

**Novel tris(trimethylsilyl)methylboron compounds.
 Crystal structures of the diborane $\{(\text{Me}_3\text{Si})_3\text{C}\}\text{HB}$
 $(\mu\text{-H})_2\text{BH}\{\text{C}(\text{SiMe}_3)_3\}$ and the bis(aminoboryl)amine
 $\{(\text{Me}_3\text{Si})_3\text{C}(\text{NH}_2)\text{B}\}_2\text{NH}$**

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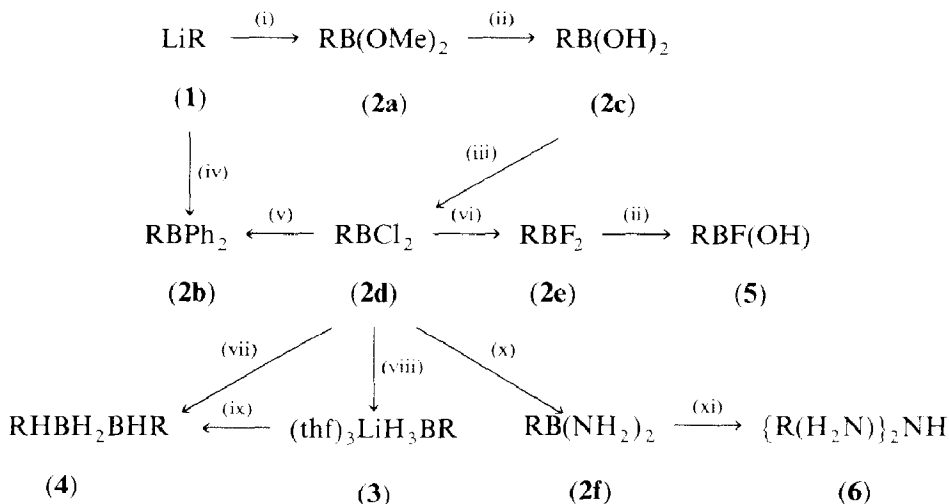
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Abstract

The dichloroborane RBCl_2 ($\text{R} = (\text{Me}_3\text{Si})_3\text{C}$) is reduced by LiBH_4 to the diborane *trans*- $\text{RHB}(\mu\text{-H})_2\text{BHR}$, which melts sharply at 183–185 °C. It also reacts with ammonia to give the diamminoborane $\text{RB}(\text{NH}_2)_2$ which on warming in vacuum gives the bis(aminoboryl)amine $\{\text{R}(\text{NH}_2)\text{B}\}_2\text{NH}$. The structures of the diborane and the bis(aminoboryl)amine have been confirmed by X-ray diffraction.

Introduction

Two independent studies [1,2] have shown that the reaction between tris(trimethylsilyl)methyl lithium (RLi (**1**), $\text{R} = (\text{Me}_3\text{Si})_3\text{C}$) and trimethoxyborane gives the dimethoxy compound $\text{RB}(\text{OMe})_2$ (**2**), which may be converted into a wide range of tris(trimethylsilyl)methylboron derivatives. Some of these are shown in Scheme 1 and others in the adjacent paper [3]. Most of the compounds RBX_2 (**2**) ($\text{X} = \text{OMe}, \text{OH}, \text{Cl}, \text{F}, \text{Ph}, \text{Me}, \text{or } \text{NH}_2$) appear from their ^{11}B NMR spectra (Table 1) to have structures similar to those of the methylboron compounds, containing three-coordinate boron [4] (confirmed for $\text{X} = \text{Ph}$ (**2b**) [6] and OH (**2c**) [1] by X-ray crystallography). The structures of compounds (**3–6**) show novel features. Those of $(\text{thf})_3\text{LiH}_3\text{BC}(\text{SiMe}_2\text{Ph})_3$ [7] and $(\text{Me}_2\text{PhSi})_3\text{CBF}(\text{OH})$ [8] have been previously discussed. In this paper we describe the synthesis and structures of **4**, the first 1,2-substituted diborane to be characterised in the crystalline state by X-ray diffraction, and of the bis(aminoboryl)amine (**6**). An independent determination of the crystal structure of **4**, at 112 K, is described in the adjacent paper [3].



