Novel heterocycles from alkylamino-bis(trifluoromethyl)borane, $(CF_3)_2BNR_2$, and isocyanides. Crystal and molecular structure of $(NC)(CF_3)_2B \cdot NHMe_2$, $\overline{(CF_3)_2B-NMe_2-B(CF_3)-NEt=C-C(NMe_2)=NEt}$ and $\overline{(CF_3)_2B-NMe_2-B(CF_3)_2-CH-C(=NMe_2)-N(CH_2Ph)-CH(Ph)-N}$ ☆

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Abstract

Dialkylamino-bis(trifluoromethyl)boranes, $(CF_3)_2BNR^1_2$ [R^1 = Me (A), Et (B)] react at $-20°C$ with ^tBuNC to form the respective adducts ($^tBuNC)(CF_3)_2BNR^1_2$ [R^1 = Me (I), Et (II)]. At 20°C these eliminate isobutylene to yield the amine boranes $(NC)(CF_3)_2B \cdot NHR^1_2$ [R^1 = Me (III), Et (IV)]. ^iPrNC combines with A in a 2:1 ratio to yield the four-membered heterocycle $\overline{(CF_3)_2B-NMe_2-C(=N^iPr)-C(=N^iPr)}$ (V) and in a 2:2 ratio to form $\overline{(CF_3)_2B-NMe_2-B(CF_3)_2-NR=C-C(NMe_2)-NR}$ [R = ^iPr (VI)]. Heterocycles corresponding to VI with R = ^nBu (VII), Et (VIII) and Me (IX) were obtained by the respective reactions of ^nBuNC, EtNC and MeNC with A. The reaction of $PhCH_2NC$ with A leads to the formation of the heterobicyclo-octane $\overline{(CF_3)_2B-NMe_2-B(CF_3)_2-CH-C(=NMe_2)-N(CH_2Ph)-CH(Ph)-N}$ (X). The novel boron compounds have been characterized by multinuclear NMR, IR and mass spectra. The structures of III, VIII and X have been investigated by single-crystal X-ray diffraction.

Keywords: Boron; Isocyanides; Heterocycles; Crystal structure

1. Introduction

Isocyanides are in some respect carbene-like species which may react as nucleophiles as well as electrophiles. Their chemistry has been reviewed [1] and their reactions with dipoles $^\oplus a-b^\ominus$ leading to cyclization are schematically shown in Scheme 1, which is taken in part from Ref. [1].

If $^\oplus a-b^\ominus$ is a diatomic dipole (e.g. the carbonyl group), a three-membered ring can be formed [pathway (a)]. More often a second molecule of either of the two partners, $^\oplus a-b^\ominus$ [pathway (b)] or isocyanide [pathway (c)], formally inserts into the three-membered ring so that ultimately a larger ring is formed. Although Scheme 1 represents common cycloaddition reactions of isocyanides fairly well, it is in general impossible to predict which of these pathways any particular reaction will choose.

The high reactivity of the boron–nitrogen double bond in $(CF_3)_2BNMe_2$ (A) is exemplified by several reactions which do not occur in general in aminoborane chemistry. Thus, A readily undergoes [2 + 4] cycloaddition reactions with dienes [2], ene-type reactions with alkenes [3], nitriles and a wide variety of carbonyl compounds [4], and forms three-membered rings which are isosteric with cyclopropane when reacted with diazoalkanes [5]. These reactions have suggested $^{\delta+}B=N^{\delta-}$ polarization in A, and we wanted to see how this dipole fits into the classification given in Scheme 1. Therefore A, and in some cases $(CF_3)_2BNEt_2$ (B) also, were reacted with several alkyl isocyanides RNC, where R was systematically varied. Details of these investigations are now reported.

☆ Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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2. Results

Reactions of **A** and **B** with alkyl isocyanides are summarized in Scheme 2. When ^{t}BuNC in pentane solution was reacted at $-20°C$, colourless solids were formed. These were shown by NMR spectroscopy to be the respective 1:1 adducts of **A** and **B**, **I** and **II**, with the C lone pair of the isocyanide coordinated to the boron atom. That no three-membered rings are formed according to pathway (a), Scheme 1, follows from the chemical shift of the NCH_3 protons of **I**, δ 2.27 ppm, and of the NCH_2 protons of **II**, δ 2.82 ppm. For a three-membered ring these signals were expected to lie close to δ 2.9 ppm and δ 3.2 ppm, respectively. Additional support for the proposed acyclic structures comes from the ^{13}C resonances of the $N=C-B$ carbons near δ 125 ppm. The resonance of an imino carbon would be expected further downfield.

Warming solutions of **I** or **II** to 20°C initiated a rapid and complete elimination of isobutylene, and the respective dimethylamine and diethylamine adducts of bis(trifluoromethyl)cyanoborane (**III** and **IV**) were formed quantitatively. The structure of **III** was confirmed by an X-ray investigation (vide infra).

The adduct formed from **A** with the less bulky isopropyl isocyanide is not susceptible to an analogous propylene elimination. The almost colourless adduct obtained at low temperature decomposes however upon warming to ambient temperature to form a black, tarry material. Work-up of this by repeated sublimation in vacuo gave two species in proportions depending on the reaction conditions. After 1 h at ambient temperature the four-membered ring **V** was obtained along with some contamination due to the cyclic 1:2 adduct **VI**.

However, when **A** and ^{i}PrNC were reacted for 2 weeks at 25°C, mainly **VI** could be isolated in a low overall yield (Scheme 2). The respective analogues **VII**,

VIII and **IX** were obtained exclusively with the less bulky n-alkyl isocyanides ^{n}BuNC, EtNC and MeNC. The formation of **VII**, **VIII** and **IX** can be regarded formally as a [2 + 3] cycloaddition reaction of **A** and the intermediate four-membered heterocycle (Scheme 2). The highest yield of these five-membered heterocycles, 27%, was obtained with EtNC because purification of **VII** was difficult and the formation of **IX** was accompanied by extensive polymerization of MeNC. Essential structural features of **VIII** were revealed by a single-crystal X-ray examination.

The correspondence of the NMR spectra of **VI–IX** strongly supports their structural analogy. A key feature is a broad ^{13}C resonance at δ 208 ppm, which is attributed to the ring-carbon atom of the $B-C=N$ fragment. Furthermore, the high deshielding of this atom provides an understanding for the reaction with benzyl isocyanide which leads to a novel bicyclooctane ring system **X**. We assume that initially a heterocycle analogous to **VI–IX** is formed. In a following step (Scheme 2) a hydride is shifted from the benzylic carbon on to the electronically poor $B-C=N$ ring-carbon. Presumably the strong difference in polarity between these carbon atoms is the driving force for this hydride shift. Concomitantly, this hydrogen migration may be assisted by a nucleophilic attack of the $NCH_2C_6H_5$ nitrogen at the benzylic carbon atom by which the ring is finally closed.

