Journal of Organometallic Chemistry, *467* (1994) 1–11

BN cleavage of the azoniaboratacyclopropane ring by H_2O and by carbonyl and nitrile derivatives: crystal structure of $(CF_3)_2B(OH)CH(SiMe_3)NHMe_2$, $(CF_3)_2\overline{BCH(SiMe_3)NMe_2CMe_2O}$ and $(MeC(O)NH)(CF_3)_2BCH(SiMe_3)NHMe_2$ *

A. Ansorge, D.J. Brauer, H. Bürger, T. Hagen and G. Pawelke

Anorganische Chemie, Fachbereich 9, Universität-GH, D-42097 Wuppertal (Germany)

(Received May 12, 1993)

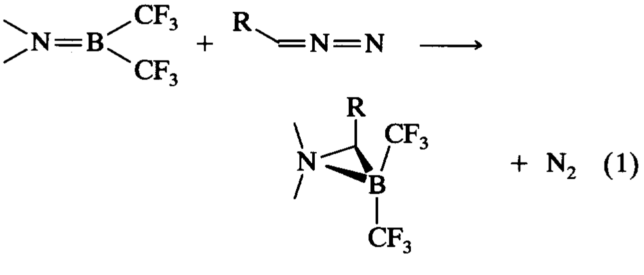
Abstract

1,1-Dimethyl-2,2-bis(trifluoromethyl)azoniaboratacyclopropane derivatives $(CF_3)_2\overline{BCHRN}Me_2$ (R = H (I), $SiMe_3$ (II)) react with H_2O with cleavage of the NB bond to form $(CF_3)_2B(OH)CHRNHMe_2$ (R = H (III), $SiMe_3$ (IV)). Carbonyl compounds $R^1R^2C{=}O$ are inserted into the NB bond of I and II to yield the five-membered heterocycles $(CF_3)_2\overline{BCHRNMe_2CR^1R^2O}$ (R = H, $R^1 = R^2 = Et$ (V); R = $SiMe_3$, $R^1 = H$, $R^2 = Me$ (VI), $R^1 = R^2 = Me$ (VII), Et (VIII), $R^1 = Me$, $R^2 = CH{=}CMe_2$ (IX), $\underline{C{=}CMe(CH_2)_2CH_2}$ (X)). Similarly nitriles insert to form $(CF_3)_2\overline{BCHRNMe_2CR^1{=}N}$ (R = H, R^1 = CHClMe (XI); R = $SiMe_3$, R^1 = Me (XII), CHClMe (XIII), Ph (XIV)). The reaction of $H_2C{=}CHCH_2CN$ with II is accompanied by a shift in the C=C bond whereby the substituent R^1 = *trans*-CH=CHMe (XV) is formed. Hydrogen cyanide combines with II to yield $(CF_3)_2B(CN)CH(SiMe_3)NHMe_2$ (XVI). The nitrile derivatives XI–XIV are hydrolysed with formation of $(R^1C(O)NH)(CF_3)_2BCHRNHMe_2$ (R = H, R^1 = CHClMe (XVII); R = $SiMe_3$, R^1 = Me (XVIII), CHClMe (XIX), Ph (XX)). The novel boranes have been characterized by elemental analyses, multinuclear NMR, IR and mass spectra. The structures of IV and VII in a mixed crystal and of XVIII have been investigated crystallographically. In the solid state, IV and XVIII show intramolecular N–H ⋯ O hydrogen bondings which leads to formation of five- and seven-membered rings respectively. Steric repulsion between the CF_3 and $SiMe_3$ groups leads to large B–C–Si bond angles (average, 124.1(8)°) and variable B–CHSiN bond distances (1.648(4) Å in VII to 1.690(4) Å in IV).

Key words: Boron; Small ring; Trifluoromethyl; Crystal structure

1. Introduction

Because of the angular strain in small ring compounds, cyclopropanes are considerably more reactive than unstrained saturated hydrocarbons. For example, a C–C bond of cyclopropane can even be cleaved by strong acids, whereas such bonds in larger essentially strain-free cycloalkanes are relatively inert. A saturated C–C bond is related isosterically to the B–N bonds in amine adducts of boranes, and such bonds are surprisingly inert if the boron atom carries trifluoromethyl substituents [1,2]. Recently the first B–N analogues of cyclopropane were prepared by reaction of dimethylamino-bis(trifluoromethyl)borane with diazoalkanes, according to eqn. (1) [3].



R = H (I), $SiMe_3$ (II)

In the light of the C–C and B–N analogy, we were interested in examining the reactivity of the B–N bonds in these new cyclic derivatives. We report below the reactions of I and II with water, carbonyl compounds and nitrile compounds.

Correspondence to: Professor H. Bürger.

* Dedicated to Professor Heinrich Nöth on the occasion of his 65th birthday.

0022-328X/94/\$7.00
SSDI 0022-328X(93)24026-2

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TABLE 1. NMR spectral data for III–XX [a]

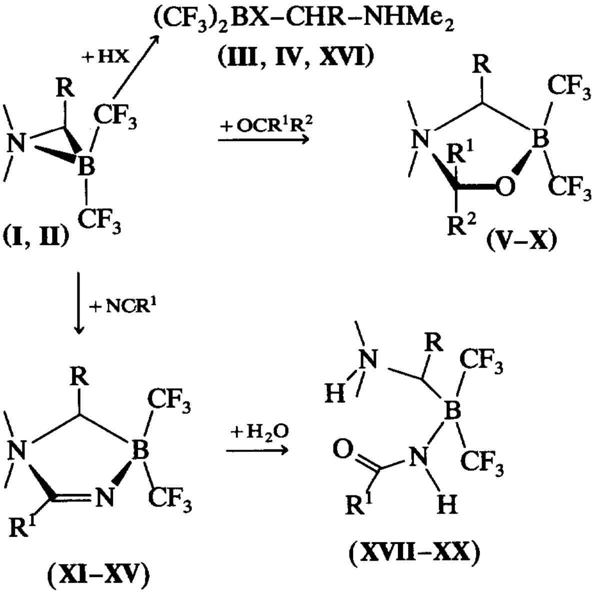
	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX
^{1}H																		
$\delta(\mathrm{NC}H_3)$	2.78	2.77 2.82	2.80	2.72 2.94	2.91 2.93	2.92 2.95	2.81 2.93	2.83 3.08	2.94 3.09	2.84 2.91	2.92 3.05 3.10 3.17	3.08	3.19 3.30	2.90 2.94	2.70	2.80 2.83	2.82 2.87	2.90 2.91
$\delta(\mathrm{BC}H_n)$	2.33	2.29	2.60	2.37	2.64	2.59	2.65	2.70	2.70	2.04	2.19 2.25	2.50	2.30	2.40	2.41	2.36	2.24	2.40
$\delta(=\mathrm{CC}H_3)$							1.80 1.98	2.0			1.76 1.78		1.92					
$\delta(\mathrm{C{=}C}H)$													6.40 7.07					
$\delta(\mathrm{CC}H_2)$			1.71 1.77			1.75 2.06		1.77 2.37 2.55										
$\delta(\mathrm{CC}H_3)$			0.82	1.41	1.58	1.00 1.03	1.53	1.65	1.69	2.07					1.56	1.99	1.70	
$\delta(\mathrm{C}H\mathrm{CH}_3)$				4.64			5.30		4.62		4.63 4.66				4.33		4.40	
$\delta(\mathrm{SiC}H_3)$		0.20		0.24	0.27	0.23	0.23	0.23		0.06	0.16	0.29	0.29	0.35		0.26	0.27	0.30
$\delta(\mathrm{C}_6H_5)$												~ 7.5						~ 7.45 ~ 7.75
$\delta(\mathrm{N}H)$	~ 7.0	~ 8.5												6.3	6.1 10.4	5.7 11.2	6.3 11.2	6.1 11.5
^{19}F																		
$\delta(\mathrm{C}F_3)$	−65.6	−66.6 −68.7	−67.4	−64.1 −67.1	−64.8	−65.3 −66.5	−65.6 −65.9	−65.2 −65.8	−62.4 −62.5	−62.8 −66.0	−61.6 −62.6 −65.8	−62.8 −65.9	−62.5 −65.6	−57.3 −61.1	−67.4	−59.3 −61.6	−59.7 −62.3	−61.8 −64.6

