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New heterocycles from the reaction of azoniaboratacyclopropane with isocyanides

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Abstract

The azoniaboratacyclopropane $(CF_3)_2\overline{B{-}NMe_2{-}C}HSiMe_3$ (**I**) combines in a 1:1 fashion with isocyanides RNC ($R = R' = p\text{-}MeC_6H_4SO_2CH_2$ and $R = R'' = PhCH_2$) to give azoniaboratacyclobutane derivatives $(CF_3)_2\overline{B{-}C(NR){-}NMe_2{-}C}HSiMe_3$ ($R = R'$ (**II**), $R = R''$ (**III**)). However, **I** reacts with two equivalents of tert-butyl isocyanide to form a novel diaza-azoniaboratabicyclo[3.3.0]octene (**IV**). The crystal structures of **II** and **IV** have been determined by X-ray methods.

Keywords: Azoniaboratacyclopropane; Heterocycles; X-ray analysis

1. Introduction

The inductive effect of trifluoromethyl substituents stabilizes amine-borane adducts like $(CF_3)_2BR^1 \cdot NHR^2R^3$ and $(CF_3)_3B \cdot NR^1R^2R^3$ to such an extent that selective reactions of their B–N bonds are unknown [1]. A conspicuous exception is the azoniaboratacyclopropane $(CF_3)_2\overline{B{-}NMe_2{-}C}HSiMe_3$ (**I**) [2], the B–N bond of which is easily cleaved. Thus H_2O and HCN add readily to **I**, which leads to opening of the three-membered ring. Furthermore, the

$$\text{I} + HX \longrightarrow (CF_3)_2B(X){-}CH(SiMe_3){-}NHMe_2 \quad (X = OH,\ CN) \qquad (1)$$

addition of ketones to **I** results in ring expansion,

$$\text{I} + R_2C{=}O \longrightarrow (CF_3)_2\overline{B{-}CH(SiMe_3){-}NMe_2{-}CR_2{-}O} \qquad (2)$$

and an analogous reaction of **I** with nitriles also yields five-membered heterocyclic rings [3]. Because of the remarkably high reactivity of the B–N bond in **I**, we were prompted to explore its behaviour towards isocyanides. The results of this investigation will now be reported.

2. Results and discussion

Isocyanides react readily with **I**. Thus *p*-methyltoluenesulfonylmethyl isocyanide and benzyl isocyanide combined with **I** according to Eq. (3) to give **II** and **III** in yields of 96% and 91%, respectively.

$$\text{I} + RNC \longrightarrow (CF_3)_2\overline{B{-}C(NR){-}NMe_2{-}C}HSiMe_3 \qquad (3)$$

II $R = p\text{-}MeC_6H_4SO_2CH_2$

III $R = PhCH_2$

The formulation of **II** and **III** as four-membered heterocyclic rings is based ultimately on the results of the X-ray study of **II** (Fig. 1, Table 1) and the internal consistency of the multinuclear NMR data (Experimental section) of these compounds. The insertion of the carbon atom of the isocyano group into the B–N bond of **I** is a novel variant of the aminometallation of isocyanides (Eq. (4)) [4] — the difference being the involvement of quaternary nitrogen in the present study.

$$Me_3SnNMe_2 + RNC \longrightarrow Me_3SnC(NR)NMe_2 \qquad (4)$$

Both reactions convert an isocyanide into an imine.

In **II**, the C(2)=N(2) bond of the imino group is short (1.249(4) Å), and the atoms of the B, N(1), C(2), N(2), C(3) fragment are coplanar to within ±0.02 Å. Because of the synperiplanar conformation of the B–

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Table 1
Selected bond distances (Å) and angles (°) in **II**

B–C(1)	1.668(5)	C(1)–N(1)	1.554(4)
B–C(2)	1.628(5)	C(2)–N(1)	1.529(4)
B–C(11)	1.596(6)	C(2)–N(2)	1.249(4)
B–C(12)	1.590(7)	C(3)–N(2)	1.450(4)
C(1)–H(1)	0.94(4)	C(13)–N(1)	1.472(5)
C(1)–Si	1.882(4)	C(14)–N(1)	1.484(5)
C(1)–B–C(2)	84.5(3)	N(1)–C(1)–Si	122.3(3)
C(1)–B–C(11)	113.3(4)	B–C(2)–N(1)	92.4(3)
C(1)–B–C(12)	118.7(4)	B–C(2)–N(2)	150.7(3)
C(2)–B–C(11)	114.5(4)	N(1)–C(2)–N(2)	116.9(3)
C(2)–B–C(12)	112.8(4)	C(1)–N(1)–C(2)	92.0(2)
C(11)–B–C(12)	110.8(3)	C(1)–N(1)–C(13)	115.9(3)
B–C(1)–H(1)	106(2)	C(1)–N(1)–C(14)	114.1(3)
B–C(1)–N(1)	90.0(2)	C(2)–N(1)–C(13)	111.3(3)
B–C(1)–Si	130.8(3)	C(2)–N(1)–C(14)	112.4(3)
H(1)–C(1)–N(1)	103(2)	C(13)–N(1)–C(14)	110.2(3)
H(1)–C(1)–Si	102(2)	C(2)–N(2)–C(3)	116.9(3)

