High-Yield Molecular Borazine Precursors for Si–B–N–C Ceramics

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The synthesis of Si–B–N–C ceramic materials can be accomplished via two different routes using B-tris(trichlorosilylvinyl)borazine (**2**) as starting material. This silyl-functionalized ethinylborazine is obtained by Pt-catalyzed hydrosilylation of B, B′, B″-tri-ethynylborazine (**1**) with $HSiCl_3$ in quantitative yield with a selectivity of 80% β-substituted product. Amminolysis of **2** with methylamine leads to the soluble silazane polymer **P3** which contains intact borazine rings connected by –CH=CH–Si–NMe linkages. In a second approach, the trichlorosilyl groups of **2** are hydrogenated to yield the B-tris(hydrosilylvinyl)borazine (**4**). With polymer **P3** or **4**, a highly durable Si–B–N–C ceramic is obtained after pyrolysis under inert atmosphere. The composition $SiBN_{1+x}C_2$ of the ceramic material corresponds exactly to the backbone of the precursor molecules **2** or **4**, and very compact materials are obtained in each case. The ceramic yield of approximately 94% starting from the silane precursor **4** sets a new standard for this type of ceramics using the pyrolysis of a single site molecular precursor. Conductivity measurements show a semiconductor behavior of the ceramic at about 10^2 $(\Omega m)^{-1}$ at room temperature. The composition of the ceramic was characterized by laser-ablation ICP-MS, which was used for that purpose for the first time. The very satisfying results demonstrate the high potential of this direct solid sampling technique.

1. Introduction

The application of molecular precursors for the synthesis of silicon- based nonoxidic ceramics with outstanding properties has been investigated intensively since the early 1990s.[1,2] Nevertheless, polycarbosilanes and related polymers are still the most important among non-oxide polymer precursors,[3,4] and since the pioneering work by Yajima (SiC-nicalon), Takamizawa (first Si–B–N–C-fibers) and others, the chemical and physical properties of binary and multinary ceramics containing Si, B, N, and/or C have been optimized.[5–7] Remarkably, using molecular monomers in the relatively recent "M-to-M" (molecules-to-materials) approach, the thermal stability of the obtained materials can be increased significantly. However, the ceramic yield is lower than that of the polymer route.[8] Multinary systems are of special interest because they represent a combination of properties of the constituting binary

phases. The stability of these materials results from a homogeneous distribution of the elements at atomic scale. The extremely low self-diffusion coefficients of silicon or boron in their respective nitrides and carbides inhibit crystallization and oxidation at temperatures up to more than 2000 °C. A detailed overview on phase equlibria and material thermodynamics of the quaternary Si–B–N–C system and its binary and ternary subsystems is given by Seifert and Aldinger.[9]

The main requirements for a molecule to be a suitable single source precursor for ceramics are (I) a functionality that allows polymerization, and (II) the presence of small and "soft" leaving groups. An overview on established molecular precursors has been given by M. Jansen et al.[8]

Borazines[10a] (often considered "inorganic arenes" although recent calculations show that these molecules are less aromatic than anticipated[10b–d]) are relatively robust when compared to other boron nitrogen compounds, and hence became interesting as precursor molecules in boron nitride (BN) materials science.[11–15] Other suitably functionalized borazines have been reported but not yet investigated for ceramic formation.[16,17] Vaultier and co-workers described the use of alkynyl- and vinyl-substituted borazines as precursors

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(1) Baldus, H. P.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 329.

(2) Jansen, M.; Baldus, H. P.; Wagner, O. European Patent EP502399. 1992.

(3) Riedel, R.; Kienzle, A.; Dressler, W.; Ruwisch, L.; Bill, J.; Aldinger, F. *Nature* **1996**, *382*, 796.

(4) Kroke, E.; Li, Y.; Konetschny, C.; Lecomte, E.; Fasel, C.; Riedel, R. *Mater. Sci. Eng.* **2002**, *26*, 97.

(5) Yajima, S.; Hayashi, J.; Omori, M.; Okamura, K. *Nature* **1976**, *261*, 683.

(6) Takamizawa, M.; Hayashida, A.; Kobayashi, T.; Takeda, Y. U.S. patent US4604367, 1986.

(7) Komeya, K.; Matsui, M. *Mater. Sci. Technol.* **1994**, *11*, 517.

(8) Jansen, M.; Jaeschke, T.; Jaeschke, B. In *High-Performance Non-Oxide Ceramics I*; Jansen, M., Ed.; Springer-Verlag: Berlin, Heidelberg, 2002; Vol. 101, p 137.

(9) Seifert, H. J.; Aldinger, F. In *High Performance Non-Oxide Ceramics I*; Jansen, M., Ed.; Springer-Verlag: Berlin, Heidelberg, 2002; Vol. 101, p 1.