^{11}B																		
δ(*B*)	−9.0	−8.0	−4.5	−4.0	−3.0	−3.2	−2.9	−2.7	−3.6	−2.4	−2.3	−2.3	−2.4	−20.9	−12.6	−10.6	−10.4	−9.7
^{13}C																		
δ(N*C*H$_3$)	47.5	42.9 48.0	49.3	43.4 51.0	47.3 49.9	47.7 50.6	48.9 51.0	48.9 52.4	51.7 52.6	48.4 52.1	49.1 50.2 52.6 53.0	51.1 54.8	50.5 53.9	44.8 49.6	45.8 46.1	43.3 48.8	42.3 48.2	41.9 47.7
δ(B*C*H$_2$)	52.5	55.0	58.5	63.0	58.0	60.0	58	59	60	59	60	60	60	54.5		56	56	56
δ(C*CH$_3$*)			7.8	16.0	23.9 24.2	8.6 8.7	25.4	23.4	23.9		24.4 24.6				22.1	24.8	22.7	
δ(C*C*H$_2$)			25.5			25.4 26.5		16.8										
δ(Si*C*H$_3$)		0.8		0.6	0.3	0.6	0.8	1.0			−0.3	0.4	1.0	1.7		2.6	2.3	1.8
δ(O*C*N)			112.4	102.9	108.3	113.9	111.6	113.6										
δ(O*C*=C)							120.3	129.9										
δ(N=*C*N)									156.8	154.5	157.6 157.8	157.7	145.9					
δ(N=C*C*)									45.3	12.5	45.4 45.5		18.9		56.2		56.7	
δ(OC=*C*)							143.4	147.0										
δ(*C*≡N)														129.5				
δ(*C*$_6$H$_5$)												129.7 130.9 131.6 133.2						126.5 128.2 131.2 134.6
δ(=C*C*H$_3$)							18.8 28.3	23.1										
δ(=C*C*H$_2$)								42.0 37.0										
δ(*C*=O)															176.7	179.4	177.5	174.1

[a] **III**, **VI**, **IX**, **XIV**, **XVI** and **XVIII** in CD$_3$CN; **V**, **XI**, **XII**, **XIII**, **XVII** and **XX** in CD$_3$CN–CDCl$_3$; **IV**, **VII**, **VIII** and **XIX** in CDCl$_3$; **X** and **XV** in (CD$_3$)$_2$CO.

2. Results

Attempts to recrystallize **II** from moist acetone yielded a crystalline material which was shown by an X-ray diffraction investigation to be a 1:2 mixture of $(CF_3)_2B(OH)CH(SiMe_3)NHMe_2$ (**IV**) and the five-membered heterocyclic species $(CF_3)_2BCH(SiMe_3)$-NMe_2CMe_2O (**VII**). While cleavage of the B–N bond in **I** and **II** was also observed in other moist solvents such as CH_2Cl_2 or $CHCl_3$ (Scheme 1), the ring expansion reaction involving incorporation of acetone was an unexpected feature. Analogous experiments employing different carbonyl derivatives, however, revealed that this ring expansion occurred generally with ketones and aldehydes, while esters and amides did not undergo similar reactions. Thus the novel heterocyclic 1,4,2-oxaazoniaboratacyclopentanes $(CF_3)_2BCHR$-$NMe_2CR^1R^2O$ (R = H, $R^1 = R^2$ = Et (**V**); R = $SiMe_3$, R^1 = H, R^2 = Me (**VI**), $R^1 = R^2$ = Me (**VII**), (**VIII**), R^1 = Me, R^2 = CH=CMe$_2$ (**IX**), R^2 = $C{=}CMe(CH_2)_2CH_2$ (**X**)) were obtained with almost quantitative yields. Of these, **VI**, **IX** and **X** can in principle exist in two diastereomeric forms, but their NMR spectra (Table 1) show no evidence for the presence of more than one isomer.



	R	X	R^1	R^2	Yield %
III	H	OH			95
IV	$SiMe_3$	OH			97
V	H		Et	Et	99
VI	$SiMe_3$		H	Me	92
VII	$SiMe_3$		Me	Me	98
VIII	$SiMe_3$		Et	Et	96
IX	$SiMe_3$		Me	$CH{=}CMe_2$	88
X	$SiMe_3$		Me	$C{=}CMe(CH_2)_2CH_2$	65
XI	H		CHClMe		88
XII	$SiMe_3$		Me		98
XIII	$SiMe_3$		CHClMe		94
XIV	$SiMe_3$		Ph		93
XV	$SiMe_3$		CH=CHMe		63
XVI	$SiMe_3$	CN			73
XVII	H		CHClMe		82
XVIII	$SiMe_3$		Me		97
XIX	$SiMe_3$		CHClMe		93
XX	$SiMe_3$		Ph		89

Scheme 1.

An analogous ring expansion reaction was observed when **I** and **II** were treated with nitriles R^1CN (Scheme 1). Thus 1,4,2-azaazoniaboratacyclopentenes $(CF_3)_2$-$BCHRNMe_2CR^1{=}N$ (R = H, R^1 = CHClMe (**XI**); R = $SiMe_3$, R^1 = Me (**XII**), CHClMe (**XIII**), Ph (**XIV**)) were formed readily and isolated with high yields. Compound **XIII**, which contains two asymmetric carbon atoms, was obtained as a mixture of all stereoisomers. In the course of the reaction of **II** with $H_2C{=}CH$–CH_2–CN the C=C double bond must have migrated because the R^1 substituent in the isolated product (**XV**) is *trans*-CH=CHMe. Rather than behaving like a nitrile, HCN reacts like a protic acid to yield $(CF_3)_2B(CN)CH(SiMe_3)NHMe_2$ (**XVI**).

The R^1C–NMe_2 bonds of **XI**–**XV** are rapidly cleaved by water, and the acetamides **XVII**–**XX** are obtained almost quantitatively (Scheme 1).

3. Properties and spectra

Compounds **III**–**XX** are colourless solids. Their melting points are given in Section 8. Except for the nitrile derivatives **XI**–**XV**, they are not sensitive towards air and moisture and are soluble in polar organic solvents such as CH_2Cl_2 and CH_3CN.

The ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **III**–**XX** were recorded. The shift data, which are set out in Table 1, are consistent with the proposed structures, and only a few comments are necessary. Although **VI**, **IX** and **X** have two asymmetric ring carbon atoms only two ^{13}C and two ^{19}F signals are observed for the NCH_3 and BCF_3 groups respectively. Obviously only one stereoisomer is formed, presumably that with the $SiMe_3$ group and the relatively bulky R^2 substituent in equatorial positions of the five-membered rings.

The nitrile derivative **XIII** has two asymmetric carbon atoms, and in this case the presence of two diastereomers is clearly revealed by its NMR spectra. Thus the ^1H and ^{13}C NMR spectra both show four signals for the NCH_3 groups and two resonances for the BCH fragments. The *trans* configuration at the C=C bond in **XV** is revealed by the typical $^3J(H,H)$ coupling constant of 15.0 Hz. Diagnostic resonances for the ring carbon atoms of the heterocycles **V**–**X** are observed between 102 and 114 ppm (B–O–*C*–N), and for **XI–XV** between 145 and 158 ppm (B–N=*C*–N), whereas the carbonyl groups in **XVII–XX** give rise to signals near 176 ppm. The ^{11}B resonance of **XVI** at -21 ppm is significantly different from that of all other species mentioned here, but typical for that of a boron atom bonded to four carbon atoms.

