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Reactions of trifluorovinyl-trifluoromethylboron derivatives, structure of $(F_2C{=}CF)(F_3C)_2B{\cdot}NHMe_2$ and $(HOOC)(F_3C)_2B{\cdot}NHMe_2$

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Dedicated to Professor Othmar Stelzer on the occasion of his 60th birthday

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Abstract

Dimethylamino-bis(trifluoromethyl)borane, $(F_3C)_2BNMe_2$ (**1**) reacts with 1,1,1,2-tetrafluoroethane in the presence of *t*BuLi to yield the dimethylamine borane $(F_2C{=}CF)(F_3C)_2B{\cdot}NHMe_2$ (**2**). Compound **2** was alkylated at nitrogen with CH_3I/KOH or benzyl chloride/KOH in ether to yield the amine boranes $(F_2C{=}CF)(F_3C)_2B{\cdot}NMe_3$ (**2a**) or $(F_2C{=}CF)(F_3C)_2B{\cdot}NMe_2Bzl$ (**2b**). Both **2** and **2a** add bromine across the C=C bond to form the respective $F_2BrC–CFBr$ derivatives **3** and **3a**. A solution of **2** in $CHCl_3$ reacts with ozone to give a 9:1 mixture of (*cyclo-O*-CF_2–CF)$(F_3C)_2B{\cdot}NHMe_2$ (**4**) and $(HOOC)(F_3C)_2B{\cdot}NHMe_2$ (**5**), and the reaction of ozone with **2a** yields a mixture of the analogous trimethylamine adducts **3b** and **5a**. Compound **4** further hydrolyzes to form the oxocarboxyborane $(HOOC–CO)(F_3C)_2B{\cdot}NHMe_2$ (**6**). The B–N bond of **2a** is cleaved by either $NEt_3 \times 3HF$ or NMe_4F to form the fluoroborate anion $[(F_2C{=}CF)B(CF_3)_2F]^-$ (**7**). The structures of **2** and **5** have been investigated by single-crystal X-ray diffraction. The B–C bond involving the trifluorovinyl group in **2** is 1.598(3) Å long, and the associated B–C–C bond angle of 134.4(2)° is remarkably large. The B–C linkage to the carboxy group in **5** is 1.620(2) Å long. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Boron; Trifluoromethyl group; Crystal structure; Small rings; Ionic liquid

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1. Introduction

Previous studies have shown that dimethylamino-bis(trifluoromethyl)borane, $(F_3C)_2BNMe_2$ (**1**), enters into numerous, novel reactions in which the boron atom increases its coordination number from three to four [1]. This electrophilic character of **1** is the driving force for its ene-type reactions with nitriles or carbonyl compounds, which readily take place to form dimethylamine boranes by C-alkylation. However, such ene-type reactions of **1** require a reactant that has sufficiently activated hydrogen atoms. Reactants that do not dispose over such hydrogen atoms can be attached to the boron atom of **1** using alkyl lithium or Grignard reagents [2]. Thus, dimethylamine boranes of the general formula $R(F_3C)_2B{\cdot}NHMe_2$ are accessible with R = alkyl, alkenyl, alkinyl and aryl. The only perfluorinated group that has been added to **1** is the CF_3 group, and adducts of $(F_3C)_3B$ with numerous amines have been shown to be thermally robust compounds [3]. We are interested in attaching functional perfluorinated groups, and the trifluorovinyl group would be one such candidate. Trifluorovinyl boranes $(F_2C{=}CF)BX_2$ (X = F, Cl, Br, Me), $(F_2C{=}CF)_2BX$ (X = F, Cl, Br, Me) and $(F_2C{=}CF)_3B$ are well characterized compounds [4–6] despite their limited thermal stability and elaborate synthesis. Little seems to be known about the chemistry of these compounds. Except for their tendency to hydrolyze under formation of $HCF{=}CF_2$, no reactions of a trifluorovinyl group bonded to boron have been reported. In the current study we have carried on the chemistry of the unique trifluoromethylboron group by adding a trifluorovinyl

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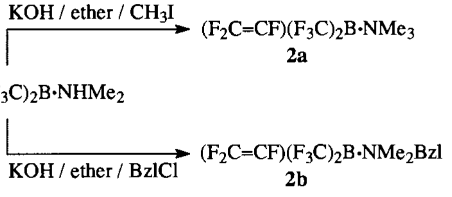
group to **1** and have investigated the properties and chemistry of the resulting borane.

2. Results

In 1997 Brisdon et al. [7] described a convenient method to generate and attach a trifluorovinyl group to elements like Hg, Sn, etc. They used 1,1,1,2-tetrafluoroethane, which is a substitute for the banned CFCs, and *n*BuLi to generate a solution of $F_2C{=}CFLi$ in ether at dry ice temperature. We have modified their method by using *t*BuLi for deprotonation. This turned out to be necessary because the deprotonation of 1,1,1,2-tetrafluoroethane with *n*BuLi was incomplete, and *n*BuLi, which was still present, also reacted with **1**. As a result a 2:8 mixture of $n\mathrm{Bu}(F_3C)_2B{\cdot}NHMe_2$ and $(F_2C{=}CF)(F_3C)_2B{\cdot}NHMe_2$ (**2**) was obtained, and separation of the two components was difficult. Because a *t*Bu group does not add to **1**, *t*BuLi proved to be the preferred deprotonating reagent; thus **2** was obtained in quantitative yield (Eq. (1)).

$$(F_3C)_2BNMe_2 + F_3CCFH_2 \xrightarrow[\text{2. }H_2O/-78°C]{\text{1. }t\mathrm{BuLi}/-78°C} \underset{\mathbf{2}}{(F_2C{=}CF)_2B{\cdot}NHMe_2} \quad (1)$$

In order to test the reactivity of the C=C bond towards bases and nucleophiles, it was necessary to methylate the acidic N–H function of **2**. This was achieved by deprotonation of the nitrogen atom with KOH in ether and subsequent alkylation of the aminoborates with CH_3I or benzyl chloride. Thus the corresponding trialkylamine boranes **2a** and **2b** were obtained (Eq. (2)).



