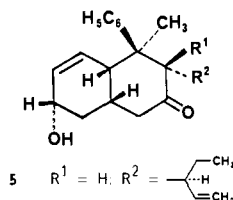


Table I. Selected Distances (Å) and Angles (deg) from **1** and **2**

	1	2
Bond Distances		
O1-C1	1.225 (3)	1.377 (5)
C1-C2	1.496 (4)	1.330 (6)
C3-C4	1.589 (4)	1.570 (7)
Nonbonded Distances		
H(C2)-H(C12)	2.038	
H(C5)-H(C12)	2.297	2.767
C11-C21	3.268	4.342
Bond Angles		
C1-C2-C3	105.3 (2)	120.0 (4)
C1-C2-C18	112.2 (3)	121.5 (4)
C1-C2-H(C2)	106 (2)	
C3-C2-C18	119.0 (2)	118.5 (3)
C3-C2-H(C2)	105 (2)	
C18-C2-H(C2)	108 (2)	
Torsional Angles		
O1-C1-C2-C18	27.9	4.0
O1-C1-C6-O2	16.1	58.1
C18-C2-C3-C11	82.4	83.1
C18-C2-C3-C17	-41.8	-39.1
C1-C2-C18-C19	58.6	-69.7
C2-C3-C11-C12	45.6	25.1

In aqueous solution, cyclohexanone is roughly 6 kcal/mol more stable than the corresponding enol.⁸ Molecular mechanics calculations (MM2) on the X-ray derived conformations find roughly this amount of destabilization of ketone **1** relative to enol **2**.⁹ The calculated strain due to angle distortion at C2 and nonbonded van der Waals contacts of H(C2) and methylene C21 in ketone **1** totaled 3.9 kcal/mol.¹⁰ A further 2.5 kcal/mol of dipole-dipole destabilization of ketone **1** was predicted for the interaction of the carbonyl group with the ether bridge C-O bonds and lone pairs.¹¹ These effects were eliminated or substantially reduced in the calculated structure of enol **2**.¹²



Experimental support for destabilization of **1** by these effects was obtained. Neither **4** nor **5** formed an isolable enol when exposed to excess NaOCH₃ in CD₃OD, although the hydrogens α to the carbonyls were exchanged for deuterium. The failure of both **4** and **5** to form a stable enol substantiates the critical roles played by the C2 side chain and ether bridge.

Acknowledgment. This work was supported by the Research Corporation. We thank Professor Gary Drobny, Jeff Bryan, Dr. Bernard Santarsiero, and Regan Shea for assistance with this project and Professor Weston Thatcher Borden for helpful dis-

cussions and a critical review of the manuscript.

Supplementary Material Available: Crystal and refinement data, tables of atomic coordinates, temperature factors, and for **1** and **2** bond distances and angles (17 pages); observed and calculated structure factors for **1** and **2** (32 pages). Ordering information is given on any current masthead page.

A New Route to Trimethylsilylated Spherosilicates: Synthesis and Structure of [Si₁₂O₁₈](OSiMe₃)₁₂, D_{3h}-[Si₁₄O₂₁](OSiMe₃)₁₄, and C_{2v}-[Si₁₄O₂₁](OSiMe₃)₁₄

P. A. Agaskar,^{1a} V. W. Day,^{*1b} and W. G. Klemperer^{*1a}

Department of Chemistry and
Materials Research Laboratory, University of Illinois
Urbana, Illinois 61801
Crystallitics Company
Lincoln, Nebraska 68501

Received February 9, 1987

Molecular polyhedral silicates (spherosilicates) whose anionic oxygen atoms have been protected by trimethylsilyl groups are convenient molecular species for examining the properties of isolated polysilicate cage frameworks.² At present, three such species are known: the trigonal prismatic [Si₆O₉](OSiMe₃)₆,³ cubic [Si₈O₁₂](OSiMe₃)₈,⁴ and pentagonal prismatic [Si₁₀O₁₅](OSiMe₃)₁₀⁵ molecules. The family of trimethylsilylated spherosilicates (Me₃SiOSiO_{1.5})_n has been restricted to $n = 6, 8,$ and 10 for purely practical reasons. These materials are prepared by trimethylsilylation of the silicate anions Si_nO_{2.5n}ⁿ⁻, and soluble anions are known only for $n = 6, 8, 4$ and 10 .⁵ We describe here a new route to trimethylsilylated spherosilicates that utilizes hydridosiloxane precursors and report the synthesis, structure, and stability of three new compounds prepared by this route, [Si₁₂O₁₈](OSiMe₃)₁₂, D_{3h}-[Si₁₄O₂₁](OSiMe₃)₁₄, and C_{2v}-[Si₁₄O₂₁](OSiMe₃)₁₄.

