic ligand are dominant in the mass spectra of **III** and **VI**.

Infrared spectra are in general complex, and only some diagnostic vibrational bands are listed in the experimental section. The presence of a B–H group is unambiguously proven by medium absorptions for ν(B–H) between 2450 and 2470 cm^{-1}. The inductive strengthening of these B–H bonds by the CF_3 groups is underscored by the fact that the B–H vibration in $F_2BH \cdot NHMe_2$ occurs at significantly lower wavenumbers (2420 cm^{-1} [8]).

4. Description of the crystal structure

Crystals of **III** are composed of discrete molecules which possess crystallographic C_s symmetry. The H, B, N, C(3), C(4) C(7) and H(7) atoms lie on the mirror plane, and the phenyl group is oriented perpendicular to this plane. As seen in Fig. 1, a staggered conformation is found for all bonds connecting four-coordinate atoms. Selected bond distances and angles are given in Table 3.

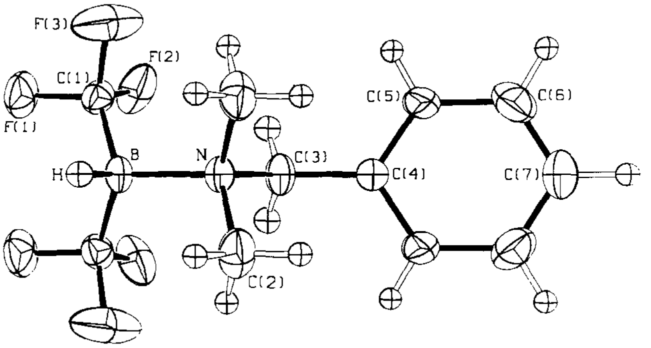


Fig. 1. A perspective drawing of III with 20% probability thermal ellipsoids except for the idealised hydrogen atoms.

Table 3
Selected bond distances (Å), and angles (°) in **III**

B–H	1.10(5)	N–C(2)	1.476(6)
B–C(1)	1.597(7)	N–C(3)	1.531(8)
B–N	1.636(8)	C(3)–C(4)	1.470(9)
C(1)–F(1)	1.328(6)	C(4)–C(5)	1.379(6)
C(1)–F(2)	1.309(6)	C(5)–C(6)	1.373(9)
C(1)–F(3)	1.320(6)	C(6)–C(7)	1.341(8)
H–B–C(1)	110(1)	B–N–C(2)	108.7(3)
H–B–N	102(2)	B–N–C(3)	113.2(5)
C(1)–B–N	112.7(4)	C(2)–N–C(2′)	106.7(6)
C(1)–B–C(1′) [a]	109.0(6)	C(2)–N–C(3)	109.7(3)
B–C(1)–F(1)	113.5(5)	N–C(3)–C(4)	116.0(6)
B–C(1)–F(2)	119.1(5)	C(3)–C(4)–C(5)	122.6(3)
B–C(1)–F(3)	115.6(5)	C(5)–C(4)–C(5′)	114.7(8)
F(1)–C(1)–F(2)	101.9(5)	C(4)–C(5)–C(6)	122.4(6)
F(1)–C(1)–F(3)	102.2(5)	C(5)–C(6)–C(7)	120.9(7)
F(2)–C(1)–F(3)	102.2(5)	C(6)–C(7)–C(6′)	118.8(9)

[a] x′, y′, z′ = x, 1.5 − y, z.

The B–N bond length in **III** is significantly longer than those reported for other acyclic amine trifluoromethylborane adducts (Table 4), but B–N distances comparable to that of **III** have been reported for some cyclic adducts in which the trifluoromethylborane coordinates to a tertiary amine (Table 4). The structure of $(CF_3)_2\overline{BNMe_2C}(SiMe_3)Bz$ presents a notable exception—its anomalously short B–N distance occurs in a three-membered ring [6].

The large spread (5.6(7)°) of the B–C–F angles might be a response to the different steric requirements of the boron substituents. These decrease in the order $NMe_2Bz > CF_3 > H$, and the CF_3 group is tilted accordingly. Similarly, the relative large B–N–C(3) angle shows that the amine substituent is tipped away from the CF_3 groups towards the B–H bond.