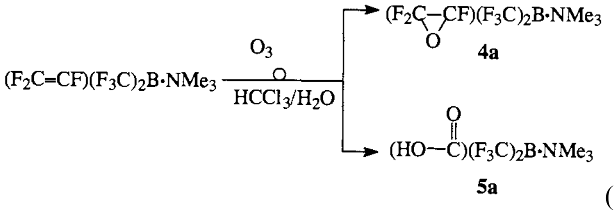
(2)

Like a typical alkene, both compounds **2** and **2a** slowly add bromine at 20°C across the C=C bond to form the respective boranes $(F_2BrC{-}CFBr)(F_3C)_2B{\cdot}NHMe_2$ (**3**) and $(F_2BrC{-}CFBr)(F_3C)_2B{\cdot}NMe_3$ (**3a**) in high yield (Eq. (3)).

$$(F_2C{=}CF)(F_3C)_2B{\cdot}L \overset{Br_2}{\rightarrow} (F_2BrC{-}CFBr)(F_3C)_2B{\cdot}L \quad (3)$$

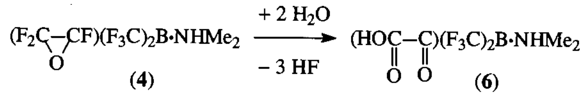
$L = NHMe_2$ (**3**), NMe_2 (**3a**)

Treatment of **2a** with O_2/O_3 in a $CHCl_3$ solution furnished both the trifluorooxiranylborane (*cyclo-O*-$CF_2{-}CF)(F_3C)_2B{\cdot}NMe_3$ (**3b**) and the carboxyborane $(HOOC)(F_3C)_2B{\cdot}NMe_3$ (**5a**) in an approximately 9:1 ratio according to Eq. (4). The latter (**5a**) results from oxidative cleavage of the C=C bond and subsequent hydrolysis of the resulting B–C(=O)F group by traces of water which were present. It should be noted that **3b** was also formed when **2a** was treated with hypochlorite in acetonitrile–water; however, the yield was lower due to hydrolytic cleavage of the $B{-}C_2F_3$ bond.



(4)

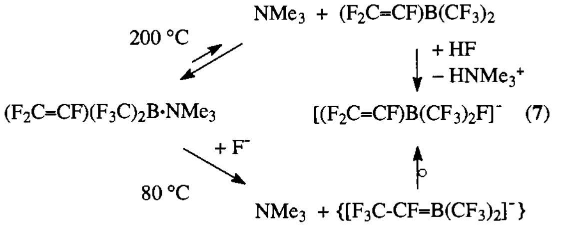
In principle, the ozonolysis of **2** proceeds analogously. If the reaction is carried out in $CHCl_3$ which has not been carefully dried, the carboxyborane $(HOOC)(F_3C)_2B{\cdot}NHMe_2$ (**5**) precipitates from the solution. The initially colorless mother liquor, which contains the trifluorooxiranylborane (*cyclo-O*-$CF_2{-}CF)(F_3C)_2B{\cdot}NHMe_2$ (**4**), slowly turns yellow. This color change results from the hydrolysis of **4** to form the yellow oxocarboxyborane $(HOOC{-}CO)(F_3C)_2B{\cdot}NHMe_2$ (**6**) according to Eq. (5).



(5)

In the course of the hydrolysis HF is formed; accordingly, once the hydrolysis has started in a glass vessel, it proceeds rapidly until all of **4** is converted into **6**. If the ozonolysis of **2** is carried out under absolutely water free conditions in a Teflon PFA reaction vessel, **4** is obtained as an oily liquid contaminated with ca. 10% of $(FOC)(F_3C)_2B{\cdot}NHMe_2$ — the complete separation of which failed. Therefore only NMR data of **4** are reported.

We found that **2a** reacts with $NEt_3 \times 3HF$ at 200°C according to Eq. (6) to form the fluoroborate ion $[(F_2C{=}CF)B(CF_3)_2F]^-$ (**7**)



(6)

Anion **7** is also formed when **2a** is treated in 2-butanone at 80°C with NMe_4F, prepared according to the procedure of Christe [8]. It seems that two mechanisms for the formation of **7** have to be considered. First, at 200°C the BN bond of **2a** is cleaved thermally, and the borane thus generated rapidly reacts with HF of $NEt_3 \times 3HF$ to form the fluoroborate anion **7**. Second, at 80°C fluoride adds first to the terminal CF_2 group of **2a**, and this adduct subsequently releases trimethylamine to form an intermediate alkylidene borate anion. This anion rearranges to yield **7**. The latter mechanism is typical of perfluorinated alkenes where 'naked' fluoride is known to add to the carbon–carbon double bond to yield perfluorinated carbanions. Despite the drastic reaction conditions, the reaction of **2a** with $NEt_3 \times 3HF$ is more convenient than that with NMe_4F because the trimethylammonium salt is readily converted in acetone solution into Cs or Li salts using Cs_2CO_3 or $LiOH \times H_2O$, respectively.

2.1. Properties and spectra

All of the novel boron compounds are air-stable solids or oily liquids (**3**, **4**, and the cesium and lithium salts of **7**). With the exception of **5**, **5a**, **6**, and **7**, they are volatile and sublime at 40°C 10^{-3} mbar. Only **4** is sensitive to water. All species mentioned here are soluble in polar solvents like acetone or acetonitrile. Compounds **5** and **5a** are weak acids with pK_a values of 5.9 and 5.4, and they are much less soluble in cold water than their sodium salts. Compound **6** is a stronger acid (pK_a 2.6), which is typical for a ketocarboxylic acid.

The NMR chemical shifts and coupling constants of **2**–**7** (Table 1) are consistent with the proposed structures. Except for the carbon atom of the trifluorovinyl group which is directly bonded to boron, all ^{13}C resonances were detected. We assume that this signal is veiled by the resonance of the CF_3 groups at 130 ppm. The assignment of the three fluorine atoms of the trifluorovinyl group was made on the generally accepted assumption that $^2J(FF) > 0$, $^3J(FF)_{trans} < 0$, $^3J(FF)_{cis} > 0$ and $|^3J(FF)_{trans}| > |^3J(FF)_{cis}|$ [9]. In trifluorovinyl derivatives $F_2C{=}CFX$, the $^3J(FF)_{cis}$ coupling constant is sensitive to the electronegativity of X — varying from 58 Hz for X = Cl [10] to 23 Hz for $X = B(CH_3)_2$ [6]. The $^3J(FF)_{cis}$ coupling constants of **2**, **2a** and **7** (ca. 26 Hz) all lie in this range. Thus the replacement of CH_3 groups by CF_3 groups and subsequent coordination to the amine has little influence on the electronegativity of the boron atom. Furthermore, we note that the fluorine atom *cis* to the $B(CF_3)_2$ group shows a $^5J(FF)$ coupling of 9–14 Hz for the amine boranes **2**, **2a** and **2b** and a coupling of 4.6 Hz for the fluoroborate anion **7**.

