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SILICON CERAMICS WITH A DASH OF BORON

by

Dietmar Seyferth, Herbert Plenio, William S. Rees, Jr. and Klaus Büchner

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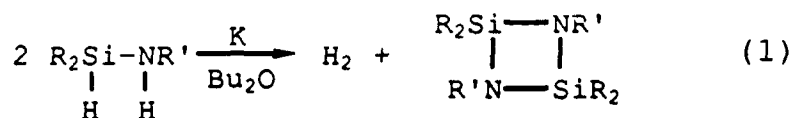
SILICON CERAMICS WITH A DASH OF BORON

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Klaus Büchner

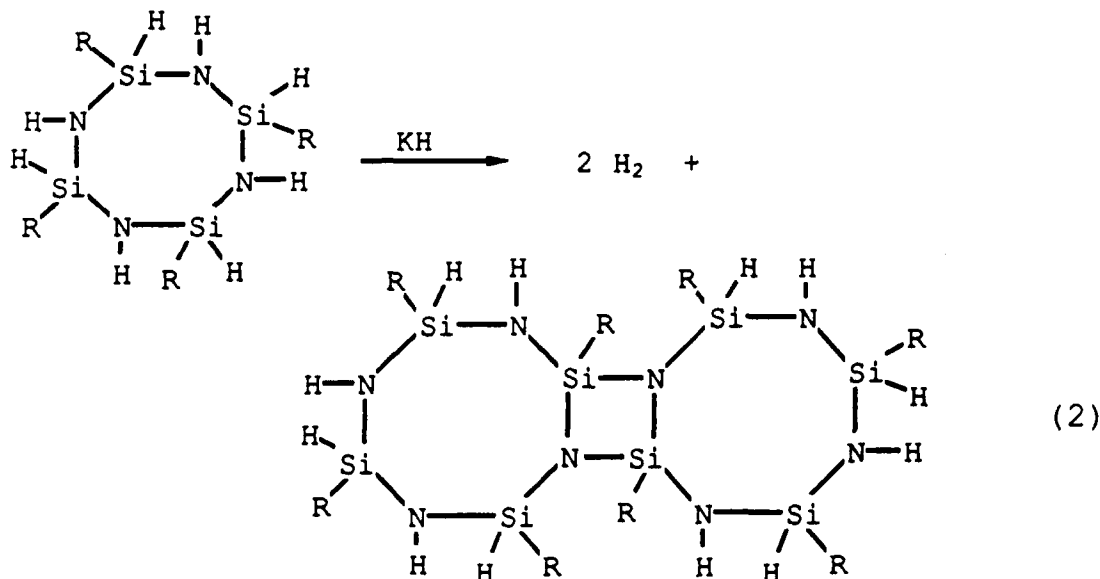
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1. INTRODUCTION

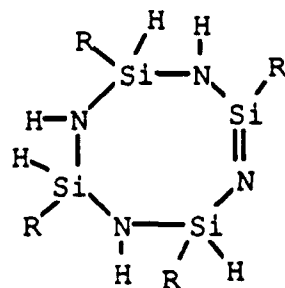
The pyrolysis of inorganic and organometallic polymers as a route to ceramics is a new area of polymer chemistry that has received much attention since the pioneering work of Yajima and his coworkers¹ and of Verbeek and Winter² in the mid-70's. Reviews that deal with preceramic polymers broadly³ or in the context of silicon-containing ceramics⁴ are available. Our own previous research has been concerned mainly with the development of useful polymers whose pyrolysis gives silicon-containing ceramics such as silicon carbide, silicon nitride, silicon carbonitride and silicon oxynitride.⁴ An approach that has shown considerable promise in terms of useful applications involves the preparation of a cross-linked but still soluble polysilazane. The first step of this procedure, the ammonolysis of methyldichlorosilane, gives a silazane product that is a mixture mainly of cyclic oligomers, cyclo-[CH₃Si(H)NH]_n (n=3,4,5,...). In order to obtain a useful preceramic material, this ammonolysis product must be converted to material of higher molecular weight. We effected such polymerization by treatment of the liquid mixture of cyclosilazanes with a catalytic quantity of a base such as KH (ca. 1 mol %), generally in an ethereal solvent such as diethyl ether or tetrahydrofuran.⁵ Hydrogen was evolved, and a "living" polymer, one that contained potassium amide functions when KH was the catalyst used, was formed. Reaction of the "living" polymer with an electrophile such as CH₃I or a chlorosilane then gave the neutral polymer whose constitution, in terms of constituent groupings, was shown by proton NMR spectroscopy to be [(CH₃Si(H)NH)_a(CH₃SiN)_b(CH₃Si(H)NCH₃)_c]_n (a + b + c = 1; c ~ 0.01, the KH catalyst concentration, a ~ 0.4, b ~ 0.6) when CH₃I was used. The treatment of the cyclo-[CH₃Si(H)NH]_n mixture with a catalytic quantity of KH was based on the report of a catalytic cyclodisilazane synthesis in a Monsanto patent⁶ (eq. 1). Our initial idea was that application of this catalytic process to the cyclo-[CH₃Si(H)NH]_n mixture would lead to the formation of



a sheet polymer. Taking the 8-membered cyclosilazane as an example, the first step in the process would be the fusion of two such rings (eq. 2). The product formed contains six sets of Si(H)-N(H) units, and if all of these reacted in this sense, a sheet polymer would result.