C(2)–N(2)–C(3) fragment, steric interactions between the CF_3 groups and the exocyclic imine substituent obviously restrict the orientation of the C(3)–S bond, and even severely short contacts would occur between the hydrogen substituents of the C(3) atom and the CF_3 groups were the B–C(2)–N(2) angle not widened to 150.7(3)°. The opening of this angle at the expense of the N(1)–C(2)–N(2) angle (116.9(2)°) is expedient for electronic reasons [5] because the nitrogen atom is much more electron demanding than the boron atom.

The relative size of the B–C(1)–Si (130.8(3)°) and N(1)–C(1)–Si (122.3(3)°) angles can be rationalized similarly. That both angles are so large indicates a flattening of the B, C(1), N(1) Si pyramid. Indeed the C(1)–Si bond is inclined by only 32.4(4)° to the B, C(1), N(1) plane rather than the 51(1)° value expected for bisecting geometry in view of the size of the H(1)–C(1)–Si angle. Thus this distortion shifts the $SiMe_3$ group towards an equatorial position of the four-membered ring and therefore alleviates $SiMe_3 \cdots CF_3$ and $SiMe_3 \cdots$ Me steric repulsions.

Usually ring puckering could be used to create an equatorial position for a bulky group, but in **II** such puckering is limited by repulsions between the F(4) atom and the C(13) methyl group. As a result, the four-membered ring remains fairly flat — the dihedral angle defined by the normals to the B, C(1), N(1) and B, C(2), N(2) planes being only 11.5(4)°.

The synperiplanar conformation of the B–C(2)–N(2)–C(3) fragment was mentioned above. NMR measurements show that the reaction in Eq. (3) produces a racemic mixture of molecules which only differ in their R and S configuration. This mixture is also present in crystals of **II**, and the molecule in the asymmetric unit depicted in Fig. 1 has the R configuration. Apparently a conformational isomer of **II** possessing an antiperiplanar B–C(2)–N(2)–C(3) fragment is not formed. In such a conformer steric repulsions between the substituents of the C(3) atom and the NMe_2 group will be important. In analogy to the distortion found in **II**, these repulsions might be relieved by opening the N(1)–C(2)–N(2) angle at the expense of the B–C(2)–N(2) angle, but this kind of change is contrary to that expected from electronic considerations.

Since the steric interactions involving the exocyclic imino substituent in **II** appears to be important, the replacement of this substituent by the sterically demanding tert-butyl group hardly appeared trivial. Indeed a different reaction took place upon combining tert-butyl isocyanide with **I**. Multinuclear NMR spectra indicated that the isocyanide had reacted with **I** in a 2:1 ratio although an equimolar reactant mixture had

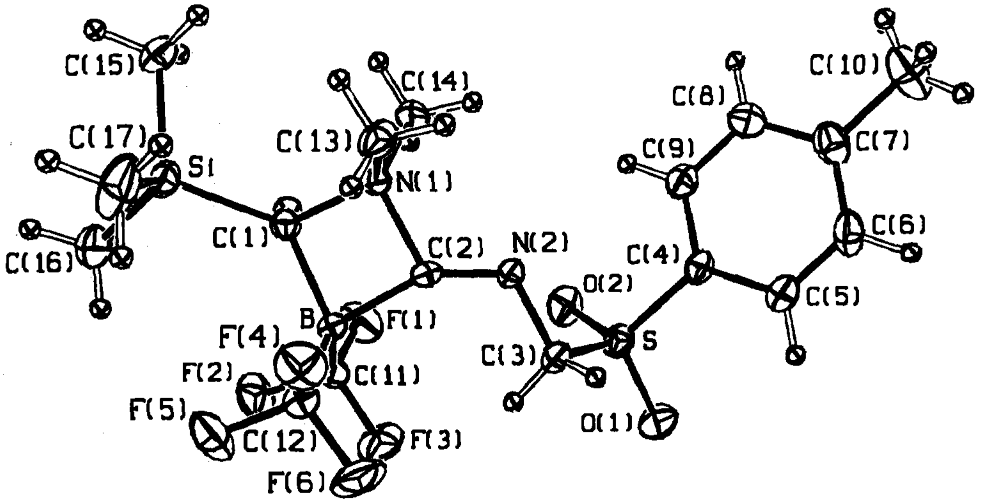
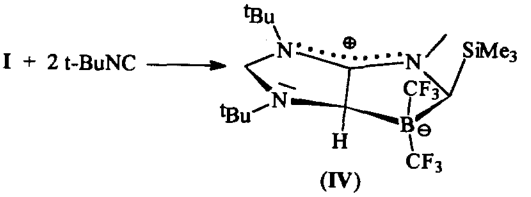


