J. Am. Chem. Soc. 1993, 115, 3586–3594

1,2-Dimethyl-1,2-disila-*closo*-dodecaborane(12), a Silicon Analog of an *o*-Carborane: Synthesis; X-ray Crystal Structure; NMR, Vibrational, and Photoelectron Spectra; Bonding

Dietmar Seyferth,[*,†] Klaus D. Büchner,[†] William S. Rees, Jr.,[†] Lars Wesemann,[†] William M. Davis,[†] S. S. Bukalov,[‡] Larissa A. Leites,[*,‡] Hans Bock,[*,§] and Bahman Solouki[§]

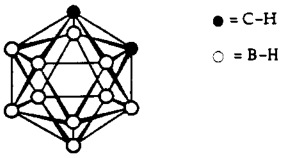
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Institute of Organo-Element Compounds, Russian Academy of Sciences, Moscow 117813, Russia, and Institut für Anorganische Chemie, Universität Frankfurt, W-6000 Frankfurt 50, Germany

Received September 4, 1992

Abstract: The reaction of $(CH_3)_2Si(NMe_2)_2$ with $B_{10}H_{14}$ yields a polymer, $-[B_{10}H_{12}{\cdot}Me_2NSi(CH_3)_2NMe_2-]_n$, whose pyrolysis in a stream of ammonia gives hexagonal boron nitride containing a small amount of silicon nitride. In contrast, $CH_3(H)Si(NMe_2)_2$ reacts with $B_{10}H_{14}$ to give 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) (DMSB), an air-sensitive solid, the structure of whose 1:1 benzene solvate was determined by X-ray diffraction. This compound crystallizes in the space group *Pccn* (#56) with $a = 10.081(1)$ Å, $b = 10.666(8)$ Å, $c = 16.130(5)$ Å, $V = 1734(2)$ Å^3, and $Z = 4$. Final $R = 0.044$ and $R_w = 0.058$. The ^1H, ^{13}C, ^{29}Si, and ^{11}B NMR spectra and mass spectrum of DSMB are reported. Its vibrational spectrum (Raman, 5–3600 cm^{-1}; IR, 200–3600 cm^{-1}) has been measured and compared with that of *o*-carborane. A study of its He(I) photoelectron spectrum led to the conclusion that DMSB is the most electron-rich cluster of type $XYB_{10}H_{10}$ with two adjacent main group element centers known.

Introduction

The icosahedral carboranes were first reported in 1963 and in the intervening years their chemistry has been highly developed.[1] They still are the subject of research today. The so-called *o*-carboranes, in which the two cluster carbon atoms occupy adjacent positions, **1**, have received by far the greatest attention.



1 (*closo*-1,2-$C_2B_{10}H_{12}$ (ortho))

Given the existence and great stability of the *o*-carboranes, one might expect that their silicon, germanium, and tin analogs might also be capable of existence. However, until the present work,[2] there has been no report of such an icosahedral heteroborane. That silicon can occupy a position (together with boron) in such an icosahedral framework was shown by the preparation of stable *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$, which contains a single silicon atom bonded within a 12-atom boron-containing cluster.[3] One reason that sila-, germa-, and stannaboranes had not yet been prepared is the lack of a suitable preparative method. The *o*-carboranes are prepared by reaction of an acetylene with $B_{10}H_{14}$ in the presence of an appropriate Lewis base or of an acetylene with a $B_{10}H_{12}{\cdot}2$ Lewis base adduct.[1] This procedure, for application to the preparation of sila-, germa-, and stannaboranes, requires the respective RM≡MR (M = Si, Ge, Sn) compounds (none of which has been reported to date) or a thermo- or photolabile precursor for such species.

We report here the serendipitous preparation of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) during the course of our investigations on the use of $[B_{10}H_{12}{\cdot}\text{diamine}]_n$ polymers as precursors for boron nitride.

Results and Discussion

1. Background. In earlier work[4] we have prepared a series of $[B_{10}H_{12}{\cdot}\text{diamine}]_n$ polymers (diamine = $H_2NCH_2CH_2NH_2$, $Me_2NCH_2CH_2NMe_2$, $HN(CH_2CH_2)_2NH$, $N(CH_2CH_2)_3N$, etc.) and found that their pyrolysis in a stream of ammonia gave hexagonal boron nitride in high yield and good purity. These polymers were soluble only in polar solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide and they melted with decomposition above 250 °C. These properties made them unsuitable for fiber spinning. In our search for lower melting, more soluble polymers of this general type, we undertook a study of the reactions of $B_{10}H_{14}$ with amino derivatives of silicon of the type $R^1R^2Si(NMe_2)_2$ since aminosilanes are less basic and less nucleophilic than their organic counterparts.[5] This should result in weaker B–N bonding in the polymer chain and, perhaps, greater solubility and a lower melting point. Such a polymer was prepared by reaction of equimolar quantities of $B_{10}H_{14}$ and $(CH_3)_2Si[N(CH_3)_2]_2$ in refluxing benzene (under nitrogen) during 48 h. After filtration and solvent evaporation, a yellow-orange, resinous solid remained in 79% yield. It was found to be very moisture-sensitive and partially soluble in aromatic hydrocarbons and more soluble in DMF and acetonitrile than the $[B_{10}H_{12}{\cdot}\text{diamine}]_n$ polymers. Furthermore, it melted in a lower temperature range. Long fibers could be drawn manually from its melt. Pyrolysis of a bulk sample of this polymer in a stream of ammonia to 1000 °C gave a foamy

---

[†] Massachusetts Institute of Technology.
[‡] Russian Academy of Sciences.
[§] Universität Frankfurt.

(1) (a) *Gmelin Handbook of Inorganic Chemistry*, ed.; Springer: Berlin; Borverbindungen, Vols. 2 (1974), 6 (1975), 11 (1977), 12 (1977) and chapters in the first and second supplements (1980–1983). (b) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970; Chapter 6 and literature cited therein.

(2) Preliminary communication: Seyferth, D.; Büchner, K.; Rees, W. S., Jr.; Davis, W. M. *Angew. Chem.* **1990**, *102*, 911; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 918.

(3) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.*, **1986**, *108*, 5369.

(4) Seyferth, D.; Rees, W. S., Jr. *Chem. Mater.* **1991**, *3*, 1106.

(5) Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960; Chapters 3 and 11.

0002-7863/93/1515-3586$04.00/0

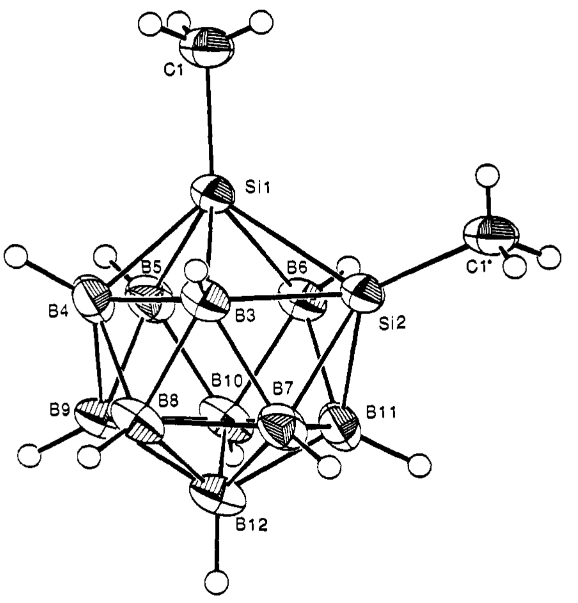


Figure 1. ORTEP representation of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) showing 35% probability ellipsoids. Hydrogen atoms have been given arbitrary thermal parameters for clarity.

Table I. Intramolecular Bond Distances[a]

Si–C(1)	1.827(3)	B(4)–B(9)	1.765(5)	B(5)–B(6)	1.849(5)
Si–B(5)	2.017(3)	B(4)–B(8)	1.774(5)	B(12)–B(9)	1.775(8)
Si–B(4)	2.018(3)	B(4)–B(3)	1.848(5)	B(12)–B(8)	1.782(5)
Si–B(6)	2.113(4)	B(4)–B(5)	1.859(5)	B(12)–B(10)	1.784(5)
Si–B(3)	2.116(3)	B(5)–B(10)	1.765(5)	B(6)–B(10)	1.771(4)
Si(1)–Si(2)	2.308(2)	B(5)–B(9)	1.769(5)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

white solid in 89% yield, which on the basis of elemental analysis was composed of 95 wt % BN and 3.6 wt % Si_3N_4. The carbon content was only 0.6%.[6] The only crystalline phase observed by powder X-ray diffraction was hexagonal BN. Pyrolysis of the polymer in a stream of argon to 1500 °C gave a black solid that contained 19.4% C.

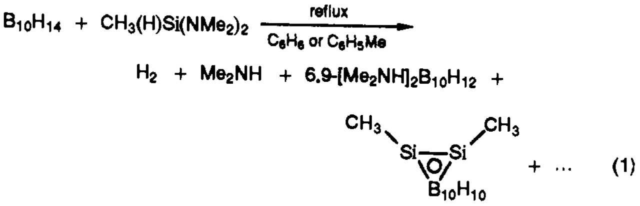
A similar polymer was prepared using $(CH_3)(CH_2{=}CH)Si[N(CH_3)_2]_2$. However, when $CH_3(H)Si[N(CH_3)_2]_2$ was the aminosilane used in a 1:1 reaction with $B_{10}H_{14}$ in refluxing toluene, the reaction proceeded differently in that during the 24-h reflux period a white solid precipitated. After filtration and removal of volatiles from the filtrate, extraction of the residue with benzene was followed by cooling and then evaporation of the benzene extracts to leave a white solid which was not immediately identified. The initial precipitate was found to contain 6,9-$[(CH_3)_2NH]_2B_{10}H_{12}$ as the major component.