The EI mass spectral data for **IV–X** and **XII–XX** are set out in Table 2. The M^+ peaks are generally weak, but the fragments $[M-CF_3]^+$ and $[M-C_2F_5]^+$ are indicative of the molecular weight. Two intense ions, often the base peaks in derivatives bearing the trimethylsilyl group, are m/e 106 $[F_2BCHN(CH_3)_2]^+$, and m/e 130 $[(CH_3)_2NCHSi(CH_3)_3]^+$. The latter corresponds to the fragment m/e 58 $[(CH_3)_2NCH_2]^+$, in non-silylated species **V** and **XVII**.

4. X-ray structure determination

Crystals were sealed in glass capillaries. The cell constants and intensity data (Table 3) were measured with a Siemens AED-1 diffractometer. The structures were solved by direct methods using the program SHELXS-86 [4] and were refined with the program SHELX-76 [5], anisotropic temperature factors being used only for the non-hydrogen atoms. While refinement of the hydrogen atoms which are bonded to the oxygen, nitrogen and methine carbon atoms was not constrained, the methyl hydrogen atoms, which were assigned group isotropic temperature factors, were placed in calculated positions (C–H, 0.95 Å) in **IV** and **VII** and refined as rigid groups in **XVIII**. The refinements converged to yield the coordinates given in Tables 4–6.

5. Description of the crystal structure of IV:2VII

The structural analysis shows that **IV** and **VII** co-crystallized serendipitously in a 1:2 ratio during an attempt to recrystallize **II**. As mentioned above, **IV** and **VII** are formed by insertion of water and acetone respectively into the B–N bond of **II**. In order to distinguish between the three molecules in the asym-

TABLE 2. EI-mass spectral data for **IV–X** and **XII–XX**

Compound	m/e (relative intensity (%)) [fragment]$^+$
IV	45(100) $[(CH_3)_2NH]^+$, 117(96) $[CH_3NH_2CHSi(CH_3)_3]^+$, 180(78) $[M-C_2F_4-OH]^+$, 179(68) $[M-C_2F_4-H_2O]^+$, 184(71) $[M-CF_3-(CH_3)_2N]^+$, 183(58) $[M-CF_3-(CH_3)_2NH]^+$, 89(58) $[OSi(CH_3)_3]^+$, 59(46) $[(CH_3)_3N\}^+$, 106(45) $[F_2BCHN(CH_3)_2]^+$, 132(34) $[OFBCHSi(CH_3)_3]^+$, 230(15) $[M-CF_2-H_2O]^+$, 229(14) $[M-CF_2-OH]^+$
V	58(100) $[(CH_3)_2NCH_2]^+$, 174(56) $[M-C_2F_5]^+$, 88(30) $[FBCH_2N(CH_3)_2]^+$, 106(10) $[F_2BCHN(CH_3)_2]^+$, 224(5) $[M-CF_3]^+$
VI	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 204(98) $[M-C_2F_5]^+$, 208(55) $[M-CH_3-C_2F_4]^+$, 106(33) $[F_2BCHN(CH_3)_2]^+$, 73(20) $[Si(CH_3)_3]^+$, 254(11) $[M-CF_3]^+$, 250(2) $[M-Si(CH_3)_3]^+$
VII	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 106(97) $[F_2BCHN(CH_3)_2]^+$, 218(79) $[M-C_2F_5]^+$, 222(46) $[M-CH_3-C_2F_4]^+$, 73(38) $[Si(CH_3)_3]^+$, 137(18) $[CF_3BCHN(CH_3)_2]^+$, 268(12) $[M-CF_3]^+$, 264(6) $[M-Si(CH_3)_3]^+$
VIII	106(100) $[F_2BCHN(CH_3)_2]^+$, 130(77) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 246(51) $[M-C_2F_5]^+$, 73(31) $[Si(CH_3)_3]^+$, 250(22) $[M-CH_3-C_2F_4]^+$, 137(16) $[CF_3BCHN(CH_3)_2]^+$, 296(9) $[M-CF_3]^+$, 292(7) $[M-Si(CH_3)_3]^+$
IX	106(100) $[F_2BCHN(CH_3)_2]^+$, 130(90) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 258(60) $[M-C_2F_5]^+$, 73(32) $[Si(CH_3)_3]^+$, 304(18) $[M-Si(CH_3)_3]^+$, 178(17) $[F_2BCSi(CH_3)_3N(CH_3)_2]^+$, 262(15) $[M-CH_3-C_2F_4]^+$, 308(14) $[M-CF_3]^+$, 137(7) $[CF_3BCHN(CH_3)_2]^+$
X	106(100) $[F_2BCHN(CH_3)_2]^+$, 130(94) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 330(44) $[M-Si(CH_3)_3]^+$, 284(35) $[M-C_2F_5]^+$, 73(27) $[Si(CH_3)_3]^+$, 109(19) $[C_7H_9O]^+$, 137(14) $[CF_3BCHN(CH_3)_2]^+$, 334(11) $[M-CF_3]^+$, 288(6) $[M-CH_3-C_2F_4]^+$
XII	106(100) $[F_2BCHN(CH_3)_2]^+$, 130(53) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 137(20) $[CF_3BCHN(CH_3)_2]^+$, 73(31) $[Si(CH_3)_3]^+$, 201(7) $[M-C_2F_5]^+$, 247(5) $[M-Si(CH_3)_3]^+$
XIII	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 106(86) $[F_2BCHN(CH_3)_2]^+$, 73(31) $[Si(CH_3)_3]^+$, 137(13) $[CF_3BCHN(CH_3)_2]^+$, 249(6) $[M-C_2F_5]^+$, 295(3) $[M-Si(CH_3)_3]^+$
XIV	103(100) $[C_6H_5CN]^+$, 106(85) $[F_2BCHN(CH_3)_2]^+$, 137(29) $[CF_3BCHN(CH_3)_2]^+$, 73(27) $[Si(CH_3)_3]^+$, 77(23) $[C_6H_5]^+$
XV	106(100) $[F_2BCHN(CH_3)_2]^+$, 227(48) $[M-C_2F_5]^+$, 73(47) $[Si(CH_3)_3]^+$, 130(44) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 96(31) $[C_6H_{10}N]^+$, 277(22) $[M-CF_3]^+$, 137(22) $[CF_3BCHN(CH_3)_2]^+$, 346(19) $[M]^+$, 273(8) $[M-Si(CH_3)_3]^+$
XVI	44(100) $[C_2H_6N]^+$, 116(97) $[CH_3NHCHSi(CH_3)_3]^+$, 45(96) $[FCN]^+$, 187(91) $[M-C_2F_5]^+$, 73(83) $[Si(CH_3)_3]^+$, 191(65) $[M-CH_3-C_2F_4]^+$, 131(35) $[(CH_3)_2NHCHSi(CH_3)_3]^+$, 291(19) $[M-CH_3]^+$
XVII	58(100) $[(CH_3)_2NCH_2]^+$, 106(40) $[F_2BCHN(CH_3)_2]^+$, 195(23) $[M-C_2F_5]^+$, 245(7) $[M-CF_3]^+$
XVIII	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 245(58) $[M-Si(CH_3)_3-HF]^+$, 116(56) $[CH_3NHCHSi(CH_3)_3]^+$, 106(42) $[F_2BCHN(CH_3)_2]^+$, 265(41) $[M-Si(CH_3)_3]^+$, 73(27) $[Si(CH_3)_3]^+$, 145(25) $[FBCHSi(CH_3)_3NCH_3]^+$, 184(23) $[HN(CH_3)_2CHSi(CH_3)_3BNCO]^+$, 178(20) $[F_2BCSi(CH_3)_3N(CH_3)_2]^+$, 219(16) $[M-C_2F_5]^+$, 323(12) $[M-CH_3]^+$
XIX	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 116(64) $[CH_3NHCHSi(CH_3)_3]^+$, 106(52) $[F_2BCHN(CH_3)_2]^+$, 73(27) $[Si(CH_3)_3]^+$, 180(30) $[F_2BCHSi(CH_3)_3NH(CH_3)_2]^+$, 293(29) $[M-Si(CH_3)_3-HF]^+$, 184(24) $[HN(CH_3)_2CHSi(CH_3)_3BNCO]^+$, 313(20) $[M-Si(CH_3)_3]^+$, 267(15) $[M-C_2F_5]^+$, 178(12) $[F_2BCSi(CH_3)_3N(CH_3)_2]^+$, 371(7) $[M-CH_3]^+$
XX	130(100) $[(CH_3)_2NCHSi(CH_3)_3]^+$, 106(46) $[F_2BCHN(CH_3)_2]^+$, 116(31) $[CH_3NHCHSi(CH_3)_3]^+$, 307(28) $[M-Si(CH_3)_3-HF]^+$, 77(18) $[C_6H_5]^+$, 327(18) $[M-Si(CH_3)_3]^+$, 73(13) $[Si(CH_3)_3]^+$, 385(8) $[M-CH_3]^+$ 178(7) $[F_2BCSi(CH_3)_3N(CH_3)_2]^+$, 184(24) $[HN(CH_3)_2CHSi(CH_3)_3BNCO]^+$