(10) (a) Muetterties, E. L. *Boron Hydride Chemistry*; Academic Press: New York, 1975. (b) Schleyer, P. v. R.; Jiao, H.; Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Kiran, B.; Phukan, A. K.; Jemmis, E. D. *Inorg. Chem.* **2001**, *40*, 3615. (d) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409.

for BNC-ceramics.[18] One main advantage of borazine precursors is the possibility of an unsymmetrical substitution at B and N, whereby the elemental ratios of the ceramic material can easily change. In a different approach, B-vinyl substituted borazines have also been used for the synthesis of polymers with pendant borazine groups.[19] Finally, we reported recently that borazines with suitable functional groups can be employed in sol−gel processes leading to functionalized silica gels containing intact borazine entities.[20]

In the present paper we are discussing two different strategies which have been investigated for the synthesis of Si−B−N−C ceramic material with β-silyl-substituted vinyl borazines as precursors. We took advantage of the high stability of borazines which therefore can be easily functionalized chemically. In the first approach, the trichlorosilylvinyl-substituted borazine derivative $[B_3N_3H_3(CH=CHSiCl_3)_3][20]$ was transformed into a soluble pre-polymer before conversion to a Si−B−N−C ceramic. In the second approach, $[B_3N_3H_3(CH=CHSiCl_3)_3]$ was reacted to the tris(trihydrosilylvinyl)-borazine $[B_3N_3H_3(CH=CHSiH_3)_3]$ which served as molecular precursor for ceramic synthesis.[21] With this method, shrinking effects should be minimized and more compact materials are produced. Previously, this concept was discussed only for polymeric precursors.[22] In either way, a high degree of cross-linking is expected because of the high degree of unsaturation in the borazine precursors to which the Si−H bonds may add in hydrosilylation reactions under thermal activation.

(11) $B_3N_3H_6$, as a precursor for the formation of pre-polymers (polborazylene $[B_3N_3H_{\sim4}]_x$) for boron nitride based polymers, see: (a) Wideman, T.; Sneddon, L. G. *Chem. Mater.* **1996**, *8*, 3. (b) Sneddon, L. G. *R. Soc. Chem.* **1997**, *201*, 491. (c) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73. (d) Volger, K. W.; Kroke, E.; Gervais, C.; Saito, T.; Babonneau, F.; Riedel, R.; Iwamoto, Y.; Hirayama, T. *Chem. Mater.* **2003**, *15*, 755 and literature cited therein.

(12) Recently, borazines of the type $[B(CH_2SiCl_2R)_3)(NH)_3)]$ were recognized as suitable single-source precursors for the formation of multinary non-oxide inorganic materials as amorphous network ceramics, see: (a) Jansen, M.; Jaeschke, T. Patent WO0222625, 2001. (b) Jansen, M.; Jaeschke, B.; Jaeschke, T. *Third International Conference on Inorganic Materials*, Konstanz, 2002. Krummland, A.; Nesper, R.; Grützmacher, H. Second International Conference on Inorganic Materials, Santa Barbara, 2000.

(13) The B-silyl substituted borazine $[B(Si(SiMe_3)_3)(BCl_2)(NH)]_3$ reacts with $HN(SiMe_3)_2$ to give a pre-polymer which is used for an amorphous $BN/Si_xN_yC_z$ composite material, see: Srivastava, D.; Duesler, E. N.; Paine, R. T. *Eur. J. Inorg. Chem.* **1998**, *1998*, 855.

(14) For other Si−B−N−C ceramics obtained from borazines see: (a) Su, K.; Remsen, E. E.; Zank, G. A.; Sneddon, L. G. *Chem. Mater.* **1993**, *5*, 547. (b) Wideman, T.; Su, K.; Remsen, E. E.; Zank, G. A.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 2203. (c) Wideman, T.; Cortez, E.; Remsen, E. E.; Zank, G. A.; Carroll, P. J.; Sneddon, L. G. *Chem. Mater.* **1997**, *9*, 2218.

(15) Coupling reactions between cyclosilazanes and borazines have also been investigated to give a special type of preceramic precursors for quaternary ceramics, see: (a) Jaeschke, B.; Klingebiel, U.; Riedel, R.; Doslik, N.; Gadow, R. *Appl. Organomet. Chem.* **2000**, *14*, 671. (b) Helmold, N.; Jaeschke, B.; Klingebiel, U. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, *168*, 569.

(16) Cheng, F.; Toury, B.; Archibald, S. J.; Bradley, J. S. *J. Organomet. Chem.* **2002**, *657*, 71.

(17) Bai, J.; Niedenzu, K.; Serwatowska, J.; Serwatowski, J. *Inorg. Chem.* **1991**, *30*, 4631.

(18) Blanchard, C.; Chassagneux, E.; Mignani, G.; Vaultier, M. European Patent EP0570247A1, 1993.

(19) Wideman, T.; Fazen, P. J.; Lynch, A. T.; Su, K.; Remsen, E. E.; Sneddon, L. G. *Inorg. Synth.* **1998**, *32*, 232.

(20) Haberecht, J.; Krummland, A.; Breher, F.; Gebhardt, B.; Rüegger, H.; Nesper, R.; Grützmacher, H. *Dalton Trans.* **2003**, *11*, 2126.

(21) Nesper, R.; Haberecht, J.; Grützmacher, H. Patent CH-0149/03, pending 2003.

(22) Weinmann, M. *Chemiedozentagung*, Chemnitz, 2003.

2. Experimental Section

2.1. General Comments. All syntheses were performed in carefully dried glassware under an argon atmosphere, which was passed through the Oxisorb gas purification system of Messer-Griesheim to remove the last traces of oxygen and moisture. All solvents were dried and purified using standard procedures and were freshly distilled under argon from sodium/benzophenone (thf, toluene) or from sodium/diglyme/benzophenone (heptane, hexane, pentane) prior to use. Air-sensitive compounds were stored and weighed in a glovebox (Braun MB 150 B-G system) and reactions on small scale were performed directly in the glovebox. Bulk pyrolyses of the precursors were performed in quartz tubes up to 1000 °C and in alumina tubes up to 1650 °C under a steady stream of argon. The samples were heated in carbon crucibles at a heating rate of 5 K/min and dwell time of 5 h at maximum temperature.