2. Isolation and Characterization of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane (12). With the major product having been identified as 6,9-$[(CH_3)_2NH]_2B_{10}H_{12}$, it was of interest to determine what the other product of the reaction was since it very likely contained the silicon portion of the $CH_3(H)Si[N(CH_3)_2]_2$ reactant. Very slow crystallization of the unknown white solid from dilute benzene solution at 3 °C gave rod-shaped crystals whose structure was determined by single-crystal X-ray diffraction. The result is shown in Figure 1: the other product is the silicon analog of 1,2-dimethyl-*o*-carborane, a "silaborane", 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12) (or 1,2-dimethyl-*o*-silaborane, DMSB), isolated as the 1:1 benzene solvate, eq 1. Observed bond distances and bond angles are given in Tables I and II, respectively. In eq 1 DMSB is shown in a simplified line drawing of the type commonly used to picture *o*-carboranes.

Table II. Intramolecular Bond Angles[a]

C(1)–Si(1)–B(5)	129.5(1)	B(6)–B(5)–Si(1)	66.1(1)
C(1)–Si(1)–B(4)	129.1(2)	B(4)–B(5)–Si(1)	62.6(1)
C(1)–Si(1)–B(6)	129.8(1)	B(11)–B(12)–B(7)	63.5(2)
C(1)–Si(1)–B(3)	128.9(1)	B(11)–B(12)–B(9)	109.3(2)
C(1)–Si(1)–Si(2)	124.3(1)	B(11)–B(12)–B(8)	110.4(2)
B(5)–Si(1)–B(4)	54.9(1)	B(11)–B(12)–B(10)	60.0(2)
B(5)–Si(1)–B(6)	53.1(1)	B(7)–B(12)–B(9)	109.1(2)
B(5)–Si(1)–B(3)	94.6(1)	B(7)–B(12)–B(8)	59.6(2)
B(5)–Si(1)–Si(2)	99.1(1)	B(7)–B(12)–B(10)	110.6(2)
B(4)–Si(1)–B(6)	94.6(1)	B(9)–B(12)–B(8)	60.2(2)
B(4)–Si(1)–B(3)	53.0(1)	B(9)–B(12)–B(10)	60.1(2)
B(4)–Si(1)–Si(2)	98.9(1)	B(8)–B(12)–B(10)	108.5(2)
B(6)–Si(1)–B(3)	95.3(1)	B(10)–B(6)–B(4)	58.6(2)
B(6)–Si(1)–Si(2)	57.0(1)	B(10)–B(6)–B(5)	58.3(2)
B(3)–Si(1)–Si(2)	56.9(1)	B(10)–B(6)–Si(1)	110.1(2)
B(9)–B(4)–B(8)	60.5(2)	B(10)–B(6)–Si(2)	110.3(2)
B(9)–B(4)–B(3)	108.2(2)	B(11)–B(6)–B(5)	105.2(2)
B(9)–B(4)–B(5)	58.4(2)	B(11)–B(6)–Si(1)	112.2(2)
B(9)–B(4)–Si(1)	113.1(2)	B(11)–B(6)–Si(2)	60.7(1)
B(8)–B(4)–B(3)	58.5(2)	B(5)–B(6)–Si(1)	60.8(2)
B(8)–B(4)–B(5)	107.0(2)	B(5)–B(6)–Si(2)	112.2(2)
B(8)–B(4)–Si(1)	114.8(2)	Si(1)–B(6)–Si(2)	66.1(1)
B(3)–B(4)–B(5)	110.1(2)	B(7)–B(8)–B(3)	63.1(2)
B(3)–B(4)–Si(1)	66.2(1)	B(7)–B(8)–B(4)	112.2(2)
B(5)–B(4)–Si(1)	62.6(1)	B(7)–B(8)–B(12)	59.8(2)
B(10)–B(5)–B(9)	60.5(2)	B(7)–B(8)–B(9)	108.9(3)
B(10)–B(5)–B(6)	58.6(2)	B(3)–B(8)–B(4)	62.9(2)
B(10)–B(5)–B(4)	106.9(2)	B(3)–B(8)–B(12)	111.1(2)
B(10)–B(5)–Si(1)	114.9(2)	B(3)–B(8)–B(9)	110.9(2)
B(9)–B(5)–B(6)	108.1(2)	B(4)–B(8)–B(12)	108.6(3)
B(9)–B(5)–B(4)	58.2(2)	B(4)–B(8)–B(9)	59.5(2)
B(9)–B(5)–Si(1)	113.0(2)	B(12)–B(8)–B(9)	59.7(2)
B(6)–B(5)–B(4)	109.9(2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.



(1)

Like the *o*-carboranes, DMSB has a slightly distorted icosahedral structure. In contrast to the *o*-carboranes, in which the C–C bond is longer (1.655 Å, on the average[7]) than the normal C(sp³)–C(sp³) distance of 1.54 Å, the Si–Si bond distance in DMSB, 2.308(2) Å, is only slightly less than that of normal Si(sp³)–Si(sp³) single bonds (2.33–2.34 Å[8]). The Si–B bond distances in the DMSB (Table I) are very close to the sum of the covalent radii of Si and B, 2.07 Å,[9] and they are very close also to the Si–B bond distances of 2.05(1) and 2.14(1) Å in *commo*-3,3′-$Si(3,1,2\text{-}SiC_2B_9H_{11})_2$.[3]

NMR spectra involving all nuclei present in DMSB were recorded. Its ^{11}B NMR spectrum, taken in acetone-d_6 solution, showed the expected four doublets in a 2:1:1:1 ratio of δ_B −14.65, −13.61, −12.79, and −11.27 ppm. In a ^{11}B NMR spectrum in methanol-d_4 solution these resonances occurred at δ_B −14.95, −14.15, −13.00, and −11.46 ppm, and in a spectrum taken in C_6D_6 solution only three resonances were observed at δ_B −14.76, −11.87, and −10.49 ppm in a 3:1:1 intensity ratio. The CH_3 singlet, seen at δ −0.07 in the ^1H NMR spectrum of DMSB in C_6D_6 solution, moved downfield as the solvent polarity was increased: to 1.13 ppm in methanol-d_4, to 1.24 ppm in THF-d_8, and to 1.34 ppm in acetone-d_6. The proton-decoupled ^{29}Si NMR spectrum of DMSB in C_6D_6 solution at 50 °C showed a singlet at δ_{Si} −37.8 ppm, the proton-decoupled ^{13}C NMR spectrum, also

---

(6) Seyferth, D.; Rees, W. S., Jr. U.S. Patent 5,026,809 (Jan. 25, 1991).

(7) Mastryukov, V. S.; Vilkov, L. V.; Dorofeeva, O. V. *J. Mol. Struct.* **1975**, *24*, 217.

(8) (a) Beagley, B.; Monaghan, J. J.; Hewis, T. G. *J. Mol. Struct.* **1971**, *8*, 401 (Me_6Si_2: 2.340(9) Å). (b) Carrell, H. L.; Donohue, J. *Acta Crystallogr. Sect. B* **1972**, *28*, 1566 (*cyclo*-$(Me_2Si)_6$: 2.338(4) Å).

(9) Using 0.89 Å as the average B covalent radius in *o*-carboranes: ref 7.

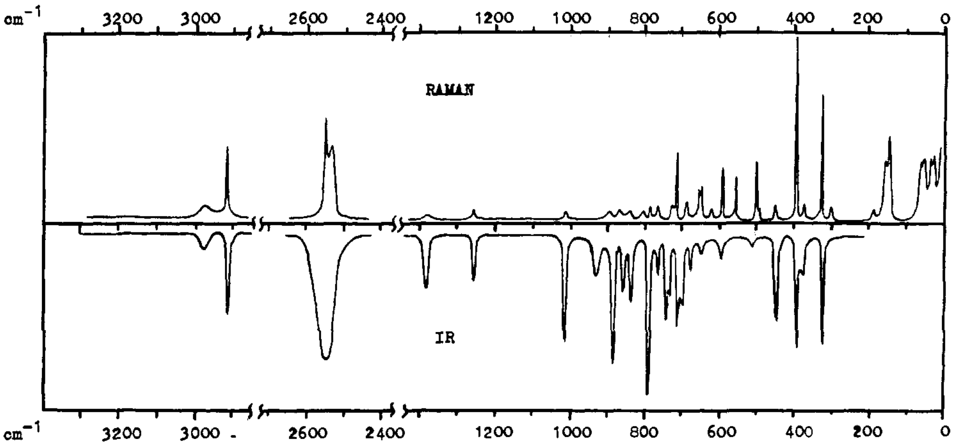


Figure 2. Raman and infrared spectra of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12).

taken in C_6D_6 at 40 °C, and a singlet at δ_C −12.80 ppm. These upfield shifts in the ^1H, ^{13}C, and ^{29}Si NMR spectra of DMSB in C_6D_6 solution, vs $(CH_3)_4Si$, are consistent with the well-documented[1] electron-deficient nature of the boron cages.