However, later studies have indicated that ring fusion polymerization via cyclodisilazane formation is not the principal polymerization process since ^{29}Si NMR studies of the products of the KH-catalyzed cyclo- $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ polymerization have failed to provide evidence for the presence of Si_2N_2 rings. Instead the polymers produced appear to be composed in the main of larger silazane rings. It may be that the KH-catalyzed reaction occurs via an intermediate that contains an $\text{Si}=\text{N}$ bond, **1** in the case of the 8-membered cyclosilazane, and that this then



1 ($\text{R} = \text{CH}_3$)

inserts into an Si-N, Si-H and/or N-H bond of another cyclosilazane molecule. (The gas phase generation of $>\text{Si}=\text{N}-$ intermediates and the study of their reactions by Sommer and his coworkers⁷ are noted in this connection.)

Regardless of polymerization mechanism and the detailed structure of the polysilazane produced in the KH-catalyzed process, the polymer is highly cross-linked, about 60 mol % of the Si(H)-N(H) units having been lost. It is a soluble solid whose pyrolysis to 1000°C in an argon stream results in a black ceramic residue (an amorphous silicon carbonitride) in about 85% yield. Pyrolysis to 1000°C in a stream of ammonia, on the other hand, gives a white ceramic residue of silicon nitride in high yield, essentially all of the methyl groups on silicon having been lost during the middle stages of the pyrolysis. The polysilazane produced in the KH-catalyzed process serves excellently as a binder for SiC and Si₃N₄ powder in the fabrication of ceramic parts, serves with advantage as the main component in coating formulations, and may be dry-spun to give fibers whose pyrolysis in argon results in silicon carbonitride ceramic fibers.

In recent research we have been interested in composites that contain a silicon ceramic and a ceramic containing another element. It is known that such composites often have better physical and mechanical properties than do the pure components of the composite, but there are few examples of polymer pyrolysis having been used to prepare such composites. We report here concerning a novel polymer system whose pyrolysis gives ceramic composites that contain silicon and boron.

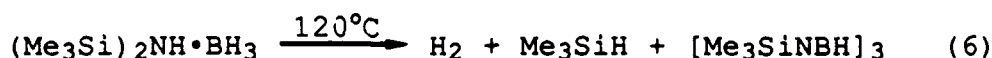
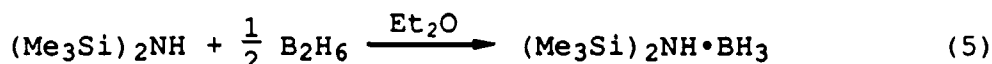
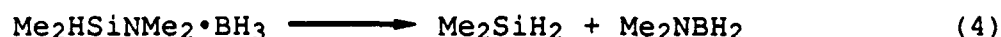
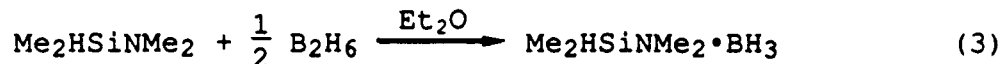
2. SILAZANE/BORAZINE POLYMERIC PRECURSORS FOR SILICON NITRIDE/BORON NITRIDE COMPOSITES

Boron nitride and silicon nitride by themselves are very useful ceramic materials. Thus boron nitride, BN, has high thermal stability (mp 2730°C), excellent high temperature strength, superior thermal shock resistance and it is chemically inert and resistant to molten metals.⁸ Furthermore, it is a high resistance electrical insulator and it exhibits high thermal conductivity. Silicon nitride⁹ also has very attractive properties, its low thermal coefficient of expansion and superior high temperature strength combining to make it one of the most thermally shock resistant ceramics known. To this can be added its high resistance to corrosion and its high temperature stability.

BN/Si₃N₄ blends are of interest. They have been prepared by chemical vapor deposition using SiCl₄/B₂H₆/NH₃/H₂¹⁰ and SiH₄/B₂H₆/N₂¹¹ as source gases. It is noteworthy that the fracture toughness of the deposited thin films improved dramatically at Si contents >10 atom %, while their hardness gradually decreased as the Si content increased from 0 to 48 atom %. Mazdiyasni and Ruh¹² fabricated high density Si₃N₄ (+ 6% CeO₂) composites with 5 to 50% BN by hot pressing. These composites, it was found, had better thermal shock resistance than a sample of commercial hot-pressed Si₃N₄. In another approach,