NMR spectra were either taken on a Bruker Avance 400 or Avance 300 system. The chemical shifts are reported on the δ scale in ppm relative to residual nondeuterated solvent signals (^{1}H) or the signals of the deuterated solvent (^{13}C) as internal standards, or relative to tetramethylsilane (^{29}Si) or $BF_3 \cdot OEt_2$ (^{11}B) as an external standard. ^{29}Si chemical shifts of the solid samples were determined relative to the external standard Q_8M_8. Values were then expressed relative to the reference compound TMS (0 ppm). ^{11}B MAS NMR spectra were determined relative to an aqueous solution of boric acid, which has a chemical shift of 19.6 ppm relative to the ^{11}B reference compound $BF_3 \cdot OEt_2$ (0 ppm). Coupling constants, J, are given in Hertz [Hz] and as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t for singlets, doublets, triplets, respectively. Broadened resonances are indicated as br. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode. IR spectra were recorded with a Perkin-Elmer Spectrum 2000 NIR-FT-Raman spectrometer. Energy values are given in cm^{-1}. Thermal analyses were taken on a Netzsch STA 409 under dynamic Ar atmosphere with a heating rate of 10 K/min in corundum crucibles (T_{max} = 1500 °C) or graphite crucibles (T_{max} = 1960 °C). TG-MS investigations have been performed on a Mettler-Toledo TGA/SDTA 851e coupled with a Balzers GSD 300T3 mass spectrometer. Density measurements were taken on a Micromeritics AccuPyc 1330 helium pycnometer. Transmission electron microscopy (TEM) and electron spectroscopic imaging (ESI) investigations were performed on a Philips Tecnai F30 microscope operated at 300 kV (field emission cathode). The material was deposited on a perforated carbon foil supported on a copper grid. For scanning electron microscopy (SEM), performed on a LEO 1530 (FEG) microscope with 1 kV electrons, samples were fixed on carbon pads. Conductivity measurements were taken on a Keithley 236-system (Van der Pauw method) in the range from 300 to 600 °C. C/N analyses were performed on a LECO CHN-900 analyzer.

2.2. Syntheses. *B, B′, B″-Tris(trichlorosilylvinyl)borazine* (**2**). Compound **2** was synthesized via hydrosilylation of B, B′, B″-triethynylborazine with $HSiCl_3$ as described in reference 20. For all experiments described in this paper, the nearly isomer-pure C_β-substituted product was used and is discussed.

$[N_3B_3H_3(CH=CHSi(NMe)_{1.5-x/2}(NHMe)_x)_3]_n$ (**P3**). In a 500-mL Schlenk flask equipped with a coolable 250-mL dropping funnel and a magnetic stirrer, 21 g (37.6 mmol) of **2** was dissolved in 300 mL of hexane and cooled to approximately −30 °C. Under vigorous stirring, 25 mL (760 mmol) of methylamine at −30 °C was added over a period of ~1 h. During the exothermic reaction, the temperature was controlled not to rise above −20 °C. After allowing the mixture to warm to room temperature, it was stirred for 1 d. The solution was then separated by filtration and the residue was carefully washed 3× with 30 mL of hexane. Finally, all volatile components were removed in a vacuum (10^{-2} mbar) to produce 13.3 g (98%) of **P3** as a colorless and highly viscous liquid that is very sensitive to moisture and air.

NMR (C_6D_6) ^{1}H: 0.37 br (Si−NH), 2.65 (s, 3H, N−CH$_3$), 5.4 br (1H, NH), 6.8 br (2H, C*H*=C*H*−Si). ^{11}B: 35.3 (br). ^{13}C: 27.2

Scheme 1. Syntheses of the Pre-Ceramic Polymer P3 via Aminolysis of 2 and Tris(trihydrosilylvinyl)Borazine 4 via Hydrogenation of 2[a]
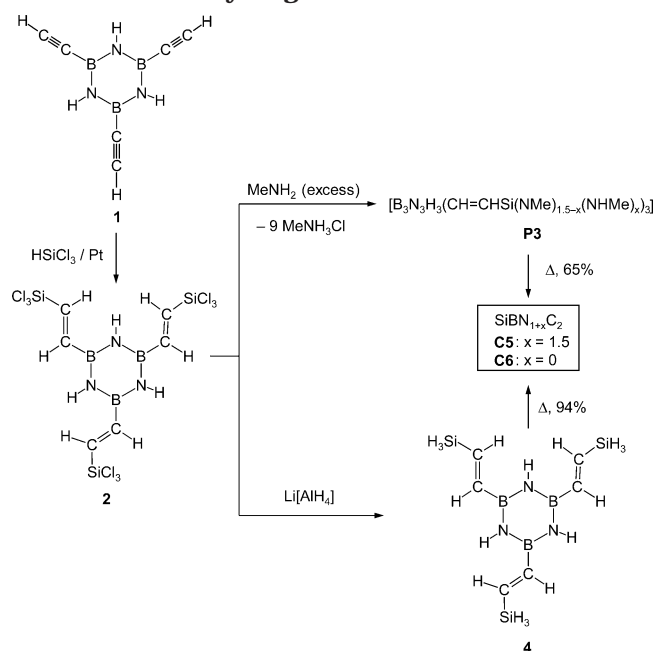
[a] Both **P3** and **4** are thermally converted to $SiBN_{1+x}C_2$ ceramics **C5** and **C6**, respectively.