3. Properties and spectra

Compounds **III**, **IV** and **X** are colourless solids. They are not sensitive towards air and moisture, and are soluble in polar organic solvents like CH_2Cl_2 and CH_3CN. The $C\equiv N$ stretching vibration of **III** and **IV** at 2248 cm^{-1} is too weak to be observable in the IR
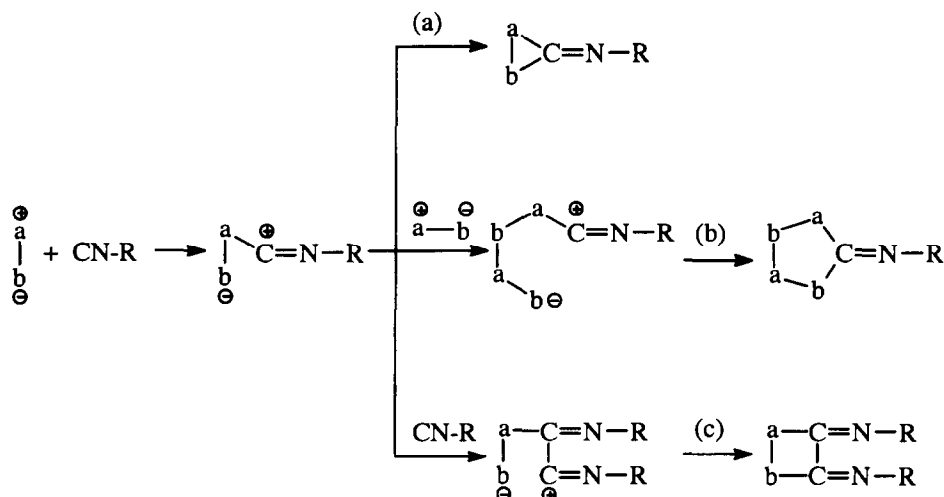
Scheme 1.

spectra but strong in the Raman spectra. Compounds VI–IX were obtained as yellow solids or oily liquids whose colour did not change upon repeated sublimation or distillation. UV–vis spectra of VIII and IX in CHCl₃ showed maxima at 320 nm ($\varepsilon = 200$–400) which can be attributed to the N=C–C=N chromophore. Melting points are given under Experimental details.

The ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectra of I–X were recorded. The shift data which are set out in Table 1 are consistent with the proposed structures, and some important features have already been discussed above. The relaxation of the boron nucleus in compounds III and

IV is sufficiently slow so that typical $1:1:1:1$ quartets are observed, e.g. ^{13}C: $^1J(\text{BC}) = 65$–70 Hz (BC=N), $^1J(\text{BC})$ ca. 80 Hz (BCF_3); ^{19}F: $^2J(\text{BF})$ ca. 30 Hz. Although VI–IX contain two magnetically non-equivalent boron atoms and four such CF₃ groups, only one broad ^{11}B resonance and only three ^{19}F resonances were observed.

EI mass spectral data of III–V and VIII–X are set out in Table 2. Compounds III and IV give an $[\text{M} + \text{H}]^+$ fragment as well as other ions not included in Table 2 with $m/e > \text{M}^+$, their intensity depending on the temperature. This indicates association in the gas phase.

Scheme 2.

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

	I	II	III	IV	V	VI	VII	VIII	IX	X
^{1}H										
$\delta(=NCH_3)$									2.96	
									3.42	
$\delta(CCH_2C)$							1.35			
							1.60			
$\delta(NCH_2CH_n)$		2.82		3.07			3.15	3.21		
				3.33			3.61	3.72		
							3.81	3.97		
$\delta[N(CH_3)_2]$	2.27		2.86		2.92	2.83	2.76	2.79	2.74	2.84
						2.94	2.99	3.01	3.03	2.88
						2.98				3.14
$\delta(CH_2CH_3)$		1.04		1.33			0.90	1.21		
							0.91	1.32		
$\delta[CH(CH_3)_2]$					3.58	4.17				
					4.76	4.48				
$\delta[CH(CH_3)_2]$					1.17	1.17				
					1.20	1.48				
						1.70				
$\delta(NH)$			6.1	5.5						
$\delta[C(CH_3)_3]$	1.55	1.61								
$\delta[C_6H_5CH_n]$										4.20
										4.84
										5.88
$\delta(BCH)$										4.81
$\delta(C_6H_5)$										7.25
										7.27
^{19}F										
$\delta(BCF_3)$	−61.8	−63.9	−63.1	−63.0	−61.2	−56.1	−56.6	−56.3	−56.5	−52.7
						−57.0	−60.0	−59.9	−56.9	−53.6
						−58.3	−60.8	−60.5	−61.0	−56.5
						−62.7				
^{11}B										
										−2.8
$\delta(B)$	−6.0	−5.7	−14.1	−13.8	−3.9	−2	−2	−2	−2	−6.3
^{13}C										
$\delta[N(CH_3)_2]$	41.3		41.3		45.0	38.1	38.2	38.1	37.1	42.6
						41.0	48.0	48.0	48.0	45.1
						46.5	48.4	48.4	48.2	46.7
						48.3				47.0
$\delta(=NCH_3)$									36.5	
									40.3	
$\delta(CCH_2C)$							20.4			
							20.6			
							29.2			
							34.0			
$\delta(NCH_2CH_n)$		41.7		47.7			49.3	43.8		
							52.9	48.1		
$\delta(CH_2CH_3)$		13.3		12.1			13.1	12.5		
							13.8	16.8		
$\delta(BC\equiv N)$	132.0	125.0	125.3	125.2						
$\delta(BCH)$										62.5
										51.2
$\delta(C_6H_5CH_n)$										87.7
$\delta(C=N)$					157.7	145.5	149.1	149.1	151.7	172.3
					171.5	∼ 208	∼ 208	∼ 208	∼ 208	
$\delta[CH(CH_3)_2]$					51.2	48.8				
					60.3	57.5				
$\delta[CH(CH_3)_2]$					23.1	24.5				
					23.4	24.8				
$\delta[C(CH_3)_3]$	29.9	28.8								

Table 1 (continued)

	I	II	III	IV	V	VI	VII	VIII	IX	X
$\delta[C(CH_3)_3]$	59.2	60.3								
$\delta(C_6H_5)$										127.7
										128.6
										128.8
										129.3
										129.5
										129.9
										135.7
										141.6

[a] I, II in CD_2Cl_2; III, IV, X in CD_3CN; V–IX in $CDCl_3$; ^1H: 250. 13 MHz, internal standard $CHCl_3$, δ 7.27 ppm; $CHDCl_2$, δ 5.35 ppm; CHD_2CN, δ 1.95 ppm. ^{13}C: 62.9 MHz, internal standard $CDCl_3$, δ 77.0 ppm; CD_2Cl_2, δ 53.8 ppm; CD_3CN, δ 1.30 ppm. ^{19}F: 235.3 MHz, internal standard $CFCl_3$. ^{11}B: 25.52 MHz, external standard $BF_3 \cdot OEt_2$.

The fragment $[M - C_2F_5]^+$, which is usually weak for boron compounds bearing two CF_3 groups, is the base peak in this case. Compounds V, VIII and IX show M^+ peaks with significant intensity; the unusual base peak of V, $m/e = 151$, results from elimination of C_2F_6 and C_3H_6. As expected, the base peak of compound X is $m/e = 91$, $[C_7H_7]^+$, the highest mass fragment being not M^+ but $[M - H_2]^+$ which is formed by elimination of hydrogen. This hydrogen seems to have its origin in the five-membered ring bearing the benzyl group because H_2 elimination can provide some kind of aromaticity. Other weak but significant fragments are also formed by elimination of CF_3 radicals.

