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From Crystalline Boryl-substituted and Boryl-coupled 2,2,4,4,6,6-Hexamethylcyclotrisilazanes to β-SiC and BN

Sabine Schaible,[a] Ralf Riedel,[b] R. Boese,[c]* E. Werner,[d] Uwe Klingebiel[d] and Martin Nieger[e]†

[a] Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany, [b] Fachbereich Materialwissenschaft, Fachgebiet disperse Feststoffe, TH Darmstadt, Hilperstraße 31, D-64295 Darmstadt, Germany, [c] Institut für Anorganische Chemie, Universität Essen, Universitätsstraße 5-7, D-45141 Essen, Germany, [d] Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany, and [e] Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

$[\mathrm{Me_2SiNBFN(SiMe_3)_2}]_3$ (1) is synthesized in the reaction of trilithiated hexamethylcyclotrisilazane with $\mathrm{F_2BN(SiMe_3)_2}$. The mono- and dilithium derivatives of the six-membered ring $\mathrm{(Me_2SiNH)_2}$ $\mathrm{Me_2SiNSiFMe_2}$ react with the $\mathrm{F_2B}$-substituted cyclotrisilazane $\mathrm{F_2B(NSiMe_2)_3(SiFMe_2)_2}$ in the molar ratio 1:1 or 1:2 to give the BF-coupled rings 2 and 3. The crystal structure analysis of 1 and 3 and pyrolysis of 1 and 3 with formation of silicon boron carbonitride and its crystallisation to composite powders at very high temperatures are reported.

Keywords: Cyclosilazane, BF-coupled rings, crystal structure, pyrolysis, β-SiC/BN composites

INTRODUCTION

In 1948 the first Si—N rings, the six-membered hexamethylcyclotri- and the eight-membered octamethylcyclotetrasilazane, were synthesized by ammonolysis of dichlorodimethylsilane,[1] Eqn [1].

$$n\,\mathrm{Me_2SiCl_2} \xrightarrow[-2n\mathrm{NH_4Cl}]{+3n\mathrm{NH_3}} \frac{1}{n}\,(\mathrm{Me_2Si-NH})_n, \qquad n=3,4 \qquad [1]$$

Because of the weakness of the Si—N bond the cyclosilazane ring is readily cleaved upon treatment with halides of the main group elements. For more than twenty years only substitution reactions of the six-membered ring with $\mathrm{Me_3SiCl}$ and $\mathrm{Me_3SnCl}$ were known. However, as we can now show, mono, di and trisubstitution of the cyclotrisilazane is possible with fluorosilanes and boranes. If the attacking ligand is a Lewis acid then the basic character of the ring nitrogen is decreased and retention of the ring size occurs.[2]

Here we describe the substitution of cyclotrisilazanes with BF-groups (**1**) and the coupling of cyclosilazanes via BF-groups (**2** and **3**). The compounds were fully characterized by mass spectra, NMR and crystal structure determinations of **1** and **3**.

Oligo- and polysilazanes have been intensively studied in recent years with regard to their application as precursors for structural ceramic materials in the ternary system Si—C—N. The synthesis proceeds by means of the thermal decomposition of silazane.[3-5] In the course of our work, we investigated molecular boron containing silazanes as precursors for the formation of materials in the quaternary system Si—B—C—N. Ceramics composed of Si—C—N or Si—B—C—N are currently being intensively investigated due to their significant potential for application as high temperature engineering materials with improved properties.[6-9]

The present work reports on the synthesis of amorphous ceramic Si—B—C—N powders starting from the readily accessible cyclosilazanes **1** and **3**. The thermal stability of the amorphous Si—B—C—N powder (silicon boron carboni-

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* Crystal structure analyses of **1**.

† Crystal structure analyses of **3**.

Further data are available from the Cambridge Crystallographic Data Centre, Cambridge, UK.

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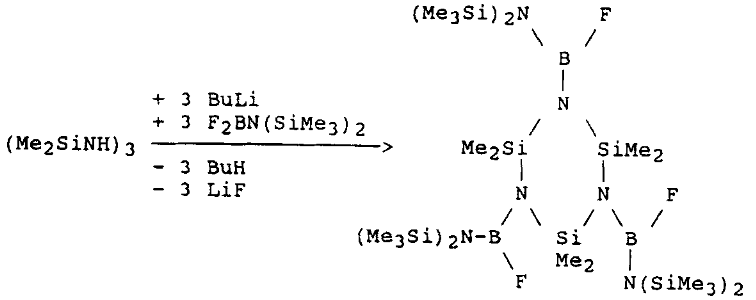


1[11]

(2)

tride) obtained is discussed in terms of its crystallisation behaviour.