DMSB is less stable thermally than the *o*-carboranes but it can be purified by sublimation at 90 °C (0.01 Torr). It melts at 201–203 °C in a sealed capillary and decomposes with gas evolution above 230 °C. Consequently, an *o*-silaborane to *m*-silaborane rearrangement, analogous to the well-known *o*-carborane to *m*-carborane rearrangement, was not observed. Contrary to what was stated in our preliminary communication,[2] DMSB is air-sensitive and is oxidized to form boric acid, especially readily when thin films are exposed to air.

3. Attempts To Improve the Yield of DMSB and To Prepare Other *o*-Silaboranes. The yield of DMSB, as prepared using the original procedure, was on the order of 15%, based on $B_{10}H_{14}$, and the yield of 6,9-$[(CH_3)_2NH]_2B_{10}H_{12}$ was 58%. A number of variants of this procedure were tried, but the only one which gave an improved yield (25%) of DMSB was one in which no solvent was used. This reaction must be carried out with care, since heating the neat reactants at 80 °C for a few minutes resulted in a vigorous gas evolution.

The attempted preparation of other silaboranes met with only limited success. A reaction of $B_{10}H_{14}$ with $Ph(H)Si[N(CH_3)_2]_2$ in refluxing toluene solution gave 6,9-$[(CH_3)_2NH]_2B_{10}H_{12}$ as the major product and a white solid, 1,2-diphenyl-1,2-disila-*closo*-dodecaborane(12), in 14% yield. This product was less stable than the dimethylsilaborane; it decomposed on attempted sublimation at 120 °C at 5×10^{-4} Torr. Its solutions were very air-sensitive. The EI mass spectrum, when the sample was not heated above 100 °C, showed highest mass peaks at *m/z* 327.2 (100), 328.3 (94.3), 329.2 (66.6), 330.2 (35.2), 331.3 (10.9), and 332.2 (4.9) ($(C_6H_5)_2{}^{28}Si_2{}^{11}B_{10}H_{10}$ = 330.28). The ^{11}B NMR spectrum (in C_6D_6) showed the expected doublets at −14.38 (J = 147 Hz), −11.41 ($J \sim$ 103 Hz), and −10.73 ppm ($J \sim$ 139 Hz) in a 3:1:1 integrated intensity ratio. Although these data are in agreement with the 1,2-diphenyl-*o*-silaborane formulation, a satisfactory analysis could not be obtained for a sample which had been recrystallized from toluene.

Attempted preparation of 1,2-diethyl-*o*-silaborane by reaction of $Et(H)Si(NMe_2)_2$ with $B_{10}H_{14}$ in toluene at reflux gave a precipitate of 6,9-$(Me_2NH)_2B_{10}H_{12}$ and a solution that contained more of the Me_2NH-decaborane(14) adduct and, apparently, the desired $Et_2Si_2B_{10}H_{10}$ (^{11}B NMR doublets at −14.92, −11.88, and −10.66 ppm (in C_6D_6)) as well. However, this mixture could not be resolved.

4. Reactivity of 1,2-Dimethyl-*o*-silaborane. If the CH_3 substituents of DMSB could be replaced by Cl or Br, then a reactive derivative would be in hand whose Si–halogen bond reactions would allow broad development of the silicon-functional chemistry of the *o*-silaboranes. However, DMSB was surprisingly resistant to all attempts to effect Si–CH_3 cleavage by literature procedures that had been applied to the demethylation of simple methylsilicon compounds. Thus the $Me_3SiCl/AlCl_3$ reagent,[10] neat, in CH_2Cl_2, or in $CHCl_3$ at reflux for up to 10 h, was without effect on DMSB, as was the $Me_3SiCl/AlBr_3$ reagent in refluxing $CHCl_3$ solution. Equally unreactive was the $HCl/AlCl_3$ (or $AlBr_3$) reagent,[11] as was the $CF_3SO_3H/AlCl_3$ reagent. No reaction occurred when a solution of DMSB and CF_3CO_2H in THF was heated at reflux for several hours. On the other hand, the action of ethanolic KOH resulted in immediate decomposition of the silaborane. While refluxing a solution of DMSB in aqueous THF was without effect, when a few drops of glacial acetic acid was added, a slow decomposition, which (by ^{11}B NMR) gave $B_{10}H_{14}$, occurred. Addition of KOH to a wet THF solution of the silaborane resulted in rapid decomposition.

5. The Vibrational Spectrum of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane (12). In view of the well-developed vibrational spectroscopy of icosahedral boron species,[12] in particular, of the dodecaborate anion, $[B_{12}H_{12}]^{2-}$,[13] and *o*-carborane, $C_2B_{10}H_{12}$,[14] it was of interest to measure the vibrational spectrum of DMSB. Its Raman spectrum in the region 5–3600 cm$^-$ was obtained for the solid sample at different temperatures; polarization measurements of Raman lines were carried out for its saturated solution in benzene. The IR spectrum of a thin film sublimed onto a cold target of the cryostat was measured in the region 200–3600 cm^{-1}. The results obtained are presented in Figure 2 and Table III.

The DMSB molecule belongs to the C_{2v} symmetry point group. The 66 normal vibrations of the $B_{10}H_{10}(SiC)_2$ moiety are distributed among the symmetry species as follows:

$$\Gamma = 21A_1 + 13A_2 + 16B_1 + 16B_2$$

All these species should be active in the Raman and all but A_2 in the IR. In fact, as is seen from Figure 2, almost all Raman lines have their IR counterparts. This is in contrast to *o*-carborane, which belongs formally to the same point group, C_{2v}, and has the same selection rules but whose spectrum really obeys the higher effective symmetry of an average icosahedron.

The most prominent features of the vibrational spectra of all *closo*-boranes are the ν(BH) multiplet in the region 2400–2600

---

[10] Bacqué, E.; Pillot, J.-P.; Birot, M.; Dunoguès, J. *Macromolecules* **1988**, *10*, 30 and references cited therein.

[11] Ishikawa, M.; Kumada, M. *Syn. Inorg. Metal-Org. Chem.* **1971**, *1*, 191.

[12] Leites, L. A. *Chem. Rev.* **1992**, *92*, 279.

[13] Leites, L. A.; Bukalov, S. S.; Kurbakova, A. P.; Kagansky, M. M.; Gaft, Yu. L.; Kuznetsov, N. T.; Zakharova, I. A. *Spectrochim. Acta* **1982**, *38A*, 1047.

[14] (a) Leites, L. A.; Vinogradova, L. E.; Alexanyan, V. T.; Bukalov, S. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2480. (b) Bukalov, S. S.; Leites, L. A. *Chem. Phys. Lett.* **1982**, *87*, 327.

Table III. Vibrational Spectrum of $B_{10}H_{10}(SiMe)_2$

Raman			IR
solid sample $\Delta\nu$, cm^{-1}	solution in benzene $\Delta\nu$, cm^{-1}	solution in benzene ρ	vacuum sublimation on a cold target ν, cm^{-1}
152 m			
186 sh			
306 w			304 w
329 s	326	0.80	328 s
379 vw			379 sh
400 vs	399	0.28	397 s
449 w			448 s
503 m	504	0.12	503 w
550 m	552	0.62	
587 m			578 w
610 w			610 vw
645 m		p	659 w
686 w			689 w
716 s	713	0.03	718 m
758 w			752 sh
			759 m
773 w			775 w
792 w			793 νs
841 w			848 m
860 w			862 w
895 w			886 s
920 w			916
			957 w
1010 w			1010 νs
1260 w			1246 w
1392 w			1395 m
2547 s	2549	0.16	2548 νs
2556 νs			
2913 m			2908 s
2994 w bp			2991 w br

cm^{-1} and the polyhedron "breathing" mode near 750 cm^{-1}. In the case of DMSB the ν(BH) multiplet is centered near 2550 cm^{-1} and the "breathing" mode at 715 cm^{-1}, both features being markedly shifted to lower frequencies compared to *o*-carborane. These modes being well-localized, this shift indicates a weakening of molecular bonding in DMSB as compared to that in *o*-carborane. However, the ν(BH) band of DMSB is shifted to higher frequencies if compared to the average ν(BH) frequency, 2480 cm^{-1}, of the $[B_{12}H_{12}]^{2-}$ anion.

The most striking difference between the spectrum of DMSB and those of $[B_{12}H_{12}]^{2-}$ and o-$C_2B_{10}H_{12}$ is the presence in the former of low-frequency modes, equally intense in the Raman and IR spectra. The most intense in the Raman spectrum is the strongly polarized narrow line at 399 cm^{-1}. Its frequency coincides with that of ν(Si–Si) mode of hexamethyldisilane.[15] Thus it seems reasonable to assign this line to the Si–Si stretching mode. However, this assignment is tentative and needs to be proved by a normal coordinate analysis, because a heavily mixed origin of this mode cannot be excluded.

It is evident that all the rest of the low-frequency bands of DMSB are associated with participation of the silicon atoms in the cage motions, because the spectra of the rigid $[B_{12}H_{12}]^{2-}$ and $C_2B_{10}H_{12}$ polyhedra exhibit no bands with frequencies lower than 450 cm^{-1}.

The polarized Raman line at 640 cm^{-1} seems to correspond to the symmetrical stretch of the exo-polyhedral Si–C bonds; its frequency lies in the usual range and is close to that of the Si–C bonds in $(CH_3)_3SiCl$.[16] The frequencies of the internal vibrations of the methyl groups attached to the silicon atoms, i.e., 1260, 1395, 2913, and 2993 cm^{-1}, also are much the same as those in the spectra of the methylchlorosilanes, in particular, CH_3SiCl_3,[16] which is in accord with the well-known electron-deficient nature of the *closo*-borane cage.