4. Description of the crystal structure of III

A crystallographic investigation of III was undertaken because initial spectroscopic evidence was also compliant with an unprecedented $(CF_3)_2B-NMe_2-CNH$ ring structure—the Raman spectrum being recorded at a later date. A drawing of III is shown in Fig. 1. The
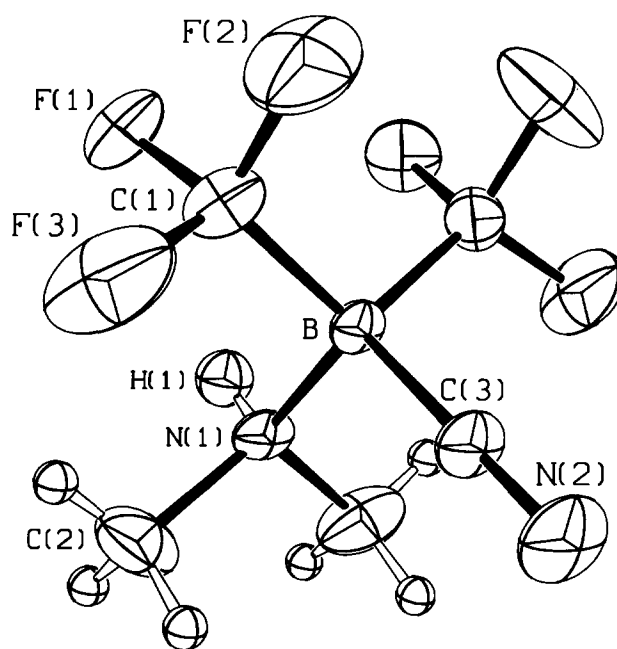

Fig. 1. A perspective drawing of III with 20% probability thermal ellipsoids for the non-idealized atoms.

Table 2

Selected electron impact mass spectral data in order of decreasing intensity m/e (relative intensity (%) [fragment]$^+$) for III–V and VIII–X

III	101 (100) $[M - C_2F_5]^+$; 44 (19) $[NC_2H_6]^+$; 94 (13) $[F_2BNH(CH_3)_2]^+$; 129 (5) $[M - CF_2 - CH_3CN]^+$; 221 (2) $[M + H]^+$; 151 (1) $[M - CF_3]^+$
IV	129 (100) $[M - C_2F_5]^+$; 101 (86) $[M - C_2F_5 - C_2H_4]^+$; 58 (57) $[C_3H_8N]^+$; 74 (36) $[FBNC_2H_6]^+$; 106 (32) $[F_2BNCH_2(C_2H_5)]^+$; 122 (11) $[F_2BNH(C_2H_5)_2]^+$; 249 (1) $[M + H]^+$; 219 (1) $[M - C_2H_5]^+$
V	151 (100) $[M - C_2F_6 - C_3H_6]^+$; 43 (95) $[C_3H_7]^+$; 193 (53) $[M - C_2F_6]^+$; 101 (32) $[FBN(CH_3)_2CNH]^+$; 92 (21) $[F_2BNCH_2(CH_3)]^+$; 71 (19) $[FBCN_2H]^+$; 74 (16) $[FBNC_2H_6]^+$; 124 (15) $[M - C_2F_6 - C_4H_7N]^+$; 262 (10) $[M - CF_3]^+$; 331 (2) $[M]^+$
VII	57 (100) $[C_4H_9]^+$; 44 (40) $[NC_2H_6]^+$; 71 (14) $[FBCN_2H]^+$; 92 (10) $[F_2BNCH_2(CH_3)]^+$; 508 (7) $[M - C_3F_8]^+$; 74 (6) $[FBNC_2H_6]^+$; 537 (4) $[M - CH_3]^+$; 495 (3) $[M - C_4H_9]^+$; 433 (2) $[M - C_2F_5]^+$; 483 (2) $[M - CF_3]^+$; 466 (2) $[M - C_4H_9 - C_2H_5]^+$; 552 (2) $[M]^+$
VIII	44 (100) $[NC_2H_6]^+$; 42 (84) $[NC_2H_4]^+$; 92 (80) $[F_2BNCH_2(CH_3)]^+$; 71 (73) $[FBCN_2H]^+$; 204 (68) $[M - 2C_2F_5 - C_3H_4N]^+$; 74 (53) $[FBNC_2H_6]^+$; 481 (52) $[M - CH_3]^+$; 377 (24) $[M - C_2F_5]^+$; 427 (14) $[M - CF_3]^+$; 496 (17) $[M]^+$
IX	44 (100) $[NC_2H_6]^+$; 42 (98) $[NC_2H_4]^+$; 74 (28) $[FBNC_2H_6]^+$; 92 (26) $[F_2BNCH_2(CH_3)]^+$; 71 (20) $[FBCN_2H]^+$; 349 (17) $[M - C_2F_5]^+$; 399 (12) $[M - CF_3]^+$; 468 (4) $[M]^+$; 453 (3) $[M - CH_3]^+$
X	91 (100) $[C_7H_7]^+$; 278 (14) $[C_{18}H_{20}N_3]^+$; 236 (10) $[F_2BC_{11}H_{13}N_3]^+$; 187 (7) $[C_{11}H_{13}N_3]^+$; 327 (3) $[F_2BC_{18}H_{20}N_3]^+$; 391 (2) $[M - C_2F_6 - C_7H_7]^+$; 482 (2) $[M - C_2F_6]^+$; 551 (2) $[M - CF_3]^+$; 618 (2) $[M - H_2]^+$; 500 (1) $[M - C_2F_5H]^+$

compound possesses crystallographic m (C_s) symmetry in the solid state with the H(1), N(1), B, C(3) and N(2) atoms lying on the mirror plane. The molecules propagate in the a direction by formation of weak hydrogen bonds, N(1) $\cdots$ N(2)($x - 1$, y, z), 2.903(6) Å. This hydrogen bonding offers an explanation for the relatively low r.m.s. torsional amplitude about the B–N(1) bond, 8.8(6)°, compared to that about the B–C(1) bond, 16.8(2)°.

The B–C(1) bond length, 1.623(4) Å, compares well with the B–CF$_3$ distances reported for numerous B(CF$_3$)$_2$(X) · NHMe$_2$ derivatives [6]. That a shorter distance is found for the B–C(3) bond [1.586(4) Å] might be attributed to the difference in hybridization of the C(1) (sp^3) and C(3) (sp) atoms. The B–N(1) bond length, 1.580(4) Å, also agrees well with those found in the above-mentioned amine–borane compounds.

5. Description of the crystal structure of VIII

Crystals of **VIII** contain two discrete, crystallographically independent molecules. A perspective drawing of the first molecule is given in Fig. 2. The labelling of the atoms in the second molecule corresponds to that of the first with the leading digit being a 2 rather than a 1. We will refer to this digit with an 'I' when features common to both molecules are discussed. The similarity

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

	$I = 1$	$I = 2$
N(I1)–B(I1)	1.60(2)	1.58(2)
N(I1)–B(I2)	1.60(2)	1.60(2)
N(I2)–B(I1)	1.58(2)	1.58(1)
N(I2)–C(I1)	1.28(1)	1.26(1)
B(I2)–C(I1)	1.64(2)	1.59(2)
C(I1)–C(I2)	1.50(1)	1.53(2)
C(I2)–N(I3)	1.28(2)	1.28(2)
C(I2)–N(I4)	1.33(1)	1.35(2)
B(I1)–N(I1)–B(I2)	107.9(8)	109.1(8)
N(I1)–B(I1)–N(I2)	102.0(8)	101.0(9)
N(I1)–B(I2)–C(I1)	100.7(7)	100.3(9)
B(I1)–N(I2)–C(I1)	115.5(8)	115.0(8)
B(I2)–C(I1)–N(I2)	112.4(8)	114.5(9)

between the two independent structures is underscored by the good agreement found for the bond distances and angles compiled in Table 3. When referring to average values, the estimated standard deviation will be taken as the larger of $\sqrt{\Sigma\sigma^2}/N$ and $\sqrt{\Sigma\Delta^2/N(N-1)}$.

