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Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Synthesis and X-ray Crystal Structure of *arachno*-6-$((CH_3)_3Si)$-6,9-$C_2B_8H_{13}$ through a Cage-Expansion Reaction of *nido*-2,3-$((CH_3)_3Si)_2$-2,3-$C_2B_4H_6$

Joseph R. Wermer, Narayan S. Hosmane,*[†] John J. Alexander,[‡] Upali Siriwardane,
and Sheldon G. Shore*

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The 10-vertex *arachno*-carborane *arachno*-6-$((CH_3)_3Si)$-6,9-$C_2B_8H_{13}$ has been prepared by the cage-expansion reaction of *nido*-$[2,3\text{-}((CH_3)_3Si)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ with B_5H_9. The carborane was isolated as well-formed, air-stable, colorless crystals by sublimation from the reaction vessel and characterized by IR, ^{11}B NMR, ^1H NMR, and 2-D ^{11}B–^{11}B NMR spectroscopy and X-ray crystallography. This molecule is isoelectronic with $[B_{10}H_{14}]^{2-}$ and the cage is very similar in appearance to that of the dianion. Crystallographic data: space group *Pbca*, $a = 12.825\ (4)$ Å, $b = 17.999\ (3)$ Å, $c = 11.335\ (1)$ Å, $V = 2616.6$ Å^3, $Z = 8$, mol wt = 196.79, $\rho_{\text{calcd}} = 0.999$ g cm^{-1}, $\mu_{\text{calcd}} = 2.3$ cm^{-1} for Mo Kα. Structural analysis is based upon 1496 independent reflections with $I > 3.00\sigma(I)$ in the range $4° \leq 2\theta \leq 55°$. Final $R_F = 3.7\%$, and $R_{wF} = 4.7\%$.

Introduction

Pentaborane(9), B_5H_9, is a useful starting material for the preparation of the higher boron hydride anions $[B_9H_{14}]^-$ and $[B_{11}H_{14}]^-$.[1-4] In the synthesis of $[B_9H_{14}]^-$ it has been shown[3] that the reaction of $[B_5H_8]^-$ with B_5H_9 is the major route leading to this anion (eq 1). It was of interest to determine whether a

$$[B_5H_8]^- + B_5H_9 \rightarrow \text{“}[B_{10}H_{17}]^-\text{”} \rightarrow [B_9H_{14}]^- + {}^1/_2B_2H_6 \qquad (1)$$

reaction similar to (1) might occur between a *nido*-carborane anion and B_5H_9 to give an expanded carborane cage. Earlier work has shown that small carboranes react with B_2H_6 to give cage-expanded species,[5-11] such as the known reactions illustrated in eq 2 and 3.

$$\text{Na}[1,3\text{-}C_2B_7H_{12}] + B_2H_6 \rightarrow$$
$$1,3\text{-}C_2B_7H_{13} + \text{NaBH}_4 + 1,6\text{-}C_2B_8H_{12} + 5,7\text{-}C_2B_8H_{12} \qquad (2)$$

$$C_2B_3H_5 + {}^3/_2B_2H_6 \rightarrow C_2B_6H_{10} + 4H_2 \qquad (3)$$

We have obtained *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$ in 21% yield from the reaction of *nido*-$[2,3\text{-}(Si(CH_3)_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ with B_5H_9. Reported here are the synthesis, characterization, and X-ray crystal structure of this carborane. This is the first reported X-ray structure of a 10-vertex *arachno*-carborane. Although many carboranes and their metalla derivatives have been reported in recent years,[12,13] only a small number of *arachno*-carboranes are known to date: 4-CB_8H_{14},[14,15] 9-L-6-CB_9H_{13},[16] 5,6-$C_2B_8H_{12}$,[17] 1,3-$C_2B_7H_{13}$ and the dimethyl derivative,[18-21] 6,9-$C_2B_8H_{14}$,[22,23] a series of 5-X-6,9-$C_2B_8H_{13}$ derivatives,[24] $(CH_3)_4C_4B_7H_9$ and a bromo derivative,[25] and σ-$(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)$-$(CH_3)_4C_4B_8H_8$.[26] X-ray structural information has been available for only three *arachno*-carboranes, 1,3-$(CH_3)_2$-1,3-$C_2B_7H_{11}$,[21] 11-Br-$(CH_3)_4C_4B_7H_8$,[25] and σ-$(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)$-$(CH_3)_4C_4B_8H_8$.[26]