The DMSB molecule obviously is "globular", in the sense of Timmermans.[17] However, unlike icosahedral carboranes,[14,18] this substance does not form a plastic phase at room temperature, which is evident from the presence of the lattice modes in the low-frequency region of its Raman spectrum (Figure 2).[19] Heating of the substance to 70 °C revealed no phase transition to a plastic phase in this temperature interval.

6. The He(I) Photoelectron Spectrum of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane and Its Koopmans' Assignment by MNDO Calculations. A variety of icosahedral 1,2-dihetero-*closo*-dodecaboranes ($XYB_{10}H_{10}$, with XY = HC–CH,[21,22] HC–P/As/Sb,[21] and As–As[21]) have been investigated PE spectroscopically. For the assignment of their ionization patterns via Koopmans' theorem, $\mathrm{IE}_n^v = -\epsilon_J^{SCF}$,[23] MNDO calculations yield satisfactory agreement and, therefore, are recommended.[21] The He(I) photoelectron spectrum of the title compound (Figure 3) can be recorded at 10^{-5} mbar pressure using a heated inlet system and is of interest due to the two silicon centers of low effective nuclear charge.

Following the literature assignment[21] for the *closo*-dodecaborane(12) framework,[21] in addition to 13 cluster and 10 BH ionizations another 14 are expected for the two H_3CSi subunits. On the basis of the relative band intensities (Figure 3), about 25 with predominant atomic orbital contributions $2s,p_B$, $1s_H,3P_{Si}$, and 2_{PC} are observed within the He(I) measurement region. The geometry-optimized MNDO calculations (Table IV) further suggest that the ionizations of lowest energy (Table IV) again[21] can be grouped into nine cluster-type ones within the band hill between 9.5 and 10.5 eV, five of BH and SiC character within the bands overlapping between 12 and 13.5 eV, as well as another five of predominant BH and CH contributions within the double band region between 14 and 16 eV (Figure 3). The next MNDO eigenvalue is calculated at 17.4 eV and, therefore, predicts, in agreement with the PE spectroscopically recorded intensities, a gap of 1.6 eV to the following band. Although the overall PES band pattern is satisfactorily reproduced by the Koopmans' correlation $\mathrm{IE}_{1-19}^v = \epsilon_{J_{1-19}}^{MNDO}$, however, considerable Koopmans' defects $\epsilon_J^{MNDO} - \mathrm{IE}_n^v \approx 1.5$ eV result (Table IV). They indicate that the sequence of the individual radical cation states assigned within the three ionization regions has to be viewed with some caution.

A comparison with the respective ionizations of the 1,2-carborane[21,22] (Table IV) demonstrates that on replacement of the cluster subunits CH by $SiCH_3$ all three ionization regions are shifted to lower energies by at least 1.5 eV. For radical cation states with large Si contribution such as the first one (Figure 3: cluster σ_{SiSi} ($12a_1$) orbital diagram), eigenvalue differences of even 1.9 eV are calculated (Table IV: $10a_1$). These observations can be traced to the considerable decrease in effective nuclear charge from carbon to silicon centers as represented by the first vertical ionization energies of the atoms (Scheme I). Accordingly, silicon cluster subunits $Si–CH_3$ are expected to act as electron donors even to the surrounding B(H) centers. This assumption is substantiated by the calculated MNDO charge distributions for both 1,2-carborane and the title compound (Scheme II).

---

(15) Fontal, B.; Spiro, T. G. *Inorg. Chem.* **1971**, *10*, 9.

(16) Dernova, V. S.; Kovalev, I. F. *Kolebatelye Spektry Soedinenii Elementov IVB Gruppy* (Vibrational Spectra of Compounds of Group IVB Elements); Saratov University Press, 1979; p 154.

(17) Timmermans, J. *J. Chem. Phys.* **1938**, *36*, 331.

(18) Leites, L. A.; Bukalov, S. S. *J. Raman Spectrosc.* **1978**, *7*, 235; **1983**, *14*, 210.

(19) Bukalov, S. S.; Leites, L. A. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1989**, *53*, 1715.

(20) Washburne, S. S.; Peterson, W. R., Jr. *J. Organomet. Chem.* **1970**, *21*, 59.

(21) Brint, P.; Sangchakr, B.; McGrath, M.; Spalding, T. R.; Suffolk, R. J. *Inorg. Chem.* **1990**, *29*, 47 and references cited therein.

(22) Vondrak, T. *Polyhedron* **1987**, *6*, 1559 and references cited therein.

(23) Cf., e.g.: Bock, H. The Photoelectron Spectra of Boron-Nitrogen Compounds. In *Gmelin Handbuch der Anorganischen Chemie*; Springer: Berlin, 1975; Erg.-Werk, 8. Aufl., Band. 23, Borverbindungen, Tl. 5, pp 170–196.

(24) Cf. the following review: Bock, H. Molecular States of Silicon-Containing Molecules. *Angew. Chem.* **1989**, *101*, 1659; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627 and references cited therein.

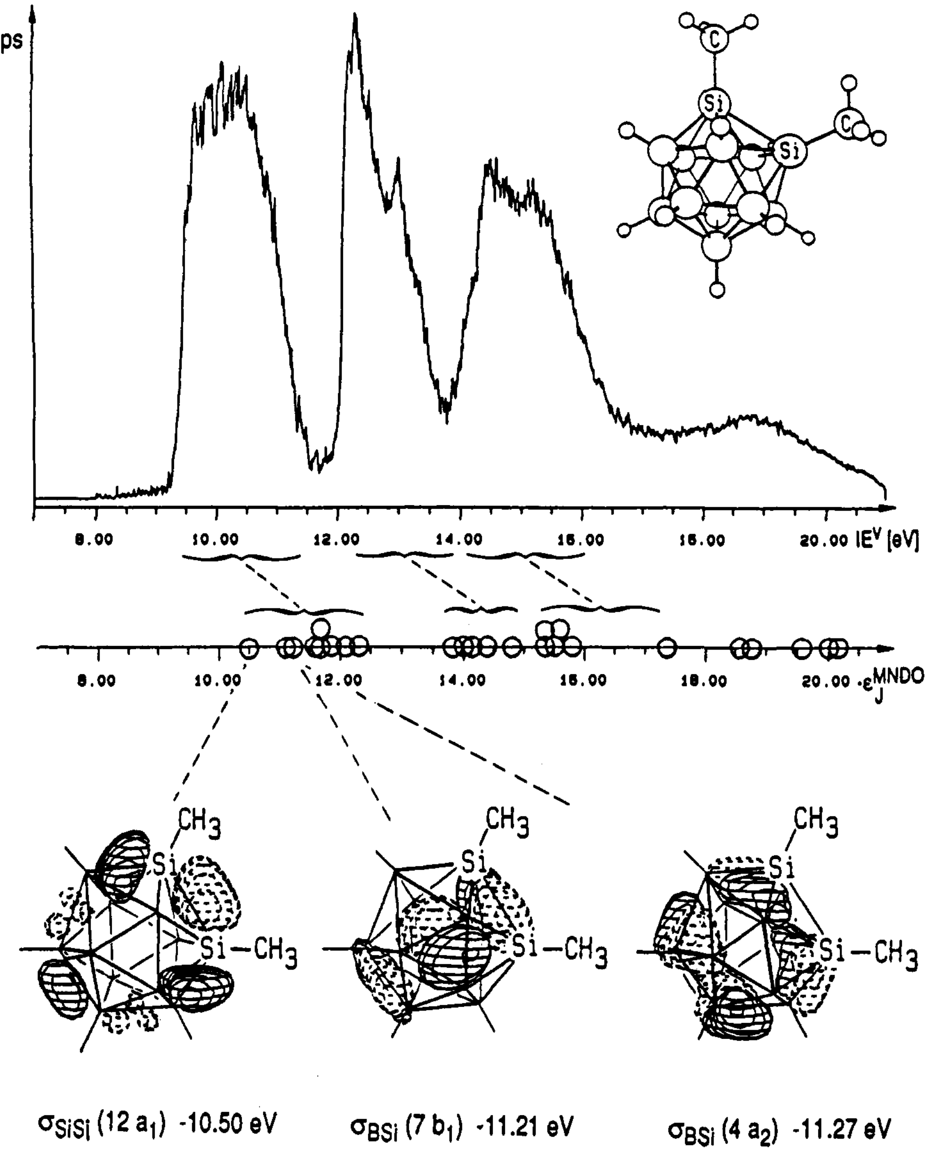


Figure 3. He(I) photoelectron spectrum of 1,2-dimethyl-1,2-*closo*-dodecaborane(12) DMSb with Koopmans' assignment by MNDO eigenvalues and cluster orbital diagrams for the three radical cation states of lowest energy.

Although the parameter-dependent MNDO charges for the individual centers should not be overemphasized, the overall effect of replacing the HC–CH group by $(H_3C)Si–Si(CH_3)$ clearly is a considerable increase of the electron density within the $(BH)_{10}$ cluster framework and thus provides a plausible explanation for the PE spectroscopically observed considerable shift of the three separated bands to lower energy (Figure 3 and Table IV).

The title compound, 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12), which exhibits in its PE spectrum at about only 9.5 eV the lowest ionization onset observed so far for analogous compounds,[21,22] therefore, may be viewed as being presently the most electron-rich cluster $XYB_{10}H_{10}$ known with two adjacent main group element centers.