(N−CH_3), 145.2 (CH=CH−Si), 147.5 (CH=CH−Si). ^{29}Si: −34.8. IR/cm^{-1}: 3415 (N−H), 1591 (C=C); 1465, 1370 (B−N); 1099 (C=C−H).

B,B′,B″-Tris(trihydrosilylvinyl)borazine *[B$_3$N$_3$H3(CH= CHSiH$_3$)$_3$] (4)*. In a 50-mL Schlenk flask equipped with a 10-mL dropping funnel and a magnetic stirrer, 306 mg (8.05 mmol) of LiAlH$_4$ was suspended in 20 mL of thf and cooled to −20 °C. Under vigorous stirring at −20 °C, 2 g (3.6 mmol) of **2** dissolved in 10 mL of thf was added over a period of 10 min. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. After adding 5 mL of pentane, the suspension was filtered over Celite. Subsequently, the solvents were removed in a vacuum and the residue was extracted with hexane to isolate the ^{1}H NMR spectroscopically pure product. After evaporation of the hexane and drying under vacuum (10^{-2} mbar), 0.4 g (1.8 mmol, 50%) of **4** was obtained as a white solid.

NMR (C$_6$D$_6$) ^{1}H: 4.16 (s, 1H, NH), 4.96 (d, 3H, SiH), 6.38 [d, 1H, CH=CH−Si, $^3J_{H,H}$ = 21.6 Hz], 6.75 [d, 1H, CH=CH−Si, $^3J_{H,H}$ = 21.6 Hz]. ^{11}B: 33.4. ^{13}C: 135.5 (CH=CH−Si), 153.7 (CH=CH−Si). ^{29}Si: −62.9 ($^1J_{Si-H}$ = 199 Hz, $^2J_{HSi-CH}$ = 13.2 Hz, $^3J_{HSi-C=CH}$ = 10.6 Hz). IR/cm^{-1}: 3432 (N−H), 2155 (Si−H$_{strech}$), 1590 (C=C); 1470, 1344 (B−N); 1007 (C=C−H); 913 (Si−H$_{bend}$). MS: *m*/*z* (%, ion) = 249 (16, M), 218 (100, M − SiH$_3$), 187 (18, M − (SiH$_3$)$_2$).

3. Results and Discussion

3.1. Syntheses. As we reported previously, the synthesis of the starting compound B,B′,B″-tri-ethynylborazine (**1**), according to the procedure described by Vaultier and co-workers, was optimized.[20] Subsequently, hydrosilylation of **1** with trichlorosilane using Pt on charcoal (1% weight, Aldrich) as heterogeneous catalyst has been performed to give the tris(trichlorosilylvinyl)-borazine (**2**) in quantitative yield (Scheme 1).

The compound **2** was obtained with a high regioselectivity of approximately 80% β-*trans* hydrosilylation product. No further hydrosilylation of the vinyl units

was observed. Pure **2** can obtained by fractional crystallization from hexane. Although we used the β-regioisomer in this work, we see no objection to using the primarily obtained mixture of α- and β-hydrosilylated products for further reactions. Two synthetic protocols were investigated in order to convert the single-source precursor molecule **2** to a preceramic polymer. In the first protocol, an excess of methylamine as linking reagent was cooled to about −30 °C to which a solution of the borazine **2** in thf was added. A slightly yellow and low-viscous liquid was obtained. Because of the excess of CH$_3$NH$_2$ present at all stages of the aminolysis, the polycondensation of **2** remains incomplete, and a relatively large amount of −Si−N(CH$_3$)H groups was detected by ^{1}H NMR (δ = 0.37 ppm) and by IR-spectroscopy [ν(N−H) ~3400 cm^{-1}]. To achieve a higher degree of condensation, the order of the addition of the reagents was inverted; i.e., CH$_3$NH$_2$ was added to the solution of **2** in hexane in order to avoid an excess of amine. With this protocol, a highly viscous, colorless oil was obtained. The polymer **P3** was purified by evaporation of the solvent indicated by its ^{1}H NMR spectrum. Nevertheless, small amounts of −Si−N(CH$_3$)H groups are detectable which are responsible for the relatively good solubility of **P3**. No residual chlorine is detected by elemental analysis and ^{29}Si NMR spectroscopy. Other solvents such as thf or toluene can also be used either for the reaction as for dissolution of the polymer. Furthermore, with ethylamine instead of methylamine very similar results are obtained in the polymer synthesis.[23]

Instead of using a pre-polymer like **P3** for the Si−B−N−C ceramic synthesis, we tested a second approach which we hoped would lead to an increase of the ceramic yield during the pyrolysis. For this purpose, the precursor molecule **2** was selectively hydrogenated to give the B,B′,B″-tris(trihydrosilylvinyl)borazine (**4**) as single-site precursor molecule (Scheme 1).[21] The hydrogenation of **2** can be carried out with different standard reagents for this type of transformation, such as LiAlH$_4$, NaAlH$_4$, or Li(BHEt$_3$) ("superhydrid"). The best yield is obtained with a small excess of LiAlH$_4$ in thf as solvent at T = −20 °C. The reaction is monitored by ^{1}H and ^{29}Si NMR spectroscopy and is complete within 1 day. Only the −SiCl$_3$ group is affected while no reaction with the vinyl groups nor the borazine core is observed. The final product **4** is a white solid, soluble in all common solvents.