The central feature of **VIII** is the slightly-puckered, N(1) B(I1) N(I2) C(I1)B(I2) five-membered ring. While the B–N and B–C bond lengths in the ring exhibit single-bond separations, the N(I2)–C(I1) distance corresponds to a double bond–the average length being 1.27(1) Å. Accordingly, the B(I1), N(I2), C(I1),
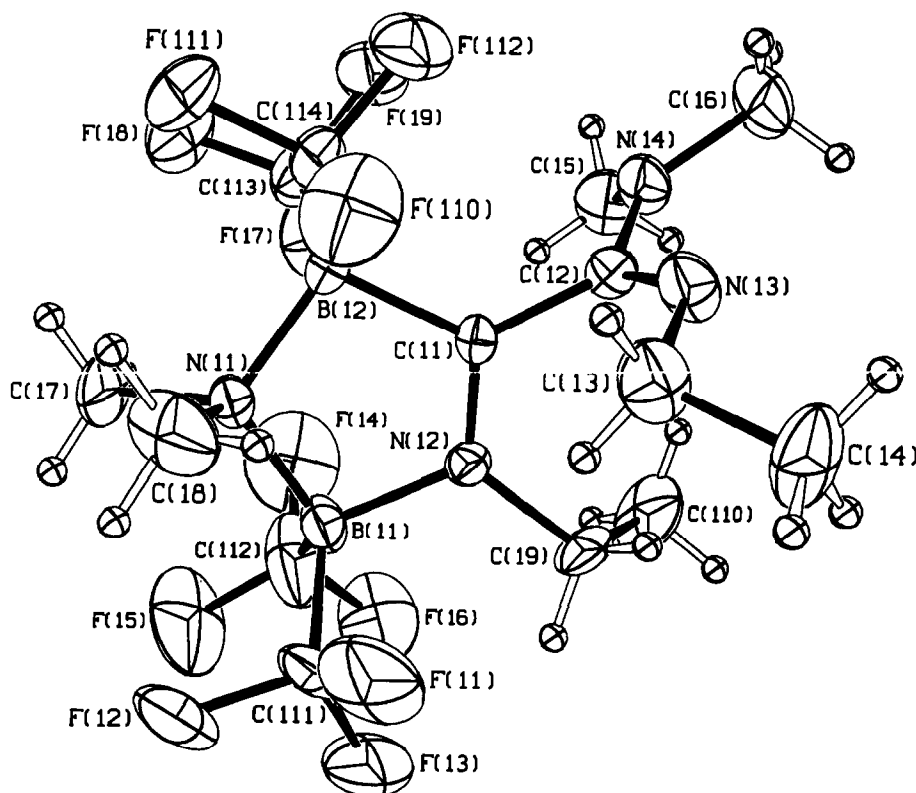

Fig. 2. A perspective drawing of the first molecule of **VIII** with 20% probability thermal ellipsoids for the non-idealized atoms.

B($I2$) fragments are planar to within the limits of experimental error.

Conjugation between the N($I2$)–C($I1$) double bonds and the exocyclic formamidine group should be minimal because the dihedral angles formed by the normals to the B($I1$), N($I2$), C($I1$), B($I2$) and corresponding C($I1$), C($I2$), N($I3$), N($I4$) fragments average 101(2)°, and indeed the average C($I1$)–C($I2$) distance assumes a normal value for a single bond, 1.51(1) Å. The formamidine group contains a C($I2$)–N($I3$) double bond averaging 1.28(1) Å, but some conjugation between the C($I2$) and N($I4$) atoms is indicated by the average C($I2$)–N($I4$) bond distance [1.34(1) Å] and the flattening of the C($I2$), N($I4$), C($I5$), C($I6$) pyramids— the average sum of the valence angles of the N($I4$) atoms being 356.5(11)°.

6. Description of the crystal structure of X

Crystals of X are composed of a racemic mixture of diastereomers–the molecule in the asymmetric unit and displayed in Fig. 3 having S and R configurations at the asymmetric carbon atoms C(5) and C(7), respectively. The compound contains two puckered, five-membered rings which are fused along the N(3)–C(5) bond.

In connecting a quaternary boron to a tertiary nitrogen atom which is not otherwise involved in formal π-bonding, the B(1)–N(3) linkage is unique in the structural chemistry of trifluoromethylborates. Its bond length of 1.476(5) Å is 0.1 Å longer than the B–N bond connecting the tertiary atoms in $(CF_3)_2BN(^iPr)_2$ [7] and 0.1 Å shorter than the bonds between four-coordinate boron and nitrogen atoms in compounds such as III. Five trifluoromethylborates containing a quaternary boron bonded to an imine nitrogen atom (e.g. the B($I1$)–N($I2$) bonds in VIII) have now been studied crystallographically [8,9], and the mean distance of such B–N bonds [1.544(7) Å] is also markedly longer than the B(1)–N(3) bond in X.

The sum of the bond angles of the N(3) atom [348.9(5)°] indicates a marked flattening of its valencies, and this fact along with the shortness of the B(1)–N(3) bond suggests some participation of the N(3) lone pair in B(1), N(3) bonding. Such a hyperconjugative interaction should weaken the B(1) bonds which are most closely aligned to the N(3) lone pair. This direction may be taken as the normal to the N(3), C(5), C(7), B(1) plane, and the respective angles formed by this normal and the B(1)–C(1), B(1)–C(2) and B(1)–N(1) bonds are 32.1(6)°, 103.4(6)° and 136.2(6)°. So N(3)pπ → B(1) bonding should mainly affect the bonds to the C(1) and N(1) atoms; therefore it might account for some pecu-