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) was prepared by the methods of Hosmane et al.[27] Pentaborane(9) (Callery Chemical Co.) was used as received. NaH (Aldrich) in mineral oil dispersion was washed repeatedly with dry pentane to remove the oil and then stored under dry, oxygen-free nitrogen; activity was determined by reaction with methanol and measurement of the H_2 evolved. A solution of $\text{Na}[2,3\text{-}(Si(CH_3)_3)_2\text{-}2,3\text{-}C_2B_4H_5]$ in glyme (1,2-dimethoxyethane) was prepared by the method of Onak and Dunks.[28] Glyme was distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were dried over 4–8-mesh molecular sieves (Davidson) and either saturated with dry nitrogen or degassed before use.

Synthetic Procedures. All experiments were carried out in a Pyrex glass round-bottom flask of 500-mL capacity, containing a magnetic stirring bar and fitted with a high-vaccum Kontes Teflon stopcock. Materials were handled by using standard vacuum line and inert-atmosphere techniques.[29]

Spectroscopic Procedures. Proton NMR spectra at 300.1 MHz were recorded on a Bruker WM300 spectrometer. Boron-11 NMR and boron-11 DFQ COSY (double quantum filter correlated spectroscopy)[30-33]

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[†] Department of Chemistry, Southern Methodist University, Dallas, TX.
[‡] Department of Chemistry, University of Cincinnati, Cincinnati, OH.

Table I. Crystallographic Data for *arachno*-6-($Si(CH_3)_3$)-6,9-$C_2B_8H_{13}$

chemical formula	$C_5B_8SiH_{22}$
mol wt	196.79
color of cryst	white
space group	*Pbca*
molecules/unit cell	8
temp. °C	−30
a, Å	12.825 (4)
b, Å	17.999 (3)
c, Å	11.335 (1)
vol of unit cell, Å^3	2616.59
cryst dimens, mm	0.31 × 0.07 × 0.41
density (calcd), g cm^{-3}	0.999
radiation	Mo Kα (0.710730 Å)
abs coeff, cm^{-1}	2.3
scan mode	ω–2θ
data collecn limits, deg	4–55
no. of unique reflecns	3436
no. of reflecns used in structure refinement (>3σ(*I*))	1496
$R_F = \sum\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.037
$R_{wF} = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{1/2}$	0.047
$w = [\sigma(I)^2 + (kI)^2]^{-1}$	$k = 0.04$

spectra at 160.4 MHz were recorded on a Bruker AM500 spectrometer. Mass spectra were obtained on a Kratos MS-30 spectrometer using heptacosafluorotributylamine as the calibrant. Infrared spectra were recorded on a Mattson-Cygnus 25 Fourier transform infrared (FT-IR) spectrometer.