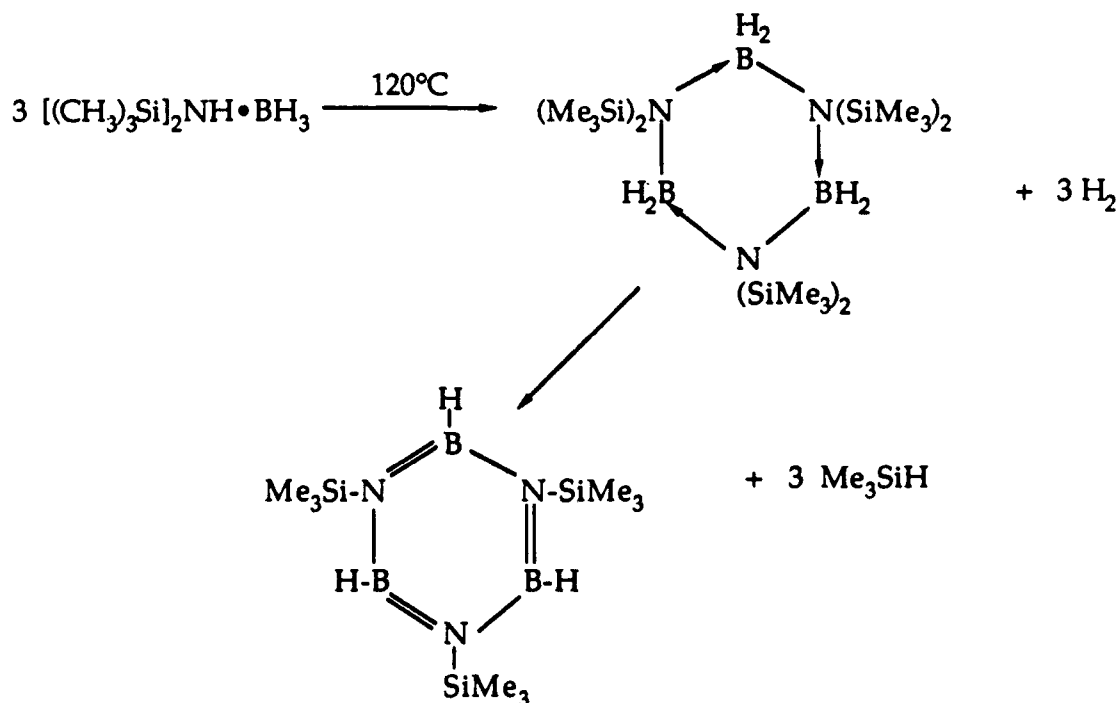
Japanese workers¹³ treated Si_3N_4 powder at high temperature with a gas containing BCl_3 and NH_3 to give $\text{BN}/\text{Si}_3\text{N}_4$ blends that could be used to make ceramic parts having high relative density and bending strength.

The entry to our synthesis of a polymer whose pyrolysis under appropriate conditions would give a $\text{Si}_3\text{N}_4/\text{BN}$ composite was provided by a 1961 paper by Nöth that reported reactions of diborane(6) in diethyl ether with various silylamines and silazanes (eq. 3-6).¹⁴ Of



particular interest was the observation that the $(\text{Me}_3\text{Si})_2\text{NH} \cdot \text{BH}_3$ adduct formed a silyl-substituted borazine, **2**, when heated to 120°C , most likely by way of an intermediate borazane (Scheme 1). If this reaction could