RESULTS

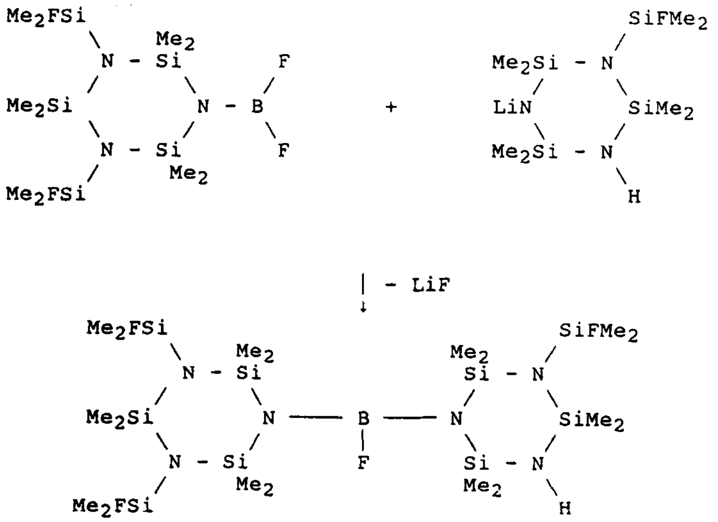
Hexamethylcyclotrisilazanes and their lithium derivatives react with $F_2BN(SiMe_3)_2$ to give the corresponding mono-, bis and tris[fluoroborylbis (trimethylsilyl) amino] hexamethylcyclotrisilazanes,[10,11] Eqn [2]. Ring coupling of two six-membered rings occurs in the reaction of lithiated 1-fluorodimethylsilylhexamethylcyclotrisilazane with 1-difluoroborylcyclotrisilazane,[11] Eqn [3].

Three six-membered rings are coupled in the reaction of the lithium derivative of **2** and the 1-difluoroborylcyclotrisilazane, Eqn [4].

DISCUSSION

Crystal Structure of 1

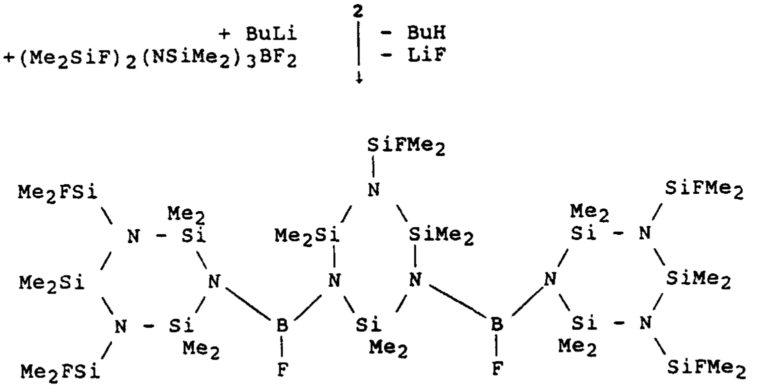
The six-membered N_3Si_3 ring adopts a distorted boat conformation with normal Si—N distances. With planar coordinated boron atoms the B—N distances are in the same range as in bis(dimethylamino)methylborane [143.4(1), 142.7(1) pm; torsion angles C(methyl)-B—N—C-17.9, 151.0° and −17.8 and 155.9°, respectively][12] although the torsion angles at the cyclic and exocyclic nitrogen atoms in **1** are greater (see Table 1). The overlap of the occupied p-orbitals on the nitrogen atoms and the vacant p-orbitals on the boron atoms in **1** is therefore reduced which should cause an increase in the B—N distances. However, the fluorine atoms increase the polarity of the B—N bonds in the σ-plane which should be responsible for a reduction of the respective distances.



(3)

2

Equation (3) here



(4)

3

X-ray structure determination of 1

$C_{24}H_{72}B_3F_3N_6Si_9$ (787.1): Nicolet R3m/V diffractometer, Mo-K_α-radiation, $T = 293$ K, monoclinic, $a = 913.1(3)$, $b = 2323.2(6)$, $c = 2300.6(4)$ pm, $\beta = 95.19(2)$, $V = 4860(2)$ Å^3; $Z = 4$, $d_{cal} = 1.076$ Mg m^{-3}, $\mu = 0.28$ mm^{-1}, $F(000) = 1704$, space group: $P2_1/n$, 8667 collected intensities, 8031 unique, ($2\theta_{max} = 50°$), 4699 observed [$F_0 \geq 4\sigma(F)$], structure solution with SHELXS, refinement with SHELXTL-PLUS (Iris Indigo), 408 parameters, anisotropic displacement parameters for all atoms except hydrogen atoms, which were treated as riding groups in calculated positions and given a common isotropic U-value, $R = 0.0516$, $R_w = 0.0491$, $w^{-1} = \sigma^2(F_0) + 0.00037 \cdot F_0^2$, maximum residual electron density 0.35 e Å^{-3}.

Table 1 Relevant distances (pm) and bond, torsion and interplanar angles (°) (mean values)

N (cycl.)—B	143.5(8)
N (exocycl.)—B	142.9 (6)
B—F	136.6 (4)
N (cycl.)—Si (cycl.)	175.7 (4)
N (exocycl.)—Si (exocycl.)	176.0 (3)
Si (cycl.)—C (methyl)	185.9 (2)
N—B—N	130.0 (3)
Si1—N1—Si2	117.5 (2)
Si2—N2—Si3	115.0 (2)
Si3—N3—Si1	117.8 (2)
N1—Si1—N3	103.0 (2)
N1—Si2—N2	106.3 (1)
N2—Si3—N3	107.2 (2)
N1—Si2—N2—Si3	−31.6
N2—Si3—N3—Si1	65.4
N3—Si1—N1—Si2	−33.1
Si1—N1—B1—N4	58.4
Si2—N2—B2—N5	31.4
Si3—N3—B3—N6	−138.7
Si1—N1—B1—F1	−120.9
Si2—N2—B2—F2	−148.4
Si3—N3—B3—F3	42.6
F1—B1—N4—Si4	−139.9
F2—B2—N5—Si7	116.0
F3—B3—N6—Si8	29.1
plane (B1, F1, N4)/plane (Si1, N1, Si2)	51.5
plane (B1, F1, N1)/plane (N4, Si4, Si5)	34.9
plane (B2, F2, N5)/plane (Si3, N2, Si2)	26.5
plane (B2, F2, N2)/plane (N5, Si7, Si6)	122.6
plane (B3, F3, N6)/plane (Si1, N3, N3)	50.6
plane (B3, F3, N3)/plane (N6, Si8, Si9)	143.7