Scheme 1. (i) B(OMe)₃; (ii) H₂O; (iii) PCl₅; (iv) Ph₂BBr; (v) LiPh; (vi) SbF₅; (vii) LiBH₄; (viii) LiAlH₄; (ix) MeSO₃H; (x) NH₃; (xi) 80 °C 0.05 Torr.

Table 1

¹¹B NMR data for compounds RBX₂^a

X	OMe	Ph	OH	Cl	F	NH ₂	Me	H
R = Me ^b	29.5	77.6	31.9	61.4	28.1	^c	86	20.5
R = (Me ₃ Si) ₃ C ^d	30.6	77.5	31.0	56.0	27.1	32.3 ^e	81	21.9 ^f

^a δ(B) in ppm relative to external BF₃OEt₂. ^b Ref. 5. ^c Compound unknown. ^d Ref. 1. ^e This work. ^f Ref. 3.

Experimental

Schlenk-tube techniques were used for manipulation of air-sensitive compounds. All NMR data were from samples in C₆D₅CD₃. Chemical shifts are relative to SiMe₄ (¹H, ¹³C, ²⁹Si), BF₃OEt₂ (¹¹B), or CH₃NO₂ (¹⁵N).

trans-1,2,-Bis{ tris(trimethylsilyl)methyl } diborane (**4**).

(a) A solution of (Me₃Si)₃CBCl₂ (**2d**) [1] (0.79 g, 2.5 mmol) in ether (10 cm³) was added slowly to a suspension of LiBH₄ (0.11 g, 5.0 mmol) in ether (20 cm³). The mixture was stirred for 3 days, the solvent removed, the residue extracted into pentane, the extract filtered, and the pentane removed. The white solid residue was sublimed at 0.05 Torr to give at 75 °C a small amount of (Me₃Si)₃CB(OH)₂, and at 120 °C the hydride **4** (0.82 g, 67%), m.p. 183–185 °C (Found: C, 49.6; H, 12.0. C₁₀H₂₉BSi₃ calc.: C, 49.1; H, 11.9%). The dimeric structure was confirmed by EI mass spectroscopy (*m/z* 487, [M – H]⁺), by cryoscopy in benzene (found *M* 520), and by an X-ray diffraction study of a sample that had been recrystallised from toluene.

(b) A similar procedure with sodium borohydride as reducing agent also gave **4** but in somewhat lower yield (38%).

(c) The diborane **4** was also obtained from the boron-lithium complex **3** [1]. Methanesulfonic acid (0.04 g, 0.42 mmol) was added from a syringe to a solution of **3** (0.20 g, 0.42 mmol) in pentane (12 cm³). There was a vigorous reaction and a white precipitate formed. The mixture was stirred for 10 min after gas evolution had ceased, the solvent was removed under vacuum, and the residue extracted into pentane. The pentane was removed to give the diborane **4** (0.05 g, 48%).

Diamino { tris(trimethylsilyl)methyl } borane (2f)

Dry ammonia was bubbled through a solution of the dichloride **2d** (1.0 g 3.2 mmol) in toluene (30 cm³) for 6 h at 20 °C. The white precipitate was filtered off, solvent evaporated from the filtrate, and the residue recrystallised from heptane to give the colourless diaminoborane **2f** (0.7 g, 80%), m.p. 220–222 °C. (Found: C, 43.5; H, 11.1; N, 9.7. C₁₀H₃₁BN₂Si₃ calc.: C, 43.8; H, 11.3; N, 10.2%); $\delta(\text{H})$ 0.23 (27H, s, SiMe₃), 2.59 (4H, br, NH₂); $\delta(\text{B})$ 32.3; $\delta(\text{C})$ 5.4 (SiMe₃); $\delta(\text{Si})$ 4.1; $\delta(\text{N})$ (INEPT) –307 ppm (t, $J(\text{NH})$ 79.4 Hz); $\nu(\text{NH})$ 3669, 3633, 3532, 3437, $\delta(\text{NH})$ 1599 cm⁻¹; m/z 259 (100% [$M - \text{Me}$]⁺), 242 (80, [$M - \text{Me} - \text{NH}_3$]⁺).