3.2. Precursor Characterization. The preceramic precursors **P3** and **4** have been characterized by NMR and FT-IR spectroscopy, and, if possible, by mass spectrometry. Selected NMR data are given in Table 1. The ^{11}B NMR shift does not change significantly and lies in the typical range of 33 to 36 ppm indicating the presence of intact borazine in all compounds **2**, **P3**, and **4**.[24] Because of the nonsymmetric substituent pattern, all ^{11}B NMR signals are broadened ($w_{1/2} \approx 390$ Hz for **2** and **4**; $w_{1/2} \geq 600$ Hz for **P3**, depending on degree of network linking). However, these results indicate the borazine ring system remains intact after the chemical reactions described in Scheme 1. Both ^{1}H and ^{13}C NMR

(23) Haberecht, J. unpublished results.
(24) Nöth, H.; Wrackmeyer, B. *NMR Spectroscopy of Boron Compounds*; 1st ed.; Springer-Verlag: Berlin, 1985; Vol. 14.

Table 1. Selected NMR Shifts for 2, P3, and 4 in C₆D₆ (δ in ppm)[a]

	^{1}H (β/α)	^{11}B	^{13}C (β/α)	^{29}Si
(N₃B₃H₃)(CH=CH(SiCl₃))₃ **(2)**[20]	6.22/6.85	34.0	137.4/153.6(b)	−3.3
[(N₃B₃H₃)(CH=CHSi(NMe)₃/₂)₃]ₙ **(P3)**	6.8(b)[b]	35.3	145.2/147.5(b)	−35.8
(N₃B₃H₃)(CH=CH(SiH₃))₃ **(4)**	6.38/6.75	33.4	135.5/153.7(b)	−62.9

[a] Further NMR data are given in the Experimental section. α/β position relative to the borazine ring. [b] Signal width ∼60 Hz, includes both β and α protons.

investigations of **2**, **P3**, and **4** reveal intact B−CH=CH−Si units (see Table 1, α /β position relative to the borazine ring). The carbon atoms attached to boron show very weak intensities because of the broadening caused by the quadrupole moment of the boron nucleus.[24] The chemical shift at 150 ± 5 ppm in **2**, **P3**, and **4** is characteristic for B−CH= units.[20] The ^{13}C chemical shift for the =CH−Si groups varies only slightly between 137.4 and 135.5 ppm in **2** and **4**, respectively, despite the rather different substituents (Cl, H) at silicon. In the polymer **P3**, this resonance is shifted to 145.2 ppm. The ^{29}Si NMR spectra show chemical shifts for **2** (−3.3 ppm), **P3** (−35.8 ppm), and **4** (−62.9 ppm) which compare well with literature values of comparable compounds.[25,26] The ^{1}H and ^{1}H coupled ^{29}Si NMR spectra of **4** are shown in Figure 1a and b, respectively.

Indicative of the stereochemistry at the C=C bond in **4** is the $^3J_{(H,H)}$ coupling constant (21.6 Hz), which is very similar to the one in tris(trichlorosilylvinyl)borazine **2** (21.8 Hz).[20] The resonance of the ^{1}H proton attached to the β-carbon (with respect to the borazine ring) is split into a doublet of quartets by an additional $^3J_{(HSi−CH)}$ coupling (2.8 Hz). The ^{1}H coupled ^{29}Si NMR spectrum shows all expected ^{1}H couplings (Figure 1b) and proves unequivocally the structure of **4**. The quartet structure of the ^{29}Si resonance stems from the large $^1J_{(Si−H)}$ coupling (199 Hz) and each line is further split into a doublet of a doublet by $^2J_{(Si−CH)}$ (13.2 Hz) and $^3J_{(Si−C=CH)}$ couplings (10.6 Hz).[27,28] The vinyl protons in the polymer **P3** are not resolved and only one broad signal is observed at 6.8 ppm ($w_{1/2} \approx$ 60 Hz).