Crystal structure of 3

Compound 3 consists of three fluoroboryl-coupled trisubstituted cyclotrisilazanes. The N atoms, if not BF substituted, are substituted by a fluorodimethylsilyl group (Fig. 2). The three six-

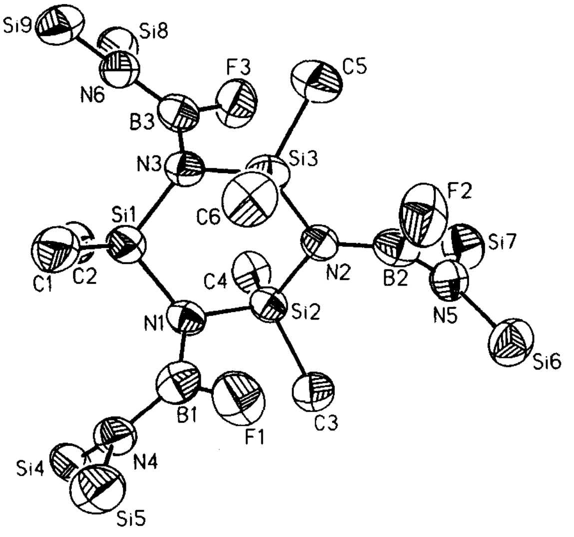


Fig. 1. Thermal ellipsoid plot of 1 (50%); hydrogen atoms and Si-bonded methyl groups are omitted for clarity.

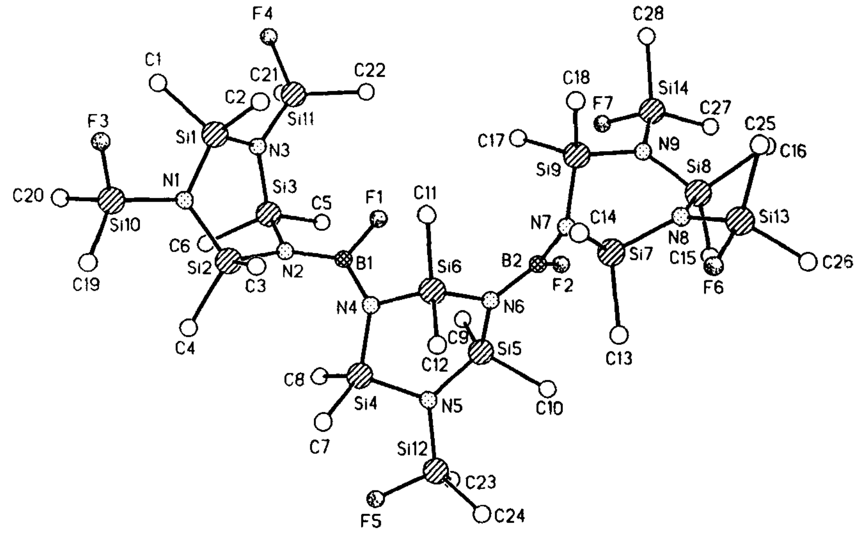


Fig. 2. Crystal structure of **3**.

membered SiN rings (A, B and C) are crystallographically independent. Unlike the NH substituted compounds,[13–15] which possess a planar annular structure, none of the Si_3N_3 rings (A–C) of compound **3** show planarity. The average deviation of the six ring atoms from the least-squares planes are 28.9 pm (A), 28.1 pm (B) and 26.5 pm (C), respectively. The deviation of each atom from the respective least-squares planes are given in Table 2. As in other *N*-silyl-substituted cyclotrisalazanes[15] a boat conformation is favoured in the SiN six-membered rings. As in comparable fluoroboryl-coupled cyclotrisilazanes,[17] the deviation of Si_3N_3 rings from an ideal boat conformation is larger than in other known compounds[16, 18] (torsion angles 0°, 60°, −60°, 0°, 60°, −60° correspond to the sequence of ring atoms). Torsion angles of the three six-membered rings are given in Table 3. The sequence of the atoms in the cyclotrisilazane A is in the opposite order to that in B and C. Although the middle SiN six-membered ring differs topologically from the outer B and C, showing two BF bridges and one silyl substituent in contrast to one BF bridge and two silyl substituents, the pattern of torsion angles and deviations from least-squares planes is comparable in all three six-membered rings. The conformation of the cyclotrisilazanes allows a description as a distorted boat form. Endocyclic SiN bond lengths (173.0–176.7 pm) are slightly larger than exocyclic bond lengths (171.0–173.1 pm). The geometry of the B and N atoms is almost planar and the sum of angles at the boron atoms is 360.0°, respectively; the average sum of angles at the nitrogen atoms is 358.2°.