metric unit, the atom numbering carries a 1, 2 or 3 as leading digit, which is occasionally abbreviated with I in the following. Relevant molecular dimensions are given in Tables 7 and 8. The shortest intermolecular contact, namely H(O1) ··· O(3) with (x, y, $z-1$), 2.21(3) Å, shows that a weak hydrogen bond is formed between **IV** and the second molecule of **VII**.

Insertion of water into the B–N bond of **II** places a hydroxy group on boron and protonates the nitrogen (Fig. 1). The B–OH linkage, 1.458(5) Å, does not differ significantly from that in $(CF_3)_2B(OH)CH(Ph)NH(Bz)$-$^tBu$ (**A**), 1.465(3) Å [6], but is significantly longer than that in $(CF_3)_2B(OH)NHMe_2$ (**B**), 1.432(3) Å [7]. Apparently the lengthening of the B–OH bond in **IV** and **A** compared with that in **B** is associated with the separation by a carbon atom of the centres of formal positive and negative charge in **IV** and **A**. The greater separation allows the formation of a five-membered ring by N(1)–H(N1) ··· O(1) hydrogen bonding. As in **A** the hydrogen bond is strongly bent but is ~0.2 Å shorter than the nearly linear (173(2)°) intermolecular hydrogen bond formed by **B**.

TABLE 3. Crystallographic data [a] for **IV**:2**VII** and **XVIII**

	IV:2**VII**	**XVIII**
Formula	$C_8H_{18}BF_6NOSi$ + $2C_{11}H_{22}BF_6NOSi$	$C_{10}H_{21}BF_6N_2OSi$
M_r	297.12 + 337.19	338.18
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.3884(8)	6.574(2)
b (Å)	17.213(2)	15.826(2)
c (Å)	18.749(2)	16.217(2)
α (°)	115.328(5)	90
β (°)	91.759(7)	100.77(2)
γ (°)	99.122(6)	90
V (Å^3)	2401.2	1657.4
Z	2	4
D_c (g cm^{-3})	1.344	1.355
T (°C)	23	24
Radiation	Cu Kα	Mo Kα
λ (Å)	1.54184	0.71073
2θ limits (°)	5–130	3–50
Reflections		
Measured	9221	6711
Unique	8138	2979
With $F \geqslant 4\sigma(F)$	5863	2041
Crystal size (mm)	0.18 × 0.30 × 0.75	0.23 × 0.23 × 0.43
μ_λ (cm^{-1})	18.53	1.92
Transmission	0.7408–0.4741	0.9735–0.9490
R (F_o)	0.054	0.051
R_w (F_o)	0.074	0.050
Parameters	580	226
Δp (e Å^{-3})	0.30 to −0.22	0.33 to −0.22

[a] Additional crystallographic data may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, by quoting the authors, the literature reference and the deposit number CSD-57456.

TABLE 4. Positional and isotropic or equivalent isotropic [a] thermal parameters for **IV**

Atom	x	y	z	U
Si(1)	0.1170(1)	0.26715(7)	0.06993(6)	0.0747(4)
F(11)	−0.1166(3)	0.1547(1)	−0.2073(1)	0.118(1)
F(12)	−0.0529(3)	0.1274(1)	−0.1112(1)	0.110(1)
F(13)	0.1286(3)	0.1887(1)	−0.1561(1)	0.118(1)
F(14)	−0.2780(2)	0.3556(1)	−0.0087(1)	0.114(1)
F(15)	−0.3391(2)	0.2667(2)	−0.1292(1)	0.116(1)
F(16)	−0.3141(3)	0.2179(2)	−0.0445(2)	0.126(2)
O(1)	−0.0096(3)	0.3489(1)	−0.1079(1)	0.069(1)
N(1)	0.1988(3)	0.3977(2)	0.0099(2)	0.063(1)
C(11)	−0.0246(4)	0.1902(2)	−0.1361(2)	0.076(2)
C(12)	−0.2437(4)	0.2806(2)	−0.0634(2)	0.075(2)
C(13)	0.0611(3)	0.3305(2)	0.0138(2)	0.057(1)
C(14)	0.3556(4)	0.3682(2)	−0.0089(2)	0.087(2)
C(15)	0.2221(4)	0.4855(2)	0.0792(2)	0.091(2)
C(16)	0.2494(5)	0.1851(3)	0.0212(2)	0.111(3)
C(17)	−0.0771(5)	0.2102(3)	0.0852(2)	0.113(3)
C(18)	0.2211(5)	0.3453(3)	0.1717(2)	0.106(2)
B(1)	−0.0520(4)	0.2861(2)	−0.0754(2)	0.060(1)
H(O1)	−0.006(4)	0.338(2)	−0.147(2)	0.07(1)
H(N1)	0.159(4)	0.403(2)	−0.030(2)	0.063(9)
H(13)	0.000(3)	0.367(2)	0.052(1)	0.055(7)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j\mathbf{a}_i \cdot \mathbf{a}_j a_i^* a_j^* U_{ij}$ for the non-hydrogen atoms.

Hydrolysis of **II** appears to cause a marked lengthening of the B(1)–C(13) bond in view of the fact that the endocyclic B–C distance in $(CF_3)_2\overline{BC(SiMe_3)(Bz)}$-$\overline{N}Me_2$ (**C**) is 0.095(6) Å shorter [3]. Steric interactions may contribute to the lengthening of the B(1)–C(13) bond in **IV**, since the B(1)–C(13)–Si(1) angle is very large, 125.2(2)°. Analogous arguments were invoked to account for the length, 1.673(4) Å, of the corresponding distance in **A**. On the contrary, the C(13)–N(1) bond in **IV** is 0.033(5) and 0.041(5) Å shorter respectively than the analogous linkages in **A** and **C**; so relatively enhanced C(13)–N(1) bonding may be compensating for the long B(1)–C(13) bond.