Fig. 1. A perspective drawing of **II** with 20% probability thermal ellipsoids for H(1) and the nonhydrogen atoms; those of the remaining hydrogen atoms are reduced for clarity.

been employed. Thus **IV** was obtained according to Eq. (5) in 82% yield.



(IV)

(5)

An X-ray study on **IV** (Fig. 2, Table 2) established its identity as a novel heterocycle containing two puckered five-membered rings which are fused along their common C(2)–C(4) bond. The formation of **IV** is surprising because even the least disruptive scenario requires the extraction of hydrogen from and fission of the N–C bond of a NMe group. Apparently the hydrogen migrates to the C(4) atom whereas the methylene carbon is found at C(3). Compound **IV** is a betain with the C(2) and B atoms being the centres of formal positive and negative charge, respectively. That the carbonium ion is stabilized by π bonding to the adjacent nitrogen atoms is indicated by the shortness of the C(2)–N(1) and C(2)–N(2) bond lengths (average 1.318(6) Å).

Table 2
Selected bond distances (Å) and angles (°) in IV

B–C(1)	1.671(8)	C(2)–N(2)	1.316(6)
B–C(4)	1.644(8)	C(3)–N(2)	1.471(6)
B–C(5)	1.614(8)	C(3)–N(3)	1.467(6)
B–C(6)	1.605(8)	C(4)–H(4)	0.91(4)
C(1)–H(1)	0.90(4)	C(4)–N(3)	1.458(7)
C(1)–N(1)	1.493(6)	C(7)–N(1)	1.469(6)
C(1)–Si	1.919(6)	C(8)–N(2)	1.508(6)
C(2)–C(4)	1.485(7)	C(12)–N(3)	1.489(6)
C(2)–N(1)	1.320(6)		
C(1)–B–C(4)	98.1(4)	B–C(4)–C(2)	101.1(4)
C(1)–B–C(5)	112.1(5)	B–C(4)–H(4)	106(3)
C(1)–B–C(6)	109.1(5)	B–C(4)–N(3)	129.1(5)
C(4)–B–C(5)	109.7(5)	C(2)–C(4)–H(4)	103(3)
C(4)–B–C(6)	115.3(5)	C(2)–C(4)–N(3)	102.3(4)
C(5)–B–C(6)	111.8(5)	H(4)–C(4)–N(3)	112(3)
B–C(1)–H(1)	108(3)	C(1)–N(1)–C(2)	112.0(4)
B–C(1)–N(1)	103.3(4)	C(1)–N(1)–C(7)	118.4(5)
B–C(1)–Si	124.9(4)	C(2)–N(1)–C(7)	125.4(5)
H(1)–C(1)–N(1)	106(3)	C(2)–N(2)–C(3)	107.3(4)
H(1)–C(1)–Si	101(3)	C(2)–N(2)–C(8)	131.3(5)
N(1)–C(1)–Si	111.9(4)	C(3)–N(2)–C(8)	121.3(4)
C(4)–C(2)–N(1)	113.6(5)	C(3)–N(3)–C(4)	105.4(4)
C(4)–C(2)–N(2)	112.4(5)	C(3)–N(3)–C(12)	112.5(4)
N(1)–C(2)–N(2)	133.9(5)	C(4)–N(3)–C(12)	120.2(4)
N(2)–C(3)–N(3)	104.2(4)		

That the N(1)–C(1) bond distance in **IV** is 0.061(7) Å shorter than in **II** probably reflects the reduced steric and/or electronic demands of the N(1) site in **IV**. The relative decrease of the latter might be related to the greater disparity between the B–C(1)–Si and N(1)–C(1)–Si bond angles in **IV** (13.0(6)°) as compared to that found in **II** (8.5(4)°).