X-ray structure determination of 3

Crystal data: $C_{28}H_{84}B_2F_7N_9Si_{14}$, $M_r = 1094.9$, colourless prisms, crystal dimension $0.4 \times 0.4 \times 1.0$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 1376.1(1)$, $b = 1606.4(1)$, $c = 1642.0(1)$ pm, $\alpha = 115.10(1)°$, $\beta = 105.23(1)°$, $\gamma = 100.84(1)°$, $V = 2.9794(5)$ nm^3, $Z = 2$, $d_{calc} = 1.22$ Mg m^{-3}, $\lambda = 71.07$ pm, μ(Mo-K) = 0.35 mm^{-1}, $F(000) = 1168$; 10880 reflections measured on an Enraf-Nonius CADA diffractometer at room temperature ($2\theta_{max} = 50°$), 10483 symmetry-independent reflections ($R_{merge} = 0.015$), 7538 reflections with $|F| \geq 4\sigma(F)$ were used for structure solution (direct methods) and refinement (541 parameters), non-hydrogen atoms refined anisotropically, H-atoms refined using a 'riding' model, $R = 0.047$ [$R_w = 0.048$, $w^{-1} = \sigma^2(F) + 0.0005\,F^2$], structure solved and refined with SHELXTL-PLUS.

Further details of the crystal structure investigations are available on request from the

Table 2 Deviation (pm) of each atom from the least-squares planes of 3

Si(1) − 30	N(2) − 41	N(4) + 46	Si(5) + 36	N(7) + 42	Si(8) + 32
N(1) + 40	Si(3) + 47	Si(4) − 2	N(6) + 2	Si(7) 0	N(9) + 5
Si(2) − 4	N(3) − 11	N(5) − 40	Si(6) − 42	N(8) − 37	Si(9) − 42

Table 3 Endocyclic torsion angles (°) of **3**

Cyclosilazane A	Si(3)—N(3)—Si(1)—N)1)	−8.5
	N(3)—Si(1)—N(1)—Si(2)	51.7
	Si(1)—N(1)—Si(2)—N(2)	−30.7
	Si(3)—N(2)—Si(2)—N(1)	−30.5
	N(3)—Si(3)—N(2)—Si(2)	69.2
	N(2)—Si(3)—N(3)—Si(1)	−44.3
Cyclosilazane B	N(5)—Si(4)—N(4)—Si(6)	−38.7
	Si(4)—N(4)—Si(6)—N(6)	69.3
	Si(5)—N(6)—Si(6)—N(4)	−32.7
	N(5)—Si(5)—N(6)—Si(6)	−21.0
	N(6)—Si(5)—N(5)—Si(4)	56.0
	N(4)—Si(4)—N(5)—Si(5)	−25.4
Cyclosilazane C	Si(9)—N(7)—Si(7)—N(8)	−35.1
	N(9)—Si(9)—N(7)—Si(7)	67.8
	Si(8)—N(9)—Si(9)—N(7)	−36.1
	Si(9)—N(9)—Si(8)—N(8)	−15.6
	N(9)—Si(8)—N(8)—Si(7)	−51.7
	N(7)—Si(7)—N(8)—Si(8)	−25.4

Table 4 Selected bond lengths (pm) and angles (°) of **3**

Bond lengths		Bond angles	
Si(1)—N(1)	175.6 (3)	N(1)—Si(1)—N(3)	109.4 (2)
Si(2)—N(1)	175.8 (3)	N(1)—Si(2)—N(2)	104.8 (1)
Si(3)—N(2)	175.3 (2)	N(2)—Si(3)—N(3)	106.9 (1)
Si(4)—N(4)	174.4 (3)	N(4)—Si(4)—N(5)	104.2 (2)
Si(6)—N(4)	176.7 (3)	N(5)—Si(5)—N(6)	109.1 (1)
Si(1)—N(3)	175.8 (3)	N(4)—Si(6)—N(6)	105.5 (1)
Si(2)—N(2)	174.7 (3)	Si(1)—N(1)—Si(2)	121.4 (2)
Si(3)—N(3)	173.0 (4)	Si(2)—N(1)—Si(10)	119.4 (2)
Si(4)—N(5)	176.3 (4)	Si(2)—N(2)—B(1)	123.2 (2)
Si(5)—N(5)	175.2 (4)	Si(1)—N(3)—Si(3)	115.3 (2)
Si(7)—N(7)	173.8 (2)	Si(3)—N(3)—Si(11)	122.4 (2)
Si(8)—N(8)	175.5 (3)	Si(1)—N(1)—Si(10)	117.9 (2)
Si(9)—N(7)	173.9 (3)	Si(2)—N(2)—Si(3)	116.0 (2)
Si(5)—N(6)	176.5 (3)	Si(3)—N(2)—B(1)	118.7 (2)
Si(6)—N(6)	174.9 (3)	Si(1)—N(3)—Si(11)	121.2 (2)
Si(7)—N(8)	176.1 (4)	Si(4)—N(4)—B(1)	123.0 (2)
Si(8)—N(9)	174.5 (3)	Si(4)—N(4)—Si(6)	117.1 (1)
Si(9)—N(9)	174.3 (4)	Si(6)—N(4)—B(1)	117.8 (3)
Si(10)—N(1)	173.1 (4)	Si(5)—N(5)—Si(12)	119.2 (2)
Si(11)—N(3)	172.0 (4)	Si(5)—N(5)—Si(4)	120.0 (2)
Si(12)—N(5)	172.0 (3)	Si(4)—N(5)—Si(12)	118.2 (2)
Si(13)—N(8)	172.4 (3)	N(2)—B(1)—N(4)	128.5 (4)
Si(14)—N(9)	171.0 (3)	N(2)—B(1)—F(1)	115.8 (3)
N(2)—B(1)	143.4 (6)	N(4)—B(1)—F(4)	115.7 (4)
B(1)—F(1)	134.7 (5)	N(6)—B(2)—N(7)	129.2 (4)
N(4)—B(1)	143.4 (4)	N(7)—B(2)—F(2)	115.2 (4)
N(6)—B(2)	141.1 (6)	N(6)—B(2)—F(2)	115.7 (4)
N(7)—B(1)	145.0 (5)		
B(2)—F(2)	135.6 (5)		