SCHEME 1



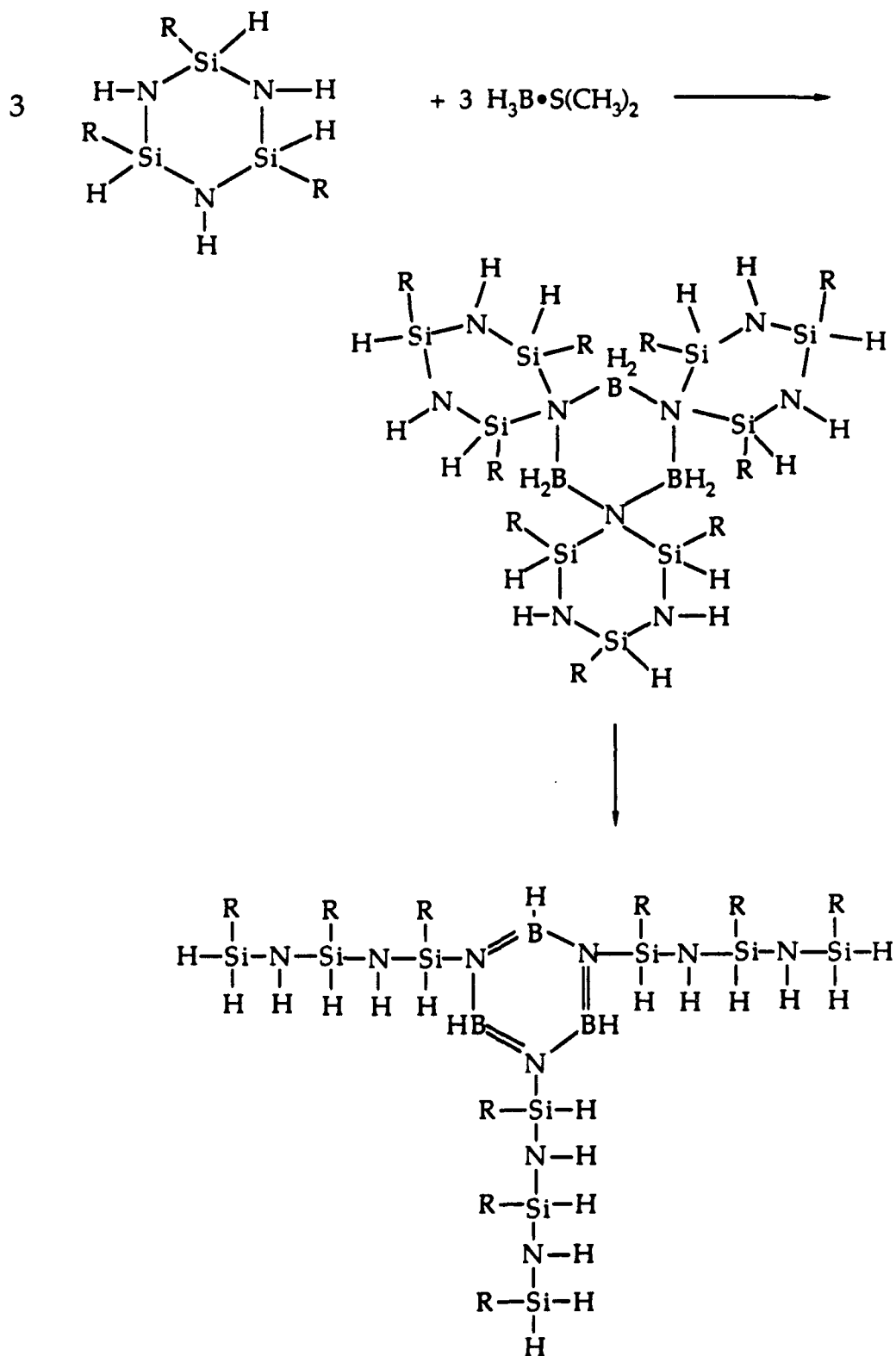
be applied to the mixture of cyclosilazanes obtained in the ammonolysis of methylchlorosilane, then a network polymer involving borazine rings and silazane units should result since the initially formed borazine contains silazanyl side-chains on the boron atoms which can react further with $\text{H}_3\text{B} \cdot \text{S}(\text{CH}_3)_2$ (Scheme 2).

In principle, the reaction of interest would be that of cyclo- $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ with diborane, B_2H_6 . In practise, the latter is dangerous to handle on a large scale, even when it is in solution, and we used instead the safer, commercially available, $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$, which is sold as a 2M solution in toluene.

The reactions are very easily effected. The prescribed amounts of the oligosilazane oil obtained by ammonolysis of methylchlorosilane in a suitable organic solvent, the 2M toluene solution of $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ and (optionally) extra toluene were charged by syringe into a three-necked, round-bottomed flask equipped with a reflux condenser topped with a nitrogen inlet/outlet tube leading to a Schlenk line, a rubber septum and a magnetic stir-bar under an atmosphere of dry nitrogen. Gas evolution began immediately at room temperature. The mixture was stirred at room temperature until the initial gas evolution had ceased (ca. 15 min. for the 30-60 mmol $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ scale used). It then was heated slowly (ca. 30 min.) to the reflux temperature and stirred at reflux for 1 hr. The resulting product was completely soluble in toluene and did not separate from solution as the released $(\text{CH}_3)_2\text{S}$ and the toluene solvent were removed at reduced pressure. The products are viscous oils or solids, depending on how much $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ was used per molar unit of $\text{CH}_3\text{Si}(\text{H})\text{NH}$. Thus, when the $\text{CH}_3\text{Si}(\text{H})\text{NH}/\text{BH}_3$ molar ratio used was 20, the product was a viscous oil with a cryoscopic molecular weight (in benzene) of 390. When the ratio used was 10, the highly viscous oil produced had an average molecular weight of 520. Use of a ratio of 4 in this reaction resulted in a soft, low-melting solid, average molecular weight 800. A further decrease in the $\text{CH}_3\text{SiHNNH}/\text{BH}_3$ molar ratio to 3 gave a solid product that, after complete solvent removal, could only be partially dissolved in hot toluene. Further decreases in the $\text{CH}_3\text{SiHNNH}/\text{BH}_3$ molar ratio used in the reaction resulted in formation of solid products that were very soluble in toluene as formed. However, once the toluene had been completely removed, they could not be redissolved in toluene. When these products retained some small amount of toluene, such that the product/toluene syrup still flows, they continue to be very soluble. Only when all of the toluene is removed do the solid products become insoluble.