In **4** and **3b** the location of the ^{19}F-NMR signals of the C_2F_3O group is in good agreement with those reported for perfluoropropene oxide: −110.95, −114.11 and −157.69 ppm [11] versus −107.0, −114.8, −140.8 ppm (**4**) and −108.8, −113.2, −132.8 ppm (**3b**). The assignment of the resonance close to −135 ppm to the BC*F* fluorine atom is unambiguous due to the broadening by the boron nucleus, whereas the assignment of the terminal CF_2 group is debatable. The geminal coupling constants $^2J(FF)$ of **4** and **3b** are 50.1 and 47.1 Hz, respectively. These values are in line with those observed for perfluoropropene oxide (+43.5 Hz). The fluorine atom of the CF_2 group with the resonance at −108 ppm shows coupling to the fluorine atoms of the $B(CF_3)_2$ groups, whereas the other fluorine atom, resonating at −114 ppm, shows no such coupling. An analogous coupling pattern is observed for perfluoropropene oxide, where the downfield signal is also split by coupling with the CF_3 group. However, based on the assumption that $^3J(FF)_{trans}$ is < 0, whereas $^3J(FF)_{cis}$ is > 0, the high field signal was assigned to the fluorine atom *cis* to the CF_3 group and the down field signal, which shows coupling with the CF_3 groups, was ascribed to the *trans* fluorine atom [11]. We would suggest a reversal of this assignment for the following reason. In the parent molecules **2** and **2a**, where the assignment of the C_2F_3 fluorine atoms is unequivocal, the $B(CF_3)_2$ group shows long range coupling to the fluorine atom *cis* to the boron substituent but not to the *trans* fluorine atom. We see no reason why this behavior should change upon epoxidation.

The EI mass spectra of **2**–**2b** were recorded. When the M^+ peaks (which are generally weak) could not be detected, the $[M^+ - Br]$ (**3** and **3a**), $[M^+ - CF_3]$ (**3b**) and $[M^+ - C_2F_5]$ peaks were taken as indicators of the molecular weight. A typical fragment of the carboxyboranes is $m/z = 222$ $[Me_2HN\text{–}B(CF_3)_2\text{–}CO^+]$ and $m/z = 236$ $[Me_3N\text{–}B(CF_3)_2\text{–}CO^+]$.

The miscibility of $Cs[(F_2C{=}CF)B(CF_3)_2F]$ (**Cs7**), which is a liquid at 20°C, with acetone and ether is remarkable. Attempts to obtain single crystals at low temperature have so far failed. The specific conductivity of a 0.01 M solution of the salt in acetone was determined to be 0.14 $\Omega^{-1}\ m^{-1}$ at 25°C. Thus, the conductivity is approximately the same as an aqueous KCl solution of equal molar concentration. However, in dry ether the specific conductivity of a 0.07 M solution of **Cs7** was determined to be only ca. 0.0015 $\Omega^{-1}\ m^{-1}$ at 25°C. This indicates that the salt dissolves as an ion pair in ether.

2.2. Description of the crystal structures of $(F_2C{=}CF)(F_3C)_2B{\cdot}NHMe_2$ and $(HOOC)(F_3C)_2B{\cdot}NHMe_2$

The structure of **2** is shown in Fig. 1, and selected structural parameters are given in Table 3. Of particular interest is the interaction between the boron atom and the trifluorovinyl group. The BC_2F_3 fragment is planar to within ± 0.02 Å, and its orientation with respect to the rest of the molecule, as shown by the anticlinal value [144.0(2)°] of the N–B–C(1)–C(2) torsion angle, precludes a nontrivial symmetry for this compound in the solid state. The B–C(1) bond length (1.598(3) Å) is not significantly shorter than that (1.608(4) Å) found for the attachment to the diazoacetic acid ester group in $B(CF_3)_2[C(N_2)C(O)OEt]{\cdot}NHMe_2$ (**A**) [12], which is the only previously reported structure of a $B(CF_3)_2R{\cdot}NHMe_2$ derivative having the R group bonded to boron via an sp^2-hybridized carbon atom.

Differences in the electronic and steric nature of the borate and fluoride substituents of the C(1) atom are reflected in its bond angles. Thus the B–C(1)–C(2) and F(1)–C(1)–C(2) angles assume relatively large and small values, 134.4(2) and 112.6(2)°, respectively. The latter is much smaller than that reported for tetrafluoroethene (**B**) in the gas phase, 123.8(6)° [13]. Substitution of a fluorine in **B** by the boryl group in **2** also leads to a marked lengthening of the C(1)–F(1) bond from 1.319(6) to 1.383(2) Å.

When the amine ligand in amine(trifluoromethyl)borates possesses an N–H bond, this bond is sufficiently acidic to take part in hydrogen bonding [1]. Three types of fluorine atoms, namely those of the CF, CF_2 and CF_3 groups, are possible proton acceptors in **2**. In order to determine if any of them take part in

Table 1
NMR spectral data for **2**–**7** [a]

	2	**2a**	**2b**	**3**	**3a**	**4**	**4a**	**5**	**5a**	**6**	**6a**	**7**
^{1}H												
$\delta(\mathrm{NC}H_3)$	2.87	2.88	2.75	3.04	3.10	2.97	3.01	2.79	2.97	2.69	2.62	
$\delta(\mathrm{NC}H_2)$			4.37									
$\delta(\mathrm{C_6}H_5)$			7.39									
			7.53									
$\delta(\mathrm{N}H)$	4.4			4.98		4.5		6.5		6.50		
$\delta(\mathrm{O}H)$								6.7		9.05		
^{19}F												
$\delta(\mathrm{BC}F_3)$	−63.2	−59.7	−58.4	−59.9	−58.8	−62.6	−61.6	−62.8	−60.3	−61.8	−60.6	−70.8
				−60.2	−59.6	−63.4	−61.9					
$^{2}J(\mathrm{BF})$								29	28			28.4
$\delta(\mathrm{C}F_2)$	−91.7	−91.4	−90.5	−51.8	−46.1	−114.8	−113.2					−99.5
$^{2}J(\mathrm{FF})$	+71.7	+64.2	+62.6	172.9	162.8	+50.1	+50.6					+87.7
$^{3}J(\mathrm{FF})_{cis}$	+25.9	+26.3	+27.5	26.5	31.8	26.9	28.2					+25.5
$\delta(\mathrm{C}F_2)$	−115.9	−111.6	−110.6	−52.6	−54.1	−107.0	−108.8					−124.3
$^{3}J(\mathrm{FF})_{trans}$	−111.4	−111.4	−111.4									−110.9
$^{4}J(\mathrm{FF})$												17.8
$^{5}J(\mathrm{FF})$	9.5	13.6	13.7			11	10					4.6
$^{3}J(\mathrm{FF})$							10					
$\delta(\mathrm{C}F\mathrm{B})$	−196.8	−187.3	−186.4	−124.9	−131.2	−140.8	−132.8					−195.7
$^{4}J(\mathrm{FF})$		8.4				5.4						
$^{2}J(\mathrm{BF})$												23
$\delta(\mathrm{B}F)$												−229.9
$^{1}J(\mathrm{BF})$												56.9
^{11}B												
$\delta(\mathrm{B})$	−11.1	−9.0	−8.1	−9.7	−7.4	−12.1	−9.6	−12.4	−10.8	−10.8	−11.4	−6.4
^{13}C												
$\delta(\mathrm{N}C\mathrm{H_3})$	40.6	52.7	46.7	42.6	55.4	41.1	53.8	41.1	53.4	41.2	40.8	
						41.2						
$\delta(\mathrm{N}C\mathrm{H_2})$			64.2									
$\delta(C\mathrm{O})$										165.0	174.5	
$\delta(\mathrm{B}C\mathrm{F_3})$	130.4	131.1	131	129.5	130.8	130	131.1	132.3	132.2	131.6	131.9	134.3
					131.1							
$^{1}J(\mathrm{CF})$		305		304	304.2		301.1	304	305.0	300		
$^{1}J(\mathrm{BC})$		78.			81.4		79.7	74	77.1	76		
					79.7							
$\delta(C\mathrm{B})$	130	130	130	106.0	107.3	98	99.5	186.5	184.4	221.3	234.1	133
$^{1}J(\mathrm{CF})$				265	266		301					
$^{1}J(\mathrm{BC})$					58		74	72	73.7	59		
$\delta(C\mathrm{F_2})$	160.5	161.5	161.4	124.4	127.3	110.5	112.2					161.6
$^{1}J(\mathrm{CF})$	297.2	280	297.5	308.2	312.3	294.5	289.4					274
	278.4	280	283.3	312.3	316.4		295.5					275
$^{2}J(\mathrm{CF})$	43.2	47	45.3	37.6	38.15	18.4	19.3					42.2
$\delta(C_6\mathrm{H}_5)$			127.4									
			129.1									
			130.4									
			133.2									