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Pyrolysis of 1 and 3

Owing to their molecular composition, compounds **1** and **3** are suitable precursors for the synthesis of $Si_3N_4/SiC/BN$ composites. The reaction in Eqns [5] and [6] represent the idealized overall thermal decomposition reaction (pyrolysis) from the oligomer to the ceramic material.

$$\mathbf{1}: C_{24}H_{72}B_3F_3N_6Si_9 \rightarrow 3BN + \tfrac{3}{4}Si_3N_4 + \tfrac{63}{4}SiC + xC + \text{volatiles} \quad [5]$$

$$\mathbf{3}: C_{28}H_{84}B_2F_7N_9Si_{14} \rightarrow 2\,BN + \tfrac{13}{4}\,Si_3N_4 + \tfrac{83}{4}SiC + xC + \text{volatiles} \quad [6]$$

At 1100 °C, **1** and **3** were pyrolysed under an argon atmosphere to give a black and X-ray amorphous ceramic residue, with fluorosilanes and alkanes as volatiles. The product formed comprised powder particles and a coating on the reaction tube wall indicating that **1** and **3** are thermally decomposed via both solid-state pyrolysis and gas phase decomposition. The yield of the powder derived from the solid-state pyrolysis of the molecular compounds **1** and **3** and that of the coating derived from the gas phase decomposition of the evaporated volume fractions of the used precursors **1** and **3** are given in Table 5.

After annealing of the synthesized amorphous Si—B—C—N powders at different temperatures (1300, 1500/1600, 1700, 1800 and 2200 °C) under a nitrogen atmosphere, the crystallisation behaviour was investigated by X-ray powder diffraction (Figs 3 and 4). In the case of **1**, crystallisation occurs at 1500 °C. The reflection lines indicate the formation of cubic β-SiC. At 2200 °C, crystalline hexagonal BN is indicated from the diffraction

Table 5 Yields (%) of powder derived from solid state pyrolysis (see text)

Compound	Theoretical yield	Yield with coating	Yield without coating
1	57.2	48.4	18.3
3	59.8	52.4	25.8

pattern (Fig. 3). In the case of **3**, the synthesized Si—B—C—N powder remains amorphous up to 1600 °C. The onset of the crystallisation of β-SiC is shifted to higher temperatures (1700 °C) whereas the formation of crystalline h-BN was also confirmed at 2200 °C. In both cases, however, the crystallisation of Si_3N_4 is completely suppressed. This finding is due to the presence of boron and to the thermodynamic instability of Si_3N_4 towards excess carbon. At 0.1 MP nitrogen pressure and at temperatures above 1440 °C, Si_3N_4 reacts with free carbon to give SiC and elemental nitrogen. Taking into account the reaction in equations [5] and [6], it is expected that a considerable amount of excess carbon is formed by the crystallisation of the amorphous Si—B—C—N material which hinders the formation of Si_3N_4.

In contrast, amorphous polysilazane-derived ceramics of the ternary system Si—C—N have been shown to crystallize at $T \geq 1440$ °C under 0.1 MPa nitrogen pressure.[8] The enhanced thermal stability of materials in the quaternary system Si—B—C—N with respect to the onset of crystallisation, as found in this work, is of great technological interest since the high-temperature application of amorphous, polymer-derived ceramics such as, e.g. inorganic fibres may be limited by the onset of crystallisation. The difference between the onset of crystallisation of the silicon boron carbonitride derived from **1** and **3** may be caused by the different molecular structure of the precursors and is presently under investigation.

