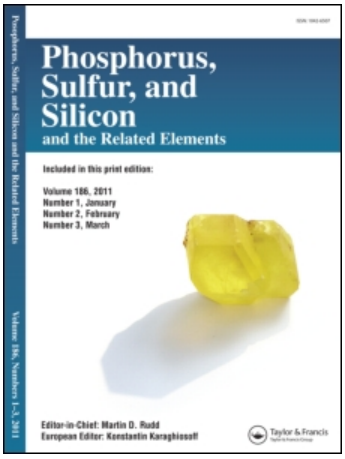


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# Cyclosilazanes and their Application as Precursors for Silicon-Based Ceramics

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The transformation of organo-element polymers into inorganic solids by pyrolysis of molecules is a new way to ceramic materials. The advantage of this method is that very pure compounds can be used, e.g. the pyrolysis of $[Me_2Si\text{-}NH]_4$ under $NH_3$ pressure above 1000°C gives $\alpha$-$Si_3N_4$. $Si_2N_2NH$ is characterized as microcrystalline material.

$$[Me_2SiNH]_4] + 2\,NH \xrightarrow[-8\,CH_4]{\Delta} Si_2N_2NH \xrightarrow[-NH_3]{>1000°C} 2\,\alpha\text{-}Si_3N_4$$

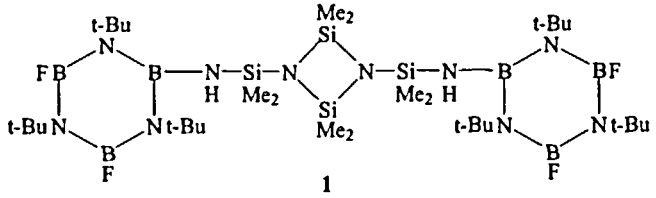
The present work reports the synthesis of a new type of precursor molecules for the ternary Si-B-N and the quaternary Si-B-C-N systems by coupling cyclosilazanes and borazines in different ratios.[1]

*Keywords:* Cyclosilazanes; Borazines; Ring-coupling



## RESULTS

Dilithiated octamethylcyclotetrasilazane reacts with 1,3,5-tri-tert.-butyl-2,4,6-trifluoroborazine to give **1** (Si:B:N = 2:3:5):




**1**

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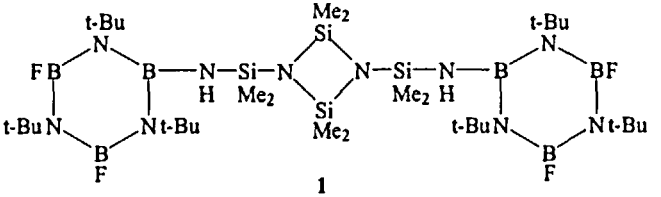


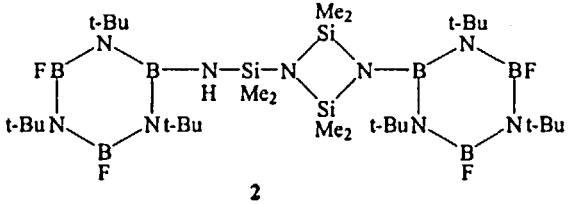
1

B–N: 141.6 – 147.4 pm, Si–N: 171.8 – 175.0 pm

The central cyclodisilazane is formed in an anionic rearrangement of the eight-membered ring system.[2] The ring contraction depends on the bulkiness of the substituents of the borazine ring, it does not occur when borazines with smaller substituents (such as ethyl) are used.

Six-membered Si–N and B–N rings are coupled in the reactions of lithiated cyclotrisilazanes with fluoroborazines.

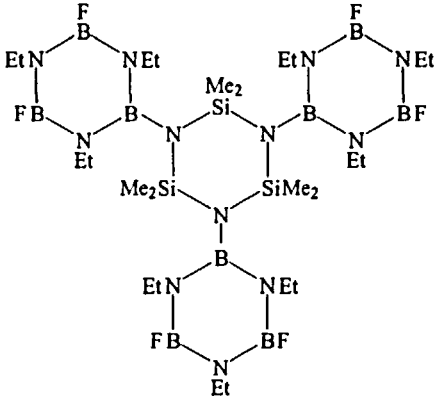
An anionic rearrangement[3] is observed in the reaction of two bulky fluoroborazines with hexamethylcyclotrisilazane (Si:B:N = 1:2:3).



2

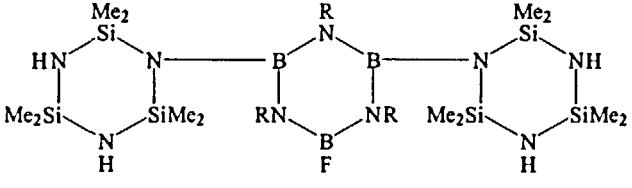
Interestingly, **2** contains non-planar N-atoms, e.g. the sum of angles. $Si_2NB$ is 352.2°.

Trilithiated hexamethylcyclotrisilazane reacts with three equivalents of 1,3,5-triethyl-2,4,6-trifluoroborazine to give compound **3** (Si:B:N = 1:3:4).



3

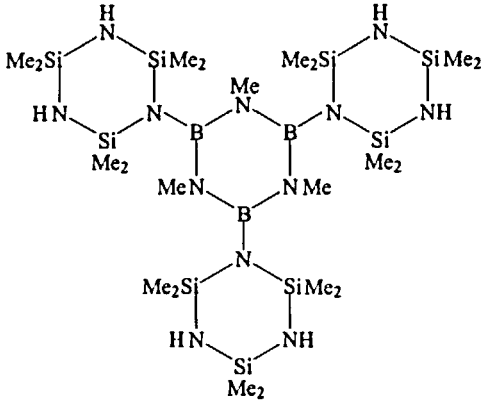
Compounds with a higher ratio of silicon (Si:B:N = 2:1:3) are obtained in the reaction of the cyclosilazane with borazines in a molar ratio 2:1.



R = Me (4), Et (5)

In compound **5** the exocyclic B–N bonds are longer than the endocyclic ones.

Compounds which are totally symmetric and free of halo atoms can be formed in reactions of cyclosilazanes and borazines in a 3:1 ratio. Compound **6** (Si:B:N = 3:1:4).



**6**

Again the exocyclic B–N bonds are found to be longer (2.4 pm) than to the endocyclic ones.

In cooperation with the groups Gadow (MPI Stuttgart), Kleebe (Universität Bayreuth) and Riedel (TU Darmstadt) these molecules will be converted into ceramic powders. Depending on the conditions of the pyrolysis Si–B–C, Si–B–C, or Si–B–C–N ceramics can be obtained. Polymer pyrolysis under $NH_3$ pressure leads to powders in the ternary system, while powders in the quaternary system are formed under $N_2$ or Ar pressure.

ACKNOWLEDGMENTS

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## *References*

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[2] K. Dippel, E. Werner, and U. Klingebiel, *Phosphorus, Sulfur, and Silicon*, 64, 15 (1992).

[3] U. Klingebiel, *Phosphorus, Sulfur, and Silicon*, 41, 361 (1989).