Synthesis of *arachno*-6-($Si(CH_3)_3$)-6,9-$C_2B_8H_{13}$. A glyme solution of Na[2,3-($(CH_3)_3Si)_2C_2B_4H_5$] was prepared by the vacuum distillation of 2,3-($(CH_3)_3Si)_2C_2B_4H_6$ (3.52 g, 16.02 mmol) into 20 mL of glyme containing 0.463 g (95% active, 18.33 mmol) of NaH. The solution was then filtered through a frit under high vacuum, and the filtrate was collected in a 500-mL round-bottom flask maintained at −196 °C. Into this reaction vessel was condensed 17.97 mmol (1.15 g) of B_5H_9 at −196 °C. *Caution*! B_5H_9 is known to be spontaneously flammable and very toxic. The mixture was warmed to room tempeature and then heated to 75 °C with stirring over a period of 19 h. After the vessel was cooled to −196 °C, the noncondensible gas produced in the reaction, H_2 (12.06 mmol), was measured with a calibrated Toepler system. Then the vessel was warmed to room temperature, and glyme and unreacted B_5H_9 (trace quantity) were pumped away. The reactor was attached to a U-trap, which was immersed in a bath at −78 °C. When the yellow residue was heated to 110 °C under high vacuum, colorless crystals and a colorless liquid collected on the inside walls and at the bottom of the U-trap, respectively. The most volatile compound, $(CH_3)_3SiH$ (3.81 mmol), passed through −78 °C and was collected at −196 °C. The main reaction products collected in the U-trap and were fractionated by passing through a series of traps held at 0, −15, and −23 °C to collect pure ($(CH_3)_3Si$)-$C_2B_8H_{13}$ (0.651 g, 3.30 mmol; 21% yield (based on the starting carborane anion) as colorless crystals), an oily liquid (0.419 g), and ($(CH_3)_3Si)_2$-$C_2B_4H_6$ (1.61 g, 7.33 mmol; 45.75% of the starting material), respectively. The GC–mass spectrum (Chemical Ionization) of the oily liquid confirmed the presence of ($(CH_3)_3Si)_2C_2B_6H_8$. A yellow air-sensitive residue (ca. 1.0 g) remained at the bottom of the reactor. The ^{11}B NMR spectrum of this residue in THF showed a number of broad doublets, which we were unable to identify. Physical properties and spectroscopic characterizations of *arachno*-6-($Si(CH_3)_3$)-6,9-$C_2B_8H_{13}$ are as follows: mp 113–114 °C; apparently air and moisture stable (^{11}B NMR spectrum showed no changes after 5-month exposure of the solid to air); highly soluble in THF, acetone, $CDCl_3$, CCl_4, CH_2Cl_2, and C_6H_6; mass spectrum M$^+$ (*m*/*z*) 198.230 found, 198.225 calculated for $[(^{12}CH_3)_3{}^{28}Si^{12}C_2{}^{11}B_8H_{13}]^+$; ^{1}H NMR ($CDCl_3$, relative to external $(CH_3)_4Si$, ^{11}B decoupled) δ 2.87 (q (br), 1 H, H_t (2)), 2.83 (q (br), 1 H, H_t (4)), 2.28 (q (br), 2 H, H_t (8,10)), 2.16 (q (br), 2 H, H_t (5,7)), 0.95 (q (br), 2 H, H_t (1,3)), 0.90 (m, 1 H, ≡SiCH), 0.03 (s, 9 H, $(CH_3)_3Si$), −0.52 (m, 1 H, CH(eq), $J_{^1H-^1H}$ = 2.4 Hz), −1.55 (d, 1 H, CH(ax), $J_{^1H-^1H}$ = 6.0 Hz), −2.74 (s (br), 2 H, B–H–B); ^{11}B NMR ($CDCl_3$, relative to external $BF_3 \cdot OEt_2$) δ 5.73 (d, 1 B, B(4), $J_{^{11}B-^1H}$ = 151 Hz), 4.80 (d, 1 B, B(2)–H, $J_{^{11}B-^1H}$ = 150 Hz), −15.03 (d, 2 B, B(8,10)–H, $J_{^{11}B-^1H}$ = 140 Hz), −16.15 (d, 2 B, B(5,7)–H, $J_{^{11}B-^1H}$ = 140 Hz), −35.58 (d, 2 B, B(1,3)–H, $J_{^{11}B-^1H}$ = 151 Hz); IR (in $CDCl_3$) 2959.51 (m), 2938.58 (w), 2927.13 (w), 2901.03 (w, ν(C–H)), 2577.07 (vs, ν(B–H)), 1612.59 (vw, ν(B–H–B)), 1403.91 (sh), 1400.99 (w, br, $\delta(CH)_{asym}$), 1261.54 (sh), 1252.49 (s, $\delta(CH)_{sym}$), 1124.67 (m), 1082.6 (m), 1065.57 (s), 1012.18 (w), 984.30 (m), 907.70 (m), 898.65 (m), 878.47 (m), 841.81 (vs, ρ-(CH)), 815.19 (m), 791.36 (s), 758.72 (s), 748.61 (w), 717.86 (w), 711.61 (w), 684.69 (w, ν(Si–C)) cm^{-1}.[17–21,27,34]