EXPERIMENTAL

Compounds were handled in a dry nitrogen atmosphere. Mass spectroscopy: Varian CH5; NMR spectroscopy; Bruker WP80 SY and AM 250 MHz instruments. The pyrolyses were carried out under a protective atmosphere (argon) using the Schlenk technique. Compounds **1** and **3** were pyrolysed in quartz glass tubes at 1100 °C for 5 h. The amorphous ceramic powders obtained were heat-treated for 5 h in a 0.1 MPa nitrogen atmosphere at different temperatures (1300, 1500/1600, 1700, 1800 and 2200 °C) in a graphite furnace. Phase analysis was conducted by X-ray diffraction

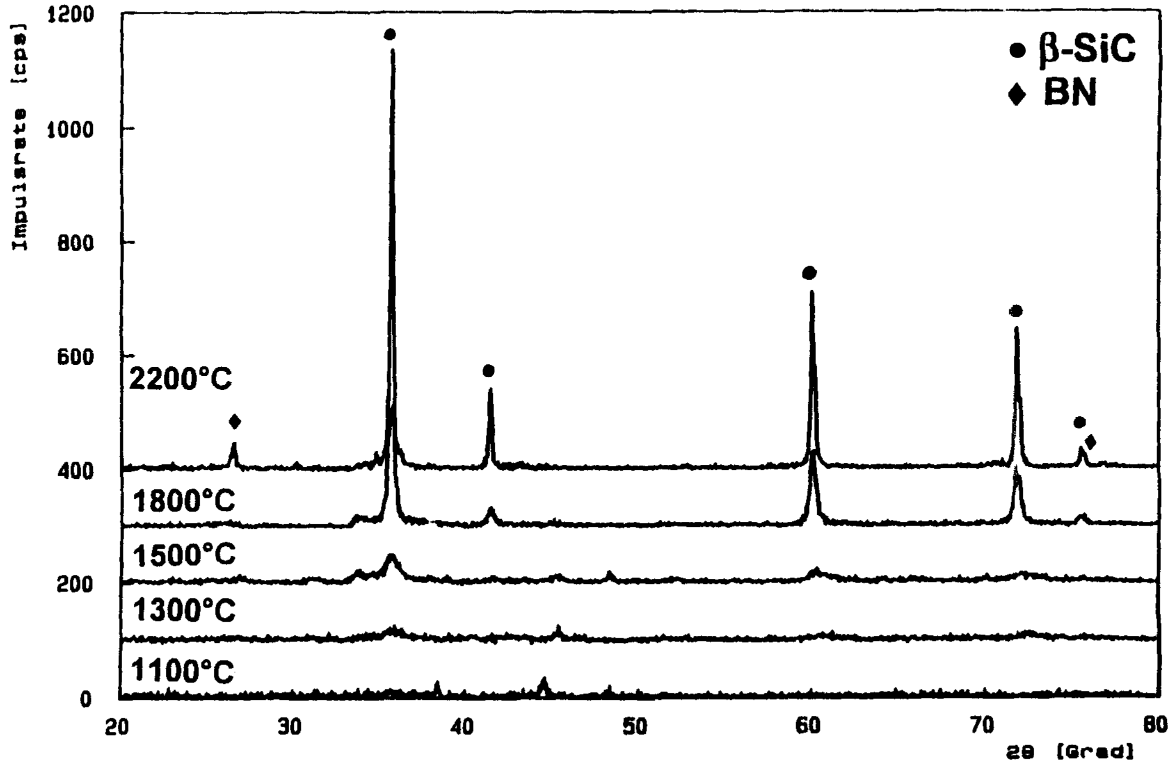


Figure 3 X-ray diffraction pattern of **1** pyrolysed at 1100 °C and subsequently annealed at 1300, 1500, 1800 and 2200 °C.