Polyhedral hydridosiloxane precursors were isolated from a mixture of species (HSiO_{1.5})_n, $n = 8, 10, 12, 14,$ and 16 , prepared by a method previously described by Frye and Collins.⁶ Gel permeation chromatography was used to obtain a fraction of this material containing largely the $n = 12, 14,$ and 16 species. Crystalline [Si₁₂O₁₈](OSiMe₃)₁₂, **1**, was separated from this mixture by slow evaporation of a saturated pentane solution. When a hot, saturated 4:1 V/V acetonitrile/tetrahydrofuran solution of the residual material was cooled to room temperature, crystalline [Si₁₄O₂₁](OSiMe₃)₁₄, **2**, was obtained. The material remaining was then separated into three fractions by using preparative gas chromatography. The central fraction contained predominantly compound **2** and a second [Si₁₄O₂₁](OSiMe₃)₁₄ isomer,⁸ **3**, according to capillary gas chromatography/mass spectrometry. Following the procedure

(8) (a) Schwarzenbach, G.; Witter, Ch. *Helv. Chim. Acta* **1947**, *30*, 669. (b) Bell, R. P.; Smith, P. W. *J. Chem. Soc. B* **1966**, 241.

(9) Although the MM2P force field is more appropriate for calculations on enols, use of the latter is unlikely to significantly alter these results, see: (a) Dodziuk, H.; von Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811. (b) Biali, S. E.; Meyer, A. Y.; Rappoport, Z.; Yuh, Y. H. *J. Org. Chem.* **1985**, *50*, 3919.

(10) Excluding 1,4-nonbonded interactions.

(11) The calculated dipole-dipole interaction energies should be taken as indicative only, since the magnitude varies inversely with the dielectric of the medium, an unknown quantity; MM2 uses a default dielectric of 1.5. Additionally, MM2 is not adequately parameterized in the dipole-dipole computation to deal with enols.⁹ On the basis of the relative dipole moments of carbonyl (2.6 D) and enol (1.0 D⁸), this term is clearly reduced on enolization.

(12) The available spectroscopic data are at this time insufficient to support or refute the possibility that enol **2** benefits in the solution phase from an intramolecular hydrogen bond to the ether bridge or side chain double bond.

(1) (a) University of Illinois. (b) Crystallitics Company.

(2) Voronkov, M. G.; Lavrent'ev, V. I. *Top. Current Chem.* **1982**, *102*, 199.

(3) (a) Hoebbel, D.; Garzo, G.; Engelhardt, G.; Ebert, R.; Lippmaa, E.; Alla, M. Z. *Anorg. Allg. Chem.* **1980**, *465*, 15. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Sov. Phys. Crystallogr.* **1984**, *29*, 421.

(4) (a) Hoebbel, D.; Wieker, W. Z. *Anorg. Allg. Chem.* **1971**, *384*, 43. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Pomes, R. *Khim. Silik. Oksidov* **1982**, *68*.

(5) Hoebbel, D.; Wieker, W.; Franke, P.; Otto, A. Z. *Anorg. Allg. Chem.* **1975**, *418*, 35.

(6) Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 5586.

(7) For spectroscopic/analytical data, see paragraph at end of paper regarding Supplementary Material.

(8) GC/MS on a 30-m Alltech DB-5 capillary column with a temperature ramp of 3 °C/min from 100 °C to 200 °C and carrier gas He at 15 psig head pressure showed two major components at 23.33 and 23.75 min with m/z 741 (M⁺ - H).