7. Possible Mechanism of Formation of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane. The observed formation of DMSB as one product of the reaction of $B_{10}H_{14}$ with $CH_3(H)Si[N(CH_3)_2]_2$ was unexpected and its mechanism of formation cannot be simple and straightforward. A rationalization of its formation is made difficult by the absence of other examples of comparable reactivity. However, a reaction course that results in formation of DMSB may be postulated.

Undoubtedly, the initial step in this reaction (eq 1) is the addition of two molar equiv of $CH_3(H)Si[N(CH_3)_2]_2$, a Lewis base, to *nido*-$B_{10}H_{14}$ which generates, via loss of H_2, an adduct of the well-known type *arachno*-6,9-$B_{10}H_{12}\cdot 2L$.[25] In the present case, L = $CH_3(H)Si[N(CH_3)_2]_2$. The boron atoms of the B_{12} cage remain fixed in their polyhedral arrangement during this net 2-electron cluster expansion. The only significant atomic displacement between the reactant and product is the relocation of the B–H–B three-center, two-electron "saddle" bridge bonds (Scheme I).

Subsequent to the formation of the $B_{10}H_{12}\cdot 2L$ adduct, deprotonation of the acidic B–H–B units by intramolecular attack by the lone electron pair of the free $(CH_3)_2N$ group of the $CH_3(H)Si[N(CH_3)_2]_2$ ligand would yield a transient zwitterionic intermediate whose anion and cation are respectively the deprotonated boron cage and the $(CH_3)_2H^+NSi(H)CH_3$ group derived from protonation of the free $(CH_3)_2NSi(H)CH_3$ group. Such deprotonation of $B_{10}H_{12}\cdot 2L$ adducts has ample precedent.[25,26] Aminosilanes, although only weakly basic, are sufficiently basic to effect such deprotonation.[5,27] Rapid expulsion of neutral $(CH_3)_2NH$ from the $(CH_3)_2H^+NSi(H)CH_3$ group and stabilization of the resulting incipient $CH_3(H)Si^+$

---

[25] *Gmelin Handbook of Inorganic Chemistry*, 8th ed., New Supplement Ser. Vol 54, Boron Compounds, Part 20; Springer: Berlin, 1979; pp 151–165 (review of $B_{10}H_{12}\cdot 2L$ compounds).

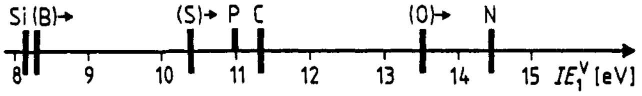
[26] Hawthorne, M. F.; Pittochelli, A. R. *J. Am. Chem. Soc.* **1962**, *84*, 1057.

[27] Aylett, B. J.; Peterson, L. K. *J. Chem. Soc.* **1965**, 4043.

Table IV. Comparison of the Vertical Ionization Energies(IE_n^v (eV)) of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane(12) and the Corresponding 1,2-Carborane Based on the Geometry-Optimized MNDO Eigenvalues ($-\epsilon_J^{MNDO}$) below 16 eV, Including Those for $H_2Si_2B_{10}H_{10}$, and on the Irreducible Representations (Ψ_J) for the Individual Radical Cation States

$(H_3C)_2Si_2B_{10}H_{10}$			$H_2Si_2B_{10}H_{10}$		$H_2C_2B_{10}H_{10}$		
IE_n^v(eV)	$-\epsilon_J^{MNDO}$	(ψ_J)	$-\epsilon_J^{MNDO}$	(ψ_J)	(ψ_J)	$-\epsilon_J^{MNDO}$	IE_n^v(eV)
9.5–11.5	10.5	($12a_1$)	10.5	($10a_1$)	($6b_1$)	12.2	10–13 eV
	11.2	($7b_1$)	11.3	($6b_1$)	($3a_2$)	12.2	
	11.3	($4a_2$)	11.3	($3a_2$)	($10a_1$)	12.4	
	11.6	($6b_1$)	11.6	($5b_1$)	($6b_2$)	12.4	
	11.7	($8b_2$)	11.7	($6b_2$)	($2a_2$)	12.7	
	11.7	($11a_1$)	11.7	($9a_1$)	($5b_1$)	12.9	
	11.8	($3a_2$)	11.8	($2a_2$)	($9a_1$)	13.2	
	12.1	($10a_1$)	12.1	($8a_1$)	($5b_2$)	13.2	
	12.3	($7b_2$)	12.2	($5b_2$)	($8a_1$)	13.7	
12–13.5	13.8	($9a_1$)					
	14.1	($6b_2$)	13.9	($7a_1$)	($4b_1$)	15.1	13.5–15.5 eV
	14.2	($5b_1$)	14.1	($4b_1$)	($4b_2$)	15.4	
	14.4	($5b_2$)	14.1	($4b_2$)	($7a_1$)	15.4	
	14.8	($8a_1$)					
14–16	15.4	($4b_1$)					
	15.4	($2a_2$)	15.8	($6a_1$)	($3b_2$)	16.3	15–19 eV
	15.4	($4b_2$)	15.8	($3b_1$)	($6a_1$)	16.6	
	15.5	($7a_1$)	15.9	($3b_2$)	($3b_1$)	17.1	
	15.8	($3b_1$)					

Scheme I. First Vertical Ionization Energies of Selected Main Group Element Atoms[a]



[a] Values in parentheses are for stabilized cations with the ns^2 or ns^2p^3 electron configuration.

silicenium ion by formation of a B–SiCH$_3$(H)–B three-center, two-electron bond produces the intermediate depicted in the lower right of Scheme I. Comparable B–SiR$_2$–B and B–SiR$_3$–B bridging units have been observed in other boron hydride cage compounds.[28]

As the final step which results in the formation of DMSB, the expulsion of Me$_2$NH from each of the two Si(IV) centers creates two closely situated silylenes which collapse to form the final closed product. The formation of germylenes[29] and stannylenes[30] by amine elimination from $R_2M(H)NR'_2$ species (M = Ge, Sn) and their subsequent reaction to form respectively polygermanes and polystannanes is a known process. In the present instance, the rather unique electron-withdrawing ability of the boron cage has created the potential for similar chemistry to occur on a silicon center. The net result is the *apparent* trapping of the as yet unknown disilyne, $CH_3Si{\equiv}SiCH_3$, by the $B_{10}H_{10}^{4-}$ cage.

This postulated mechanism admittedly is speculative, but its various steps are based on known chemistry. In view of the complexity of this mechanism, the low DMSB yields are not surprising.

Experimental Section

General Comments. All manipulations were performed in an inert atmosphere of argon or nitrogen following standard techniques. All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. NMR chemical shifts are reported relative to external $F_3B{:}OEt_2$ (^{11}B), external $Si(CH_3)_4$(^{29}Si), internal solvent (^{13}C), or residual ^1H in deuterated solvents (^1H). Ceramic analyses were performed by Galbraith Laboratories, Knoxville, TN and C, H, and N analyses of non-ceramic materials by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points were measured using samples in sealed capillaries and are uncorrected.

All NMR measurements were obtained using either a Varian XL-300 or VXR-500 NMR spectrometer, IR measurements at MIT with a Perkin-Elmer Model 1430 spectrophotometer. Raman spectra were obtained using a Ramanov HG-2S spectrometer equipped with an ILA-2 argon ion laser operating at 5145 Å as the exciting source. The exciting power was less than 100 mW. IR spectra in the vibrational spectroscopy study in Moscow were measured with a M-80 Karl Zeiss spectrophotometer and a Bruker IFS-113v Fourier transform spectrometer. The He(I) PE spectrum was recorded with a Leybold Heraeus UPG 200 spectrometer using a heated inlet system and calibrated by the Xe and Ar ($^2P_{3/2}$) peaks at 12.13 and 15.76 eV; the MNDO calculations were performed on an IBM RISC 6000/320 work station using the SCAMP program version 4.1 (author: Dr. T. Clark, University of Erlangen). TGA measurements were obtained on a Perkin-Elmer Model TGS-2 equipped with a Thermal Analysis System 4 controller. Lindberg tube furnaces with Eurotherm controllers were used for all preparative-scale pyrolyses. For pyrolyses to 1000 °C, 1.5-in. diameter quartz tubes and fused silica boats were used for all samples (powders, bars, and fibers); for pyrolyses to 1500 °C, 2.5-in.-diameter mullite tubes and boron nitride boats supported on alumina dee tubes were used. All pyrolyses were carried out under a flowing gas stream. For experiments to 1000 °C a flow rate of ca. 6–8 L/h was used and for ones to 1500 °C it was ca. 16–20 L/h. Unless otherwise stated, all pyrolyses performed between 1000 and 1500 °C were carried out under a flowing argon atmosphere. A Rigaku rotating-anode X-ray powder diffractometer was used to obtain and computer match and simulate diffraction patterns.