Table 4
B–CF_3 and B–N bond distances (Å) in amine trifluoromethylborane complexes

	B–C	B–N	Ref.
Acyclic			
$(CF_3)_2BF \cdot NHMe_2$	1.612(8)	1.584(7)	[1]
$(CF_3)_2BOH \cdot NHMe_2$	1.624(4)	1.602(3)	[1]
$(CF_3)_3B \cdot NH_3$	1.612(9)	1.595(8)	[9]
$(CF_3)_3B \cdot NH_2Et$	1.615(6)	1.589(5)	[5b]
$(CF_3)_3B \cdot NHEt_2$	1.613(6)	1.596(8)	[5b]
$(CF_3)_3B \cdot NH(CH_2)_6$	1.631(7)	1.606(8)	[10]
$(CF_3)_2BC(N_2)C(O)OEt \cdot NHMe_2$	1.620(6)	1.612(4)	[6]
$(CF_3)_2BCH_2CN \cdot NHMe_2$	1.627(3)	1.600(3)	[3]
$(CF_3)_2BH \cdot NMe_2Bz$	1.597(7)	1.636(8)	
Cyclic			
$(CF_3)_2\overline{BNMe_2C}(SiMe_3)Bz$	1.612(6)	1.560(5)	[6]
$(CF_3)_2\overline{BNMe_2C(O)N}{}^tBu$	1.619(7)	1.635(8)	[11]
$(CF_3)_2\overline{BNMe_2C(S)N}{}^tBu$	1.63(1)	1.61(1)	[11]
$(CF_3)_2\overline{BNMe_2CH_2CMeCMeCH_2}$	1.638(3)	1.621(3)	[12]
$(CF_3)_2\overline{BNEt_2CH_2CMeCMeCH_2}$	1.64(1)	1.633(6)	[12]
$(CF_3)_2\overline{BNEt_2CH_2CMeCMeO}$	1.64(2)	1.64(1)	[12]

Although the B–C(1) distance in **III** is measurably shorter than those of the other compounds listed in Table 4, values of several entries are not significantly longer. The apparent shortness of the C–F distance in **III** (average 1.319(9) Å) is probably an artefact of the large fluorine thermal displacements. The remaining structural parameters are normal.

5. Discussion

Compounds with a B–H bond are potential hydroboration reagents. Such reducing agents fall into categories, such as hydroborates, boranes (three coordinate species with B–H bonds), and borane complexes with amines, ethers, etc. While hydroborates are viewed as nucleophilic reducing agents, boranes are their electrophilic counterpart. Borane complexes with e.g. amines are somewhere in between, depending on the steric and electronic properties of the amine.

The presence of two CF_3 groups attached to boron influences the character of the B–H bond in **I** remarkably. Attempts to use **I** for hydroboration reactions with alkenes and alkynes failed. Even **IV** and **V**, which contain olefinic and acetylenic bonds respectively, show no tendency to undergo such reactions even when heated to 100°C for a week. This failure is due to the strengthened B–N bond in bis(trifluoromethyl)borane-amines which are better characterised as 'neutral ammonium salts' rather than as amine adducts. A requirement for the hydroboration reaction is that boron can exist in the tricoordinated state. Therefore the deficient reactivity of **I–VI** is further proof for the absolute integrity of their B–N bond.

6. Experimental section

6.1. *Dimethylamine-bis(trifluoromethyl)borane (I)*

Under stirring 12.5 g (65 mmol) $(CF_3)_2BNMe_2$ were added dropwise to 19.2 g (66 mmol) Bu_3SnH (Aldrich) at 10°C. Volatile by-products and other impurities were removed in vacuo and 4 ml H_2O was added while stirring was continued for 20 min. Excess water was removed at 45°C/10^{-1} torr and the lower layer, which was almost pure **I**, was separated and washed twice with 25 ml pentane. Distillation at 65°C/10^{-2} torr yielded 10.9 g (86%) **I**: mp. 8°C; IR (cm^{-1}): 3280s ν(NH), 2471m ν(BH), 1098vs, 1050 vs $\nu(CF_3)$.

Table 5
Elemental analyses

Compound	Formula	Analyses (Found(calc.)%)		
		C	H	N
I	$C_4H_8BF_6N$	24.53 (24.65)	4.19 (4.14)	7.20 (7.19)
II	$C_5H_{10}BF_6N$	28.81 (28.74)	4.79 (4.82)	6.76 (6.70)
III	$C_{11}H_{14}BF_6N$	46.73 (46.35)	4.89 (4.95)	4.97 (4.91)
IV	$C_7H_{12}BF_6N$	35.66 (35.78)	5.21 (5.15)	5.95 (5.96)
V	$C_7H_{10}BF_6N$	36.04 (36.09)	4.42 (4.33)	5.98 (6.01)
VI	$C_{12}H_{16}BF_6NO$	45.52 (45.75)	5.06 (5.12)	4.47 (4.45)

6.2. *Potassium bis(trifluoromethyl)dimethylaminohydridoborate (Ia), trimethylamine-bis(trifluoromethyl)borane (II), Benzyldimethylamine-bis(trifluoromethyl)borane (III), Allyldimethylamine-bis(trifluoromethyl)borane (IV), Dimethylpropargylamine-bis(trifluoromethyl)-borane (V). General procedure*

To a stirred solution of 2.0 g (10.3 mmol) **I** in 30 ml ether, 4 g powdered KOH were added as stirring was continued for 15 min. The solution was filtered and removal of the ether in vacuo at ambient temperature left pure **Ia**. To a stirred solution prepared as described above (11 mmol) CH_3I, $ClCH_2C_6H_5$, $ClCH_2CH{=}CH_2$, $BrCH_2C{\equiv}CH$ were added respectively. After 2 h the solution was filtered, and ether and excess alkylating agent were removed in vacuo at ambient temperature and the products were sublimed at 45°C C/10^{-2} torr. Yields: **II** 96% m.p. 53°C; **III** 89% m.p. 44°C; **IV** 94% m.p. 14°C; **V** 92% m.p. 37°C.