That borazine rings are present in the $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n/\text{H}_3\text{B}\cdot\text{SMe}_2$ products was shown by their ^{11}B NMR spectra. The ^{11}B NMR resonance in borazines generally is observed between 29.1 ppm ($[\text{HBNH}]_3$) and 35.8 ppm ($[\text{CH}_3\text{BNCH}_3]_3$) (downfield from external $\text{F}_3\text{B}\cdot\text{OEt}_2$).¹⁵ Our products showed the main ^{11}B NMR resonances in the 32-34 ppm range. In addition, there were less intense signals in the ^{11}B NMR spectra around 26 ppm, indicative of the presence of some species with BN_3 connectivity.

SCHEME 2



$\text{CH}_3\text{SiHNH}/\text{BH}_3$ molar ratios ranging between 20 and 1 were used in these experiments. As the ratio decreased, the yield of ceramic produced on pyrolysis in a stream of argon to 1000°C increased from 52% for a ratio of 20 to 91% for a ratio of 1. The ceramic residues were amorphous, black in color and contained boron, silicon, carbon and nitrogen, thus were borosilicon carbonitrides.

Pyrolysis of these $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n/\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ products in a stream of ammonia to 1000°C left a white ceramic residue that in most cases contained less than 0.5% by weight of carbon. Thus the pyrolysis product was a borosilicon nitride. As expected, as the $\text{CH}_3\text{Si}(\text{H})\text{NH}/\text{BH}_3$ ratio that was used was decreased, the boron content of the ceramic product increased: from 1.72% when this ratio was 10 (equivalent to $2.5 \text{ Si}_3\text{N}_4 + 1.0 \text{ BN}$) to 11.42% for a $\text{CH}_3\text{Si}(\text{H})\text{NH}/\text{BH}_3$ ratio of 1 (equivalent to $0.42 \text{ Si}_3\text{N}_4 + 1.0 \text{ BN}$). These are nominal compositions since the ceramic obtained is amorphous. No separation of phases into Si_3N_4 and BN had occurred. In fact, experiments in which such ceramic samples were heated up to 1700°C showed no crystallization of Si_3N_4 ; only broad features attributable to turbostratic BN were observed in the X-ray powder pattern. The amorphous ceramic products of the pyrolysis of our polysilazane alone in a stream of ammonia to 1000°C crystallize to form $\alpha\text{-Si}_3\text{N}_4$ between 1450 and 1500°C , so it appears that BN retards the crystallization of Si_3N_4 .

The simple chemistry described here also can be applied to mixed systems such as the coammonolysis products of $\text{CH}_3\text{SiHCl}_2$ and CH_3SiCl_3 and of $\text{CH}_3\text{SiHCl}_2$ and $(\text{CH}_3)_2\text{SiCl}_2$, as well as siloxazanes, such as the ammonolysis product of $\text{O}[\text{SiCH}_3(\text{H})\text{Cl}]_2$. We note, however, that the reaction of $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ with cyclo- $[(\text{CH}_3)_2\text{SiNH}]_n$ ($n=3,4$) alone was much less facile, requiring long (ca. 72 hr) heating at reflux in toluene solution. Furthermore, the white solid product that was obtained in a reaction where the Si/B ratio was 2 left only a 2% yield of residual solid on pyrolysis to 1000°C in a stream of argon.