Decaborane(14) was purchased from Callery Chemical Co. and sublimed prior to use. The bis(dimethylamino)silanes were prepared by the procedure of Washburne and Peterson.[20]

Radiation of $B_{10}H_{14}$ with $(CH_3)_2Si[N(CH_3)_2]_2$. A 500-mL, three-necked, round-bottomed flask equipped with an addition funnel containing the benzene solution of the aminosilane, a reflux condenser, a nitrogen inlet/outlet tube, and a magnetic stir-bar was charged with a solution of 5.00 g (41 mmol) of $B_{10}H_{14}$ in 150 mL of dry benzene. A solution of 6.00 g (41 mmol) of $(CH_3)_2Si[N(CH_3)_2]_2$ in 50 mL of benzene was added dropwise with stirring under nitrogen. During the addition, the reaction mixture became pale yellow. The reaction mixture was stirred at ambient temperature for 2 h after the addition was complete and at reflux for 48 h. After the mixture was cooled to ambient temperature and filtered through Celite (to remove ~200 mg of precipitate), the solvent was removed under reduced pressure. (This solution instantaneously becomes cloudy upon exposure to moist air.) The resulting deep yellow-orange, resinous solid was dried at ambient temperature at 0.01 Torr for 4 h. The product, 8.66 g (79%), melted between 80 and 110 °C. It was insoluble in aliphatic hydrocarbons, partially soluble in aromatic hydrocarbons, and soluble in DMF and MeCN. Anal. Calcd for

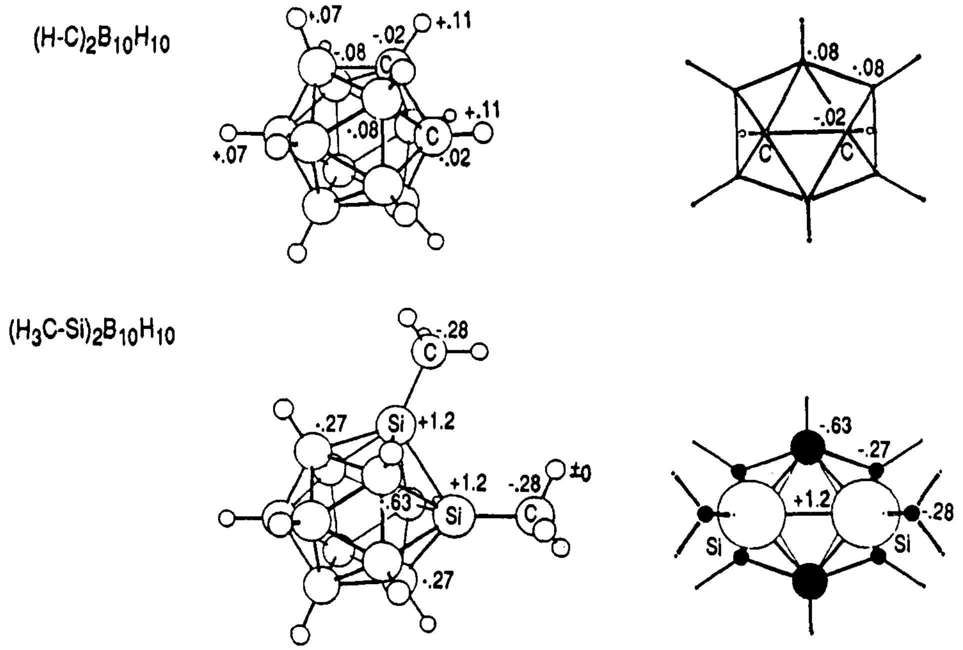
---

(28) (a) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* **1971**, *93*, 522. (b) Loffredo, R. E.; Norman, A. D. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 599. (c) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1972**, 919. (d) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925. (e) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792.

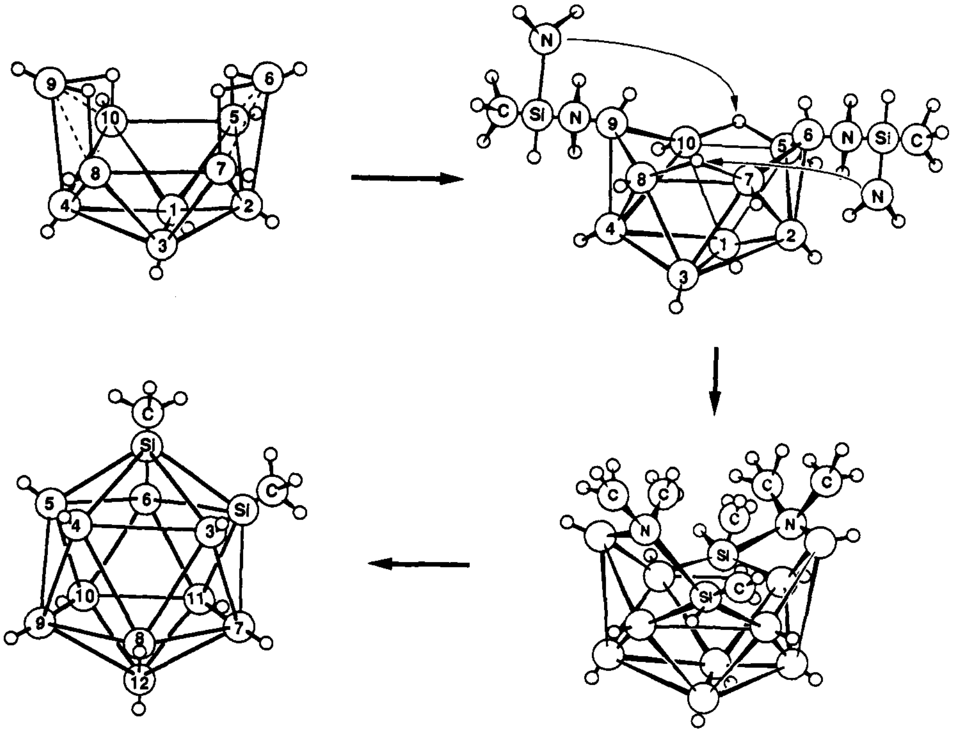
(29) Rivière, P.; Rivière-Baudet, M.; Couret, C.; Satgé, J. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 295.

(30) (a) Neumann, W. P.; Schneider, B.; Sommer, R. *Liebigs Ann. Chem.* **1966**, *692*, 1. (b) Sommer, R.; Schneider, B.; Neumann, W. P. *Liebigs Ann. Chem.* **1966**, *692*, 12.

Scheme II. MNDO-Calculated Charges for 1,2-carborane and 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12)



Scheme III



$-\{B_{10}H_{12}\cdot(CH_3)_2Si[N(CH_3)_2]_2-\}_n$: C, 27.0; H, 11.4; N, 10.5; B, 40.6; Si, 10.6. Found: C, 27.4; H, 10.2; N 10.6; B, 40.3; Si, 9.5. ^1H NMR after 15 h at reflux: δ 2.20, 2.14 (NMe); 0.22 (SiMe) (C_6D_6) ^1H NMR after 48 h at reflux: δ 2.09 (s), 2.06 (s), 1.94 (d), 1.87 (d) (N–Me, 3.0); 0.20 (s, 1.0), 0.05 (d, 0.2) (Si–Me) (C_6D_6). $^{11}B\{^1H\}$ NMR: δ_B 16.5, 14.7, 13.3, 10.8, 8.8, 7.4, 4.5, 3.1, 0.0, −1.5, −3.6, −5.9, −15.1, −16.6, −23.6, −31.6, −38.1 (C_6D_6). ^{29}Si NMR: δ_{Si} 13.35. $^{13}C\{^1H\}$ NMR: δ_C 45.86, 44.94, 39.14 ($N-CH_3$), −4.31 ($Si-CH_3$). IR: 3225 (impurity), 2500, 1297, 1265, 1075, 905, 808 cm^{-1}.

The material obtained from this anaerobic treatment is unsuited for melt-spinning of polymer fibers. However, after a brief (<1 min) exposure to humid (relative humidity <40%, $T \sim 20$ °C) air, the material could be melt-spun. A broad absorption at 700–1150 cm^{-1}, absent in the spectrum of the anhydrous material, was observed in the IR spectrum of the moist-air-treated material. Found elemental composition of such moist-air-treated material: C, 26.9; H, 10.3; N, 10.2; B, 37.8; Si, 9.4. This elemental composition was little changed after the material had been kept molten and used for 0.5 h as the source for melt-spun fibers. Anal. Found: C, 24.5; H, 10.2; N, 10.4; B, 40.0; Si, 7.7. The polymeric material was rendered infusible when it was heated to temperatures >250 °C. Anal. Found: C, 24.3; H, 10.7; N, 11.0; B, 41.9; Si, 4.6. During this conversion of the initial polymer to infusible material, the only significant change was a slight decrease in the amount of Si, relative to B.

A 0.852-g sample, when pyrolyzed to 1000 °C under an argon atmosphere, produced 0.724 g (85%) of a lustrous, black residue that contained only crystalline BN by XRD. Anal. Found: C, 18.0; B, 57.9; Si, 6.4; N, 11.8; H, 1.0. Further heating to 1500 °C of a 0.500 g sample of the material thus produced yielded 0.485 g (97%) of a fine, black powder. The crystalline phases observed were hexagonal BN and minor amounts of an unidentified phase, which did not match with any of the reported nitrides or carbides of either boron or silicon. Anal. Found:

C, 19.4; B, 57.6; Si, 10.0; N, 12.9. A 1.02-g sample of the precursor, when pyrolyzed to 1000 °C under ammonia, produced 0.908 g (89%) of a white foamy solid. Anal. Found: C, 0.6; B, 39.8; Si, 2.1; N, 55.4; H, 0.8. The crystalline phases observed were hexagonal BN and minor amounts of the above described unidentified phase. Further heating to 1500 °C of a 0.500-g sample of the material thus produced yielded 0.460 g (92%) of a very light grey powder. The only crystalline phases observed were hexagonal BN and the above described unidentified phase. Anal. Found: C, 0.3; B, 40.9; Si, 4.1; N, 54.7. This corresponds to a nominal formulation of $(BN)_{1.000}(Si_3N_4)_{0.008}(Si)_{0.004}$.