Excellent agreement is found between the molecular dimensions of the two crystallographically independent molecules of **VII** except for the fact that an enantiomorphic pair was chosen for the asymmetric unit. Thus the twist conformation found for the five-membered ring of **VII** (Figs. 2 and 3) appears to be quite rigid.

This ring is somewhat smaller and, because of the two additional methyl substituents, sterically more obstructed than that of **IV**. Nevertheless the B(I)–C(I3) bonds are significantly shorter (0.042(6) Å average shortening) in **VII** than in **IV**. The other bonds formed by boron tend to be longer in **VII** than in **IV**, the difference being significant for the B–O distances (0.024(6) Å). While the C(I4)–O(I) distances (average,

TABLE 5. Positional and thermal [a] parameters for **VII**

Atom	*x*	*y*	*z*	*U*
Si(2)	0.4207(1)	0.09423(7)	0.20493(6)	0.0824(5)
F(21)	0.4179(3)	0.2631(1)	0.3860(1)	0.121(1)
F(22)	0.6654(3)	0.2515(1)	0.4003(1)	0.105(1)
F(23)	0.5191(4)	0.2670(1)	0.4941(1)	0.132(1)
F(24)	0.1955(3)	0.0193(2)	0.3715(2)	0.148(2)
F(25)	0.1788(3)	0.1505(2)	0.4044(2)	0.153(2)
F(26)	0.2887(4)	0.1157(2)	0.4853(2)	0.168(2)
O(2)	0.5860(2)	0.0932(1)	0.4191(1)	0.0706(9)
N(2)	0.6130(3)	0.0159(2)	0.2854(2)	0.075(1)
C(21)	0.5135(5)	0.2242(2)	0.4145(2)	0.085(2)
C(22)	0.2828(5)	0.1006(3)	0.4099(2)	0.088(2)
C(23)	0.4644(3)	0.0575(2)	0.2852(2)	0.057(1)
C(24)	0.6237(4)	0.0140(2)	0.3689(2)	0.073(2)
C(25)	0.5950(6)	−0.0741(3)	0.2183(2)	0.122(2)
C(26)	0.7613(4)	0.0726(3)	0.2789(3)	0.113(3)
C(27)	0.7954(4)	0.0109(3)	0.3964(3)	0.109(2)
C(28)	0.5034(5)	−0.0637(2)	0.3668(3)	0.102(2)
C(29)	0.4361(7)	0.0089(3)	0.1036(2)	0.138(3)
C(210)	0.2048(5)	0.1079(3)	0.2125(2)	0.107(2)
C(211)	0.5488(6)	0.1980(3)	0.2153(3)	0.127(3)
B(2)	0.4605(4)	0.1190(2)	0.3807(2)	0.060(1)
H(23)	0.379(3)	0.009(2)	0.270(1)	0.053(7)
Si(3)	0.2433(1)	0.47127(7)	0.61042(6)	0.0798(5)
F(31)	0.1029(2)	0.5188(1)	0.8144(1)	0.099(1)
F(32)	0.3569(2)	0.5427(1)	0.8051(1)	0.098(1)
F(33)	0.2673(3)	0.4776(1)	0.8749(1)	0.105(1)
F(34)	0.4010(3)	0.2797(2)	0.6680(1)	0.117(1)
F(35)	0.5130(2)	0.4020(2)	0.7553(2)	0.139(2)
F(36)	0.3721(3)	0.3128(2)	0.7867(2)	0.158(2)
O(3)	0.0636(2)	0.3337(1)	0.7390(1)	0.0589(8)
N(3)	−0.0115(3)	0.3350(1)	0.6192(1)	0.059(1)
C(31)	0.2356(4)	0.4812(2)	0.8050(2)	0.073(1)
C(32)	0.3724(4)	0.3445(2)	0.7346(2)	0.077(2)
C(33)	0.1695(3)	0.3793(2)	0.6394(2)	0.056(1)
C(34)	−0.0341(3)	0.2795(2)	0.6683(2)	0.060(1)
C(35)	−0.0579(4)	0.2777(2)	0.5318(2)	0.088(2)
C(36)	−0.1175(4)	0.4019(2)	0.6453(2)	0.079(2)
C(37)	−0.2075(4)	0.2635(2)	0.6855(2)	0.084(2)
C(38)	0.0233(4)	0.1930(2)	0.6248(2)	0.080(2)
C(39)	0.1855(6)	0.4369(3)	0.5027(2)	0.133(3)
C(310)	0.4702(5)	0.4875(3)	0.6256(2)	0.114(3)
C(311)	0.1737(6)	0.5774(2)	0.6668(3)	0.109(2)
B(3)	0.2111(4)	0.3860(2)	0.7285(2)	0.057(1)
H(33)	0.219(3)	0.337(2)	0.607(1)	0.050(7)

[a] See Table 4.

TABLE 6. Positional and thermal [a] parameters for **XVIII**

Atom	*x*	*y*	*z*	*U*
Si	0.0247(1)	0.05151(5)	0.83677(5)	0.0536(3)
F(1)	0.1887(3)	0.2657(1)	0.7938(1)	0.0766(8)
F(2)	−0.0619(4)	0.3367(1)	0.7245(1)	0.0864(9)
F(3)	−0.1192(4)	0.2509(1)	0.8196(1)	0.093(1)
F(4)	−0.4204(3)	0.1542(2)	0.7010(2)	0.120(1)
F(5)	−0.3562(3)	0.1290(1)	0.5819(2)	0.105(1)
F(6)	−0.3795(3)	0.2560(1)	0.6201(2)	0.110(1)
O	0.0395(4)	0.1119(1)	0.5236(1)	0.073(1)
N(1)	0.0547(4)	0.2183(2)	0.6156(1)	0.048(1)
N(2)	0.0202(4)	0.0244(1)	0.6587(1)	0.0414(8)
C(1)	−0.0112(6)	0.2582(2)	0.7565(2)	0.063(1)
C(2)	−0.2998(5)	0.1813(2)	0.6484(2)	0.069(1)
C(3)	0.0495(5)	0.0932(2)	0.7272(2)	0.040(1)
C(4)	0.0814(5)	0.1859(2)	0.5436(2)	0.049(1)
C(5)	0.1698(6)	0.2414(2)	0.4840(2)	0.066(1)
C(6)	−0.1577(5)	−0.0336(2)	0.6579(2)	0.061(1)
C(7)	0.2125(5)	−0.0249(2)	0.6562(2)	0.062(1)
C(8)	−0.2460(6)	0.0453(2)	0.8555(2)	0.079(2)
C(9)	0.1435(7)	−0.0560(2)	0.8580(2)	0.078(2)
C(10)	0.1835(7)	0.1184(2)	0.9191(2)	0.084(2)
B	−0.0530(5)	0.1835(2)	0.6865(2)	0.045(1)
H(1)	0.085(4)	0.267(2)	0.620(2)	0.044(9)
H(2)	−0.005(5)	0.054(2)	0.604(2)	0.07(1)
H(3)	0.195(4)	0.104(1)	0.738(1)	0.028(6)

[a] See Table 4.

1.385(7) Å) are short for an ether-like bond, the C(*I*4)–N(*I*) bond lengths (average, 1.582(4) Å) are markedly long. The length of the C(*I*4)–N(*I*) interaction may reflect in part the ability of the C–O linkage to stabilize a positive charge on the C(*I*4) atom via O(pπ) → C(pπ) bonding—the tendency for a hesitant approach of a carbonyl to an amine group being well documented [8]. The short contacts between the F(*I*4) atoms and the hydrogen atoms bonded to C(*I*3) and C(*I*8) should be noted. They cause a ~24° rotation of the trifluoromethyl groups about the B(*I*)–C(*I*2) bonds away from the staggered conformation, whereas the conformation of the B(*I*)–C(*I*1) bonds lies within 4° of being exactly staggered.