Table II. Positional Parameters (Esd's) and Isotropic Equivalent Thermal Parameters for *arachno*-6-($Si(CH_3)_3$)-6,9-$C_2B_8H_{13}$[a]

atom	*x*	*y*	*z*	*B*, Å^2
B(1)	0.3216 (2)	0.3204 (1)	0.5300 (2)	3.18 (4)
B(2)	0.3492 (2)	0.2262 (1)	0.5178 (2)	2.54 (4)
B(3)	0.4500 (2)	0.2889 (1)	0.4914 (2)	2.86 (4)
B(4)	0.4322 (2)	0.3640 (1)	0.5841 (2)	3.33 (4)
B(5)	0.2709 (2)	0.2562 (1)	0.6356 (2)	3.04 (4)
C(6)	0.3601 (1)	0.18215 (9)	0.6440 (2)	2.55 (3)
B(7)	0.4751 (2)	0.2057 (1)	0.5726 (2)	2.95 (4)
B(8)	0.4689 (2)	0.7013 (1)	0.3815 (2)	3.42 (5)
C(9)	0.0451 (2)	0.6580 (1)	0.2231 (2)	3.83 (4)
B(10)	0.1731 (2)	0.6520 (1)	0.1814 (2)	3.73 (5)
Si	0.31519 (4)	0.08211 (3)	0.64795 (5)	2.965 (9)
C(1)	0.1757 (2)	0.4198 (1)	0.1926 (3)	6.24 (7)
C(2)	0.3935 (2)	0.4663 (1)	0.2608 (2)	4.60 (5)
C(3)	0.1669 (3)	0.5371 (1)	0.5028 (3)	7.79 (8)
H(10)	0.226 (1)	0.653 (1)	0.966 (2)	3.3 (4)*
H(20)	0.185 (1)	0.6899 (9)	0.452 (2)	3.2 (4)*
H(30)	0.481 (1)	0.2964 (9)	0.409 (2)	3.5 (4)*
H(40)	0.044 (2)	0.577 (1)	0.065 (2)	4.3 (5)*
H(50)	0.311 (1)	0.755 (1)	0.138 (2)	3.5 (4)*
H(61)	0.383 (1)	0.305 (1)	0.213 (2)	4.3 (5)*
H(70)	0.022 (1)	0.3369 (9)	0.465 (2)	3.1 (4)*
H(80)	0.389 (1)	0.6876 (9)	0.393 (2)	3.1 (4)*
H(91)	0.054 (2)	0.701 (1)	0.277 (2)	4.9 (5)*
H(90)	0.017 (1)	0.616 (1)	0.265 (2)	4.0 (5)*
H(100)	0.223 (2)	0.609 (1)	0.208 (2)	4.6 (5)*
H(510)	0.207 (1)	0.7102 (9)	0.225 (2)	3.9 (5)*
H(78)	0.972 (2)	0.767 (1)	0.153 (2)	4.2 (5)*
H(11)	0.149 (2)	0.472 (1)	0.201 (2)	8.8 (8)*
H(12)	−0.165 (3)	0.604 (2)	−0.253 (4)	16 (1)*
H(13)	0.145 (3)	0.095 (2)	0.618 (3))	12 (1)*
H(21)	0.372 (2)	0.516 (1)	0.264 (2)	6.4 (6)*
H(22)	0.459 (2)	0.468 (1)	0.237 (2)	9.4 (8)*
H(23)	0.396 (2)	0.446 (2)	0.334 (2)	10.4 (9)*
H(31)	0.175 (2)	0.487 (1)	0.510 (3)	8.3 (7)*
H(32)	0.223 (2)	0.551 (2)	0.456 (3)	12 (1)*
H(33)	0.089 (2)	0.540 (1)	0.489 (2)	8.1 (7)*