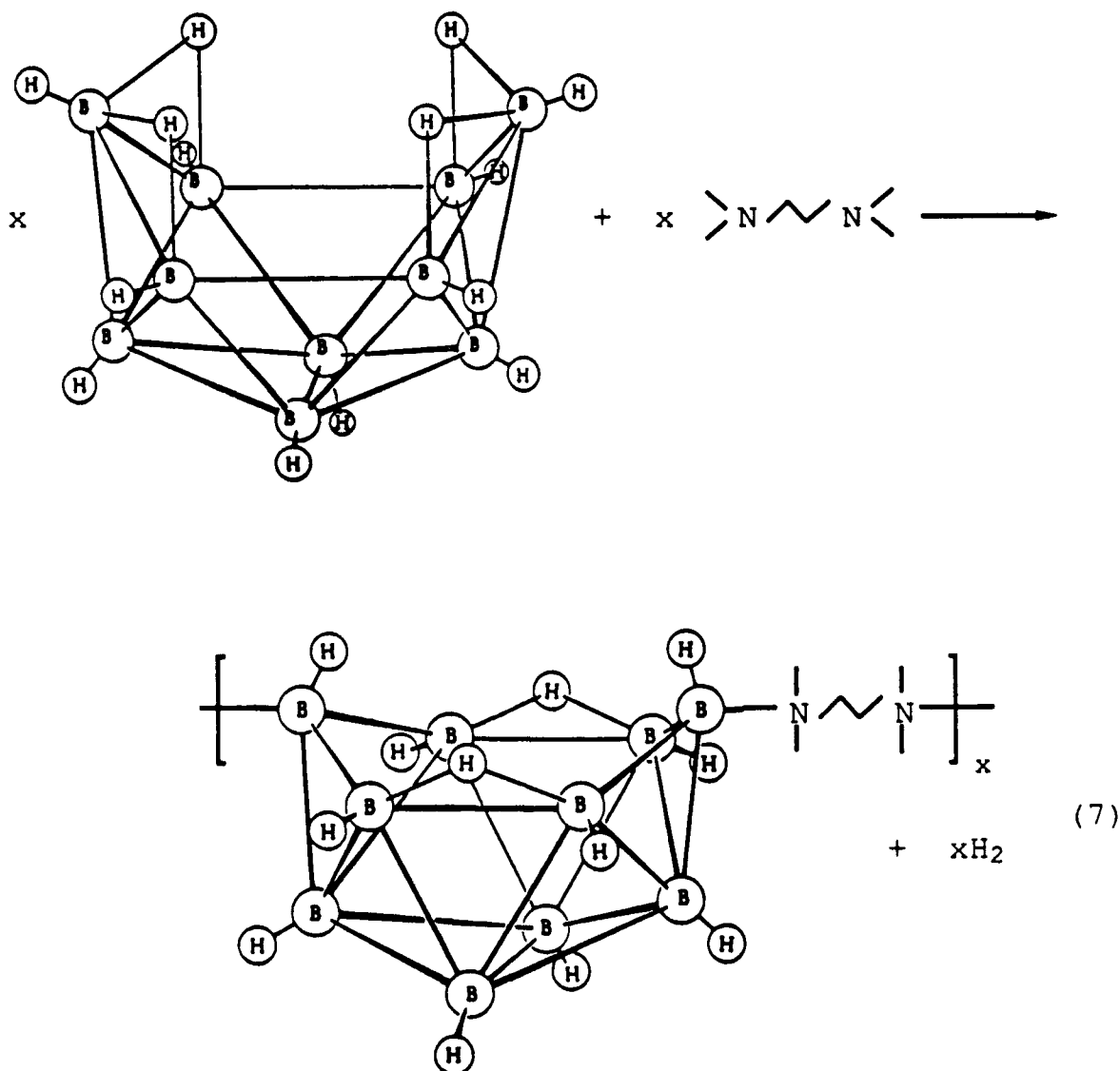
The use of $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$ is especially favorable for two reasons: (1) its reaction with $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ is facile and (2) if, after the reaction with the borane adduct, there is unreacted, latent $\text{Si}(\text{H})\text{-N}(\text{H})$ functionality left, further elimination of hydrogen can take place during the initial stages of pyrolysis, leading to even further cross-linking, hence very high ceramic yields. The Si-H bond appears to be of critical importance in the chemistry we describe here.

To date, not much research on applications of these new polymers has been carried out. They serve well as binders for ceramic powders. In another experiment, the polymer from such a 2:1 Si/B preparation was pressed into a rectangular bar weighing 3.42 g ($3.84 \times 1.32 \times 0.69$ cm; density 0.98 g cm^{-3}). Pyrolysis to 1000°C in a stream of argon gave a black bar of the same shape ($3.00 \times 1.03 \times$

0.55 cm; 50% reduction in volume) that weighed 3.0 g and had a density of 1.76 cm^{-3} . From a toluene-containing thick syrup of the same polymer long thin fibers could be hand-drawn. When these were fired in a stream of ammonia to 1000°C , white ceramic fibers were obtained.

3. FROM BORON NITRIDE PRECURSORS TO AN α -SILABORANE

In research directed toward the preparation of polymers whose pyrolysis will give boron nitride, we prepared decaborane/diamine polymers of type 3 by the reaction of decaborane(14) with various diamines (eq. 7).¹⁶



The $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers thus prepared are soluble in polar organic solvents such as dimethylformamide, dimethyl sulfoxide, hexamethylphosphoric triamide and acetone, but not in hydrocarbon solvents such as benzene, toluene or hexane. Their molecular weights appear to be in the 300,000+ range. Such $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers were prepared using $H_2NCH_2CH_2NH_2$, $(CH_3)_2NCH_2CH_2N(CH_3)_2$, $(CH_3)_2NCH_2CH_2NH_2$, and triethylenediamine. In the case of the $[B_{10}H_{12} \cdot H_2NCH_2CH_2NH_2]_x$ polymer, pyrolysis under argon to 1500°C ($10^\circ\text{C}/\text{min}$) left a brown, crystalline ceramic residue, whose examination by powder X-ray diffraction showed the presence of B_4C and BN . Examination of both the amorphous and crystalline pyrolysis products by diffuse reflection infrared Fourier transform spectroscopy showed absorptions due to B-C and B-N bonds. Similarly, pyrolysis of $[B_{10}H_{12} \cdot (CH_3)_2NCH_2CH_2N(CH_3)_2]_x$ gave an amorphous ceramic product of nominal composition $(B_4C)_1(BN)_1(C)_{0.53}$ (80% yield) at 1000°C and $(B_4C)_1(BN)_1(C)_{0.17}$ at 1500°C . High ceramic yields were observed in the pyrolysis to 1000°C under argon of the other diamine systems.