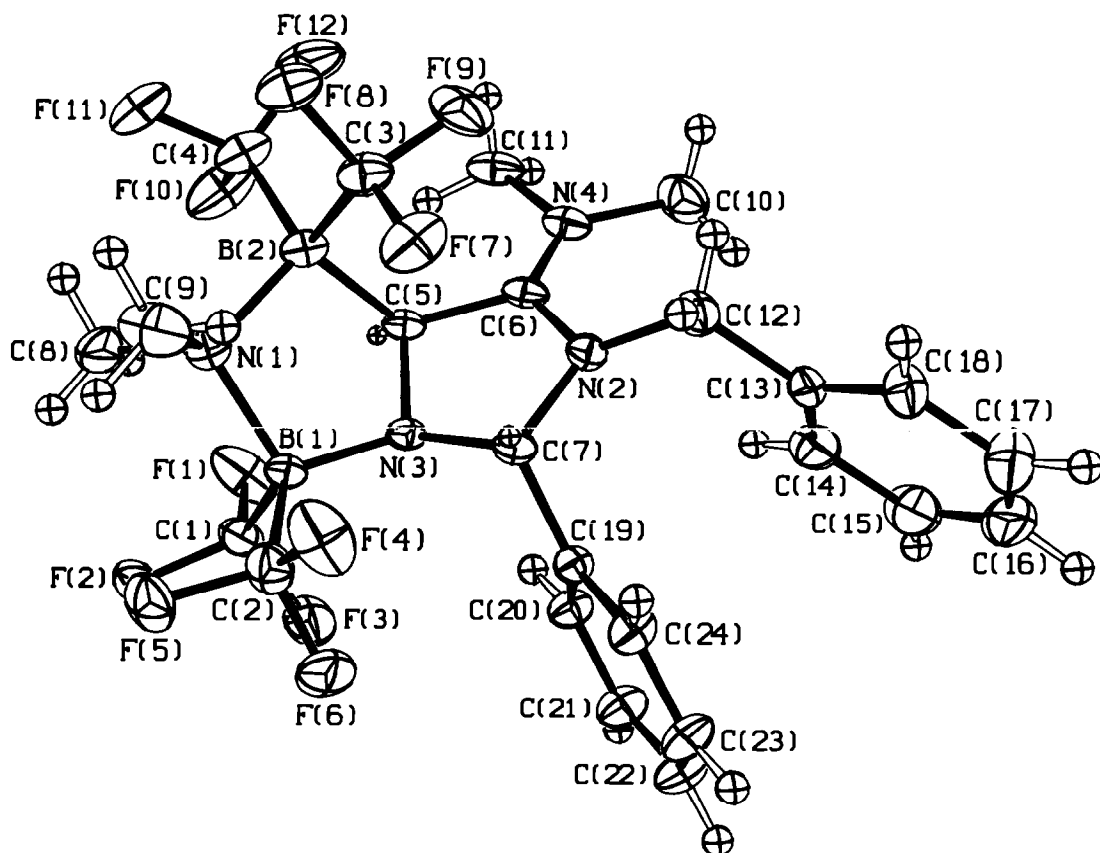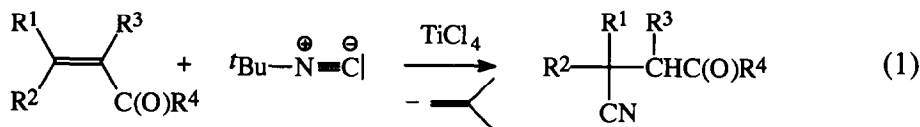Fig. 3. A perspective drawing of X with 20% probability thermal ellipsoids for the non-idealized atoms.

$$R^2\underset{C(O)R^4}{\overset{R^1}{\diagdown}}\diagup^{R^3} + \ {}^tBu\!-\!\overset{\oplus}{N}\!\!=\!\!\overset{\ominus}{C}| \ \xrightarrow[-\diagup\diagdown]{TiCl_4} \ R^2\!-\!\!\overset{R^1}{\underset{CN}{\overset{|}{\underset{|}{C}}}}\!-\!\overset{R^3}{\overset{|}{C}}HC(O)R^4 \qquad (1)$$

Table 4
Selected bond distances (Å) and angles (°) in **X**

N(1)–B(1)	1.669(5)	B(1)–C(1)	1.662(6)
N(1)–B(2)	1.639(6)	B(1)–C(2)	1.621(6)
N(3)–B(1)	1.476(5)	B(2)–C(3)	1.636(6)
N(3)–C(5)	1.468(4)	B(2)–C(4)	1.629(6)
N(3)–C(7)	1.439(4)	B(2)–C(5)	1.655(6)
B(1)–N(1)–B(2)	104.4(3)	B(1)–N(3)–C(7)	128.0(3)
N(1)–B(1)–N(3)	104.9(3)	B(2)–C(5)–C(6)	121.1(3)
N(1)–B(2)–C(5)	101.4(3)	C(5)–N(3)–C(7)	110.2(3)
B(1)–N(3)–C(5)	110.7(3)	N(3)–C(5)–C(6)	102.1(3)
B(2)–C(5)–N(3)	104.1(3)		

liar trends in the bond distances listed in Table 4. In particular, the B(1)–C(1) bond is 0.041(8) Å longer than the B(1)–C(2) valency, which possesses a normal value for such a linkage [6]. Furthermore, the B(1)–N(1) bond is 0.030(8) Å longer than the B(2)–N(1) distance. If hyperconjugation is affecting these bond lengths, then the effect is quite subtle. Indeed we have not found trends of comparable significance in the structures of the above-mentioned compounds in which boron is bonded to an imine nitrogen.

7. Discussion

The formation of **III** and **IV** can be regarded as a boron version of the $TiCl_4$-promoted hydrocyanation of α,β-unsaturated ketones [10] according to Eq. (1). Here

$TiCl_4$ forms a complex with the carbonyl group, thus polarizing the C=C double bond. Presumably the strong polarity of the B=N double bond in **A** and **B** induces an analogous reaction even in the absence of a catalyst.

The formation of **V** from a hypothetical adduct follows pathway (c), Scheme 1. This is in line with the observation of Tapper, Schmitz and Paetzold [11] who reported that ${}^iPr_2N\!=\!B\!=\!C(SiMe_3)_2$ adds two molecules of ${}^tBuNC$ to yield a related four-membered heterocycle according to Eq. (2).

The [2 + 3] cycloaddition of **A** to the four-membered rings which yields **VI–X** requires the cleavage of a B–N bond. This bond-breaking most likely follows a concerted mechanism because intermediates with tricoordinated boron are rare and are so far restricted to the aminoboranes $CF_3B(NR_2)_2$ and $(CF_3)_2BNR_2$ (R = alkyl). A rupture of a B–N bond has already been observed in trifluoromethyl boron chemistry [8]. Here [Eq. (3)] the primary adduct of a [2 + 2] cycloaddition of **A** and MeNCO rearranges at room temperature under cleavage of a B–N bond to yield a thermodynamically more stable isomer. This reaction sequence is in support of the proposed mechanism.

The present study reveals that in the hydrocyanation reaction the B=N bond in **A** behaves like a polarized C=C double bond. Apparently all reactions of isocyanides with **A** are in line with those depicted in Scheme 1. The variety of products obtained either directly or by secondary reactions seems to be mainly governed by the steric demand of the ligand R linked to
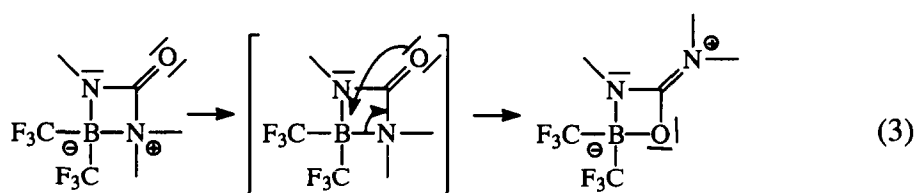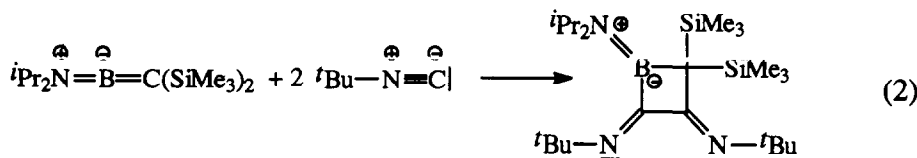

$$^iPr_2N\!=\!\overset{\oplus}{B}\!=\!\overset{\ominus}{C}(SiMe_3)_2 + 2 \ {}^tBu\!-\!\overset{\oplus}{N}\!\!=\!\!\overset{\ominus}{C}| \ \longrightarrow \qquad (2)$$

$$(3)$$

Table 5
Elemental analyses

Compound	Formula	Analysis: (Found; Calc.)(%)		
		C	H	N
III	$C_5H_7BF_6N_2$	27.3; 27.31	3.2; 3.21	12.6; 12.74
IV	$C_7H_{11}BF_6N_2$	33.7; 33.91	4.5; 4.47	11.7; 11.30
VII	$C_{18}H_{30}B_2F_{12}N_4$	40.4; 39.16	5.6; 5.48	10.4; 10.15
VIII	$C_{14}H_{22}B_2F_{12}N_4$	33.6; 33.91	4.5; 4.47	11.2; 11.30
IX	$C_{12}H_{18}B_2F_{12}N_4$	29.1; 30.80	3.6; 3.88	10.0; 11.97
X	$C_{24}H_{26}B_2F_{12}N_4$	45.8; 46.48	4.1; 4.23	9.4; 9.04

the NC group although, to a lesser extent, electronic effects also displayed by the R group may be of importance.