$BN(Si_3N_4)$ fibers could be obtained from the $[B_{10}H_{12}\cdot(CH_3)_2Si(NMe_2)_2]_n$ polymer as follows. About 2.0 g of the polymer was placed, in an inert-atmosphere box, in a 250 mL Schlenk flask equipped with a rubber septum. After removal from the inert-atmosphere box, the flask containing the polymer then was partly submerged in a sand bath in a heating mantle and slowly (~5 deg C/min) heated under an argon atmosphere until the polymer visibly softened. The septum was removed, and fibers were drawn using a glass rod dipped into the molten polymer and withdrawn manually at a rate which produced suitably shaped fibers. The bath temperature was maintained (within ±10 °C) and fibers were drawn until the molten polymer began to show signs of decomposition (significant thickening), presumably due to exposure to small amounts of atmospheric oxygen and/or water vapor. The polymer fibers were harvested in air using scissors and were stored in an inert-atmosphere box until pyrolyzed to prevent any reaction with water or atmospheric oxygen.

As-harvested polymer fibers, on exposure to a flowing stream of ammonia at ambient temperature, reacted within <5 min to produce a bubbly mass, and those which were heated in a flowing stream of argon remelted below 100 °C. Thus, a cure was needed for the polymer fibers to render them infusible. It was found that maintaining them at 15–20 °C and 40% relative humidity for 3 h or longer was a suitable cure. Subsequent pyrolysis to 1000 °C (10 deg C/min, ammonia atm) gave white ceramic fibers. SEM analysis showed the fibers to be ~20 μm in diameter, rough surfaced, partially spherical, and flawed at a level of ~1 μm.

Reaction of $B_{10}H_{14}$ with $CH_3(H)Si[N(CH_3)_2]_2$. Isolation of 1,2-Dimethyl-*o*-silaborane. A 250-mL, three-necked flask equipped as above was charged with 6.6 g (54.0 mmol) of $B_{10}H_{14}$ and 120 mL of dry toluene. To the resulting solution was added dropwise (with stirring at room temperature) 7.1 g (53.7 mmol) of $CH_3(H)Si[N(CH_3)_2]_2$. A pale yellow reaction mixture resulted. The solution became cloudy after some minutes of stirring and slow gas evolution was observed. The reaction mixture was stirred and heated at reflux under argon for 24 h. During this time a white solid precipitated. The reaction mixture was filtered and the filtrate evaporated at reduced pressure. The residue from the evaporation was extracted with two 100-mL portions of hot benzene. Filtration of the extracts and cooling to 3 °C resulted in deposition of 1.45 g of DMSB as an amorphous white powder that contained a small amount of white needles. Evaporation of the remaining benzene solution gave 0.6 g of white solid, identified as $6,9\text{-}(Me_2NH)_2B_{10}H_{12}$ on the basis of its ^1H and ^{11}B NMR and mass spectra. The solid that had precipitated during the reaction was sublimed at 90 deg C/0.01 Torr to give an additional 0.15 g of DMSB. The 6.0-g sublimation residue was $6,9\text{-}(Me_2NH)_2B_{10}H_{12}$. The total yield of the latter was 6.6 g (58%). The total yield of DMSB was 1.60 g (15% yield, based on $B_{10}H_{14}$).

Bulk samples of DMSB appear to oxidize slowly on storage. Thin films oxidize more rapidly, as the vibrational spectroscopy study showed. After a thin film of DMSB obtained by sublimation in vacuo on to a cold target of the cryostat was exposed to the atmosphere, its IR spectrum soon acquired some "extra" bands, namely ~3200 cm⁻ [ν(B–OH)], ~1200 cm^{-1} [δ(B–OH)], and ~1100 cm^{-1} [ν(SiOSi)], which indicated partial oxidation of the material. The intensity of the "extra" bands slowly increased with time (see Figure 4).

Characterization of 1,2-Dimethyl-*o*-silaborane. (a) Melting point (sealed capillary): 201–203 °C; decomposition with gas evolution above 230 °C. **(b) Anal.** (sublimed sample). Calcd for $C_2H_{16}B_{10}Si_2$ (204.42 g/mol): C, 11.75; H, 7.89; Si, 27.48; B, 52.88. Found: C, 11.64; H, 7.75; Si, 27.62; B, 48.31. **(c) Mass spectrometry** (high-resolution EI) [formula, exact mass, observed mass]: $C_2H_{16}{}^{11}B_{10}{}^{28}Si_2$, 206.17211, 206.1720; $C_2H_{16}{}^{11}B_{10}{}^{28}Si^{29}Si$, 207.17168, 207.1715; $C_2H_{16}{}^{11}B_{10}{}^{28}Si^{30}Si$, 208.16898, 208.1688; $C_2H_{16}{}^{11}B_{10}{}^{29}Si^{30}Si$, 209.16855, 209.1685. The peaks at the highest masses observed in the EI mass spectrum are at m/z = 206 (26.1% relative intensity), 207 (5.3) and 208 (1.4). **(d) ^1H NMR spectrum** (300 MHz): Large solvent-induced shifts of the CH_3 resonance were observed, with more polar solvents causing a downfield shift [solvent, $\delta(Si\text{–}CH_3)$ in ppm]: C_6D_{12}, –0.08; C_6D_6, –0.07; CD_3OD, 1.13; $CDCl_3$, 1.15; CD_2Cl_2, 1.19; $DC(O)N(CD_3)_2$, 1.21; THF-d_8, 1.24; $(CD_3)_2CO$, 1.34. Adding small amounts of CD_3OD to 0.5 mL of a saturated solution of DMSB in C_6D_6 resulted in shifts of the CH_3 resonance to lower field [mL of CD_3OD added, $\delta(Si\text{–}CH_3)$ in ppm]: 0.05, 0.19; 0.10, 0.31; 0.15, 0.39; 0.20, 0.48; 0.30, 0.56; 0.45, 0.64; 0.60, 0.70; 0.80, 0.75; 1.00, 0.79; 1.50, 0.83. Removing the solvent from a $CDCl_3$ solution of DMSB in vacuo and replacing it with C_6D_6 resulted in the expected upfield shift of the Si–CH_3 resonance to –0.07 ppm. **(e) ^{29}Si NMR spectrum**: (i) 99.34 MHz, proton-decoupled, at 50 °C in C_6D_6, –37.77 ppm; (ii) CP/MAS, –36 ppm. **(f) ^{13}C NMR spectrum**, 75.43 MHz, proton-decoupled, at 40 °C in C_6D_6, –12.80 ppm. **(g) ^{11}B NMR spectrum**, 160.35 MHz, in C_6D_6 at room temperature, δ_B –14.76 (d, J = 147.6 Hz), –11.87 (d, J = 159.8 Hz), –10.49 (d, J = 159.8 Hz) in the 3:1:1 intensity ratio. In the proton-coupled ^{11}B NMR spectra (at 160.35 MHz) taken in $(CD_3)_2CO$ and in CD_3OD solution the resonances overlapped. In $(CD_3)_2CO$ solution they were estimated as follows: δ_B –14.65 (d, J = 147 Hz, B 4, 5, 7, 11), –13.61 (d, J = 152 Hz, B 3, 6), –12.79 (d, J = 144 Hz, B 8, 10), –11.27 (d, J = 147 Hz, B 9, 12). ^{11}B NMR spectrum in CD_3OD: –14.95, –14.15, –13.00, and –11.46 (doublets in the 4:2:2:2 intensity ratio). **(h) X-ray Crystal Structure Determination.** Very slow crystallization of DMSB from dilute benzene solution at 3 °C gave the 1:1 solvate, $(CH_3)_2Si_2B_{10}H_{10}\cdot C_6H_6$, as white rods. The molecule crystallizes with crystallographic 2-fold symmetry. The benzene is found in two sites of equal occupancy and each site has the same crystallographic 2-fold symmetry. This limited the refinement of benzene carbons to isotropic scatterers. The remaining non-hydrogen atoms were refined as anisotropic scatterers. The DMSB hydrogen atoms were located on a difference Fourier map and placed in those positions with no further refinement. Hydrogen atoms in the disordered benzene molecule were placed in calculated positions.

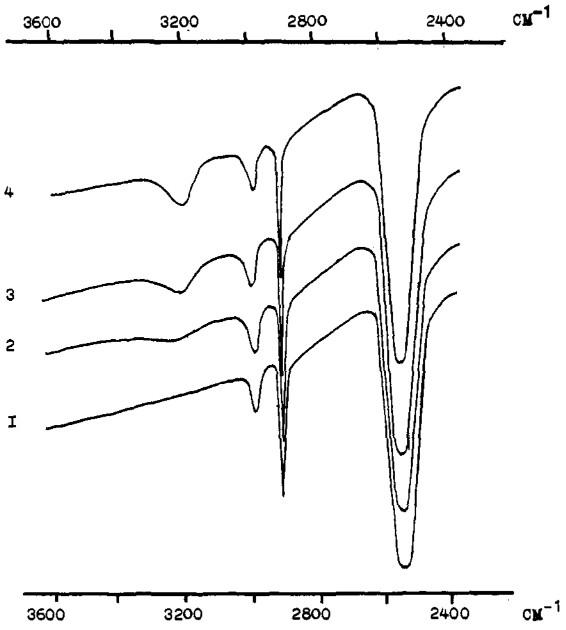


Figure 4. Process of oxidation of DMSB in air as shown by the IR spectrum of a thin film: (1) just after sublimation in vacuum (no $\nu_{B\text{–}OH}$ band at ~3200 cm^{-1}); (2) after 5 h of exposure to air; (3) after 24 h; and (4) after 1 week.