Usually, linear, noncross-linked polymers are not useful preceramic precursors, but in the case of the $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers a unique pyrolysis mechanism is operative. At temperatures above 150°C proton transfer from boron (the bridging H atoms) to nitrogen takes place, converting the covalent polymer to a diammonium salt of the $[B_{10}H_{10}]^{2-}$ anion. Such salts are not volatile, hence remain in the hot zone and are converted to a ceramic in high yield.

Ceramic monoliths could be produced by pyrolysis (under argon) of rectangular polymer bars. These $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers can serve as good to excellent binders for boron carbide powder.

The $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers also serve as boron nitride precursors. Their pyrolysis to 1000°C in a stream of ammonia (rather than argon) results in displacement of the diamine linker and reaction of ammonia with the B_{10} cage, leaving a white ceramic residue. The latter was spectroscopically and analytically indistinguishable from authentic boron nitride. For instance, the pyrolysis of $[B_{10}H_{12} \cdot N(CH_2CH_2)_3N]_x$ in a stream of ammonia gave a powdery ceramic residue in 70% yield which contained B and N in 0.99:1.0 ratio and only a slight amount of carbon. In a manner like that described above, a white ceramic bar was produced by pyrolysis (to 1000°C under ammonia) of a rectangular bar of BN powder/polymer binder that was of excellent strength and that exhibited shape retention in all dimensions.

Unfortunately, the $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers were not suitable for the preparation of ceramic fibers. They melted at higher temperatures with decomposition, so melt-

spinning was not an option. In order to obtain $[B_{10}H_{12} \cdot \text{diamine}]_x$ polymers with lower melting points, we replaced the organic diamines with dimethylbis(dimethylamino)silane. The latter reacted with $B_{10}H_{14}$ in refluxing benzene solution to give a pale yellow, resinous material that was soluble in polar organic solvents and melted in the range 80-110°C. Analytical and NMR spectroscopic data indicated that the moisture-sensitive product was the desired $[B_{10}H_{12} \cdot (CH_3)_2NSi(CH_3)_2N(CH_3)_2]_x$. Pyrolysis of this polymer to 1000°C in a stream of argon left an amorphous black residue in 85% yield. Its analysis (18.0% C, 11.8% N, 6.4% Si, 57.9% B) established the formation of a borosilicon carbonitride, boron-rich, rather than silicon rich as was the case for the $[CH_3Si(H)NH]_n/H_3B \cdot S(CH_3)_2$ products. Pyrolysis to 1000°C in a stream of ammonia gave a white ceramic residue in 89% yield whose analysis (40% B, 55% N, 2% Si, 0.6% C) was fairly close to that required for BN (43.6% B, 56.4% N). Obviously, not all of the $(CH_3)_2Si[N(CH_3)_2]_2$ linker was displaced by the high temperature reaction with ammonia.

Long fibers could be drawn from a melt of this polymer. A moist air cure, followed by pyrolysis in a stream of ammonia to 1000°C gave white ceramic fibers. Since the T_g of the polymer was below room temperature, multifilament spinning proved to be impractical. In a search for a more suitable polymer (which is still in progress), we have varied the substituents on silicon in the bis(dimethylamino)silane linker. The results obtained when $CH_3(H)Si[N(CH_3)_2]_2$ was used are noteworthy.¹⁷

The reaction of this silane with $B_{10}H_{14}$ in refluxing benzene or toluene solution resulted in the formation of a mixture of white solid products. The major product was identified as $B_{10}H_{12} \cdot 2(CH_3)_2NH$ (58% yield). The product formed in lesser (~15%) yield could be crystallized from benzene or sublimed at 90°C at 0.01 mm Hg. Very slow crystallization from dilute benzene gave diffraction-quality crystals which an X-ray diffraction study showed to be the 1:1 benzene solvate of 1,2-dimethyl-1,2-disilacloso-dodecaborane(12) (or 1,2-dimethyl- α -silaborane, in analogy to carborane nomenclature) whose structure is shown in Fig. 1. This is the first silicon analog of an ortho-carborane. Like the α -carboranes, it has a slightly distorted icosahedral structure. The Si-Si bond distance of 2.308(2)Å is slightly less than that of normal Si-Si single bonds (~2.33-2.34Å)¹⁸ but significantly longer than those of known Si-Si double bonds.¹⁹ In comparison, the C-C bond distances in α -carboranes (1.655Å, the mean value found in X-ray and gas phase electron diffraction studies²⁰) are longer than the normal $C(sp^3)-C(sp^3)$ distance of 1.54Å. This is understandable in terms of the larger size of a silicon atom (covalent radius 1.18Å), compared with a carbon atom (covalent radius 0.77Å). The Si-B bond distances in **1** [2.017(3), 2.018(3), 2.113(4) and 2.116(3)Å] are very close to the sum of the covalent radii of Si and B, 2.07Å (using 0.89Å as the average boron