When heated under vacuum at 80 °C and 0.05 Torr for 3 h, compound **2f** gave a white sublimate which appeared from NMR and mass spectroscopy to be mainly unchanged bis(amino) derivative together with a second compound having an almost identical ¹¹B chemical shift (28.3 ppm). After recrystallisation from heptane a crystal selected for study by X-ray diffraction was shown to be bis(amino{tris(trimethylsilyl)methyl}boryl)amine (**6**), but we were unable to detect the ammonia which must have accompanied the formation of **6** from **2f**.

Crystal structure determinations

(1) {(Me₃Si)₃C}HB(μ-H)₂BH{(SiMe₃)₃} (4)

Crystal data: C₂₀H₅₈B₂Si₆, M 488.8, triclinic, space group $P\bar{1}$, a 8.915(6), b 8.982(2), c 11.478(3) Å, 100.76 (14), β 100.71(7), γ 107.63(12). U 831.2 Å³, Z = 1, D_c 0.98 g cm⁻³, $F(000)$ = 272, Mo- K_α radiation, λ 0.71069 Å, μ 2.52 cm⁻¹.

Data were measured with an Enraf–Nonius CAD 4 diffractometer on a crystal of size 0.4 × 0.33 × 0.4 mm. Intensities for h , $\pm k$, $\pm l$ reflections with $2 < \theta < 25^\circ$ were measured with a $\theta/2\theta$ scan with $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$: two standard reflections, monitored every 30 min showed no change. After correction for Lorenz and polarization effects but not for absorption, 1889 reflections with $|F|^2 > \sigma(F^2)$ were used for the structure analysis. The positions of C, Si, and B atoms were found by direct methods [9]. The hydrogen atoms H and H(1) were found on a difference map: although the position of H refined satisfactorily that of H(1) did not, and it was fixed at the position indicated by the map. H atoms for the methyl groups were held at calculated positions with $U_{\text{iso}} = 1.3 U_{\text{eq}}$ for the C atoms to which they were bonded. Full matrix least squares refinement, with anisotropic temperature factors, converged at $R = (\sum \|F_o\| - |F_c|) / \sum |F_o| = 0.11$ and $R' = \{\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2\}^{1/2} = 0.13$ with $w = 1/\sigma^2(F)$. All final shift to error ratios were < 1.06 and a final difference map was everywhere $< 0.5 \text{ e \AA}^{-3}$. Fractional atomic coordinates are given in Table 2, and bond lengths and angles in Table 3.

(2) {(Me₃Si)₃C(H₂N)B}₂NH (6)

Crystal data: C₂₀H₅₉B₂N₃Si₆, M 531.85, triclinic, space group $P\bar{1}$, a 9.262(5), b 12.649(9), c 15.730(11) Å, α 104.73(6), β 90.63(5), γ 102.81(5)°, U 1733.4 Å³, Z = 2,