In addition to the NMR data, some absorptions in the IR spectra are useful indicators for the structures of the investigated compounds. For comparison, the IR spectra of **2**, **P3**, and **4** are shown in Figure 2 and clearly demonstrate that the basic functionalities, i.e., the borazine ring and the vinyl groups, are present in all compounds. The È N−B−N vibration modes of the B₃N₃ ring at about 1470 and 1340 cm^{-1} are typical for borazines and observed in all three samples. Furthermore, the C=C stretching vibration at about 1590 cm^{-1} and the H−C=C bending mode at about 1020 cm^{-1} is observed. In **4**, two additional strong absorptions are observed which are indicative of the SiH₃ groups. The mode at 2155 cm^{-1} is assigned to the Si−H stretching vibration, the second one at lower energy (913 cm^{-1}) is assigned to the Si−H bending vibration.[29,30]
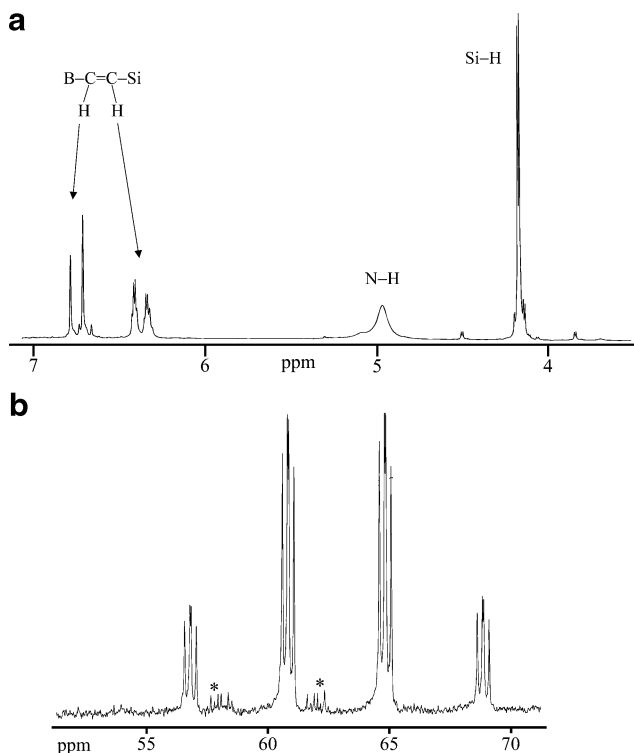
Figure 1. a and b. ^{1}H and ^{29}Si NMR (Si−H coupled) spectra (C₆D₆) of B-tris(trihydrosilylvinyl)borazine (**4**). (*) denotes signals from residual α-hydrosilylation product.
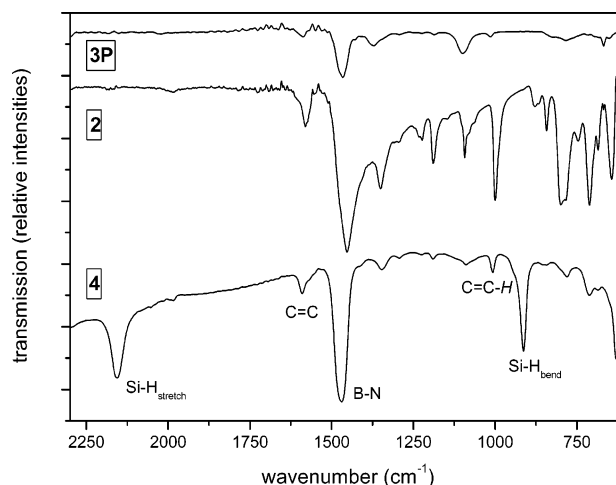
Figure 2. IR spectra of the initial molecule **2** (middle) and the ceramic precursors **P3** (up) and **4** (down).

The mass spectrum of **4** shows the molecule ion at m/z = 249 and the fragments [M − SiH₃] and [M − 2 SiH₃)₂] at m/z = 218 and 187, respectively.

3.3. Ceramic Material Characterization. The conversion of either the polymeric precursor **P3** or molecular precursor **4** to the ceramics (**C5** and **C6**, respectively) has been carried out in carbon crucibles (Sigradur) under argon atmosphere. Applying a heating rate of 5 K/h, the samples were pyrolyzed in a first step up to

(25) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; John Wiley: Chichester, 2001; Vol. 3.
(26) Marsmann, H. In *NMR−Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, Heidelberg, 1987; Vol. 17, p 65.
(27) Schrock, R.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch. (B)* **1994**, *49*, 1036.
(28) Hassler, K.; Köll, W.; Pöschel, U. In *Organosilicon Chemistry III*; Auner, N., Weiss, J., Eds.; Wiley-VCH: Weinheim, 1997; p 301.
(29) Rudinger, C.; Beruda, H.; Schmidbaur, H. *Chem. Ber.-Recl.* **1992**, *125*, 1401.
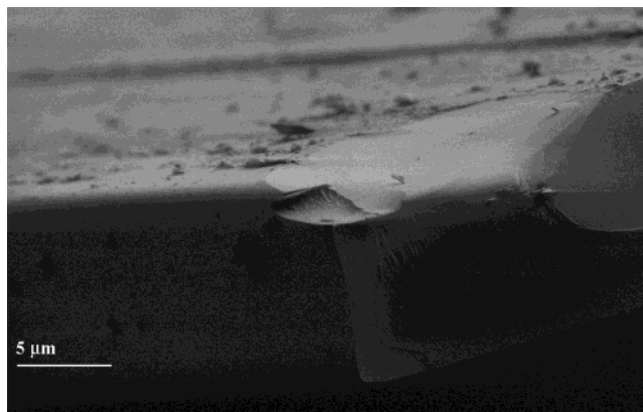(30) Beach, D. B. *Inorg. Chem.* **1992**, *31*, 4174.

Figure 3. SEM image of the ceramic material **C6** as obtained from **4** after heating under Ar at 1650 °C.
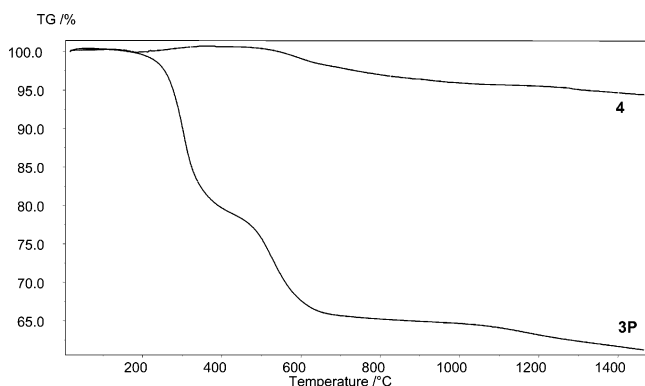

Figure 4. Thermogravimetric analyses of **P3** and **4**. Heating rate 10 K/min; flowing argon.

1000 °C in quarz tubes, and then up to 1650 °C in alumina tubes. After this thermal treatment, both polymeric (**P3**) or molecular precursor **4** gave black and dense amorphous ceramic materials (Scheme 1 and Figure 3).