[a] **2**, **2a**, **2b**, **3**, **4**, in $CDCl_3$, **6**, **3a**, **3b**, **7** in [D_3]acetonitrile; **5**, **5a** in [D_6]acetone; **6a** in D_2O/[D_3]acetonitrile.

Table 2
Crystal data

Compound	**2**	**5**
Empirical formula	$C_6H_7BF_9N$	$C_5H_8BF_6NO_2$
Formula weight	274.94	238.93
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.1079(13)	6.904(2)
b (Å)	8.2451(10)	7.308(2)
c (Å)	12.545(2)	10.825(2)
α (°)	90	89.78(2)
β (°)	106.597(10)	74.50(2)
γ (°)	90	61.947(14)
V (Å^3)	1002.0(2)	459.6(2)
Z	4	2
D_{calc} (g cm^{-3})	1.823	1.726
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
Wavelength (Å)	0.71073	0.71073
T (K)	295(2)	293(2)
Diffractometer	Siemens P3	Siemens P3
Scan mode	θ–2θ	θ–2θ
Theta range (°)	2.10–25.04	3.19–25.05
Limiting indices	$0 \leq h \leq 12$, $0 \leq k \leq 9$, $-14 \leq l \leq 14$	$-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$
Reflections collected	1865	3566
Unique	1765	1636
R_{int}	0.0122	0.0262
Observed ($I > 2\sigma$)	1297	1261
Crystal size (mm)	$0.46 \times 0.24 \times 0.20$	$0.42 \times 0.20 \times 0.10$
μ (mm^{-1})	0.225	0.201
Transmission	0.9590–0.9495	0.9776–0.9639
R_1 (all data)	0.0454	0.0441
wR_2 (all data)	0.0818	0.0848
Goodness-of-fit on F^2	1.044	1.018
Parameters	167	153
ΔF map (e Å^{-3})	0.200 to -0.137	0.251 to -0.145
Extinction coefficient	0.020(2)	0.020(6)

hydrogen bonding, the coordinates of the hydrogen atom were first corrected for the systematic shortening of the N–H bond, which arises in an X-ray experiment [14]. Accordingly, the hydrogen atom was pushed along the N–H vector to a position 1.033 Å [15] from the nitrogen atom. The nearest fluorine atoms to this position are F(1) (2.21 Å) and F(9) ($1-x$, $y-0.5$, $1.5-z$) (2.23 Å). These hydrogen bonds are shown in Fig. 1. The former completes a five-membered ring and accordingly is sharply bent (111°), while the latter links the molecules to chains and is more stretched (161°). While the basicity of the F(1) and F(9) atoms should be enhanced over those of the CF_2 group by the inductive effect of the boron atom, the lengths involved in this bifurcated interaction indicate that the hydrogen bonding must be considered feeble [16].

A view of **5** is given in Fig. 2, and selected distances and angles are listed in Table 4. While the CF_3 and NMe_2H groups adopt roughly staggered conformations

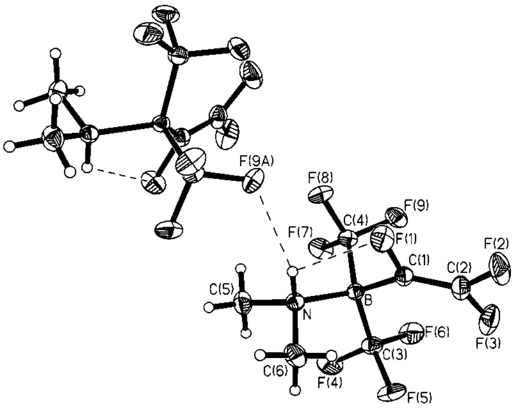


Fig. 1. A perspective drawing showing two screw-related molecules of **2**. Broken lines delineate hydrogen bonds, and the positions of the non-hydrogen atoms are indicated by 20% probability thermal ellipsoids.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
B–N	1.608(2)	N–H	0.84(2)
B–C(1)	1.598(3)	C(1)–C(2)	1.293(3)
B–C(3)	1.622(3)	C(1)–F(1)	1.383(2)
B–C(4)	1.627(3)	C(2)–F(2)	1.314(2)
N–C(6)	1.493(2)	C(2)–F(3)	1.313(3)
N–C(5)	1.496(2)		
Bond angles			
N–B–C(1)	105.66(14)	B–N–C(6)	113.2(2)
N–B–C(3)	111.4(2)	B–N–H	101.9(14)
N–B–C(4)	108.62(14)	B–C(1)–C(2)	134.4(2)
C(1)–B–C(3)	113.6(2)	B–C(1)–F(1)	112.99(14)
C(1)–B–C(4)	108.44(14)	F(1)–C(1)–C(2)	112.6(2)
C(3)–B–C(4)	108.93(14)	C(1)–C(2)–F(2)	126.2(2)
C(5)–N–C(6)	109.6(2)	C(1)–C(2)–F(3)	124.2(2)
B–N–C(5)	118.0(2)	F(2)–C(2)–F(3)	109.6(2)

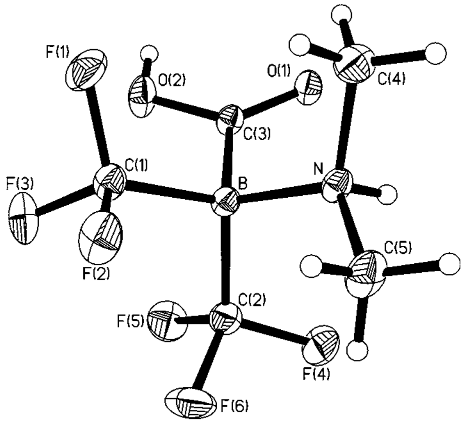


Fig. 2. A perspective drawing of **5** employing 20% probability thermal ellipsoids for the non-hydrogen atoms.