Table 2

Fractional atomic coordinates ($\times 10^4$ for Si, B; $\times 10^3$ for H) for **4** with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	2007(3)	1724(2)	3547(2)
Si(2)	4663(3)	2619(3)	2104(2)
Si(3)	2287(3)	4564(2)	2266(2)
C(1)	3447(8)	3422(7)	3089(6)
C(2)	474(14)	2326(14)	4205(10)
C(3)	3065(14)	954(9)	4739(9)
C(4)	829(15)	-71(10)	2228(11)
C(5)	5409(12)	1079(11)	2703(12)
C(6)	6588(12)	4242(15)	2126(10)
C(7)	3526(13)	1669(12)	462(9)
C(8)	3545(14)	5891(11)	1479(9)
C(9)	1708(11)	5977(9)	3367(10)
C(10)	388(11)	3266(10)	1113(9)
B	4764(13)	4793(11)	4200(9)
H	573(1)	459(1)	497(1)
H(1)	584	584	391

Table 3

Intramolecular distances (Å) and angles ($^\circ$) for **4** with estimated standard deviations in parentheses ^a

<i>(a) Bonds</i>			
Si(1)–C(1)	1.901(7)	Si(1)–C(2)	1.846(14)
Si(1)–C(3)	1.873(11)	Si(1)–C(4)	1.862(9)
Si(2)–C(1)	1.897(8)	Si(2)–C(5)	1.890(12)
Si(2)–C(6)	1.878(11)	Si(2)–C(7)	1.864(9)
Si(3)–C(1)	1.912(8)	Si(3)–C(8)	1.861(11)
Si(3)–C(9)	1.875(11)	Si(3)–C(10)	1.836(8)
C(1)–B	1.582(9)	B...B'	1.747(14)
B–H	1.195(12)	B–H'	1.231(13)
B–H(1)	1.267		
<i>(b) Angles</i>			
C(1)–Si(1)–C(2)	113.2(5)	C(1)–Si(1)–C(3)	113.5(4)
C(1)–Si(1)–C(4)	112.7(5)	C(2)–Si(1)–C(3)	105.0(6)
C(2)–Si(1)–C(4)	105.7(5)	C(3)–Si(1)–C(4)	105.9(4)
C(1)–Si(2)–C(5)	112.0(5)	C(1)–Si(2)–C(6)	112.2(4)
C(1)–Si(2)–C(7)	114.0(5)	C(5)–Si(2)–C(6)	103.6(5)
C(5)–Si(2)–C(7)	107.5(5)	C(6)–Si(2)–C(7)	106.9(5)
C(1)–Si(3)–C(8)	112.3(5)	C(1)–Si(3)–C(9)	111.8(4)
C(1)–Si(3)–C(10)	114.6(4)	C(8)–Si(3)–C(9)	104.4(5)
C(8)–Si(3)–C(10)	106.9(5)	C(9)–Si(3)–C(10)	106.0(4)
Si(1)–C(1)–Si(2)	111.0(3)	Si(1)–C(1)–Si(3)	111.1(4)
Si(1)–C(1)–B	114.8(6)	Si(2)–C(1)–Si(3)	110.9(4)
Si(2)–C(1)–B	105.1(6)	Si(3)–C(1)–B	103.6(5)
C(1)–B–H	125.6(8)	C(1)–B–H(1)	115.6(8)
H–B–H(1)	93.9(7)	H–B...B'	44.8(6)
H(1)–B...B'	108.1(6)	C(1)–B...B'	136.2(8)
H–B–H'	87.9(7)	H(1)–B–H'	112(7)
C(1)–B–H'	117.3(9)	B'...B–H'	43.1(6)
B–H–B'	92.1(8)		