The density of the ceramics was determined to be 1.6−1.7 g/cm^{-3}. As expected and known from literature, thermal conversion of both polymer **P3** and molecule **4** result in an amorphous ceramic material.[1] The conversion process was monitored by thermal analyses and the final product was characterized by X-ray powder diffraction, MAS NMR spectroscopy, and electron microscopy (SEM and TEM). The weight loss and amount of gaseous byproducts during pyrolysis are of crucial importance for the ceramic formation and determine the suitability of a precursor.[31] As shown in Figure 4, TG measurements with **P3** up to 1500 °C reveal a total weight loss of approximately 37% in the case of **P3**. As is seen in Figure 4, three steps of thermal degradation are clearly distinguished during the formation of **C5**.[31]

The thermal process detected in the first step can be assigned to the completion of the polycondensation (250−400 °C) whereby methylamine and small amounts of HCN are liberated (weight loss ∼20%). In the second step, in the range of 400 to 600 °C, fragmentations in the pre-polymer lead to a further weight loss (∼14%) and mainly methane and also HCN are split off. In the final step, the elimination of residual hydrogen occurs at temperatures >1000 °C (weight loss ∼3%). On the
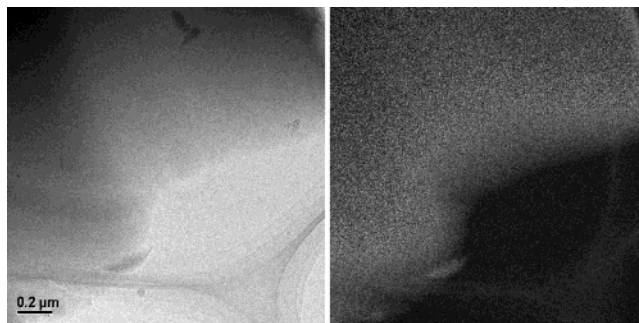

Figure 5. Ceramic material after pyrolysis at 1650 °C; TEM image showing the amorphous structure (left) and Si map (right), obtained at the K ionization edge by ESI, demonstrating the homogeneous Si distribution.

other hand, only ∼6% weight loss between 600 and 1500 °C is observed when the silylvinyl borazine **4** is used. This loss corresponds to the elimination of hydrogen. The obtained excellent ceramic yield is unprecedented for processes where molecular precursors were employed for Si−B−N−C ceramics and reaches the benchmarks previously set by polysilazanes and its derivatives for the preparation of Si−N ceramics.[32,33]

X-ray powder investigations of **C5** and **C6** after thermal treatment up to 1650 °C, as well as DTA/TG measurements, indicate that the amorphous state of the ceramic material is maintained in all cases. For more detailed structure characterization, TEM investigations have been performed for ceramics obtained from **P3** and **4**.

As shown for one example in Figure 5, HRTEM reveals the completely amorphous state at atomic scale of the samples heated to 1650 °C. Furthermore, elemental maps of Si, B, N, and C (Figure 5), recorded from the selected area by electron spectroscopic imaging confirm a homogeneous distribution of the elements. Thus, the formation of boron nitride domains was not observed as was previously suspected as an undesired effect when borazines were employed as precursors for ceramics.[34]

To characterize the properties of the ceramic material obtained from **P3** at high-temperatures, a DTA/TG measurement up to 2000 °C was performed. The weight loss between 1000 °C and 2000 °C amounts to about 2%. A subsequent powder X-ray diffraction analysis as well as HRTEM investigations of the sample indicates the crystallization of Si_3N_4 and SiC up to these temperatures.

Amorphous materials can be advantageously investigated by ^{11}B- and ^{29}Si-MAS NMR experiments.[35,36] The ^{29}Si NMR spectra of the ceramic materials obtained with **4** or **P3** show one signal at −43 ppm ($w_{1/2}$ = 1400 Hz), a chemical shift typical for silicon in 4-fold coordination site. The chemical shifts and the shapes of the signals in [11]B−NMR spectra (δ_{iso}= 30 ppm, qcc = 2.8 MHz) indicate boron nuclei in a trigonal-planar coordination

(31) van Wüllen, L.; Müller, U.; Jansen, M. *Chem. Mater.* **2000**, *12*, 2347.

(32) Weinmann, M.; Schuhmacher, J.; Kummer, H.; Prinz, S.; Peng, J. Q.; Seifert, H. J.; Christ, M.; Mueller, K.; Bill, J.; Aldinger, F. *Chem. Mater.* **2000**, *12*, 623.

(33) Weinmann, M.; Kamphowe, T. W.; Schuhmacher, J.; Müller, K.; Aldinger, F. *Chem. Mater.* **2000**, *12*, 2112.

(34) Krummland, A. Ph.D. Thesis, ETH Zurich, No. 14179, 2001.

(35) Müller, U. Ph.D. Thesis, University of Bonn, 2002.