6. Description of the crystal structure of XVIII

A view of **XVIII** is given in Fig. 4, and important dimensions are listed in Table 9. The structure of **XVIII** is closely related to that of **IV**, the hydroxy group of **IV** being replaced by an acetamido fragment. The carbonyl function of the latter accepts a proton from the ammonium centre to form an O ··· H(2)–N(2) hydrogen bond that completes a seven-membered ring. This hydrogen bond is not nearly as bent (160(3)°) and

TABLE 7. Selected bond distances and angles in **IV**

B(1)–C(11)	1.612(5)	C(13)–H(13)	0.95(3)
B(1)–C(12)	1.624(5)	N(1)–C(14)	1.483(4)
B(1)–C(13)	1.690(4)	N(1)–C(15)	1.490(5)
B(1)–O(1)	1.458(5)	N(1)–H(N1)	0.85(3)
C(13)–Si(1)	1.906(4)	O(1)–H(O1)	0.68(3)
C(13)–N(1)	1.526(4)	O(1)–H(N1)	1.82(3)
O(1)–B(1)–C(13)	104.9(2)	B(1)–C(13)–N(1)	105.4(3)
C(11)–B(1)–C(13)	115.0(3)	B(1)–C(13)–Si(1)	125.2(2)
C(12)–B(1)–C(13)	110.1(2)	B(1)–C(13)–H(13)	107(2)
C(13)–N(1)–C(14)	115.8(3)	N(1)–C(13)–Si(1)	115.9(2)
C(13)–N(1)–C(15)	114.0(3)	N(1)–C(13)–H(13)	102(2)
C(13)–N(1)–H(N1)	99(2)	Si(1)–C(13)–H(13)	98(2)
B(1)–O(1)–H(N1)	88(1)	N(1)–H(N1)–O(1)	139(3)

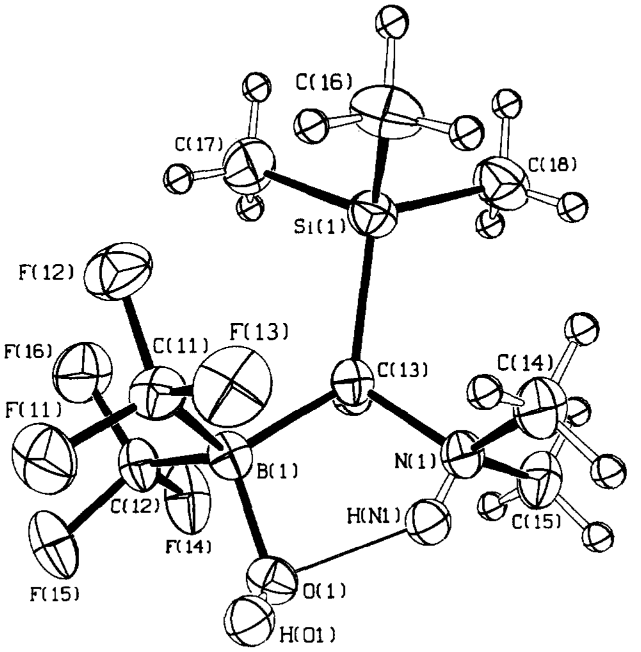


Fig. 1. A perspective drawing of **IV** with ellipsoids of the methyl hydrogen atoms reduced for clarity.

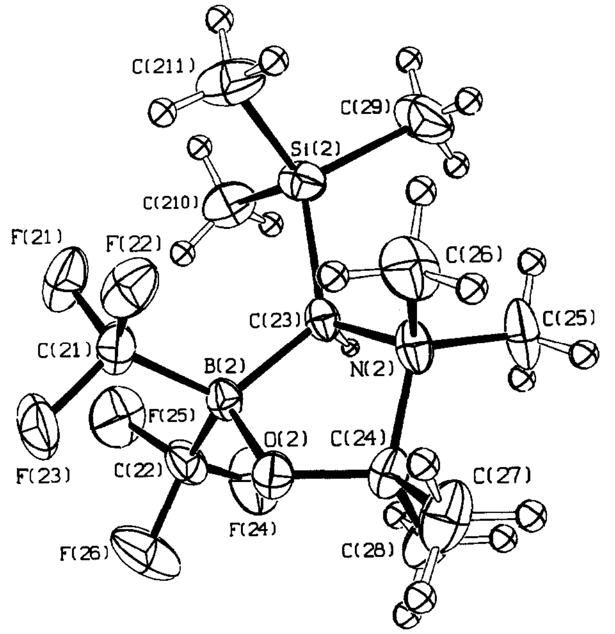


Fig. 2. A view of the first molecule of **VII** from above the ring.

is significantly shorter (0.16(4) Å) than that found in the five-membered ring of **IV**. On the contrary, the hydrogen atom bonded to N(1) forms no hydrogen bond in the solid state.

The H(1), N(1), C(4), C(5), O fragment is planar to within the limits of experimental error, and the boron atom is displaced by 0.158(3) Å from this plane. The B–N(sp^2) distance does not differ significantly from those reported in other bis(trifluoromethyl)borate structures [9]. The C(3)–B bond length lies between those found in **IV** and **VII** whereas the C(3)–N(2) distance is similar to those of **VII**.

7. Discussion

Reactions of the azoniaboratacyclopropanes **I** and **II** result in fission of the B–N bond. This reactivity is significantly higher than that of the less-strained bis(trifluoromethyl)alkylborane-amines. The latter are generally stable to water, their B–N bonds being remarkably inert, since the trifluoromethyl substituents

TABLE 8. Selected bond distances and angles in **VII**

	I = 2	*I* = 3		*I* = 2	*I* = 3
B(*I*)–C(*I*1)	1.620(6)	1.628(5)	C(*I*4)–O(*I*)	1.380(4)	1.390(3)
B(*I*)–C(*I*2)	1.634(5)	1.650(5)	C(*I*4)–N(*I*)	1.581(4)	1.583(4)
B(*I*)–C(*I*3)	1.649(4)	1.647(4)	C(*I*4)–C(*I*7)	1.531(5)	1.508(4)
B(*I*)–O(*I*)	1.483(4)	1.481(4)	C(*I*4)–C(*I*8)	1.528(6)	1.525(5)
C(*I*3)–Si(*I*)	1.912(3)	1.906(4)	N(*I*)–C(*I*5)	1.500(5)	1.506(4)
C(*I*3)–N(*I*)	1.534(4)	1.543(4)	N(*I*)–C(*I*6)	1.496(6)	1.492(4)
C(*I*3)–H(*I*3)	0.94(2)	0.90(2)			
O(*I*)–B(*I*)–C(*I*3)	103.3(3)	103.3(2)	B(*I*)–C(*I*3)–N(*I*)	102.1(2)	102.1(2)
C(*I*1)–B(*I*)–C(*I*3)	118.5(3)	118.9(3)	B(*I*)–C(*I*3)–Si(*I*)	123.3(2)	123.7(2)
C(*I*2)–B(*I*)–C(*I*3)	112.2(2)	112.3(2)	B(*I*)–C(*I*3)–H(*I*3)	107(2)	104(2)
C(*I*3)–N(*I*)–C(*I*4)	103.8(2)	104.2(2)	N(*I*)–C(*I*3)–Si(*I*)	120.4(2)	118.9(2)
C(*I*3)–N(*I*)–C(*I*5)	112.3(3)	112.9(2)	N(*I*)–C(*I*3)–H(*I*3)	101(2)	103(2)
C(*I*3)–N(*I*)–C(*I*6)	109.5(3)	110.8(2)	Si(*I*)–C(*I*3)–H(*I*3)	100(2)	102(2)
B(*I*)–O(*I*)–C(*I*4)	112.3(2)	113.3(2)	N(*I*)–C(*I*4)–O(*I*)	103.0(3)	102.7(2)