Table 4
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths			
B–N	1.589(2)	O(2)–C(3)	1.315(2)
B–C(1)	1.630(2)	N–C(4)	1.498(2)
B–C(2)	1.620(3)	N–C(5)	1.503(2)
B–C(3)	1.620(2)	N–H(N)	0.85(2)
O(1)–C(3)	1.231(2)	O(2)–H(O2)	0.83(2)
Bond angles			
N–B–C(1)	112.45(14)	B–C(3)–O(2)	115.10(14)
N–B–C(2)	109.22(14)	O(1)–C(3)–O(2)	121.0(2)
N–B–C(3)	107.82(13)	B–N–C(4)	114.12(14)
C(1)–B–C(2)	109.7(2)	B–N–C(5)	117.1(2)
C(1)–B–C(3)	110.02(14)	B–N–H(N)	104.5(13)
C(2)–B–C(3)	107.53(14)	C(4)–N–C(5)	108.8(2)
B–C(3)–O(1)	123.86(14)	C(3)–O(2)–H(O2)	112(2)

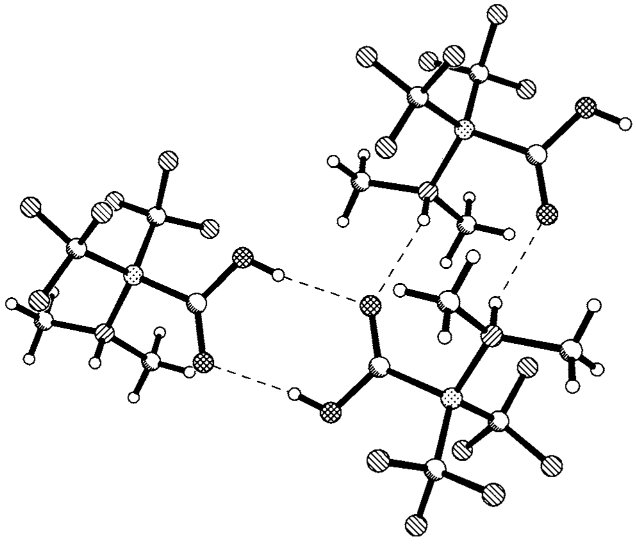


Fig. 3. A packing diagram of **5** showing the formation of centrosymmetric hydrogen-bonded eight- and ten-membered rings.

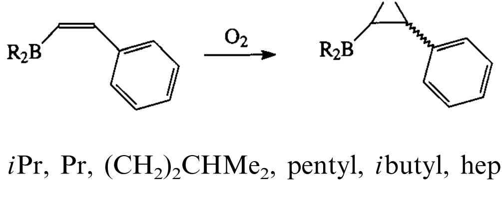
with respect to the bonds radiating from the boron atom, the plane of the carboxy group is oriented nearly perpendicular to the B–CF_3 bond of the C(2) atom. The attachment of the carboxy group to boron, 1.620(2) Å, is slightly but significantly longer than the B–C(sp^2) bond in **2** and is probably longer than that of **A**. Bonding to the boryl fragment does not lead to significant lengthening of the C–O bonds in **5**, 1.231(2) and 1.315(2) Å, when compared with those of carboxy groups that are directly bonded to a saturated carbon atom, 1.214(19) and 1.308(19) Å, respectively [15].

Before checking for possible proton acceptors in **5**, the N–H(N) and O(2)–H(O2) bond lengths were lengthened as described for **2** to 1.033 and 0.967 Å, respectively. A scan of the interatomic distances showed that only the O(1) atom is functioning as a hydrogen bond acceptor. It interacts weakly with the H(N) atom (2.14 Å, 154°) to form a centrosymmetric, eight-membered ring and stronger with the H(O2) atom (1.81 Å, 169°) to form a centrosymmetric, ten-membered ring, Fig. 3. Thus hydrogen bonding couples the molecules to zigzag chains, which propagate in the *b* direction. This structure further underscores the weak hydrogen-acceptor properties of organic fluorine [16] because the O(1) atoms accepts both protons although it is outnumbered by fluorine by a factor of six.

3. Discussion

The thermal stability and chemical inertness of the amine trifluorovinylboranes **2** and **2a** is in contrast to the sensitivity of the uncomplexed trifluorovinylboranes reported in the literature. It has been mentioned that $C_2F_3BMe_2$ and $(C_2F_3)_2BMe$ react with NMe_3 to form the corresponding trimethylamine boranes [6]. However, no information about the properties of these adducts was given. A comparison of the properties of $(F_2C{=}CF)Me_2B{\cdot}NMe_3$ with those of **2a** should give further insight into the CH_3/CF_3 substitution effect. Although a direct comparison is not possible, the C_2F_3 group at tetracoordinated boron is drastically stabilized by the CF_3 groups in **2** and **2a**. The addition of bromine to the C=C bond of **2a** is a typical reaction of both fluorinated and nonfluorinated alkenes. The epoxidation of **2** and **2a** using ozone is typical for perfluorinated terminal alkenes, e.g. tetrafluoro-oxirane has been obtained from tetrafluoroethene and ozone [17]. The side reaction with oxidative cleavage of the C=C bond and the formation of a C(=O)F group, which hydrolyses to form **5** and **5a**, is also known in perfluoroalkene chemistry [17,18]. Amine carboxyboranes, $R^1R^2R^3N{-}BH_2{-}COOH$ ($R^1R^2R^3 = H$, Me), are well characterized compounds which exhibit remarkable physiological properties [19]. They are very weak acids with pK_a values of 8.14–8.38. Compounds **5** and **5a** are related derivatives in which the boron-bonded hydrogen has been substituted by CF_3 groups. The electron withdrawing power of these two groups increases the acid strength considerably — the pK_a values being 5.9 and 5.4, respectively.