8. Experimental details

8.1. Dimethylamine bis(trifluoromethyl)cyanoborane (III) and diethylamine bis(trifluoromethyl)cyanoborane (IV)

To a stirred solution of 1.0 g (12 mmol) of ^tBuNC in 10 ml of dry pentane, 10 mmol of either **A** or **B** were added dropwise at −20°C. The respective adducts **I** and **II** precipitated immediately and were isolated by pumping off all volatile material at −20°C. Upon warming of a solution in CH_2Cl_2 to room temperature, **I** and **II** eliminated isobutylene to yield **III** and **IV**, respectively, quantitatively.

Table 7
Atomic coordinates and isotropic or equivalent [a] isotropic temperature factors for the non-idealized atoms of **III**

Atom	x	y	z	U
F(1)	0.6942(5)	0.1203(2)	0.8001(5)	0.106(1)
F(2)	1.0429(7)	0.1391(5)	0.9427(6)	0.171(2)
F(3)	0.907(1)	0.0375(3)	0.6718(8)	0.181(3)
N(1)	0.6471(5)	0.2500	0.4112(5)	0.059(1)
N(2)	1.2324(7)	0.2500	0.4961(9)	0.102(2)
C(1)	0.8785(6)	0.1357(3)	0.7559(6)	0.078(1)
C(2)	0.6201(8)	0.1454(6)	0.2785(7)	0.115(2)
C(3)	1.0804(6)	0.2500	0.5444(7)	0.066(1)
B	0.8684(6)	0.2500	0.6141(6)	0.048(1)
H(1)	0.55(1)	0.2500	0.455(9)	0.07(1)

[a] $U = U_{iso}$ for H(1), otherwise $U = U_{eq} = 1/3\Sigma_i\Sigma_j\bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$.

Compound **III**: m.p. 159°C. IR/Raman (cm^{-1}): $\nu(N-H)$ 3080 (s/−); $\nu(C\equiv N)-/2248(s)$; $\nu(C-F)$ 1135 (vs/−), 1107 (vs/−), 1070 (s/−).

Compound **IV**: m.p. 165°C. IR/Raman (cm^{-1}): $\nu(N-H)$ 3100 (s/−); $\nu(C\equiv N)-/2248(s)$; $\nu(C-F)$ 1115(vs/−), 1070(s/−).

8.2. 1,1-Dimethyl-2,2-bis(trifluoromethyl)-3,4-bis(isopropylimino)-1-azonia-2-borata-cyclobutane (V), 1-isopropyl-2,2,4,4-tetrakis(trifluoromethyl)-3,3-dimethyl-5-(2,5-dimethyl-2,4-diazahex-3-en-3-yl)-1,3-diazonia-2,4-diborata-cyclopent-1-ene (VI): General procedure

To a stirred solution of 1.4 g (20 mmol) of ^iPrNC in 15 ml of dry pentane, 10 mmol **A** were added dropwise

Table 6
Crystal data and refinement details for **III**, **VIII** and **X**

	III	VIII	X
Formula	$C_5H_7BF_6N_2$	$C_{14}H_{22}B_2F_{12}N_4$	$C_{24}H_{26}B_2F_{12}N_4$
MW	219.92	495.96	620.10
Space group	$P2_1/m$	$P\bar{1}$	$P2_1/n$
$a(\mathring{A})$	6.3716(3)	8.837(2)	12.711(2)
$b(\mathring{A})$	11.5298(4)	14.253(3)	13.037(4)
$c(\mathring{A})$	6.8317(2)	17.879(4)	16.920(4)
$\alpha(°)$	90	79.47(1)	90
$\beta(°)$	111.212(3)	79.22(2)	102.21(2)
$\gamma(°)$	90	85.67(2)	90
Z	2	4	4
D_c (g cm^{-3})	1.561	1.516	1.503
t (°C)	26	24	24
λ (Å)	1.54184	0.71073	0.71073
2θ limits (°)	3–130	5–45	5–50
Measured reflections	1865	6624	5224
Unique reflections	838	6103	4806
Observed $(F \geqslant 4\sigma(F))$	769	2736	2511
Crystal size (mm^3)	0.14 × 0.17 × 0.61	0.19 × 0.49 × 0.81	0.23 × 0.26 × 0.75
μ_λ (cm^{-1})	16.3	1.6	1.4
Transmission	0.804–0.655		0.976–0.960
R	0.072	0.106	0.056
R_w	0.111	0.110	0.052
$\Delta\rho$ (e Å^{-3})	0.43 to −0.29	0.44 to −0.32	0.24 to −0.23
Parameters	74	597	400

at $-20°C$. Upon warming the reaction mixture to room temperature for 1 h, the colourless precipitate formed initially turned into a dark brown, tarry material. All volatile material was removed in vacuo and the tarry reaction product was subjected to a sublimation at

Table 8

Atomic coordinates and equivalent isotropic temperature factors [a] for the non-hydrogen atoms of **VIII**