^a Symmetry element: ' is 1 - *x*, 1 - *y*, 1 - *z*

Table 4

Fractional atomic coordinates ($\times 10^4$) for **6** with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	2593(11)	2492(7)	2109(5)	C(8)	-1486(36)	1033(24)	1105(19)
Si(2)	-9(11)	2659(7)	3334(6)	C(9)	-1844(35)	3313(25)	1222(18)
Si(3)	-506(13)	2469(8)	1306(6)	C(10)	501(33)	2475(26)	263(16)
Si(4)	5398(15)	6840(10)	3620(7)	C(11)	4189(22)	7037(16)	2716(14)
Si(5)	3348(13)	8227(8)	3143(7)	C(12)	3981(33)	6101(20)	4334(15)
Si(6)	5588(17)	7343(10)	1821(8)	C(13)	6693(32)	5913(25)	3259(21)
N(1)	2705(17)	4998(12)	2567(10)	C(14)	6453(37)	8214(23)	4426(16)
N(2)	2356(29)	5897(20)	1289(14)	C(15)	2471(35)	8206(22)	4268(17)
N(3)	156(21)	5044(15)	2859(13)	C(16)	1698(32)	8156(22)	2370(19)
C(1)	878(23)	3066(16)	2290(14)	C(17)	4514(32)	9681(21)	3367(18)
C(2)	3888(30)	3193(21)	1386(17)	C(18)	5962(37)	6073(20)	1120(17)
C(3)	3827(28)	2798(19)	3085(14)	C(19)	7465(35)	8368(23)	2409(20)
C(4)	2287(31)	951(21)	1555(15)	C(20)	4677(34)	8133(21)	1071(15)
C(5)	920(31)	3637(22)	4406(16)	B(1)	1217(34)	4424(23)	2566(20)
C(6)	128(36)	1248(22)	3407(18)	B(2)	2980(46)	5882(34)	2180(27)
C(7)	-1973(29)	2672(22)	3432(14)				

D_c 1.02 g cm⁻³, $F(000) = 588$, Mo- K_α radiation, λ 0.710 69 Å, μ 5.0 cm⁻¹.

Data from a crystal of size 0.5 × 0.3 × 0.1 mm were collected as for **4**: 1038 reflections with $|F|^2 > 3\sigma(F^2)$ were used in the structure analysis. The C, Si, N, and B atoms were found by direct methods [9] and refined by full matrix least squares with anisotropic temperature factors except for B(1) and B(2), which were left isotropic. Hydrogen atoms within (Me₃Si)₃C groups were placed at calculated positions (C–H 1.08 Å, B_{iso} 8.0 Å³); those attached to nitrogen could not be found and were omitted.

Refinement converged at $R = 0.13$, $R' = 0.11$. Final shifts to error were < 0.15 , and a final difference map was everywhere < 0.6 e Å⁻³. Atomic coordinates are given in Table 4, and bond lengths and angles in Table 5.

A PDP 11/34 computer and the Enraf–Nonius Structure Determination Package was used for both structures. Lists of hydrogen atom coordinates, temperature factors, and structure factors are available from the authors.

Results and discussion

The 1,2-dialkyldiborane (**4**) is readily made by reduction of the dichloride **2d** with lithium borohydride. The stronger reducing agent lithium aluminium hydride gives the boron-lithium complex $L_n\text{LiH}_3\text{BR}$ (**3**) ($L_n = (\text{thf})_3$) but this can be converted into **4** by treatment with a stoichiometric quantity of methanesulfonic acid. The diborane **4**, which is also obtained by treatment of compounds **3** ($L_n = (\text{Et}_2\text{O})_2$) with Me₃NHCl or I₂ [3], shows good thermal stability, and melts at 183–185 °C.

The structure of the diborane is shown in Fig. 1. In the crystal the molecules are required by the space group to be centrosymmetric. The B...B and B–C distances are in excellent agreement with those found for (MeBH₂)₂ in the gas phase by electron diffraction [10], and although the B–H distances were obtained with low precision there is some evidence that they are slightly shorter than those from electron diffraction, as was found earlier for diborane. The most notable difference

Table 5

Intramolecular distances (Å) and angles (°) for **6** with estimated standard deviations in parentheses