As in **II** the geometry of the C(1) atom is distorted

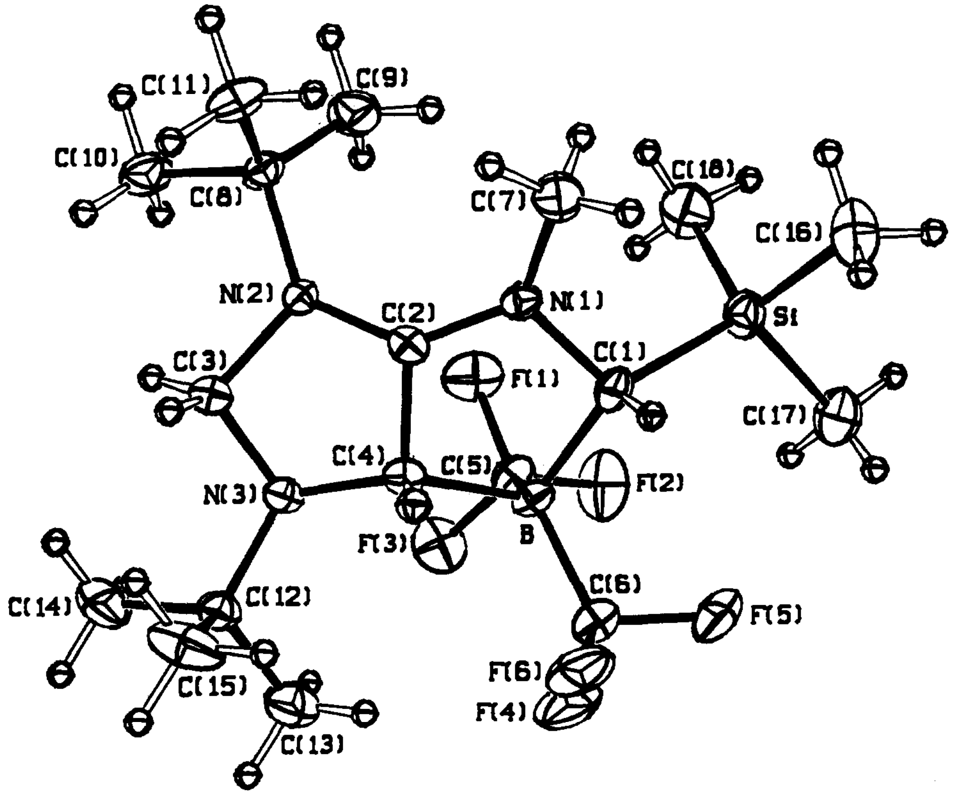


Fig. 2. A perspective drawing of IV with 20% probability thermal ellipsoids for H(1), H(4) and the nonhydrogen atoms; those of the remaining atoms are reduced for clarity.

so as to compress those bond angles involving the C(1)–H(1) bond. One result of this compression is the shift of the $\mathrm{SiMe_3}$ group towards an equatorial position of the five-membered ring. This shift is evident from the angle between the B, C(1), N(1) plane and the C(1)–Si bond (38.2(5)°), which is less than half (50(1)°) the value of the H(1)–C(1)–Si bond angle. The analogous discrepancy was larger than in **II**, but in **IV** two exocyclic substituents (C(6) and C(7)) adjacent to the $\mathrm{SiMe_3}$ group also occupy equatorial positions.

If tert-butyl isocyanide would have reacted with **I** according to Eq. (3), then the tert-butyl group would have come into close proximity to either the $\mathrm{B(CF_3)_2}$ or $\mathrm{NMe_2}$ entities. The likelihood of such conformations may be judged from a perusal of the structural parameters of **IV** because it contains a t-Bu–N–C–$\mathrm{B(CF_3)_2}$ and a t-Bu–N–C–NMe fragment. The main reason for the absence of severely repulsive t-Bu ··· $\mathrm{CF_3}$ contacts in **IV** is that the C(12)–N(3)–C(4)–B torsion angle assumes a value (91.8(8)°) which lies far from that of the sterically catastrophic synperiplanar conformation required by a derivative of **II**. Nevertheless, markedly short F(3) ··· C(13) and F(4) ··· C(13) distances would arise were the C(4)–N(3)–C(12) and B–C(4)–N(3) angles not so wide (120.2(4)° and 129.1(5)°, respectively). However, severely short t-Bu ··· NMe contacts are avoided despite the synperiplanar conformation of the N(1)–C(2)–N(3)–C(8) fragment because large bond angles (> 125°) are formed along this sequence. However, a derivative of **II** will have two methyl groups bonded to the N(1) atom, and the second exocyclic site of this atom in **IV** is blocked by the methyl groups C(9) and C(18). This analysis of **IV** therefore indicates that the exocyclic imine substituent of **II** can hardly be replaced by a tert-butyl group.