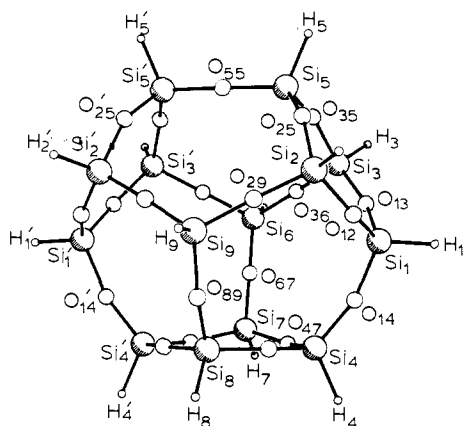


Figure 1. Perspective drawing of the D_{3h} isomer of $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**2**). Silicon atoms are represented by large shaded circles, oxygen atoms by medium-sized open circles, and hydrogen atoms by small open circles. Atoms labeled with a prime (') are related to those without a prime by the crystallographic mirror plane at $z = 1/4$ in unit cell which contains $\text{Si}_6, \text{Si}_7, \text{Si}_8, \text{Si}_9, \text{O}_{55}, \text{O}_{67}, \text{O}_{89}, \text{H}_6, \text{H}_7, \text{H}_8,$ and H_9 .

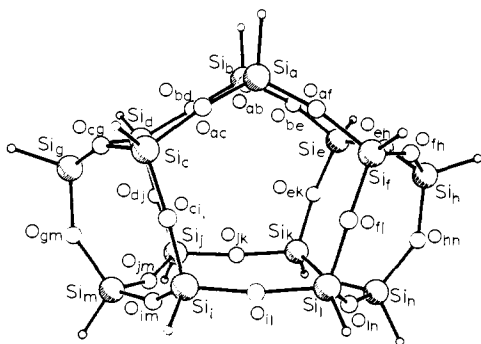
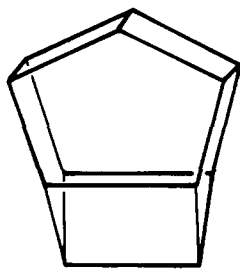


Figure 2. Perspective drawing of the C_{2v} isomer of $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**3**). Silicon atoms are represented by large shaded circles, oxygen atoms by medium-sized open circles and hydrogen atoms by small open circles.

just described, compounds **1** and **2** could be prepared as pure materials on a gram scale, but **3** was obtained only as an approximately 1:1 mixture of **2** and **3**. Single crystals of **3** could be manually separated, however, following crystallization of the mixture by slow evaporation of a pentane solution.

The hydridosiloxanes **1**–**3** have been structurally characterized by using NMR spectroscopy and X-ray crystallography. Compound **1** displays two ^{29}Si NMR resonances⁷ with relative intensities of 1:2 and is assumed to have the C_{2v} polyhedral framework **a** adopted by its phenyl analogue, $[\text{Si}_{12}\text{O}_{18}](\text{C}_6\text{H}_5)_{12}$.⁹

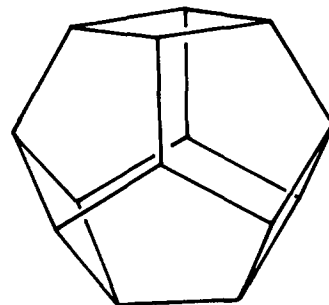


a

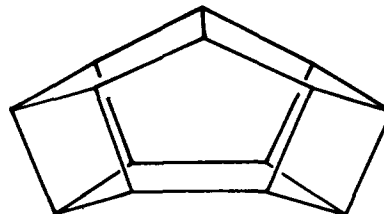
The structures of compounds **2** and **3**, determined by single-crystal X-ray diffraction studies,¹⁰ are shown in Figures 1 and 2, respectively. Compound **2** is seen to have the D_{3h} polyhedral framework **b**, while **3** adopts the less symmetric C_{2v} framework **c**. To the best of our knowledge, neither of these polyhedral frameworks has heretofore been observed in chemical structures.

(9) Clegg, W.; Sheldrick, G. M.; Vater, N. *Acta Crystallogr., Sect. B: Struct. Crystallog. Cryst. Chem.* **1980**, *B36*, 3162.

(10) See paragraph at end of paper regarding Supplementary Material.

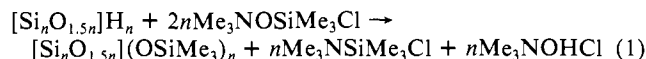


b



c

When tetrahydrofuran solutions of $[\text{Si}_{12}\text{O}_{18}]\text{H}_{12}$ (**1**), D_{3h} - $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**2**), and C_{2v} - $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**3**) are treated with 2 equiv of $\text{Me}_3\text{NOSiMe}_3\text{Cl}$ ¹¹ per hydride group, the corresponding trimethylsiloxy derivatives $[\text{Si}_{12}\text{O}_{18}](\text{OSiMe}_3)_{12}$ (**4**), D_{3h} - $[\text{Si}_{14}\text{O}_{21}](\text{OSiMe}_3)_{14}$ (**5**), and C_{2v} - $[\text{Si}_{14}\text{O}_{21}](\text{OSiMe}_3)_{14}$ (**6**) are obtained in >95% yield following removal of solvent and pentane extraction.⁷ Since this reaction requires 2 equiv of $\text{Me}_3\text{NOSiMe}_3\text{Cl}$ to reach completion, it is believed to proceed as indicated in (1)