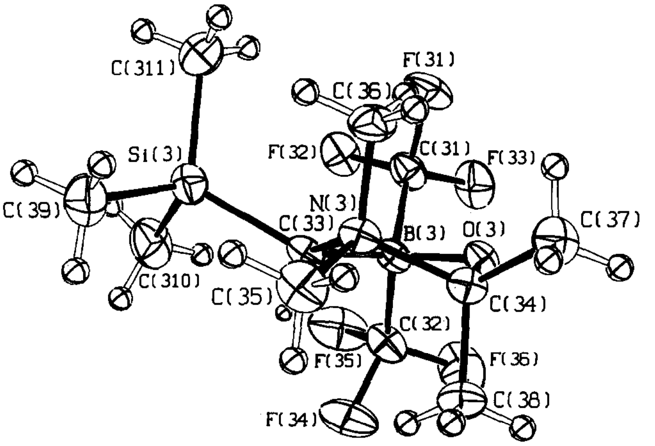


Fig. 3. A side-on view of the ring of the second molecule of **VII**.

TABLE 9. Selected bond distances and angles in **XVIII**

B–C(1)	1.627(4)	C(4)–N(1)	1.317(4)
B–C(2)	1.626(5)	C(4)–C(5)	1.501(4)
B–C(3)	1.663(4)	N(1)–H(1)	0.80(3)
B–N(1)	1.558(4)	N(2)–C(6)	1.485(4)
C(3)–Si	1.930(3)	N(2)–C(7)	1.493(4)
C(3)–N(2)	1.541(3)	N(2)–H(2)	0.99(3)
C(3)–H(3)	0.95(2)	O–H(2)	1.66(3)
C(4)–O	1.233(3)		
N(1)–B–C(3)	113.0(2)	B–C(3)–N(2)	109.5(2)
C(1)–B–C(3)	110.1(2)	B–C(3)–Si	124.2(2)
C(2)–B–C(3)	115.7(2)	B–C(3)–H(3)	103(1)
B–N(1)–C(4)	132.0(3)	N(2)–C(3)–Si	113.7(2)
B–N(1)–H(1)	114(2)	N(2)–C(3)–H(3)	104(1)
C(4)–N(1)–H(1)	113(2)	Si–C(3)–H(3)	99(1)
C(3)–N(2)–C(6)	115.8(2)	N(1)–C(4)–O	123.0(3)
C(3)–N(2)–C(7)	113.3(2)	N(1)–C(4)–C(5)	118.3(3)
C(3)–N(2)–H(2)	107(2)	O–C(4)–C(5)	118.7(3)
C(4)–O–H(2)	112(1)	N(2)–H(2)–O	160(3)

effectively limit adduct dissociation via their inductive-withdrawing effect. Thus a $\overset{\delta+}{B}-\overset{\delta-}{N}$ charge distribution is to be expected in these molecules despite fourfold coordination of both the boron and nitrogen atoms. Thus the reactions of **I** and **II** may have been initiated by a nucleophilic attack at the boron atoms. This might explain why only carbonyl and nitrile compounds undergo a ring expansion reaction while the formally related but less nucleophilic 1-alkenes such as $H_2C{=}CHC_4H_9$ and 1-alkynes such as $HC{\equiv}CC_6H_5$ do not. An analogous insertion of aldehydes into the phosphorus–boron bond has been observed in 1-boryl-2-phosphinoethylenes [10]. In this connection the tendency for cyclopropanes to open heterolytically as in eqn. (2)

(2)

should be noted. The importance of such zwitterionic transition states is enhanced by placing electron donors at the cationic site (*e.g.*, R = Me, Ph) and electron acceptors at the anionic site (*e.g.*, X = CN) [11]. Whether a ring-strain-promoted heterolytic cleavage of the NB bonds in **I** and **II** must occur before nucleophilic attack can proceed awaits to be seen. Until now no stable three-coordinated trifluoromethylborane had ever been observed without an amino group bonded directly to boron. Since these B–N bonds were usually retained in subsequently formed borate derivatives, the cleavage of the B–N bond in **I** and **II** reported here makes these three-membered rings versatile building blocks in bis(trifluoromethyl)boron chemistry.

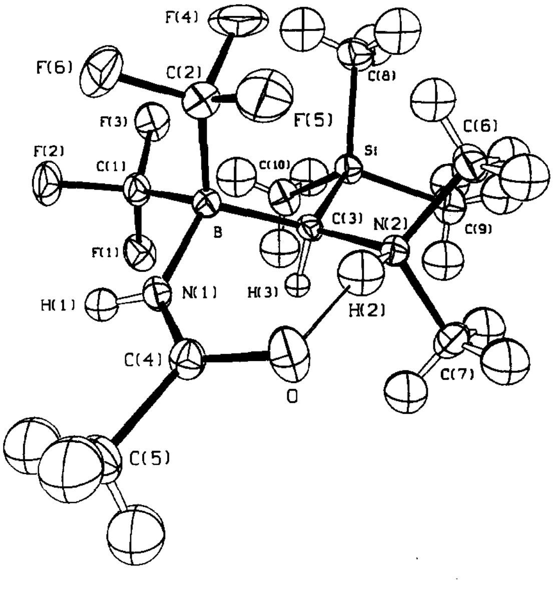


Fig. 4. A perspective drawing of **XVIII**.

8. Experimental details

8.1. 4-Hydroxy-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-2-azonia-4-boratapentane (III) and 4-hydroxy-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-3-trimethylsilyl-2-azonia-4-boratapentane (IV)

A solution of 0.52 g (2.5 mmol) of **I** or 0.56 g (2 mmol) of **II** in 10 ml of CH_2Cl_2 was stirred with 3 mmol of H_2O for 4 h at ambient temperature. After removal of the solvent and the water *in vacuo*, pure **III** and **IV** respectively were obtained.

III: Mp. 92°C. IR: ν(OH) 3660w, ν(NH) 3280w, ν(CF) 1080vs, br cm^{-1}.

IV: Mp. 80°C. IR: ν(OH) 3668w, ν(NH) 3080w, br, ν(CF) 1080vs, br cm^{-1}.

8.2. 2,2-Bis(trifluoromethyl)-5,5-diethyl-4,4-dimethyl-1-oxa-4-azonia-2-boratacyclopentane (V), 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VI), 2,2-bis(trifluoromethyl)-4,4,5,5-tetramethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VII), 2,2-bis(trifluoromethyl)-5,5-diethyl-4,4-dimethyl-3-trimethylsilyl-1-oxa-4-azonia-2-boratacyclopentane (VIII), 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-5-(2-methyl-propenyl)-1-oxa-4-azonia-2-boratacyclopentane (VIII) and 2,2-bis(trifluoromethyl)-4,4,5-trimethyl-3-trimethylsilyl-5-(2-methylcyclopentenyl)-1-oxa-4-azonia-2-boratacyclopentane (X)

A solution of 0.52 g (2.5 mmol) of **I** or 0.56 g (2 mmol) of **II** in 10 ml of $CHCl_3$ was stirred with one equivalent of the respective anhydrous carbonyl reactant for 12 h at ambient temperature. After removal of the solvent *in vacuo*, compounds **V–X** were obtained.

V: Mp. 132°C. IR: δ(CH) 1270m, ν(CF) 1098vs, 1080vs, br cm^{-1}.

VI: Mp. 119°C. IR: δ(CH) 1258m, ν(CF) 1080vs, br, $\rho(Si(CH_3)_3)$ 845vs cm^{-1}.