Little is known about the formation of these compounds. We assume that the reaction of **I** with isocyanides starts with nucleophilic attack on the boron atom by the isocyano carbon. The latter would then add to the amino group if formation of a four-membered ring is possible as it was for **II** and **III**. Though the primary step in the formation of **IV** might be the same as for **II** and **III**, several rearrangements and uptake of another molecule of the isocyanide are required. Since no information is now available about intermediates involved further speculation about the mechanism is presently unwarranted.

3. Experimental section

The isocyanides were purchased from Aldrich, and **I** was prepared as described previously [1]. ^{1}H NMR (250 MHz), ^{13}C NMR (62.9 MHz), ^{19}F NMR (235.2 MHz) and ^{11}B NMR (25.52 MHz) spectra were recorded at 25°C on Bruker AC 250 and Varian FT 80A spectrometers using $\mathrm{CDCl_3}$ as a solvent. All chemical shifts are reported in ppm, the positive sign indicating higher resonance frequency with regard to the standard. ^{1}H NMR shifts are reported relative to internal $\mathrm{CHCl_3}$ ($\delta(\mathrm{CHCl_3}) = 7.27$), ^{13}C NMR against $\mathrm{CDCl_3}$ ($\delta(\mathrm{CDCl_3}) = 77.0$), ^{19}F NMR against internal $\mathrm{CFCl_3}$ and ^{11}B NMR against external $\mathrm{BF_3 \cdot OEt_2}$. ^{13}C NMR spectra were broadband decoupled from hydrogen nuclei. The ^{13}C resonances of the $\mathrm{CF_3}$ groups were not detected. The IR spectra were obtained from KBr pellets using a Perkin Elmer 580B spectrometer. Mass spectral data were measured with a Varian MAT 311A apparatus operating at 70 eV. X-ray data were collected with a Siemens AED 1 diffractometer employing zirconium filtered Mo Kα radiation (λ 0.71073 Å) — the intensities being corrected for absorption.

Preparations of 2(RS)-1,1-dimethyl-4-[(4-toluenesulfonyl)methyl]imino-3,3-bis(trifluoromethyl)-2-trimethylsilyl-1-azonia-3-boratacyclobutane (**II**), 2(RS)-4-benzylimino-1,1-dimethyl-3,3-bis(trifluoromethyl)-2-trimethylsilyl-1-azonia-3-boratacyclobutane (**III**) and 1(SR)-7(RS)-2,4-di-tert-butyl-6-methyl-8,8-bis(trifluoromethyl)-7-trimethylsilyl-2,4-diaza-6-azonia-8-boratabicyclo-[3.3.0]oct-5-ene (**IV**) were as follows.

At room temperature 10 mmol of the isocyanide was added dropwise to a stirred solution containing 2.8 g (10 mmol) of **I** in 10 ml of $\mathrm{CHCl_3}$. After stirring for 5 h, the solvent and unreacted material was pumped off in vacuo (2d/10^{-2} torr) to yield **II** (96%, m.p. 135°C), **III** (91%, m.p. 111°C). Compound **IV** (m.p. 139°C) was obtained analogously in 82% yield from **I** and t-BuNC in a 1:2 ratio as a colourless solid. Elemental analyses: found (calc.): **II** C, 43.13(43.05), H, 5.27(5.31), N, 5.86(5.91); **III** C, 48.24(48.50), H, 5.66(5.85), N, 6.89(7.07); **IV** C, 48.80(48.54), H, 7.59(7.69), N, 9.61(9.43)%.

3.1. Spectra of II

^{1}H NMR: $\delta = 0.16$ (s, 9H; $\mathrm{Si(C}H_3)_3$), 2.43 (s, 3H; $\mathrm{C}CH_3$), 2.81 (s, 3H; $\mathrm{N}CH_3$), 2.83 (s, 3H; $\mathrm{N}CH_3$), 3.04 ((broad), 1H; $\mathrm{BC}H$), 4.82 (s, 2H; $\mathrm{NC}H_2\mathrm{S}$), 7.34 ('d' 8.1 Hz, 2H; $\mathrm{C_6}H_4$), 7.74 ('d' 8.2 Hz, 2H, $\mathrm{C_6}H_4$); ^{13}C{^{1}H} NMR: $\delta = -0.9$ (s; $\mathrm{Si}C_3$), 21.5 (s; $\mathrm{C_6H_4}C\mathrm{H_3}$), 46.6 (q; $\mathrm{N}C\mathrm{H_3}$, $^5J(\mathrm{CF}) = 1.6$ Hz), 50.7 (s; $\mathrm{N}C\mathrm{H_3}$), 61.2 ((broad); $\mathrm{B}C\mathrm{H(Si)N}$), 71.1 (s; $\mathrm{N}C\mathrm{H_2S}$), 128.9 (s; $C_6\mathrm{H_4}$), 129.7 (s; $C_6\mathrm{H_4}$), 133.8 (s; $C_6\mathrm{H_4}$), 145.4 (s; $C_6\mathrm{H_4}$), 182.0 ((broad); $\mathrm{B}C\mathrm{{=}N}$); ^{11}B NMR: $\delta = -12.0$; ^{19}F NMR: $\delta = -58.3$ ('d', $^2J(\mathrm{BF}) \approx 33$ Hz), -62.7 ('d', $^2J(\mathrm{BF}) = 33$ Hz). IR (KBr): ν (cm^{-1}) 1719 (C=N), 1089 (C–F). MS (70 eV): m/z 401 ($M^{\oplus} - \mathrm{Si(CH_3)_3}$, 5%), 130 ($\mathrm{(H_3C)_2N{=}CH{-}Si(CH_3)_3^{\oplus}}$, 100), 106 ($\mathrm{F_2BCH{=}N(CH_3)_2^{\oplus}}$, 80).