Compounds **4** and **3b** are the first well-characterized species in which an epoxide ring is directly attached to boron. It has been reported that styrylboranes add molecular oxygen to form epoxides according to Eq. (7) [20], but these products were only characterized by their refractive indices, densities, boiling points and elemental analyses.



(7)

R = *i*Pr, Pr, $(CH_2)_2CHMe_2$, pentyl, *i*butyl, heptyl

Thus the characterization of these compounds gave no indication of the oxygen connectivity. In light of boron chemistry this reaction seems strange because trialkylboranes are known to react readily with oxygen under insertion into the carbon–boron bond.

The difference in the hydrolytic stability of **3b** and **4** is remarkable. Whereas **3b** is water-stable, **4** rapidly adds water, the epoxide ring being cleaved. We assume that this divergent behavior is due to either intramolecular or intermolecular hydrogen bridging between the acidic NH function and the oxygen atom of the epoxide ring. Such bridging increases the nucleophilicity of the CF_2 group and lowers the barrier for a nucleophilic attack. That the hydrolytic stability of the epoxide ring is due to the quaternization of the nitrogen is further established by the fact that the ozonolysis of **2b** results in the formation of a stable oxiranylborane. This was shown by epoxidation experiments run on an NMR scale.

4. Experimental

4.1. General

NMR: Bruker ARX 400 (400, 100.6 and 376.5 MHz, for ^1H, ^{13}C and ^{19}F, respectively), Bruker AC 250 (79.8 MHz for ^{11}B): $CDCl_3$ (^1H: $\delta_H = 7.27$, ^{13}C: $\delta_C = 77.0$), [D_3]acetonitrile (^1H: $\delta_H = 1.95$, ^{13}C: $\delta_C = 1.30$), [D_6]acetone (^1H: $\delta_H = 2.05$, ^{13}C: $\delta_C = 30.5$) as solvent and internal standard, ^{19}F: external standard $CFCl_3$, ^{11}B: external standard BF_3OEt_2. —IR: Bruker IFS 25; —Raman: Cary 82 Kr^+ 647.1 nm. —UV–vis: Schimadzu UV-160 A. —MS: Varian MAT 311 (70 eV). —Thermogravimetry: Netzsch STA 409. —Ozone Generator: Fischer 501.

4.2. X-ray structural determination

Crystals of **2** were grown by sublimation and sealed in a glass capillary while those of **5**, which crystallized from a solution in acetonitrile, were glued to a glass fiber. Diffraction measurements were made at room temperature (r.t.) using a Siemens P3 diffractometer employing graphite monochromatized Mo–K_α radiation. Intensities were derived by profile analysis and corrected for absorption. The structures were solved by direct methods and refined with all non-hydrogen atoms assigned anisotropic temperature factors. The hydrogen atoms bonded to the nitrogen and oxygen atoms were located by difference Fourier techniques and refined isotropically, while those of the methyl groups were idealized. Crystal data are given in Table 2. Structural solution, refinement and display were carried out with a SHELXTL, version 5.03, program package.

4.3. Preparation of compounds

4.3.1. Dimethylamine-trifluoroethenylbis-(trifluoromethyl)borane (*2*)

To a stirred solution of 20 g of 1,1,1,2-tetrafluoroethane in 100 ml of dry ether, $(CF_3)_2BNMe_2$ (**1**) (7.1 g, 36.8 mmol) and 50 g *t*BuLi (15% solution in pentane) were added dropwise at − 78°C. The reaction mixture was stirred for 20 min, 30 ml of water added at − 78°C and the mixture was allowed to warm to r.t. The pH was adjusted to ca. 4 using diluted HCl, the organic phase separated, dried over Na_2SO_4 and taken to dryness. The brown oily residue was sublimed in vacuo at 50°C. Yield: 9.0 g (32.7 mmol) 89% colorless solid, m.p. 48°C. IR (film)/Ra: 3272 cm^{-1} s/- (NH), 1753 s/m (C=C), 1104 vs/- (CF). —MS (70 eV); *m/z* (%): 275 (22) [M^+], 206 (11) [$M^+ - CF_3$], 156 (93) [$M^+ - C_2F_5$], 94 (100) [$F_2BNH(CH_3)_2^+$], 44 (66) [$C_2H_6N^+$]. —$C_6H_7BF_9N$ (274.92): Anal. Calc.: H, 2.57; C, 26.21; N, 5.09. Found: H, 2.6; C, 25.6; N, 4.8%.

4.3.2. Trimethylamine-trifluoroethenylbis-(trifluoromethyl)borane (*2a*), benzyldimethylamine-trifluoroethenylbis(trifluoromethyl)borane (*2b*)

A solution of **2** (8 g, 29 mmol) in 100 ml of ether (dried over KOH) was stirred with 4.0 g of KOH pellets and 10 ml of CH_3I at 20°C for ca. 2 h. The reaction mixture was filtered, all volatile material removed in vacuo and **2a** crystallized from $CHCl_3$. **2a**: Yield 7.9 g (27 mmol) 94% colorless solid, m.p. 94°C. IR (film)/Ra: 1741 cm^{-1} s/m (C=C), 1105 vs/- (CF). —MS (70 eV); *m/z* (%): 289 (5) [M^+], 220 (2) [$M^+ - CF_3$], 170 (53) [$M^+ - C_2F_5$], 108 (100) [$F_2BN(CH_3)_3^+$], 58 (91) [$C_3H_8N^+$]. —$C_7H_9BF_9N$ (288.95): Anal. Calc.: H, 3.14; C, 29.10; N, 4.85. Found: H, 3.1; C, 28.8; N, 4.6%. Compound **2b** was prepared analogously by stirring 3.9 g (14 mmol) of **2**, 4.4 g of benzyl chloride and 4 g of KOH pellets in 60 ml of ether for 14 h. Crystallization from ether at − 78°C furnished **2b** (4.6 g, 12.9 mmol) in 90% yield as a colorless solid, m.p. 59°C. —IR 1736 cm^{-1} (C=C), 1112, 1090 (CF). —MS (70 eV); *m/z* (%): 365 (3) [M^+], 246 (1) [$M^+ - C_2F_5$], 135 (19) [$C_9H_{13}N^+$], 134 (10) [$C_9H_{12}N^+$], 92 (21) [$F_2BNCH_2(CH_3)^+$], 91 (100) [$C_7H_7^+$], 58 (59) [$C_3H_8N^+$]. —$C_{13}H_{13}BF_9N$ (365.05): Anal. Calc.: H, 3.59; C, 42.77; N, 3.84. Found: H, 3.5; C, 42.6; N, 4.0%.