<i>(a) Bonds</i>			
Si(1)–C(1)	1.88(2)	Si(1)–C(2)	1.89(3)
Si(1)–C(3)	1.81(3)	Si(1)–C(4)	1.88(2)
Si(2)–C(1)	1.98(2)	Si(2)–C(5)	1.88(2)
Si(2)–C(6)	1.85(3)	Si(2)–C(7)	1.83(3)
Si(3)–C(1)	1.88(2)	Si(3)–C(8)	1.79(3)
Si(3)–C(9)	1.83(4)	Si(3)–C(10)	1.90(3)
Si(4)–C(11)	1.90(3)	Si(4)–C(12)	1.97(3)
Si(4)–C(13)	1.85(4)	Si(4)–C(14)	1.92(3)
Si(5)–C(11)	1.83(2)	Si(5)–C(15)	1.96(3)
Si(5)–C(16)	1.91(3)	Si(5)–C(17)	1.86(3)
Si(6)–C(11)	1.98(3)	Si(6)–C(18)	1.81(3)
Si(6)–C(19)	1.98(3)	Si(6)–C(20)	2.01(3)
N(1)–B(1)	1.41(3)	N(1)–B(2)	1.38(5)
N(2)–B(2)	1.52(5)	N(3)–B(1)	1.40(4)
C(1)–B(1)	1.62(3)	C(11)–B(2)	1.65(4)
<i>(b) Angles</i>			
C(1)–Si(1)–C(2)	112(1)	C(1)–Si(1)–C(3)	115(1)
C(1)–Si(1)–C(4)	116(1)	C(2)–Si(1)–C(3)	100(1)
C(2)–Si(1)–C(4)	104(1)	C(3)–Si(1)–C(4)	108(1)
C(1)–Si(2)–C(5)	113(1)	C(1)–Si(2)–C(6)	113(1)
C(1)–Si(2)–C(7)	116(1)	C(5)–Si(2)–C(6)	105(1)
C(5)–Si(2)–C(7)	104(1)	C(6)–Si(2)–C(7)	105(1)
C(1)–Si(3)–C(8)	118(1)	C(1)–Si(3)–C(9)	115(1)
C(1)–Si(3)–C(10)	109(1)	C(8)–Si(3)–C(9)	109(2)
C(8)–Si(3)–C(10)	103(1)	C(9)–Si(3)–C(10)	102(2)
C(11)–Si(4)–C(12)	104(1)	C(11)–Si(4)–C(13)	116(1)
C(11)–Si(4)–C(14)	114(1)	C(12)–Si(4)–C(13)	106(1)
C(12)–Si(4)–C(14)	105(1)	C(13)–Si(4)–C(14)	109(1)
C(11)–Si(5)–C(15)	113(1)	C(11)–Si(5)–C(16)	110(1)
C(11)–Si(5)–C(17)	119(1)	C(15)–Si(5)–C(16)	104(1)
C(15)–Si(5)–C(17)	103(1)	C(16)–Si(5)–C(17)	106(1)
C(11)–Si(6)–C(18)	112(1)	C(11)–Si(6)–C(19)	110(1)
C(11)–Si(6)–C(20)	108(1)	C(18)–Si(6)–C(19)	110(2)
C(18)–Si(6)–C(20)	109(1)	C(19)–Si(6)–C(20)	108(1)
B(1)–N(1)–B(2)	118(3)	Si(1)–C(1)–Si(2)	107(1)
Si(1)–C(1)–Si(3)	112(1)	Si(1)–C(1)–B(1)	114(2)
Si(2)–C(1)–Si(3)	110(1)	Si(2)–C(1)–B(1)	103(2)
Si(3)–C(1)–B(1)	110(2)	Si(4)–C(11)–Si(5)	110(1)
Si(4)–C(11)–Si(6)	104(1)	Si(4)–C(11)–B(2)	114(2)
Si(5)–C(11)–Si(6)	111(1)	Si(5)–C(11)–B(2)	113(2)
Si(6)–C(11)–B(2)	103(2)	N(1)–B(1)–N(3)	119(2)
N(1)–B(1)–C(1)	117(2)	N(3)–B(1)–C(1)	124(2)
N(1)–B(2)–N(2)	127(3)	N(1)–B(2)–C(11)	117(3)
N(2)–B(2)–C(11)	116(3)		