VII: Mp. 168°C (decomposition). IR: δ(CH) 1255s, ν(CF) 1075vs, br, $\rho(Si(CH_3)_3)$ 835s cm^{-1}.

VIII: Mp. 144°C. IR: δ(CH) 1260m, ν(CF) 1080vs, br, $\rho(Si(CH_3)_3)$ 855s cm^{-1}.

IX: Mp. 133°C. IR: ν(C=C) 1668w, δ(CH) 1257s, ν(CF) 1095vs, 1075vs, $\rho(Si(CH_3)_3)$ 855s cm^{-1}.

X: Mp. 150°C (decomposition). IR: ν(C=C) 1645vw, δ(CH) 1260s, ν(CF) 1075vs, br, $\rho(Si(CH_3)_3)$ 852s cm^{-1}.

8.3. 2,2-Bis(trifluoromethyl)-5-(1-chloroethyl)-4,4-dimethyl-1-aza-4-azonia-2-boratacyclopentene (XI), 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-methyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XII), 2,2-bis(trifluoromethyl)-5-(1-chloroethyl)-4,4-dimethyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XIII), 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-phenyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XIV) and 2,2-bis(trifluoromethyl)-4,4-dimethyl-5-propenyl-3-trimethylsilyl-1-aza-4-azonia-2-boratacyclopentene (XV)

A solution of 0.52 g (2.5 mmol) of **I** or 0.56 g (2 mmol) of **II** in 10 ml of $CHCl_3$ was stirred with one equivalent of the respective anhydrous nitrile reactant for 5 h at ambient temperature. After removal of the solvent *in vacuo* the pure compounds **XI–XV** were obtained.

XI: Mp. 111°C. IR: ν(C=N) 1730m, δ(CH) 1275s, ν(CF) 1085vs, br cm^{-1}.

XII: Mp. 168°C. IR: ν(C=N) 1745m, δ(CH) 1270s, ν(CF) 1085vs, br, $\rho(Si(CH_3)_3)$ 845s cm^{-1}.

XIII: Mp. 123°C. IR: ν(C=N) 1738s, δ(CH) 1265s, ν(CF) 1090vs, br, $\rho(Si(CH_3)_3)$ 845s cm^{-1}.

XIV: Mp. 97°C. IR: ν(C=N) 1745m, δ(CH) 1275s, ν(CF) 1090vs, 1080vs, $\rho(Si(CH_3)_3)$ 845s cm^{-1}.

XV: Mp. 113°C. IR: ν(C=N) 1720w, ν(C=C) 1625vw, δ(CH) 1260s, ν(CF) 1090vs, 1080vs, $\rho(Si(CH_3)_3)$ 845s cm^{-1}.

TABLE 10. Elemental analyses for **III–XX**

Compound	Formula	Found (%) (calc. (%))		
		C	H	N
III	$C_5H_{10}BF_6NO$	26.79 (26.70)	4.42 (4.48)	6.20 (6.23)
IV	$C_8H_{18}BF_6NOSi$	32.40 (32.34)	6.07 (6.11)	4.59 (4.71)
V	$C_{10}H_{18}BF_6NO$	41.22 (40.98)	6.37 (6.19)	4.73 (4.78)
VI	$C_{10}H_{20}BF_6NOSi$	36.68 (37.17)	5.99 (6.24)	4.20 (4.33)
VII	$C_{11}H_{22}BF_6NOSi$	39.09 (39.18)	6.51 (6.58)	4.19 (4.15)
VIII	$C_{13}H_{26}BF_6NOSi$	42.84 (42.75)	7.02 (7.17)	3.92 (3.83)
IX	$C_{14}H_{26}BF_6NOSi$	44.21 (44.57)	6.78 (6.95)	3.98 (3.71)
X	$C_{15}H_{28}BF_6NOSi$	47.09 (47.65)	6.73 (7.00)	3.91 (3.47)
XI	$C_8H_{12}BClF_6N_2$	32.64 (32.41)	4.28 (4.08)	9.22 (9.45)
XII	$C_{10}H_{19}BF_6N_2Si$	37.48 (37.52)	6.05 (5.98)	8.93 (8.75)
XIII	$C_{11}H_{20}BClF_6N_2Si$	35.49 (35.84)	5.35 (5.47)	7.38 (7.60)
XIV	$C_{15}H_{21}BF_6N_2Si$	47.00 (47.14)	5.67 (5.54)	7.50 (7.33)
XV	$C_{12}H_{21}BF_6N_2Si$	42.32 (41.63)	6.50 (6.11)	8.48 (8.09)
XVI	$C_9H_{17}BF_6N_2$	35.67 (35.31)	5.73 (5.60)	9.00 (9.15)
XVII	$C_8H_{14}BClF_6N_2O$	35.33 (35.52)	6.38 (6.26)	8.45 (8.28)
XVIII	$C_{10}H_{21}BF_6N_2OSi$	30.19 (30.56)	4.28 (4.49)	9.14 (8.91)
XIX	$C_{11}H_{22}BClF_6N_2OSi$	34.33 (34.17)	5.55 (5.73)	7.39 (7.25)
XX	$C_{15}H_{23}BF_6N_2OSi$	44.92 (45.01)	5.69 (5.79)	6.18 (7.00)

8.4. 4-Cyano-2-methyl-5,5,5-trifluoro-4-trifluoromethyl-3-trimethylsilyl-2-azonia-4-boratapentane (XVI)

A solution of 0.56 g (2 mmol) of **II** in 10 ml CH_2Cl_2 was stirred under an atmosphere of HCN for 12 h at ambient temperature. After removal of the solvent *in vacuo*, **XVI** was obtained as analytically pure crystals.

XVI: Mp. 178°C (decomposition). IR/Raman: ν(NH) 3165m/—, ν(CH) 2960m/w, ν(C≡N) 2220vw/s, ν(CF) 1090vs, br/vvw, $\rho(Si(CH_3)_3)$ 845s/m, $\delta_s(CF_3)$ 690m/s cm^{-1}.

8.5. 4,4-Bis(trifluoromethyl)-7-chloro-2-methyl-5-aza-2-azonia-4-borata-octane-6-one (XVII), 4,4-bis(trifluoromethyl)-2-methyl-3-trimethylsilyl-5-aza-2-azonia-4-borataheptan-6-one (XVIII), 4,4-bis(trifluoromethyl)-7-chloro-2-methyl-3-trimethylsilyl-5-aza-2-azonia-4-borata-octan-6-one (XIX) and 4,4-bis(trifluoromethyl)-2-methyl-6-phenyl-3-trimethylsilyl-5-aza-2-azonia-4-borata-hexan-6-one (XX)

At ambient temperature, **XI–XIV** were dissolved in $(CH_3)_2CO-H_2O$. Removal of the solvents yielded pure **XVII–XX**.

XVII: Mp. 74°C. IR: ν(NH) 3445w, 3100w, ν(C=O) 1635m, ν(CF) 1095vs cm^{-1}.

XVIII: Mp. 100°C. IR: ν(NH) 3420m, 3100w, ν(C=O) 1615m, ν(CF) 1090vs cm^{-1}.

XIX: Mp. 92°C. IR: ν(NH) 3430w, 3090w, ν(C=O) 1620 m, ν(CF) 1090vs, 1085vs cm^{-1}.

XX: Mp. 87°C. IR: ν(NH) 3420w, 3080w, ν(C=O) 1625s, ν(CF) 1095vs, 1085vs cm^{-1}.

For elemental analyses see Table 10.

Acknowledgments

We thank Dr. D. Henneberg, Mülheim/Ruhr, for recording the mass spectra. Financial support by the Fonds der Chemie and the Ministerium für Wissenschaft und Forschung NW is gratefully acknowledged.

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