According to ^{29}Si NMR spectroscopy,⁷ the conversion of **1**–**3** to **4**–**6** proceeds in each case with preservation of the polyhedral siloxane framework: **4** displays two resonances having equal intensities in both the silicate and trimethylsilyl regions, consistent with structure **a**; **5** displays three resonances in each region with relative intensities of 3:3:1 (see **b**); and **6** displays five resonances in each region with relative intensities of 1:1:2:2:1 (see **c**).

Acknowledgment. This work was supported at the University of Illinois by the U.S. Department of Energy, Division of Material Science, under Contract DE-AC02-76ER01198. Gas chromatographic mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (GM-27029). Dr. Paul Gaus contributed to the initial phases of the GC/MS studies.

Registry No. **1**, 330-26-7; **2**, 109494-91-9; **3**, 109468-83-9; **4**, 109468-84-0; **5**, 109494-92-0; **6**, 109468-85-1; $\text{Me}_3\text{NOSiMe}_3\text{Cl}$, 109468-86-2.

Supplementary Material Available: Crystal structure report for the D_{3h} isomer of $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**2**), Table I (Atomic Coordinates for Non-Hydrogen Atoms in **2**), Table II (Anisotropic Thermal Parameters for Non-Hydrogen Atoms in **2**), Table III (Atomic Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms in **2**), Table IV (Bond Lengths and Bond Angles in **2**), crystal structure report for the C_{2v} isomer of $[\text{Si}_{14}\text{O}_{21}]\text{H}_{14}$ (**3**), Table V (Atomic Coordinates for Non-Hydrogen Atoms in **3**), Table VI (Anisotropic Thermal Parameters for Non-Hydrogen

(11) The adduct $\text{Me}_3\text{NOSiMe}_3\text{Cl}$ was prepared by reacting anhydrous Me_3NO with excess Me_3SiCl in tetrahydrofuran for 30 min and then removing solvent and excess Me_3SiCl under vacuum. Anal. Calcd for $\text{C}_6\text{H}_{18}\text{NClOSi}$: C, 39.22; H, 9.87. Found: C, 39.03; H, 9.88. cf. (a) Graddon, D. P.; Rana, B. A. *J. Organomet. Chem.* **1977**, *140*, 21. (b) Issleib, K.; Reinhold, H. *Z. Anorg. Allg. Chem.* **1962**, *314*, 113.

Atoms in 3), Table VII (Atomic Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms in 3), Table VIII (Bond Lengths and Bond Angles in 3), and spectral/analytical data for compounds 1, 2, 4, 5, and 6 (23 pages); structure factor amplitude tables for 2 and 3 (18 pages). Ordering information is given on any current masthead page.

Synthesis of Boron Nitride Ceramics from Poly(borazinylamine) Precursors

Chaitanya K. Narula, Riley Schaeffer, and Robert T. Paine*

Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

Abhaya Datye

Department of Chemical Engineering
University of New Mexico
Albuquerque, New Mexico 87131

William F. Hammett

Sandia National Laboratory
Albuquerque, New Mexico 87185

Received April 20, 1987

Several simple monomeric boron and nitrogen reagents have been utilized as starting materials in high-temperature pyrolyses or chemical vapor deposition schemes to prepare hexagonal boron nitride.^{1,2} However, extensive applications and demands for new forms (films, gels, foams, fibers) have recently led to searches for improved syntheses and processing techniques for BN. Polymeric precursors might offer alternate low-energy syntheses of BN,³ but, unfortunately, the oligomer and polymer chemistry of boron-nitrogen compounds is not well developed.⁴ Several substituted borazenes have been examined as BN precursors;⁴⁻⁶ however, recent thorough studies indicate that carbon-contaminated, boron-rich materials are typically obtained from pyrolyses of these reagents.^{7,8} Nevertheless, the proposed mechanism for borazene thermal condensation^{4h,8} and chemistry for organoborazinylamines reported by Meller and co-workers⁹ suggest that amino cross-linked borazenes, without organic substituent groups, might lead to oligomeric gel precursors for pure boron nitride. Furthermore,