between **4** and $(\text{MeBH}_2)_2$ is in the values of the B...B–C and B...B–H angles (136.2(8) and 108°, respectively for **4**; and 121.8(8) and 118.5(27)° for $(\text{MeBH}_2)_2$), which reflect the effect of the larger alkyl group in **4**. Indeed, the distance from C(1) to the molecular centre of inversion (2.29 Å) is only slightly larger than those (2.05–2.18 Å) in the species MR_2 (M = Mg, Mn, or Hg) or $[\text{M}'\text{R}_2]^-$ (M' = Li, Cu,

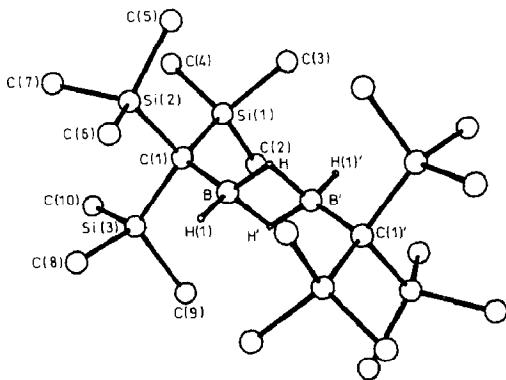


Fig. 1.

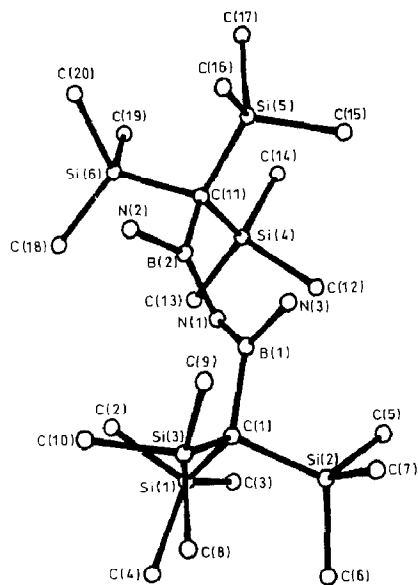


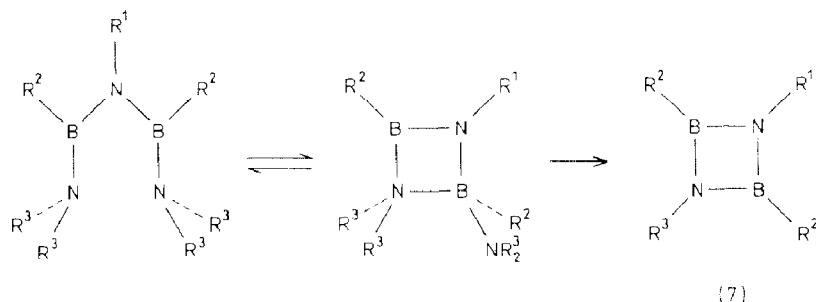
Fig. 2.

or Ag), in which the methyl groups of adjacent R interlock to fill the space around the centres of the molecules [11,12]. The mean Si–C distances (Si–C(1) 1.90(1), Si–Me 1.86(1) Å) and angles within the $(\text{Me}_3\text{Si})_3\text{C}$ groups (C–Si–C 105.7(5) and Si–C(1)–Si 111.0(5)°) in **4** show no unusual features.

The product of the reaction between the dichloride **2d** and ammonia appears from elemental analysis and mass and NMR spectroscopy to be the bis(amino) derivative **2f**. The natural abundance ^{15}N NMR spectrum, enhanced by the INEPT procedure, shows a single triplet, suggesting that all the nitrogen atoms are chemically equivalent and attached to two protons. The X-ray structure of a crystal obtained by heating **2f** under vacuum showed that ammonia had been eliminated with formation of $\{(\text{Me}_3\text{Si})_3\text{C}(\text{NH}_2)\text{B}\}_2\text{NH}$ (**6**), but we have not been able to isolate a bulk sample of **6** which is free from **2f** and so do not have satisfactory analytical and spectroscopic data.