3.2. Spectra of III

^{1}H NMR: $\delta = 0.25$ (s, 9H; $\mathrm{Si(C}H_3)_3$), 2.97 (s, 6H; $\mathrm{N(C}H_3)_2$), 3.05 ((broad), 1H; $\mathrm{BC}H$), 4.71 (s, 2H;

$\mathrm{NC}H_2$), 7.34 (m, 5H; C_6H_5); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = -0.3$ (s; $\mathrm{Si}C_3$), 48.0 ((broad); $\mathrm{N}C\mathrm{H}_3$), 51.6 ((broad); $\mathrm{N}C\mathrm{H}_3$), 55.2 (s; $\mathrm{N}C\mathrm{H}_2\mathrm{C}_6\mathrm{H}_5$), 60.9 (q; $\mathrm{B}C\mathrm{H(Si)N}$ $^1J(\mathrm{CB}) \approx 36$ Hz), 128.2 (s; $C_6\mathrm{H}_5$), 128.8 (s; $C_6\mathrm{H}_5$), 129.6 (s; $C_6\mathrm{H}_5$), 139.7 (s; $C_6\mathrm{H}_5$), 177.0 ((broad); $\mathrm{B}C\mathrm{=N}$); $^{11}\mathrm{B}$ NMR: $\delta = 11.6$ (sept, $^2J(\mathrm{BF}) \approx 30.8$ Hz); $^{19}\mathrm{F}$ NMR: $\delta = -58.5$ (q, $^2J(\mathrm{BF}) \approx 29.7$ Hz), -63.1 (q, $^2J(\mathrm{BF}) \approx 30.7$ Hz). IR (KBr): ν (cm^{-1}) 1716 (C=N), 1086 (C–F). MS (70 eV): m/z 323 ($\mathrm{M}^{\oplus} - \mathrm{Si(CH_3)_3}$, 12), 130 ($\mathrm{(H_3C)_2N{=}CH{-}Si(CH_3)^{\oplus}}$, 58), 106 ($\mathrm{F_2BCH{=}N(CH_3)_2^{\oplus}}$, 20), 91 ($\mathrm{C_7H_7^{\oplus}}$, 100).

3.3. Spectra of IV

$^1\mathrm{H}$ NMR: $\delta = 0.16$ (s, 9H; $\mathrm{Si(C}H_3)_3$), 1.09 (s, 9H; $\mathrm{C(C}H_3)_3$), 1.50 (s, 9H; $\mathrm{C(C}H_3)_3$), 2.83 ((broad), 1H; $\mathrm{BC}H$), 3.15 (s, 3H; $\mathrm{NC}H_3$), 3.72 ((broad), 1H; $\mathrm{BC}H$), 4.42 ('t', $^2J(\mathrm{HH}) \approx {}^4J(\mathrm{HH}) = 5.4$ Hz, 1H; $\mathrm{C}H_2$), 4.80 (d, $^2J(\mathrm{HH}) = 5.4$ Hz, 1H; $\mathrm{C}H_2$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = 0.59$ (s; $\mathrm{Si}C_3$), 26.0 (s; $\mathrm{C(}C\mathrm{H_3)_3}$), 29.8 (s; $\mathrm{C(}C\mathrm{H_3)_3}$), 44.1 (s; $\mathrm{N}C\mathrm{H}_3$), 52.8 (s; $C\mathrm{(CH_3)_3}$), 57.9 (s; $C\mathrm{(CH_3)_3}$), 58.4 (q; $\mathrm{B}C\mathrm{H}$, $^1J(\mathrm{CB}) \approx 33$ Hz), 65.0 (q; $\mathrm{B}C\mathrm{H}$, $^1J(\mathrm{CB}) \approx 37$ Hz), 74.4 (s; $\mathrm{N}C\mathrm{H_2N}$), 181.0 (s; $\mathrm{N{=}}C\mathrm{N}$); $^{11}\mathrm{B}$ NMR: $\delta = -14.0$ (sept, $^2J(\mathrm{BF}) \approx 25.8$ Hz); $^{19}\mathrm{F}$ NMR: $\delta = -57.05$ (q, $^2J(\mathrm{BF}) = 24.4$ Hz), -57.10 (q, $^2J(\mathrm{BF}) = 25.9$ Hz). IR (KBr): ν (cm^{-1}) 1647 (C=N), 1083 (C–F). MS (70 eV): m/z 388 ($\mathrm{M}^{\oplus} - \mathrm{C_4H_9}$, 10), 332 ($\mathrm{M}^{\oplus} - \mathrm{C_8H_{17}}$, 7), 57 ($\mathrm{C_4H_9^{\oplus}}$, 100).