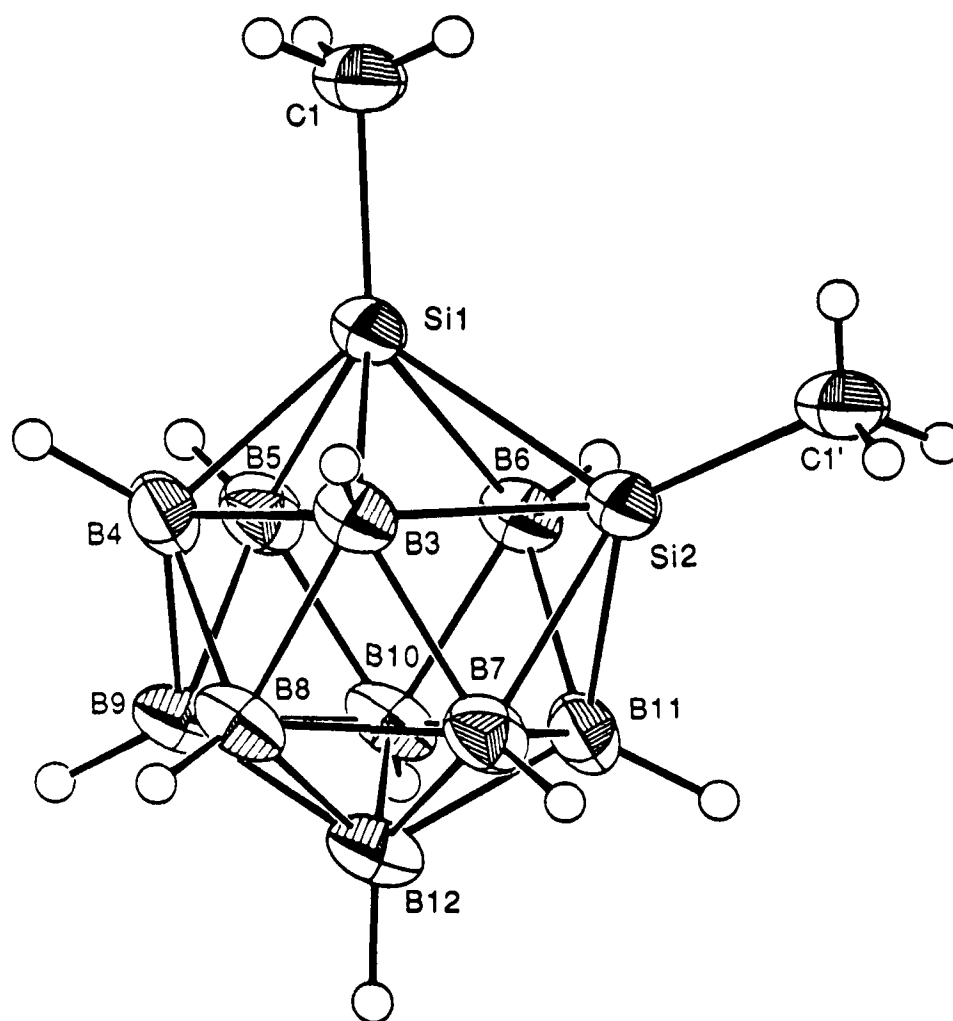
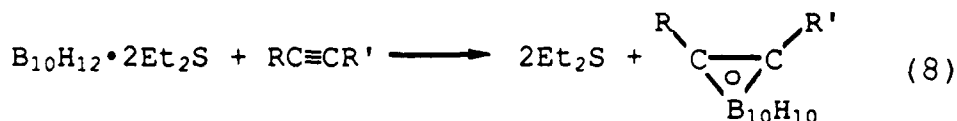


Fig. 1 ORTEP representation of 1,2-dimethyl-1,2-disila-closo-dodecaborane(12), drawn with 35% probability ellipsoids. Hydrogen atoms have been given arbitrary thermal parameters for clarity.

covalent radius in α -carboranes). These distances may be compared to those of the Si-B bonds in compo-3,3'-Si(3,1,2-SiC₂B₉H₁₁)₂, which contains a single silicon atom bonded within a 12-atom boron-containing cluster: 2.051(1) and 2.14(1) Å.²¹

1,2-Dimethyl- α -silaborane is less stable than the α -carboranes. It melts at 201-203°C (sealed capillary) and decomposes with gas evolution above 230°C. It remains undecomposed when heated at reflux in wet tetrahydrofuran solution for several days. It was unaffected when treated with an excess of CH₃CO₂H in THF at room temperature and remained largely undecomposed when this solution was heated at reflux for 14 hr. It was found to be stable toward AlCl₃ in refluxing benzene. It reacts with and is degraded by alcoholic KOH in THF at room temperature within minutes and it decolorizes a solution of bromine in carbon tetrachloride after several hours at reflux.

The α -carboranes are derivatives of acetylenes (eq. 8), and thus 1,2-dimethyl- α -silaborane may be regarded



as a formal derivative of a disilyne, CH₃Si≡SiCH₃, although its formation in the reaction of B₁₀H₁₄ with CH₃(H)Si[N(CH₃)₂]₂ need not involve such an intermediate.

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