Both **2f** and **6** are unusual compounds. The only other bis(amino)boranes without substituents on nitrogen appear to be $\text{BH}(\text{NH}_2)_2$, which slowly loses ammonia in the liquid state but is stable in the vapour phase or in solution in liquid ammonia [13], and the thermally stable tris(amino) compound $\text{B}(\text{NHAr})(\text{NH}_2)_2$ (Ar = 2, 4, 6-Bu^tC₆H₂), which has been characterised by an X-ray diffraction study [14]. As far as we are aware, no stable crystalline bis(aminoboryl)amine without N-substituents has hitherto been described. The compounds $\{\text{R}(\text{Me}_2\text{N})\text{B}\}_2\text{NH}$ (R = Me, [15] or Ph [15,16]) are known, but apparently decompose readily to give borazenes. A large number of diborylamines have recently been described [17,18], including several having chains of alternate boron and nitrogen atoms: there is a tendency for such compounds to cyclise (Scheme 2) or give clusters.

The X-ray study of **6** does not give bond lengths and angles with sufficient accuracy to permit detailed comparison with those for other compounds, but the molecular structure (Fig. 2) is clearly defined. The sum of the angles at boron (361° at B(1) and 360° at B(2)) shows that the coordination is planar. The boron-contain-



Scheme 2

ing planes are inclined at $46.5 \pm 2^\circ$ to the plane defined by B(1)N(1)B(2). The molecule has no crystallographically required symmetry but the conformation is such that the overall symmetry is close to C_2 , with all the Me_3Si groups twisted in the same direction from the fully staggered positions [19]. The B–N distances are similar to those in $\text{HB}(\text{NH}_2)_2$ (1.419(2)), $\text{MeB}(\text{NHMe})_2$ (1.418(4)) [20], or $(\text{Pr}_2\text{N})\text{B}\text{NBu}^1\text{B}(\text{NPr}_2^1)\text{EPh}$ (1.463(4), E = P; 1.451(5), E = As) [21], $\text{B}(\text{NHAr})(\text{NH}_2)_2$ (1.412(4), 1.437(4), 1.470(4) Å), and are close to the value (1.41 Å) given for the B–N double bond [22]. As in **4** and other tris(trimethylsilyl)methylboron derivatives [6], the mean $\text{Me}_3\text{Si}-\text{C}$ distance (1.91(3) Å) is greater than the Si–Me distance (1.88(3) Å). The mean C–Si–C and Si–C–Si angles (106(1) and 109(1)°, respectively) are normal.

Ring closure (Scheme 2; $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = (\text{Me}_3\text{Si})_3\text{C}$) requires nucleophilic attack by nitrogen on boron and subsequent elimination of ammonia. The first step is probably prevented both by restricted rotation about B–N bonds and by steric hindrance from the large alkyl groups. A molecular model shows that attack on B(2) by the lone pair of N(3) from a direction perpendicular to the plane defined by the three bonds at boron is restricted by the proximity of the methyl groups of the $(\text{Me}_3\text{Si})_3\text{C}$ ligand. However, the distance from the central carbon atom of $(\text{Me}_3\text{Si})_3\text{C}$ to the centroid of the hypothetical molecule $(\text{RBNH})_2$ (7), obtained from **6** by elimination of NH_3 , is 2.6 Å. This is considerably greater than that for **4** or the species R_2Mg . There is thus probably no steric reason why $(\text{RBNH})_2$ should not be stable, and it would be of interest to see whether ammonia could be eliminated from **6** at higher temperatures than have been used so far.

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