Table 3
Atomic coordinates and thermal parameters (Å^2) of the nonidealized atoms of **II**

Atom	x	y	z	U
S	0.3580(1)	0.6899(1)	0.6004(1)	0.0644(6)
Si	−0.3197(1)	0.9221(1)	0.2427(1)	0.0620(6)
F(1)	0.0822(3)	1.0082(3)	0.3122(3)	0.102(2)
F(2)	0.0611(3)	1.0191(3)	0.1347(2)	0.107(2)
F(3)	0.2494(3)	0.8842(3)	0.2395(3)	0.117(2)
F(4)	0.0082(3)	0.6257(3)	0.2580(3)	0.097(2)
F(5)	0.0273(4)	0.7856(3)	0.1030(2)	0.116(2)
F(6)	0.2084(3)	0.6610(4)	0.2183(3)	0.134(2)
O(1)	0.5110(3)	0.6475(4)	0.5775(3)	0.094(2)
O(2)	0.2798(3)	0.8286(3)	0.5731(3)	0.086(2)
N(1)	−0.1186(3)	0.7811(3)	0.4593(2)	0.045(1)
N(2)	0.1247(3)	0.6658(3)	0.5307(3)	0.050(2)
C(1)	−0.1488(4)	0.8808(4)	0.3275(3)	0.049(2)
H(1)	−0.160(3)	0.963(4)	0.335(3)	0.04(1)
C(2)	0.0453(3)	0.7376(4)	0.4395(3)	0.044(2)
C(3)	0.2802(4)	0.6311(4)	0.5129(3)	0.058(2)
C(4)	0.3299(4)	0.6032(4)	0.7511(3)	0.055(2)
C(5)	0.4342(5)	0.4879(5)	0.8153(4)	0.073(2)
C(6)	0.4103(6)	0.4207(5)	0.9329(5)	0.087(3)
C(7)	0.2846(6)	0.4650(5)	0.9898(4)	0.082(3)
C(8)	0.1828(5)	0.5818(6)	0.9251(5)	0.089(3)
C(9)	0.2035(5)	0.6513(5)	0.8067(4)	0.075(3)
C(10)	0.2594(8)	0.3884(7)	1.1205(5)	0.131(4)
C(11)	0.1040(4)	0.9313(5)	0.2457(4)	0.067(2)
C(12)	0.0672(5)	0.7262(5)	0.2181(4)	0.068(2)
C(13)	−0.1744(4)	0.6682(4)	0.4919(4)	0.073(2)
C(14)	−0.1600(4)	0.8452(5)	0.5512(4)	0.073(2)
C(15)	−0.4787(4)	0.9882(5)	0.3283(4)	0.083(3)
C(16)	−0.3057(5)	1.0562(6)	0.1013(4)	0.109(3)
C(17)	−0.3466(6)	0.7844(6)	0.2128(6)	0.124(4)
B	0.0252(4)	0.8206(5)	0.2953(4)	0.048(2)

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

Table 4
Atomic coordinates and thermal parameters (Å^2) of the nonidealized atoms of **IV**