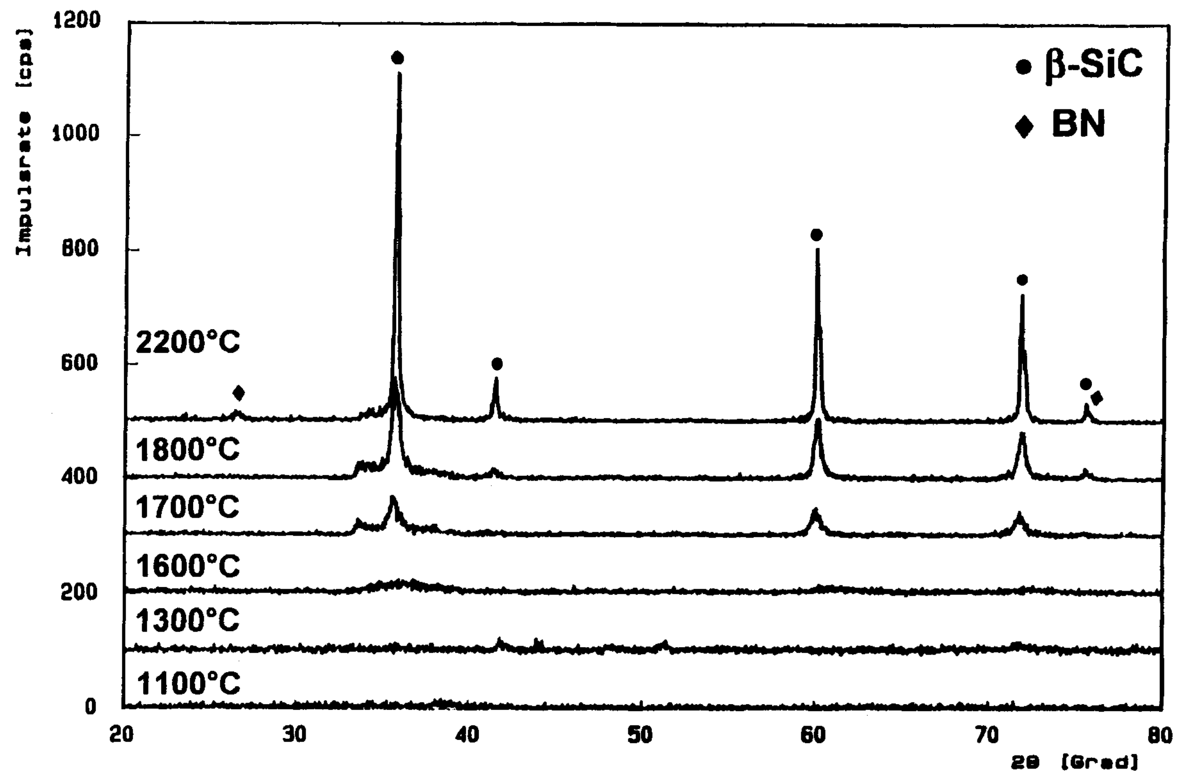


Figure 4 X-ray diffraction pattern **3** pyrolysed at 1100 °C and subsequently annealed at temperatures between 1100 and 2200 °C.

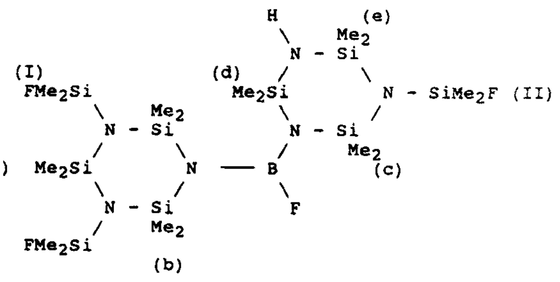
with Cu-K radiation ($\lambda = 154.056$ pm) using a scintillation counting detector.

1,3,5-Tris[bis(trimethylsilyl)aminofluoroboryl]-2,2,4,4,6,6-hexamethylcyclotrisilazane 1

A solution of 0.1 mol of $(Me_2SiNH)_3$ in 50 ml THF was treated with 0.3 mol of n-C_4H_9Li, boiled under reflux for 3 h, and treated with 0.3 mol of $F_2BN(SiMe_3)_2$. Compound **1** was isolated by crystallisation from hexane. Yield: 50.3 g (64%).

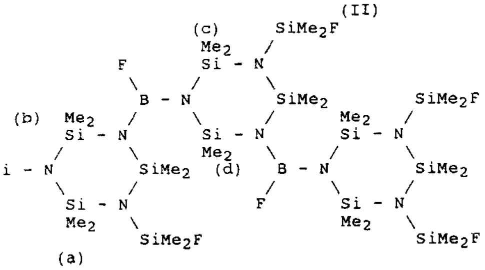
Compounds **2** and **3**: a solution of 0.1 mol $(Me_2SiNH)_2Me_2SiNSiFMe_2$ in 100 ml hexane was treated with 0.1 mol (**2**) or 0.2 mol (**3**) n-C_4HgLi, boiled under reflux for 3 h, and treated with 0.1 mol (**2**) or 0.2 mol (**3**) $F_2B(NSIMe_2)_3SiFMe_2$[8] in 50 ml THF. Products **2** and **3** were purified by crystallisation from hexane.

1-[Fluoro-(3′-fluorodimethylsilyl-2′,2′,4′,4′,6′,6′-hexamethylcyclotrisilazane1′-yl)-boryl]-3,5-fluorodimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane 2



$C_{18}H_{55}BF_4N_6Si_9$(695.3); yield: 54.2 g (78%), m.p.: 69 °C, MS (70 eV, FJ): *m/z* (%) = 695 (100) M^+, NMR ($CDCl_3$); ^1H: $\delta = 0.19$ $SiMe_2$ (e), 6 H (d, $^5J_{HF} = 1.6$ Hz); 0.24 $SiMe_2$ (d), 6 H; 0.25 $SiMe_2F$ (II), 6 H (d, $^3J_{HF} = 7.3$ Hz); 0.29 $SiMe_2F$ (I), 12 H (d,d, $^3J_{HF} = 7.3$ Hz, $^7J_{HF} = 1.8$ Hz); 0.32 $SiMe_2$ (b), 12 H (d, $^{5}J_{\mathrm{HF}} = 1.2$ Hz); 0.36 SiMe$_2$ (c), 6 H (d, $^{5}J_{\mathrm{HF}} = 1.5$ Hz); 0.37 SiMe$_2$ (a), 6 H(t, $^{5}J_{\mathrm{HF}} = 1.1$ Hz); 0.68 (NH, 1 H) ^{13}C: $\delta = 2.50$ SiC$_2$F (II), (d, $^{2}J_{\mathrm{CF}} = 18.4$ Hz); 3.10 SiC$_2$F (I), (d,d, $^{2}J_{\mathrm{CF}} = 18.4$ Hz, $^{6}J_{\mathrm{CF}} = 3.5$ Hz); 4.15 SiC$_2$ (d), (d, $^{4}J_{\mathrm{CF}} = 1.6$ Hz); 4.72 SiC$_2$ (e), (d, $^{4}J_{\mathrm{CF}} = 2.9$ Hz); 4.92 SiC$_2$ (b), (m); 5.49 SiC$_2$ (c), (d,d, $^{4}J_{\mathrm{CF}} = 3.0$ Hz, $^{4}J_{\mathrm{CF}} = 2.4$ Hz); 6.54 1/2 SiC$_2$ (a), (t, $^{4}J_{\mathrm{CF}} = 3.2$ Hz); 6.67 1/2 SiC$_2$ (a), (t, $^{4}J_{\mathrm{CF}} = 2.8$ Hz). ^{11}B: $\delta = 26.3$ BF. ^{19}F: $\delta = 27.08$ SiMe$_2$F (II), (sept. $^{3}J_{\mathrm{HF}} = 7.2$ Hz); 29.60 SiMe$_2$F (I), (sept., m, $^{3}J_{\mathrm{HF}} = 7.8$ Hz, $^{5}J_{\mathrm{HF}} = 1.2$ Hz); 101.8 BF. ^{29}Si: $\delta = -7.73$ SiMe$_2$ (c), (d, d, $^{3}J_{\mathrm{SiF}} = 6.1$ Hz, $^{3}J_{\mathrm{SiF}} = 4.2$ Hz); -4.27 SiMe$_2$ (a), (t, $^{3}J_{\mathrm{SiF}} = 4.6$ Hz); -4.23 SiMe$_2$ (b), (d, d, $^{3}J_{\mathrm{SiF}} = 8.9$ Hz, $^{3}J_{\mathrm{SiF}} = 4.5$ Hz); -3.45 SiMe$_2$ (e), (d, $^{3}J_{\mathrm{SiF}} = 5.7$ Hz); -2.90 SiMe$_2$ (d), (d, $^{3}J_{\mathrm{SiF}} = 5.5$ Hz); 8.36 SiMe$_2$F (II), (d, sept., $^{1}J_{\mathrm{SiF}} = 267.4$ Hz, $^{2}J_{\mathrm{SiH}} = 7.1$ Hz); 8.99 SiMe$_2$F (I), (d, sept., $^{1}J_{\mathrm{SiF}} = 268.3$ Hz, $^{2}J_{\mathrm{SiH}} = 7.0$ Hz).