Experimental details (crystal data, intensity measurements, structure solution and refinement) are given in Table V. Table VI lists positional parameters, Table I non-hydrogen atom bond distances, and Table II intramolecular bond angles involving the non-hydrogen atoms.

Characterization of $6,9\text{-}(Me_2NH)_2B_{10}H_{12}$. (a) Melting point (sealed capillary): decompostion at 243 °C with vigorous gas evolution. (b) **Analysis**: Calcd for $C_4H_{26}B_{10}N_2$: C, 22.84; H, 12.46; N, 13.32; B, 51.39. Found: C, 21.70; H, 12.26; N, 13.03; B, 49.16. (c) **IR** (Nujol, cm^{-1}): 3234 (s, ν_{NH}), 2542 (s), 2482 (s), 2360 (s), 2341 (s), several medium to weak bands in the 1297–914-cm^{-1} region. (d) **NMR spectra**: ^1H (300 MHz, $(CD_3)_2CO$) δ –5.20 (s, br, 2 H, BHB), –1.40 to 2.22 (several broad signals, BH), 2.67 (d, J = 5.7 Hz, 12 H, NCH_3), 5.18 (s, br, 2 H, NH); ^{11}B (96.24 MHz), $(CD_3)_2CO$) δ_B –42.10 (d, J = 140 Hz, 1 B), –20.6 (d, J = 131 Hz, 2 B), –17.5 (d, J = 127 Hz, 1 B), –6.51 (d, J = 131 Hz, 1 B).

Table V. Crystal Structure Determination

A.Crystal Data	
empirical formula	$C_2H_{16}B_{10}Si_2C_6H_6$
formula wt	282.53
cryst color, habit	white, rod
cryst dimensions (mm)	0.120 × 0.120 × 0.380
cryst system	orthorhombic
no. of reflcns used for unit cell determination (2θ range)	25 (25.0–32.0°)
ω scan peak width at half-height	0.28
lattice parameters	
a (Å)	10.081(1)
b (Å)	10.666(8)
c (Å)	16.130(5)
V (Å^3)	1734(2)
space group	*Pccn* (#56)
Z value	4
D_{calc} (g/cm^3)	1.082
F_{000}	592
$\mu_{(Mo\ K\alpha)}$ (cm^{-1})	1.78
B.Intensity Measurements	
diffractometer	Rigaku AFC6R
radiation	Mo Kα (λ = 0.71069 Å)
temp (°C)	23
take-off angle (deg)	6.0
detector aperture (mm)	6.0 horizontal; 6.0 vertical
cryst-to-detector dist (cm)	31 cm
scan type	ω–2θ
scan rate (deg/min)	32.0 (in ω) (8 rescans)
scan width (deg)	$(0.94 + 0.35 \tan \theta)$
$2\theta_{max}$ (deg)	55.0
total no. of reflcns measd	2291
corrections	Lorentz–polarization, secondary extinction (coeff: 0.28680E-06)
C.Structure Solution and Refinement	
structure solution	direct methods
H atom treatment	included in diff map of calcd positions (d_{C-H} = 0.95 Å)
refinement	full-matrix least-squares
function minimized	$\omega w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.05
anomalous dispersion	all non-H atoms
no. of observations ($I > 3.00\sigma(I)$)	1050
no. of variables	89
reflcn/parameter ratio	11.80
residuals: R; R_w	0.044; 0.058
goodness-of-fit indicator	1.40
max shift/error in final cycle	0.00
max peak in final diff map (e$^-$/Å^3)	0.25
min peak in final diff map (e$^-$/Å^3)	–0.25

[a] Based on the systematic absences of $0kl$: $1 \neq 2n$; $h0l$: $1 \neq 2n$; $hk0$: $n + k \neq 2n$. [b] MITHRIL: Gilmore, J. C. *J. Appl. Crystallogr.* **1984**, *17*, 42. DIRDIF: Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Technical Report 1984/1. [c] Neutral atom scattering factors from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, Table 2.2A values for $\Delta f'$ and $\Delta f''$, Table 2.3.1. Also anomalous dispersion effects included in F_{calc}: Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. Calculations: TEXSAN-TEXRAX Structure Analysis Package, Molecular Structure Corp., 1985.

Table VI. Positional Parameters[a]

atom	x	y	z
Si	0.16614(7)	0.67636(7)	0.35177(4)
C(1)	0.0923(3)	0.6097(3)	0.4454(2)
C(11)	0.2889(8)	0.1966(7)	0.0798(5)
C(12)	0.3300(8)	0.1434(8)	0.0057(5)
C(13)	0.2915(8)	0.1967(8)	–0.0670(5)
C(11′)	1/4	1/4	0.0915(7)
C(12′)	0.3175(9)	0.1578(8)	0.0493(6)
C(13′)	0.321(1)	0.163(1)	–0.0347(6)
C(14′)	1/4	1/4	–0.0765(7)
B(1)	0.2063(4)	0.5925(3)	0.2425(2)
B(2)	0.0804(3)	0.7198(4)	0.2425(2)
B(3)	0.3142(4)	0.8069(4)	0.1566(2)
B(4)	0.1443(3)	0.8572(3)	0.2999(2)
B(5)	0.3483(4)	0.6512(4)	0.1904(2)

[a] Complete positional parameters, including those for the H atoms, are given in the supplementary material.

Reaction of $B_{10}H_{14}$ with $CH_3(H)Si[N(CH_3)_2]_2$ (No Solvent). A 100-mL Schlenk Flask equipped with a reflux condenser topped with a gas inlet/outlet tube, a rubber septum, and a magnetic stir-bar was flushed well with nitrogen and charged with 3.0 g (24.6 mmol) of $B_{10}H_{14}$. Methylbis(dimethylamino)silane (6.48 g) was added slowly by syringe. The reaction mixture was stirred while the temperature was raised slowly to 80 °C. After 5 min of stirring at 80 °C, vigorous gas evolution commenced, accompanied by a color change from pale yellow to orange. The oil bath was removed until gas evolution had ceased and then heating was continued. The mixture was stirred at 110 °C for 48 h. The now pale yellow reaction mixture was cooled to room temperature. All volatiles were removed at reduced pressure, leaving 6.3 g of pale yellow solid. To the latter was added (in a 500-mL flask) 400 mL of toluene, and the resulting suspension was stirred at room temperature overnight to dissolve the DMSB. After filtration, the filtrate was stored at 3 °C for 8 h and then at –12 °C. Filtration was followed by concentration of the solution and further cooling. Repetition of this procedure several times gave 1.25 g (25%) of DMSB. Complete evaporation of toluene left a 3.7-g residue (72%) of 6,9-$(Me_2NH)_2B_{10}H_{12}$.

Reaction of $B_{10}H_{14}$ with $C_6H_5(H)Si[N(CH_3)_2]_2$ in Toluene. The same procedure used in the synthesis of DMSB was used in a reaction of 9.53 g (49.1 mmol) of $B_{10}H_{14}$ in 150 mL of toluene with 6.00 g (49.1 mmol) of the aminosilane. The reaction mixture was stirred and heated at 100–110 °C for about 48 h under nitrogen. The reaction mixture, which contained a pale yellow solid, was cooled to room temperature and filtered to give 6.4 g (62%) of 6,9-$(Me_2NH)_2B_{10}H_{12}$, identified by ^{11}B and ^1H NMR spectroscopy. The filtrate was concentrated to about one-third of its volume and then stored at 3 °C overnight. A white precipitate resulted. Further steps of concentration and cooling gave more of this solid. A total of 2.22 g (14%) of 1,2-diphenyl-*o*-silaborane was thus obtained. Complete removal of the toluene left a pale yellow, waxy solid, which ^{11}B NMR spectroscopy showed to be a mixture. The silaborane product could be recrystallized (with exclusion of air) from toluene. Its solutions appeared to be quite air-sensitive. Attempted sublimation resulted in decomposition. A satisfactory analysis could not be obtained. ^1H NMR (300 MHz, C_6D_6) δ 1.8–4.2 (several broad signals, BH), 6.72 (m, 2 H, CH), 6.92 (m, 1 H, CH), 7.30 (m, 2 H, CH). ^{11}B NMR (96.24 MHz, C_6D_6) δ_B –14.4 (d, J = 147 Hz, 3 B), –11.41 (d, J = 130 Hz, 1 B), –10.7 (d, J = 139 Hz, 1 B). (Due to extensive overlap of the doublets and the breadth of the resonances, the coupling constants are estimates.) $^{29}Si\{^1H\}$ NMR (59.95 MHz, C_6D_6) δ_{Si} –44.64. $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ_C 115.51, 129.63, 133.66, 136.71 (C_6H_5). EI MS (temperature <100 °C), highest mass peaks at 327.2 (100), 328.3 (94.3), 329.2 (66.6), 330.2 (35.2), 331.3 (10.9), 332.2 (4.9). IR (Nujol, cm^{-1}) 2522 (s), 2359 (s), 2341 (s), 1456 (s), 1430 (s), 1418 (m), 1394 (w), 1375 (s), 1112 (m), 996 (w), 730 (w), 668 (w).

Acknowledgment. The MIT authors are grateful to the Office of Naval Research for support. K.D.B. thanks the Alexander von Humboldt Foundation for the award of a Feodor Lynen Fellowship and L.W. the Deutscher Akademischer Austauschdienst for the award of a NATO postdoctoral fellowship.

Supplementary Material Available: X-ray structure report including experimental details and tables of positional parameters, *U* values, and benzene C–C bond distances and C–C–C angles (9 pages); structure factor tables (14 pages). Ordering information is given on any current masthead page.