Atom	x	y	z	U
Si	0.2081(2)	0.5272(1)	0.3418(1)	0.0649(7)
F(1)	0.6156(4)	0.5298(2)	0.3293(2)	0.089(2)
F(2)	0.4956(4)	0.4262(2)	0.2679(2)	0.113(2)
F(3)	0.6768(4)	0.4915(2)	0.2215(2)	0.090(2)
F(4)	0.4336(5)	0.4953(3)	0.0995(2)	0.124(2)
F(5)	0.2280(5)	0.4959(3)	0.1495(2)	0.127(2)
F(6)	0.2988(5)	0.6105(3)	0.0964(2)	0.109(2)
N(1)	0.3749(5)	0.6844(3)	0.3215(2)	0.046(2)
N(2)	0.6190(5)	0.7584(3)	0.3229(2)	0.046(2)
N(3)	0.6813(5)	0.6956(3)	0.2114(2)	0.051(2)
C(1)	0.3044(7)	0.6078(4)	0.2781(3)	0.051(2)
C(2)	0.5018(6)	0.7110(3)	0.2950(3)	0.041(2)
C(3)	0.7197(7)	0.7699(4)	0.2626(3)	0.064(2)
C(4)	0.5216(7)	0.6762(4)	0.2186(3)	0.045(2)
C(5)	0.5541(7)	0.5071(4)	0.2593(4)	0.065(3)
C(6)	0.3533(8)	0.5459(5)	0.1424(4)	0.073(3)
C(7)	0.2779(8)	0.7390(4)	0.3654(4)	0.076(3)
C(8)	0.6619(7)	0.7937(4)	0.4012(3)	0.053(2)
C(9)	0.6211(8)	0.7264(4)	0.4586(3)	0.082(3)
C(10)	0.8343(7)	0.8066(4)	0.4118(3)	0.076(3)
C(11)	0.5897(7)	0.8842(4)	0.4116(3)	0.076(3)
C(12)	0.7344(7)	0.7096(4)	0.1355(3)	0.057(2)
C(13)	0.7009(9)	0.6300(5)	0.0869(4)	0.106(4)
C(14)	0.9055(9)	0.7231(5)	0.1467(4)	0.113(4)
C(15)	0.662(1)	0.7900(5)	0.0952(3)	0.116(4)
C(16)	0.0232(7)	0.5722(5)	0.3674(4)	0.109(4)
C(17)	0.1568(9)	0.4191(4)	0.2960(4)	0.113(4)
C(18)	0.3312(8)	0.5077(4)	0.4308(3)	0.098(3)
B	0.4363(7)	0.5797(4)	0.2213(3)	0.049(2)
H(1)	0.223(5)	0.629(2)	0.250(2)	0.02(1)
H(4)	0.458(5)	0.711(3)	0.188(2)	0.03(1)

$U = U_{iso}$ for H(1) and H(4), otherwise $U = U_{eq}$ as in Table 3.

3.4. Crystal structure of II

Triclinic crystals of **II** were grown from a $\mathrm{CHCl_3}$ solution and have $a = 9.795(3)$, $b = 11.404(5)$, $c = 11.963(4)$ Å, $\alpha = 68.25(2)$, $\beta = 83.58(2)$, $\gamma = 70.12(2)°$, $V = 1167$ Å^3, $Z = 2$, $\rho_{\mathrm{cal}} = 1.352$ g cm^{-3}, $P\bar{1}$ (No. 2) at 299 K. A total of 4814 reflections ($5° \leq 2\theta \leq 45°$) was measured from a crystal of dimensions 0.32 × 0.30 × 0.08 mm. Of these reflections, 3042 were unique, and 2072 with $F_0 \geq 4\sigma$ (F_0) were used in the refinement. The structure was solved by direct methods and refined with all nonhydrogen atoms anisotropic and hydrogen atoms isotropic. While parameters of the H(1) atom were not constrained, the other hydrogen atoms were idealized (C–H 0.95 Å) and allowed to ride on the carbon atoms to which they were attached. Convergence of the 287 parameters was reached with $R = 0.047$ and $R_w = 0.054$. Coordinates of the refined atoms are listed in Table 3, and the labelling is defined in Fig. 1 [8].

3.5. *Crystal structure of IV*

Monoclinic crystals of **IV** were obtained using an acetone/ethanol/petroleum ether solvent mixture. Crystal data are $a = 8.826(3)$, $b = 15.114(5)$, $c = 17.824(7)$ Å, $\beta = 95.64(3)°$, $V = 2366$ Å^3, $Z = 4$, $\rho_{cal} = 1.247$ g cm^{-3}, $P2_1/n$ (No. 14) at 298 K. A total of 6963 reflections ($5° \le 2\theta \le 45°$) was measured from a crystal of dimensions 0.57 × 0.20 × 0.12 mm. Of these data, 3093 are unique, and 1921 with $F_0 \ge 4\sigma(F_0)$ were used to refine the structure. The solution and refinement of this structure follows that of **II** with H(1) and H(4) being refined freely. Refinement of the 284 parameters converged with $R = 0.075$ and $R_w = 0.061$. Coordinates of the refined atoms are listed in Table 4, and Fig. 2 defines the numbering scheme [8].

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[8] Additional crystallographic data may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the deposit number CSD 380068 for II and 380069 for VI, the names of the authors and the literature reference.