4.3.3. Dimethylamine-1,2-dibromotrifluoroethylbis-(trifluoromethyl)borane (*3*), trimethylamine-1,2-dibromotrifluoroethylbis(trifluoromethyl)borane (*3a*)

A solution of **2** (1.1 mmol) or **2a** in 5 ml of $CHCl_3$ was mixed with 0.4 g (2.5 mmol) of Br_2 and kept for 3 days at 20°C. All volatile material was removed in vacuo. Compound **3** was distilled at 50°C 10^{-3} mbar and **3a** was crystallized from $CHCl_3$. Yield **3a**: 0.38 g

(0.85 mmol) 77% colorless solid, m.p. 112°C. IR (KBr)/Ra: 1110 vs/- (CF), $-$/296 vs (CBr). —MS (70 eV); m/z (%): 370 (30) [$M^+ - \text{Br}$], 289 (1) [$M^+ - \text{Br}_2$], 222 (10) [$\text{C}_2\text{F}_2\text{Br}_2^+$], 170 (16) [$M^+ - \text{C}_2\text{F}_5\text{–Br}_2$], 108 (100) [$\text{F}_2\text{BN(CH}_3)_3^+$], 58 (98) [$\text{C}_3\text{H}_8\text{N}^+$]. —$\text{C}_7\text{H}_9\text{BBr}_2\text{F}_9\text{N}$ (448.76): Anal. Calc.: H, 2.02; C, 18.74; N, 3.12. Found: H, 2.0; C, 18.5; N; 3.6%. Yield **3**: 0.35 g (0.80 mmol) 73% colorless oil. —IR (film)/Ra: 1110 vs/- (CF), $-$/295 vs (CBr). MS (70 eV); m/z (%): 356 (1) [$M^+ - \text{Br}$], 275 (5) [$M^+ - \text{Br}_2$], 222 (37) [$\text{C}_2\text{F}_2\text{Br}_2^+$], 162 (28) [$\text{C}_2\text{F}_3\text{Br}^+$], 156 (23) [$M^+ - \text{C}_2\text{F}_5\text{–Br}_2$], 94 (100) [$\text{F}_2\text{BNH(CH}_3)_2^+$], 44 (92) [$\text{C}_2\text{H}_4\text{N}^+$]. —$\text{C}_6\text{H}_7\text{BBr}_2\text{F}_9\text{N}$ (434.73): Anal. Calc.: H, 1.62; C, 16.58; N, 3.22. Found: H, 1.6; C, 16.8; N, 3.2%.

4.3.4. *Trimethylamine-bis(trifluoromethyl)-trifluorooxiranylborane (**3b**), trimethylamine-carboxybis(trifluoromethyl)borane (**5a**), dimethylamine-carboxybis(trifluoromethyl)borane (**5**), dimethylamine-bis(trifluoromethyl)oxocarboxyborane (**6**)*

A flow of ozone/oxygen (ca. 2 g O_3/h) was introduced into a solution of **2** (4.0 g, 13.8 mmol) in 10 ml of CHCl_3 at 20°C. The progress of the reaction was monitored by running ^{19}F-NMR spectra and stopped when the signals of **2a** had disappeared. The solution was cooled to 0°C and **5a** was removed by filtration. The filtrate was concentrated to 5 ml and upon cooling to -20°C most of **3b** crystallized (colorless thin plates). Yield **3b**: 3.1 g (10.1 mmol) 73%: m.p. 113°C. —IR/Ra: 1500 cm^{-1} s/- (C–O), 1123, 1095 vs/- (CF). —MS (70 eV); m/z (%): 236 (3) [$M^+ - \text{CF}_3$], 186 (3) [$M^+ - \text{C}_2\text{F}_5$], 170 (3) [$M^+ - \text{OC}_2\text{F}_5$], 108 (100) [$\text{F}_2\text{BN(CH}_3)_3^+$], 58 (74) [$\text{C}_3\text{H}_8\text{N}^+$]. —$\text{C}_7\text{H}_9\text{BF}_9\text{NO}$ (304.95): Anal. Calc.: H, 2.97; C, 27.57; N, 4.59. Found: H, 3.1; C, 27.4; N, 4.6%.

Yield **5a**: 0.49 g (1.9 mmol) 14%: dec. 201°C. —IR (KBr): 1671 cm^{-1} s, 1629 m (C=O), 1105 vs (CF). —MS (70 eV); m/z (%): 253 (10) [M^+], 236 (6) [$M^+ -$ OH], 189 (4) [$M^+ - \text{CO}_2\text{–HF}$], 170 (3) [$M^+ - \text{CO}_2\text{–HF}_2$], 139 (3) [$M^+ - \text{CO}_2\text{–HCF}_3$], 108 (100) [$\text{F}_2\text{BN(CH}_3)_3^+$], 58 (76) [$\text{C}_3\text{H}_8\text{N}^+$]. —$\text{C}_6\text{H}_{10}\text{BF}_6\text{NO}_2$ (252.95): Anal. Calc.: H, 3.98; C, 28.49; N, 5.54. Found: H, 3.9; C, 28.5; N; 5.3%. —pK_a 5.9.

The epoxidation of **2** was carried out analogously with 4.0 g (14.5 mmol). After **5** has been isolated by filtration, the filtrate became yellow and was stirred for 2 h with aqueous CsOH solution. The pH was of the aqueous phase was adjusted to **9** using CsOH, and the reaction mixture was taken to dryness in vacuo. The residue was stirred with 150 ml of hot acetonitrile, and the slurry was hot filtered. Upon cooling the filtrate to -20°C Cs[$\text{HMe}_2\text{N–B(CF}_3)_2\text{–CO–CO}_2$] (**6a**) precipitated. The salt was dissolved in 50 ml of 2 M HCl and the acid extracted with two portions of ether. The organic phase was taken to dryness and **6** dried at 60°C. Yield: 2.0 g (7.56 mmol) 52% yellow powder; m.p. 108°C; pK_a 2.6. IR: $\nu = 3343$ cm^{-1} (OH), 3185 (NH), 1746, 1686 (C=O), 1102 (CF). —MS (70 eV); m/z (%): 222 (10) [$M^+ - \text{CO}_2\text{H}$], 94 (100) [$\text{F}_2\text{BNH(CH}_3)_2^+$], 74 (3) [$\text{FBN(CH}_3)_2^+$], 44 (15) [$\text{C}_2\text{H}_6\text{N}^+$]. Elemental analyses $\text{C}_6\text{H}_8\text{BF}_6\text{NO}_3$ (266.93): Anal. Calc. H, 3.02; C, 27.00; N, 5.25. Found: H, 2.9; C, 26.5; N, 4.9%. Cs[$\text{HMe}_2\text{N–B(CF}_3)_2\text{–CO–CO}_2$] (**6a**): UV–vis (water): λ_max (ε) = 365 nm (27), 410 nm (14). Elemental analyses $\text{C}_6\text{H}_7\text{CsBF}_6\text{NO}_3$ (398.83): Anal. Calc.: H, 1.77; C, 18.07; N, 3.51. Found: H, 1.7; C, 17.7; N, 3.5%.