Atom	x	y	z	U
F(11)	0.602(2)	0.5685(8)	0.9033(9)	0.213(8)
F(12)	0.548(1)	0.5025(5)	0.8166(6)	0.190(6)
F(13)	0.707(1)	0.6164(9)	0.781(1)	0.252(9)
F(14)	0.350(2)	0.766(1)	0.7021(6)	0.230(9)
F(15)	0.468(2)	0.628(1)	0.6889(6)	0.263(8)
F(16)	0.581(2)	0.751(1)	0.6961(6)	0.214(7)
F(17)	0.109(1)	0.8295(7)	0.7873(7)	0.174(6)
F(18)	-0.057(1)	0.7326(8)	0.8506(8)	0.212(8)
F(19)	-0.0151(9)	0.8509(7)	0.8981(7)	0.177(6)
F(110)	0.173(1)	0.6351(8)	1.0400(5)	0.178(6)
F(111)	-0.031(1)	0.6338(7)	0.9889(6)	0.187(5)
F(112)	0.030(1)	0.7600(7)	1.0234(5)	0.171(5)
N(11)	0.2664(9)	0.6365(6)	0.8572(5)	0.078(4)
N(12)	0.4542(8)	0.7549(5)	0.8598(4)	0.057(3)
N(13)	0.393(1)	0.8247(6)	1.0190(6)	0.098(5)
N(14)	0.260(1)	0.9336(6)	0.9445(6)	0.089(4)
C(11)	0.332(1)	0.7814(5)	0.9029(5)	0.045(3)
C(12)	0.337(1)	0.8498(6)	0.9568(6)	0.063(4)
C(13)	0.461(2)	0.730(1)	1.0454(8)	0.112(7)
C(14)	0.590(2)	0.7437(9)	1.0838(9)	0.140(8)
C(15)	0.247(2)	0.9829(9)	0.869(1)	0.128(8)
C(16)	0.242(2)	0.9955(9)	1.002(1)	0.154(9)
C(17)	0.182(2)	0.598(1)	0.808(1)	0.18(1)
C(18)	0.279(2)	0.5447(8)	0.920(1)	0.156(9)
C(19)	0.607(1)	0.7954(8)	0.8528(8)	0.097(6)
C(110)	0.617(2)	0.896(1)	0.8130(9)	0.152(9)
C(111)	0.575(2)	0.586(1)	0.836(1)	0.134(9)
C(112)	0.462(3)	0.700(2)	0.728(1)	0.18(1)
C(113)	0.053(2)	0.783(1)	0.860(1)	0.117(8)
C(114)	0.091(2)	0.685(1)	0.989(1)	0.137(9)
B(11)	0.438(2)	0.6679(9)	0.8193(7)	0.078(6)
B(12)	0.184(1)	0.7182(9)	0.9033(8)	0.073(5)
F(21)	1.024(1)	0.4910(6)	0.5775(5)	0.181(6)
F(22)	1.019(1)	0.5162(4)	0.6913(4)	0.131(4)
F(23)	1.228(1)	0.4887(6)	0.6223(6)	0.184(6)
F(24)	1.320(1)	0.350(8)	0.7212(5)	0.160(6)
F(25)	1.207(2)	0.2339(7)	0.7685(6)	0.214(8)
F(26)	1.125(1)	0.3654(5)	0.8039(4)	0.129(4)
F(27)	0.756(1)	0.322(1)	0.5508(8)	0.39(2)
F(28)	0.744(1)	0.172(1)	0.573(1)	0.43(2)
F(29)	0.612(1)	0.254(1)	0.6506(6)	0.26(1)
F(210)	0.958(1)	0.095(1)	0.7502(9)	0.33(1)
F(211)	0.858(2)	0.0641(9)	0.6602(8)	0.43(2)
F(212)	0.719(1)	0.1226(7)	0.7516(6)	0.234(7)
N(21)	0.907(1)	0.3094(7)	0.6988(6)	0.104(5)
N(22)	1.1452(9)	0.2876(5)	0.6090(4)	0.063(3)
N(23)	1.191(1)	0.0871(8)	0.5555(7)	0.118(6)
N(24)	1.059(1)	0.1809(7)	0.4698(6)	0.103(5)
C(21)	1.054(1)	0.2309(6)	0.5958(5)	0.065(4)
C(22)	1.109(1)	0.1633(8)	0.5381(7)	0.079(5)
C(23)	1.241(2)	0.057(1)	0.632(1)	0.16(1)
C(24)	1.396(3)	0.007(1)	0.610(1)	0.23(1)
C(25)	1.012(2)	0.273(1)	0.4315(9)	0.134(8)

Table 8 (continued)

Atom	x	y	z	U
C(26)	1.092(2)	0.114(1)	0.4160(7)	0.155(9)
C(27)	0.854(3)	0.285(2)	0.7799(9)	0.38(3)
C(28)	0.795(2)	0.384(1)	0.682(2)	0.40(4)
C(29)	1.306(1)	0.297(1)	0.5669(8)	0.111(7)
C(210)	1.329(2)	0.350(2)	0.4889(9)	0.19(1)
C(211)	1.087(2)	0.4614(9)	0.6416(8)	0.105(7)
C(212)	1.183(2)	0.326(1)	0.7431(9)	0.113(8)
C(213)	0.746(1)	0.2465(9)	0.6056(7)	0.19(1)
C(214)	0.855(1)	0.127(1)	0.7063(7)	0.18(1)
B(21)	1.076(1)	0.3474(8)	0.6742(6)	0.067(5)
B(22)	0.890(1)	0.2281(8)	0.6507(6)	0.091(7)

[a] See footnote to Table 7.

$60°C/10^{-1}$ mbar. According to NMR spectra this sublimate consisted of a 4 : 1 mixture of **V** and **VI**. After repeated sublimation the 1 : 1 adduct **V**, which is slightly more volatile than **VI**, was obtained in $\sim 90\%$ purity, yield 12%. In order to increase the portion of **VI**, ¹PrNC and **A** were sealed in an ampoule in a 1 : 1 ratio and kept for 2 weeks at 25°C. The black tarry reaction mixture was then sublimed and the product thus obtained consisted of **V** and **VI** in a 1 : 2.5 ratio.

Compound **V**: IR (cm^{-1}): $\nu(C=N)$ 1624(s); $\nu(C-F)$ 1115 (vs), 1076 (s), 1048 (s).

8.3. 1-n-Butyl-2,2,4,4-tetrakis(trifluoromethyl)-3,3-dimethyl-5-(2-methyl-2,4-diazaoct-3-en-3-yl)-1,3-diazonia-2,4-diborata-cyclopent-1-ene (VII), 1-ethyl-2,2,4,4-tetrakis(trifluoromethyl)-3,3-dimethyl-5-(2-methyl-2,4-diazahex-3-en-3-yl)-1,3-diazonia-2,4-diborata-cyclopent-1-ene (VIII), 1-methyl-2,2,4,4-tetrakis(trifluoromethyl)-3,3-dimethyl-5-(2-methyl-2,4-diazapent-3-en-3-yl)-1,3-diazonia-2,4-diborata-cyclopent-1-ene (IX)

Compound **A** (15 mmol) was added dropwise at $-20°C$ to a stirred solution of 13 mmol of the respective isocyanide in 15 ml of dry pentane. When the reaction mixture was brought to room temperature for 1 h, the initially formed precipitate turned into a dark brown tarry residue. All volatile material was removed in vacuo $(10^{-2}$ mbar) and **VIII** and **IX** sublimed at $60°C/10^{-2}$ mbar. Compounds **VIII** and **IX** were recrystallized from $CHCl_3$/pentane and after resublimation obtained as yellow crystals in yields of 27% and 22%, respectively.

Because of its low volatility, **VII** was not further purified and was obtained as a dark oil. Despite its appearance, NMR spectroscopy showed it to be at least 95% pure. Yield 30%.

Compound **VII**: IR (cm^{-1}): $\nu(C=N)$ 1615(s); $\nu(C-F)$ 1114 (vs), 1050 (s).

Compound **VIII**: m.p. 53°C. IR (cm^{-1}): $\nu(C=N)$ 1614 (s); $\nu(C-F)$ 1113 (vs), 1080 (s), 1052 (s).

Compound **IX**: m.p. 79°C. IR (cm^{-1}): $\nu(C=N)$ 1625 (s); $\nu(C-F)$ 1117 (vs), 1074 (s), 1051 (s).

8.4. 2,2,4,4-Tetrakis(trifluoromethyl)-3,3-dimethyl-6-dimethylimino-7-benzyl-8-phenyl-1,7-diaza-3-azonia-2,4-diborata-bicyclo[3.3.0]octane (X)

To a stirred solution of 2 g (10 mmol) of **A** in 10 ml of dry pentane, 10 mmol of benzylisocyanide were added dropwise at −20°C. The reaction mixture was warmed to room temperature and stirred for 1 h. After removal of volatile material in vacuo, the tarry residue was dissolved in acetone. Then water was added. Com-

pound **X**, which precipitated after 1 d, was filtered and recrystallized from acetone/water. Yield, 87%.

Compound **X**: m.p. 143°C (dec.) IR (cm^{-1}): ν(C=N) 1650(s); ν(C–F) 1090 (vs), 1080 (vs sh), 1070 (vs sh). For elemental analyses see Table 5.