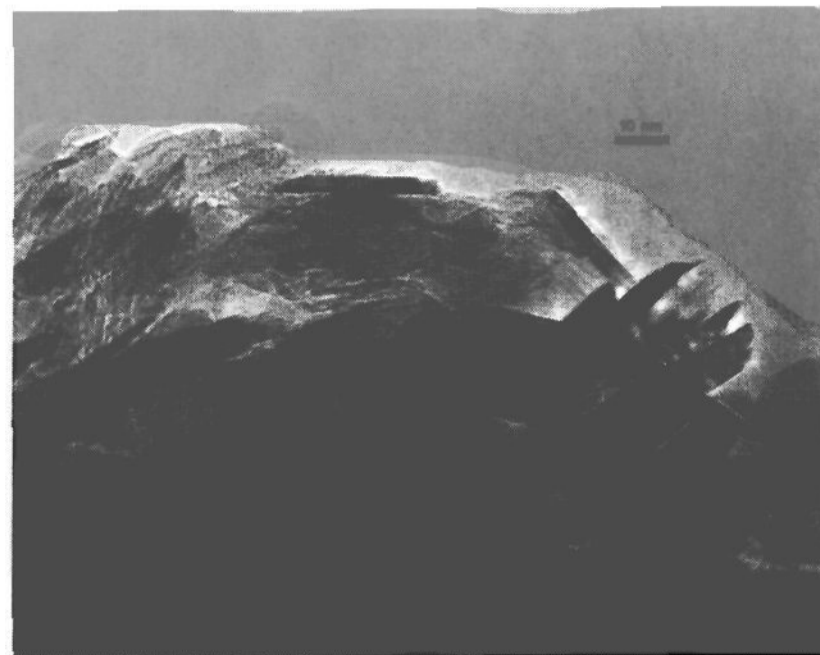
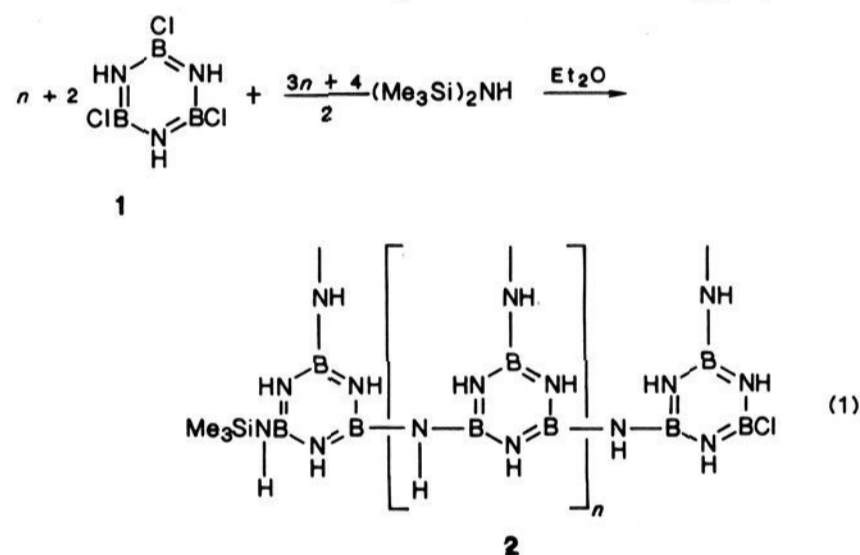


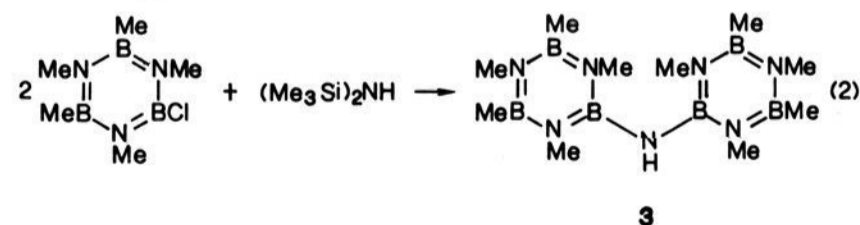
Figure 1. Transmission electron micrograph of sample 5.

such a synthesis should lend itself to modern nonaqueous sol-gel processing techniques.¹⁰