(36) van Wüllen, L.; Müller, U.; Jansen, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2519.
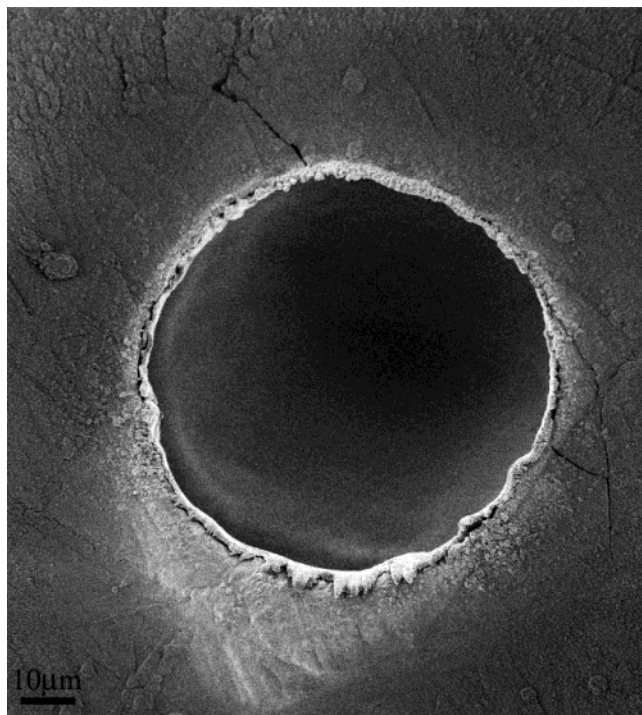
Figure 6. SEM image of the ceramic material **C5** as obtained from **P3** after LA-ICP-MS analysis.

sphere spanned by nitrogen atoms.[37] Thus, results of NMR spectroscopic investigations of our Si−B−N−C ceramics are confirmed with previous results from literature.[38] Thus, it is not possible to distinguish between **C5** and **C6** by powder investigations.

Because of constantly encountered difficulties and high costs with the elemental analyses for boron and silicon of ceramic materials, we applied a laser-ablation technique (LA-ICP-MS)[39,40] to obtain more precise information about the elemental composition of our material. Pieces of the ceramics were placed into the ablation cell of the apparatus. The sampling on the ceramic surface was carried out using a 193 nm Excimer laser ablation system (GeoLas, MicroLas, Göttingen, Germany). The interaction of the laser with the sample produces an aerosol which was transported using helium as carrier gas to an inductively coupled plasma mass spectrometer (ICP-MS, ELAN 6100, Perkin-Elmer, Norwalk, CT). Here the aerosol was vaporized, atomized, and ionized. The NIST 610 reference glass material was used as external standard for calibrating the instrument. Every sample was analyzed at five different positions using a spatial resolution of 80 μm (see Figure 6). At all positions, the measured Si/B weight ratios result in 2.55 for **C5** and 2.64 for **C6**, respectively, with standard deviations of 0.04. Thus, the expected Si/B ratio from the borazine precursors (2.6) is found in the ceramic material. In accord with the results of the ESI investigations (vide supra), the spatially resolved analyses indicate a homogeneous distribution of the elemental composition. The laser ablation technique which we

Table 2. Calculated and Measured Elemental Composition (wt %) of Ceramics C5 and C6 and the Corresponding Formulas[a]

material	C5		C6	
	calc.	meas.	calc.	meas.
Si	28.7	ratio 2.55	36.5	ratio 2.64
B	11.2		14.1	
N	35.7	37.2	18.2	14.8
C	24.5	24.1	31.2	36.8
calc. formula	$SiBN_{2.5}C_2$		$SiBNC_2$	
empir. formula	$SiBN_{2.7}C_2$		$SiBN_{0.9}C_{2.5}$	

[a] Oxygen values are <1% and are omitted.

applied is very sensitive to trace elements and, importantly, no residual chlorine was detected in our products. In combination with the results of the C/N analyses, the overall composition of the material can be described as $SiBN_{1+x}C_2$ (for **C6** $x = 0$; for **C5** $x = 1.5$) within the experimental errors (see Table 2).

In view of the possible applications of amorphous Si−B−N−C ceramics, conductivity measurements of our ceramic material were performed and gave promising results. The amorphous ceramics show a semiconductor behavior in the temperature range of 300 to 600 °C. At room temperature, the specific conductivity is approximately 10^2 $(\Omega m)^{-1}$, comparable to that of typical III/V semiconductors.[41] In further investigations, tuning of this behavior will be tested.

Conclusions

Our synthetic route opens a new and wide range for syntheses of further precursor molecules for Si−B−N−C ceramics. Starting by hydrosilylation of **1** with dichloroalkylsilanes $H(Cl)_2SiR$, the chemical composition of the ceramic material could be varied by changing the silyl-substituents R (Cl, alkyl, phenyl). In every case, a linking reaction forming a polymer or a hydrogenation is possible (similar to Scheme 1). Thus, according to the carbon content, the nitrogen content also can be tuned. Detailed investigations are in progress. Possibly because of the high amount of multiple bonds in the borazine molecules, a very high degree of cross-linking and thermal stability was achieved. The backbone of the precursor molecules (elemental composition is given by $SiBNC_2$) remains intact during pyrolysis. Furthermore, it was possible to increase the ceramic yield up to 94% by using tris(silylvinyl)borazine, which demonstrates for the first time that quaternary Si−B−N−C materials can be produced very efficiently from molecular precursors.

(37) Jansen, M.; Kroschel, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1634.
(38) Schuhmacher, J. Ph.D. Thesis, University of Stuttgart, 2000.
(39) Günther, D.; Horn, I.; Hattendorf, B. *Fresenius' J. Anal. Chem.* **2000**, *368*, 4.
(40) Günther, D.; Frischknecht, R.; Heinrich, C. A.; Kahlert, H. J. *J. Anal. At. Spectrom.* **1997**, *12*, 939.
(41) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL, 2002.