8.5. X-Ray structural studies of III, VIII and X

The crystals were mounted in thin-walled glass capillaries and X-ray data were measured with a Siemens AED-1 diffractometer. The structures were solved by direct methods using the program SHELXS-86 [12] and refined with anisotropic temperature factors for all non-hydrogen atoms using the program SHELX-76 [13]. While the coordinates of the H(1) atom in **III** and H(5) and H(7) atoms in **X** were refined conventionally, the methyl groups of the C(10) and C(11) atoms in **X** were treated as rigid groups whereas all other hydrogens were handled with the riding model (C–H, 0.95 Å). Since a conventional refinement of **VIII** showed poor convergence, the coordinates of the NMe$_2$ group of the N(21) atom and the B(CF$_3$)$_2$ group of the B(22) atom were varied under the constraints of equal N–C, B–C and C–F bond lengths and equal F–F distances in the CF$_3$ groups. Least-squares optimization gave 1.42(1), 1.61(1), 1.312(6) and 2.110(9) Å for the values of the respective distances. Crystal data and details of the refinements are set out in Table 6, and coordinates of the refined atoms are listed in Tables 7, 8 and 9 [14]. The thermal parameters of the non-hydrogen atoms of **III** were fitted excellently ($R = 0.023$) by a rigid-body motion model which was augmented by correlated oscillations [15] about the B–C(1) and B–N(1) bonds using the program THMA11 [16].

Table 9
Atomic coordinates and temperature factors [a] for the non idealized atoms of **X**

Atom	x	y	z	U
F(1)	0.0666(2)	0.7983(2)	0.2557(2)	0.117(1)
F(2)	−0.0584(2)	0.7082(2)	0.1835(1)	0.080(1)
F(3)	0.0856(2)	0.7389(2)	0.1431(2)	0.105(1)
F(4)	0.1314(2)	0.4293(2)	0.2076(2)	0.113(2)
F(5)	−0.0269(2)	0.4905(2)	0.1749(2)	0.091(1)
F(6)	0.0949(2)	0.5407(2)	0.1151(2)	0.108(1)
F(7)	0.2803(2)	0.4461(2)	0.3921(2)	0.095(1)
F(8)	0.2206(2)	0.4611(2)	0.5012(1)	0.086(1)
F(9)	0.3610(2)	0.5425(2)	0.4869(2)	0.108(1)
F(10)	0.1311(3)	0.7722(2)	0.4732(2)	0.124(2)
F(11)	0.0867(3)	0.6303(2)	0.5202(2)	0.103(1)
F(12)	0.2504(3)	0.6811(2)	0.5501(2)	0.113(2)
N(1)	0.0815(3)	0.5875(3)	0.3427(2)	0.063(1)
N(2)	0.4088(2)	0.6129(2)	0.3187(2)	0.052(1)
N(3)	0.2284(2)	0.6363(2)	0.2726(2)	0.044(1)
N(4)	0.4426(3)	0.7388(3)	0.4212(2)	0.063(1)
C(1)	0.0494(4)	0.7137(4)	0.2095(3)	0.067(2)
C(2)	0.0778(4)	0.5178(4)	0.1892(3)	0.071(2)
C(3)	0.2613(4)	0.5163(3)	0.4465(3)	0.068(2)
C(4)	0.1643(5)	0.6748(4)	0.4878(3)	0.080(2)
C(5)	0.2586(3)	0.6836(3)	0.3530(2)	0.044(2)
C(6)	0.3782(3)	0.6801(3)	0.3685(2)	0.050(2)
C(7)	0.3167(3)	0.5770(3)	0.2529(2)	0.048(2)
C(8)	−0.0149(4)	0.6473(6)	0.3525(3)	0.154(4)
C(9)	0.0496(5)	0.4783(5)	0.3529(3)	0.139(3)
C(10)	0.5593(4)	0.7434(4)	0.4322(3)	0.095(3)
C(11)	0.3989(4)	0.8083(3)	0.4743(3)	0.079(2)
C(12)	0.5056(3)	0.5468(3)	0.3355(3)	0.066(2)
C(13)	0.5821(3)	0.5603(4)	0.2792(2)	0.062(2)
C(14)	0.5897(4)	0.6496(4)	0.2379(3)	0.084(2)
C(15)	0.6605(5)	0.6553(6)	0.1866(4)	0.116(3)
C(16)	0.7217(5)	0.5716(8)	0.1755(4)	0.128(4)
C(17)	0.7150(5)	0.4836(7)	0.2169(4)	0.125(4)
C(18)	0.6460(4)	0.4771(4)	0.2693(3)	0.085(2)
C(19)	0.3360(3)	0.5939(3)	0.1711(2)	0.047(1)
C(20)	0.3275(3)	0.6904(3)	0.1366(2)	0.058(2)
C(21)	0.3467(4)	0.7050(3)	0.0611(3)	0.071(2)
C(22)	0.3738(4)	0.6237(4)	0.0174(3)	0.075(2)
C(23)	0.3805(4)	0.5279(4)	0.0502(3)	0.074(2)
C(24)	0.3617(3)	0.5125(3)	0.1269(3)	0.060(2)
B(1)	0.1128(4)	0.6104(3)	0.2534(3)	0.048(2)
B(2)	0.1911(4)	0.6169(3)	0.4091(3)	0.053(2)
H(5)	0.233(2)	0.757(3)	0.351(2)	0.05(1)
H(7)	0.311(2)	0.502(3)	0.262(2)	0.05(1)

[a] $U = U_{iso}$ for H(5) and H(7), otherwise $U = U_{eq}$ as in Table 7.

References and notes

[1] I. Ugi, Isonitrile Chemistry, Academic Press, New York/London, 1971.
[2] A. Ansorge, D.J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter, J. Organomet. Chem., 396 (1990) 253.
[3] H. Bürger, T. Hagen and G. Pawelke, J. Organomet. Chem., 456 (1993) 19.
[4] A. Ansorge, D.J. Brauer, H. Bürger, T. Hagen and G. Pawelke, J. Organomet. Chem., 444 (1993) 5.
[5] A. Ansorge, D.J. Brauer, H. Bürger, T. Hagen and G. Pawelke, Angew. Chem., 105 (1993) 429.
[6] D.J. Brauer and G. Pawelke, J. Organomet. Chem., 486 (1995) 129.
[7] D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke and W. Weuter, J. Organomet. Chem., 378 (1989) 125.

[8] A. Ansorge, D.J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter, *J. Organomet. Chem., 407* (1991) 283.

[9] A. Ansorge, D.J. Brauer, H. Bürger, B. Krumm and G. Pawelke, *J. Organomet. Chem., 446* (1993) 25.

[10] Y. Ito, H. Kato, H. Imai and T. Saegusa, *J. Am. Chem. Soc., 104* (1982) 6449.

[11] A. Tapper, T. Schmitz and P. Paetzold, *Chem. Ber., 122* (1989) 595.

[12] G.M. Sheldrick, *SHELXS-86: Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1986.

[13] G.M. Sheldrick, *SHELX-76: Program for Crystal Structure Determination*, University of Cambridge, Cambridge, UK, 1976.

[14] Additional crystallographic details may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Informationen mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the deposit number CSD-401974 for **III**, CSD-401992 for **VIII** and CSD-401991 for **X**, the authors and the literature reference.

[15] J.D. Dunitz, V. Schomaker and K.N. Trueblood, *J. Phys. Chem., 92* (1988) 856.

[16] E. Huber-Buser and K.N. Trueblood, *THMA11: Program for Thermal Motion Analysis*, ETH Zürich, Zürich, Switzerland, 1987.