In a typical experiment, trichloroborazene 1 (10.4 g, 56.5 mmol) in dry diethyl ether (100 mL) is cooled to $-78\text{ }^{\circ}\text{C}$, and hexamethyldisilazane (17.7 g, 84.9 mmol) is added. The mixture is agitated and allowed to warm slowly to $25\text{ }^{\circ}\text{C}$ (2 h). A white gel is isolated by vacuum evaporation of the solvent and Me_3SiCl . The reaction is outlined in eq 1. This cross-linking proposal is



supported by model reactions with substituted borazenes (eq 2), in which bis(pentamethylborazinyl)amine (3) is isolated.¹¹ The gel 2 would be expected to have a N/B ratio of 1.5 with small amounts of C, Si, and Cl present in oligomer-capping groups. Indeed, elemental analyses¹² indicate a partial formula $\text{BN}_{1.49}\text{Cl}_{0.06}\text{Si}_{0.09}$.



The infrared spectrum of 2 is similar to a spectrum of 1¹³ except that $\nu_{\text{B-Cl}}$, 741 cm^{-1} , present for 1, is absent in 2. Thermogravi-

(1) Balmain, J. J. *Prakt. Chem.* 1982, 27, 422.

(2) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds* 1974, 13, 1; first supplement 1980, 2, 1; second supplement 1983, 1, 304.

(3) Wynne, K. J.; Rice, R. W. *Ann. Rev. Mater. Sci.* 1984, 14, 297 and references therein.

(4) The majority of this chemistry is summarized in the following: (a) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975. (b) Steinberg, H.; Brotherton, R. J. *Organoboron Chemistry*; Wiley: New York, 1966; Vol. 2. (c) Lappert, M. F. *Developments in Inorganic Polymer Chemistry*; Lappert, M. F., Leigh, G. J., Eds.; Elsevier: New York, 1962; p 20. (d) Lappert, M. F. *Proc. Chem. Soc.* 1959, 59. (e) Aubrey, D. W. *J. Chem. Soc.* 1959, 2927. (f) Laubengayer, A. W.; Moews, P. C.; Porter, R. F. *J. Am. Chem. Soc.* 1961, 83, 1337. (g) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* 1962, 1, 99. (h) Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* 1963, 2, 29.

(5) Taniguchi, I.; Harada, K.; Maeda, T. *Jpn. Kokai* 7653 000, 1976; *Chem. Abstr.* 1976, 85, 96582v.

(6) Constant, G.; Feurer, R. J. *Less-Common Met.* 1981, 82, 113.

(7) Bender, B. A.; Rice, R. W.; Spann, J. R. *Ceram. Eng. Sci. Proc.* 1985, 6, 1171.

(8) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Smythe, M. E.; Kimble, P. F. U.S. Patent 4581 468, 1986. Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci.* 1986, 24, 173.

(9) (a) Gutmann, V.; Meller, A.; Schlegel, R. *Monatsh. Chem.* 1963, 94, 1071. Gutmann, V.; Meller, A.; Schlegel, R. *Monatsh. Chem.* 1964, 95, 314. Meller, A.; Füllgrabe, H.-J. *Angew. Chem., Intl. Ed. Engl.* 1975, 14, 359. Meller, A.; Füllgrabe, H.-J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1978, 33B, 156. Meller, A.; Füllgrabe, H.-J.; Habben, C. D. *Chem. Ber.* 1979, 112, 1252.

(10) The term sol-gel processing refers to the method of preparing glasses or ceramics from the chemical conversion (usually solvolysis) of an appropriate precursor. For example, the alcohol conversion of silicon tetraalkoxides produces a sol, then a gel, and finally a glass at temperatures usually well below the temperatures normally employed to make a glass or ceramic product. Brinker, C. J.; Drotning, W. D.; Sherer, G. W. *Mat. Res. Soc. Symp. Proc.* 1984, 32, 25. Hench, L. L.; Ulrich, D. R. *Ultrastructure Processing of Ceramics, Glasses and Composites*; Wiley: New York, 1984.

(11) Narula, C. K.; Paine, R. T.; Schaeffer, R., Manuscript in preparation.

(12) Elemental Anal. Found: C, 11.07; H, 5.91; B, 24.00; N, 46.53; Cl, 4.92; Si, 5.83.

(13) Meller, A. *Organomet. Chem. Rev.* 1967, 2, 1. Although B-Cl bonds are present in end-capping groups, their number are estimated to be few: B/Cl ~20:1 to 40:1.