Crystals of **5** were grown from acetonitrile. Yield **5**: 0.42 g (1.74 mmol) 12%: dec. 144°C IR (KBr): 3202 cm^{-1} m (NH), 1691 m, 1664 s (C=O), 1099 vs (CF). —MS (70 eV); m/z (%): 239 (4) [M^+], 222 (1) [$M^+ -$ OH], 175 (2) [$M^+ - \text{CO}_2\text{–HF}$], 156 (1) [$M^+ - \text{CO}_2\text{–HF}_2$], 94 (100) [$\text{F}_2\text{BNH(CH}_3)_2^+$], 44 (22) [$\text{C}_2\text{H}_6\text{N}^+$]. —$\text{C}_5\text{H}_8\text{BF}_6\text{NO}_2$ (238.92): Anal. Calc.: H, 3.37; C, 25.14; N, 5.86. Found: H, 3.3; C, 24.7; N, 5.8%. —pK_a 5.4.

4.3.5. *Tetramethylammonium-fluoro-(trifluoroethenyl)bis(trifluoromethyl)borate (NMe₄7)*

Anhydrous tetramethylammonium fluoride (6 g), prepared according to Ref. [8], was stirred with 30 ml of anhydrous 2-butanone and 2 g (6.9 mmol) of **2a** at reflux for 20 min. Most of the solvent was removed in vacuo, and the residue was stirred with ca. 60 ml of anhydrous acetone and filtered. The filtrate was taken to dryness in vacuo. Yield: 1.2 g (3.7 mmol) 54% light yellow waxy solid. IR (KBr): 1746 cm^{-1} s (C=C), 1488 s ($\delta_\text{as}\text{CH}_3$), 1277, 1091, 1034 vs (CF). —$\text{C}_8\text{H}_{12}\text{BF}_{10}\text{N}$ (322.98): Anal. Calc.: H, 3.74; C, 29.75; N, 4.34. Found: H, 4.1; C, 30.4; N, 4.5%.

4.3.6. *Cesium-fluoro(trifluoroethenyl)bis-(trifluoromethyl)borate (Cs7)*

Compound **2a** (0.85 g, 2.94 mmol) and $\text{NEt}_3 \times 3\text{HF}$ (2.0 g, 12.4 mmol) were heated in a Teflon PFA reaction vessel to 200°C for 7 h. The excess of $\text{NEt}_3 \times 3\text{HF}$ and eventually unreacted **2a** were distilled off in vacuo at 150–160°C, and the residue was stirred with 4 g of Cs_2CO_3 in 30 ml of acetone for 4 h to remove $\text{NEt}_3 \times 3\text{HF}$ and to prepare the Cs salt. The slurry was filtered over charcoal and the filtrate was taken to dryness in vacuo at 60°C. Yield: 0.96 g (2.53 mmol) 86% colorless oil, dec.170–175°C. IR (film): 1751 cm^{-1} vs (C=C), 1283, 1093, 1031 vs (CF). —$\text{C}_4\text{CsF}_{10}\text{B}$ (381.74): Anal. Calc.: C, 12.59. Found: C, 12.2%.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 134641 and 134642, respectively, for compounds **2** and **5**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] G. Pawelke, H. Bürger, Appl. Organomet. Chem. 10 (1996) 147.

[2] (a) G. Pawelke, J. Fluorine Chem. 42 (1989) 429. (b) D.J. Brauer, H. Bürger, F. Dörrenbach, B. Krumm, G. Pawelke, W. Weuter, J. Organomet. Chem. 385 (1990) 161. (c) A. Ansorge, D.J. Brauer, H. Bürger, F. Dörrenbach, B. Krumm, G. Pawelke, Z. Naturforsch. Teil B 47 (1992) 772. (2) A. Ansorge, D.J. Brauer, H. Bürger, B. Krumm, G. Pawelke, J. Organomet. Chem. 446 (1993) 25.

[3] G. Pawelke, J. Fluorine Chem. 73 (1995) 51.

[4] H.D. Kaesz, S.L. Stafford, F.G.A. Stone, J. Am. Chem. Soc. 81 (1959) 6336.

[5] S.L. Stafford, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 6238.

[6] E.J. Stampf, J.D. Odom, J. Organomet. Chem. 108 (1976) 1.

[7] K.K. Banger, A.K. Brisdon, A. Gupta, Chem. Commun. 1 (1997) 139.

[8] K.O. Christe, W.W. Wilson, R.D. Wilson, R. Bau, J. Feng, J. Am. Chem. Soc. 112 (1990) 7619.

[9] S. Berger, S. Braun, H.O. Kalinowski, ^{19}F-NMR-Spekroskopie, Verlag, New York, 1994.

[10] P.W. Jolly, M.T. Bruce, F.G.A. Stone, J. Chem. Soc. (1965) 5830.

[11] K.W. Jolley, L.H. Sutcliffe, K.L. Williamson, Spectrochim. Acta Part A 30 (1974) 1455.

[12] A. Ansorge, D.J. Brauer, H. Bürger, T. Hagen, G. Pawelke, Angew. Chem. 105 (1993) 429.

[13] J.L. Carlos, R.R. Karl, S.H. Bauer, J. Chem. Soc. Faraday Trans. II 70 (1974) 177.

[14] R. Taylor, O. Kennard, Acta Crystallogr. Sect. B 39 (1983) 133.

[15] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, J. Chem. Soc. Perkin Trans. 2 (1987) S1–S19.

[16] J.D. Dunitz, R. Taylor, Chem. Eur. J. 3 (1997) 89.

[17] J.W. Agopovich, C.W. Gillies, J. Am. Chem. Soc. 102 (1980) 7572.

[18] P.R. Resnick, in: M. Howe-Grant (Ed.), Fluorine Chemistry: A Comprehensive Treatment, Wiley, New York, 1995, p. 294.

[19] (a) B.F. Spielvogel, in: J.F. Liebman, A. Greenberg, R.E. Williams (Eds.), Advances in Boron and the Boranes, VCH, New York, 1988, pp. 329. (b) B. Györi, Z. Berente, Z. Kovács, Inorg. Chem. 37 (1998) 5131.

[20] G.E. Kacheishvili, N.I. Pritskhalava, S.P. Kandelaki, N.A. Tupinashvili, Tr. Tbilis. Univ. 4 (1972) 127.