IR(cm^{-1}): **II** 2459m ν(BH), 1104vs, 1049vs $\nu(CF_3)$; **III** 2452m ν(BH), 1102vs; 1062vs $\nu(CF_3)$; **IV** 2468m ν(BH), 1644w ν(C=C), 1102vs, 1062vs $\nu(CF_3)$; **V** 3307m ν(≡CH), 2467m ν(BH), 2134vw ν(C≡C), 1108vs, 1057vs $\nu(CF_3)$.

6.3. *N,N-dimethyl-2-phenyl-2-hydroxyethylamine-bis(trifluoromethyl)borane (VI)*

To a solution of **Ia** prepared from 4.7 g (24 mmol) **I** as described above 2-phenyloxirane (24 mmol) was added and stirred overnight at ambient temperature. The reaction mixture was was brought to pH 6 using dil. HCl, the organic layer separated and dried over $MgSO_4$. Distillation at 10^{-2} torr yielded at 65–70°C, 0.3 g **I** and at 90–95°C 5.9 g **VI** (78%). IR(cm^{-1}): 2465m ν(BH), 1102vs, 1060vs $\nu(CF_3)$; for elemental analyses see Table 5.

6.4. *X-ray structural determination of* III

A crystal of **III** having the dimensions 0.35 × 0.48 × 0.56 mm^3 was grown by slow sublimation and sealed in a glass capillary. Crystallographic data were determined at 24°C with a Siemens AED-1 diffractometer employing Zr filtered Mo K_α radiation (λ 0.71073 Å). Crystals of **III** belong to the orthorhombic space group *Pnma* with $a = 9.874$ (3), $b = 12.122(4)$, $c = 11.132$ (3) Å, $Z = 4$ and $D_c = 1.42$ g cm^{-3}. The 2764 reflections measured (hkl, $\bar{h}$kl, $5 \leq 2\theta \leq 50°$) were corrected for

Table 6
Coordinates and temperature factors [Å^2] for the non-idealised atoms of **III**

Atom	x	y	z	U
F(1)	0.0131(4)	0.6384(3)	−0.2853(3)	0.136(2)
F(2)	−0.0715(5)	0.6255(4)	−0.1178(3)	0.149(2)
F(3)	0.1080(5)	0.5476(3)	−0.1533(5)	0.199(3)
N	0.1783(5)	0.7500	0.0064(4)	0.061(2)
C(1)	0.0456(6)	0.6428(5)	−0.1697(5)	0.081(2)
C(2)	0.2641(7)	0.8477(5)	0.0279(5)	0.109(3)
C(3)	0.0593(7)	0.7500	0.0947(6)	0.078(3)
C(4)	0.0951(6)	0.7500	0.2228(6)	0.060(2)
C(5)	0.1106(7)	0.6543(5)	0.2882(5)	0.099(3)
C(6)	0.1436(7)	0.6548(6)	0.4080(6)	0.120(3)
C(7)	0.1616(8)	0.7500	0.4672(7)	0.095(4)
B	0.1307(8)	0.7500	−0.1344(6)	0.064(3)
H	0.229(5)	0.7500	−0.182(4)	0.04(1)

$U = U_{iso}$ for H, otherwise $U = \frac{1}{3}\Sigma_i U_{ii}$.

the variations (0.98–1.08) found for the three hourly monitored standard reflections and absorption (μ = 1.4 cm^{-1}, transmission:0.9348–0.9663). The data were merged to give 1230 unique reflections, of which 794 were considered observed ($F_o \geq 4\ \sigma(F_o)$).

The structure was solved by direct methods and refined by least-squares techniques using the programs SHELXS-86 [13a] and SHELX-76 [13b], respectively. The coordinates of the hydrogen atoms bonded to the boron and nitrogen atoms were taken from a difference Fourier synthesis and refined isotropically. The other hydrogen atoms were positioned geometrically (C–H 0.95 Å) and allowed to ride on the corresponding carbon atoms. Refinement of the 100 parameters converged with $R = 0.084$ and $R_w = 0.105$. The final difference Fourier synthesis (0.37 to −0.36 e/Å^3) revealed no chemically significant feature. The coordinates of the nonidealised atoms are given in Table 6, and the numbering scheme is defined in Fig. 1 — nonlabelled hydrogen atoms are numbered after the carbon atom to which they are bonded [14].

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References and notes

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[14] Additional crystallographic details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the deposit number CSD-401167, the names of the authors and the literature reference.