1,3-Bis[fluoro-[3′,5′bis(fluorodimethylsilyl)-2′,2′,4′,4′,6′,6′-hexamethylcyclotrisilazane-1′-yl]boryl]-5-fluorodimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane 3



$C_{28}H_{84}B_2F_7N_9Si_{14}$(1094.8); yield: 65.7 g (60%), m.p.: 130 °C, MS (70 eV, FJ): m/z (%) = 1094(6) M$^+$, 1079 (100) [M − CH$_3$]$^+$; NMR (CDCl$_3$); ^{1}H: $\delta = 0.30$ SiMe$_2$F (I), 24 H (d, $^{3}J_{\mathrm{HF}} = 7.6$ Hz); 0.30 SiMe$_2$F (II), 6 H (d, $^{3}J_{\mathrm{HF}} = 7.6$ Hz); 0.36 SiMe$_2$ (a), 12 H (d, t, $^{7}J_{\mathrm{HF}} = 2.8$ Hz, $^{5}J_{\mathrm{HF}} = 1.3$ Hz); 0.38 SiMe$_2$ (c), 12 H (d, $^{5}J_{\mathrm{HF}} = 1.3$ Hz); 0.39 SiMe$_2$ (b), 24 H (d, $^{5}J_{\mathrm{HF}} = 1.3$ Hz); 0.40 SiMe$_2$ (d), 12 H. ^{13}C: $\delta = 3.06$ SiC$_2$F (I), (d,d, $^{2}J_{\mathrm{CF}} = 18.4$ Hz, $^{6}J_{\mathrm{CF}} = 2.0$ Hz); 3.09 SiC$_2$F (II), (d, $^{2}J_{\mathrm{CF}} = 18.4$ Hz); 3.78 SiC$_2$ (c); 5.11 SiC$_2$ (b); 5.25 SiC$_2$ (a), (t, $^{4}J_{\mathrm{CF}} = 2.1$ Hz); 6.56 SiC$_2$ (d), (d,d, $^{4}J_{\mathrm{CF}} = 5.4$ Hz, $^{4}J_{\mathrm{CF}} = 2.8$ Hz). ^{11}B: $\delta = 26$ BF. ^{19}F: $\delta = 29.72$ SiMe$_2$F (I), (sept. $^{3}J_{\mathrm{HF}} = 7.6$ Hz); 29.94 SiMe$_2$F (II), 103.65 BF. ^{29}Si: $\delta = -4.37$ SiMe$_2$ (b), (d,d, $^{3}J_{\mathrm{SiF}} = 4.8$ Hz, $^{3}J_{\mathrm{SiF}} = 4.8$ Hz); -4.03 SiMe$_2$ (a), (t, $^{3}J_{\mathrm{SiF}} = 4.5$ Hz); -3.22 SiMe$_2$ (c), (d,d, $^{3}J_{\mathrm{SiF}} = 4.7$ Hz, $^{3}J_{\mathrm{SiF}} = 4.7$ Hz); -2.84 SiMe$_2$ (d), (d,d, $^{3}J_{\mathrm{SiF}} = 5.2$ Hz, $^{3}J_{\mathrm{SiF}} = 5.2$ Hz); 9.00 SiMe$_2$F (I), (d, $^{1}J_{\mathrm{SiF}} = 268.3$ Hz), 9.27 SiMe$_2$F (II), (d, $^{1}J_{\mathrm{SiF}} = 268.1$ Hz).

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