[a] Values marked with an asterisk were for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Crystal Structure Determination of 6-($(CH_3)_3Si$)-6,9-$C_2B_8H_{13}$. Large, well-formed, clear, colorless crystals of the title compound were grown by vacuum sublimation onto a glass surface. A specimen was mounted in a 0.3-mm glass capillary for X-ray examination and data collection. All data were collected at −30 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by least-squares refinement of the angular settings from 25 reflections, well-distributed in reciprocal space and lying in a 2θ range of 24–30°. Crystal parameters are given in Table I. Six standard reflections were monitored and showed no significant decay (0.5%). The data were corrected for Lorentz and polarization effects. All crystallographic computations were carried out by using the "Structure Determination Package" (SDP).[35]

The structure was solved by a combination of direct methods (MULTAN 11/82) and the difference Fourier technique. Refinement was by full-matrix least squares. Analytical atomic scattering factors were used throughout the structure refinement. Since an extinction correction was found to have no effect on the parameters, none was included in the final refinement. Full-matrix least-squares refinement was carried out by using anisotropic thermal parameters for B, C, and Si atoms and isotropic

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(35) SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, apply corrections, solve and refine the structures, produce drawings, and print tables.

Table III. Selected Bond Distances (Å) and Esd's for *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$

B(1)–B(2)	1.738 (3)	B(1)–H(10)	1.07 (2)
B(1)–B(3)	1.795 (3)	B(2)–H(20)	1.08 (2)
B(1)–B(4)	1.733 (3)	B(3)–H(30)	1.03 (2)
B(1)–B(5)	1.787 (3)	B(4)–H(40)	1.12 (2)
B(1)–B(10)	1.791 (3)	B(5)–H(50)	1.07 (2)
B(2)–B(3)	1.742 (2)	B(5)–H(510)	1.22 (2)
B(2)–B(5)	1.758 (3)	C(6)–H(61)	0.87 (2)
B(2)–C(6)	1.643 (2)	C(6)–Si	1.891 (2)
B(2)–B(7)	1.768 (3)	B(7)–H(70)	1.06 (2)
B(3)–B(4)	1.727 (3)	B(7)–H(78)	1.24 (2)
B(3)–B(7)	1.789 (3)	B(8)–H(78)	1.25 (2)
B(3)–B(8)	1.787 (3)	B(8)–H(80)	1.06 (2)
B(4)–B(8)	1.772 (3)	C(9)–H(91)	0.99 (2)
B(4)–C(9)	1.652 (3)	C(9)–H(90)	0.96 (2)
B(4)–B(10)	1.768 (3)	B(10)–H(100)	1.05 (2)
B(5)–C(6)	1.760 (2)	B(10)–H(510)	1.24 (2)
B(5)–B(10)	1.875 (3)	Si–C(1)	1.859 (2)
C(6)–B(7)	1.734 (2)	Si–C(2)	1.846 (2)
B(7)–B(8)	1.894 (3)	Si–C(3)	1.850 (3)
B(8)–C(9)	1.724 (3)		
C(9)–B(10)	1.712 (3)		

Table IV. Selected Bond Angles (deg) and Esd's Involving Cage Atoms for *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$

B(2)–B(1)–B(3)	59.0 (1)	B(3)–B(4)–C(9)	111.8 (1)
B(2)–B(1)–B(4)	107.6 (1)	B(3)–B(4)–B(10)	110.8 (1)
B(2)–B(1)–B(5)	59.8 (1)	B(8)–B(4)–C(9)	60.4 (1)
B(2)–B(1)–B(10)	109.8 (1)	B(8)–B(4)–B(10)	107.6 (1)
B(3)–B(1)–B(4)	58.6 (1)	C(9)–B(4)–B(10)	60.0 (1)
B(3)–B(1)–B(5)	107.1 (1)	B(1)–B(5)–B(2)	58.7 (1)
B(3)–B(1)–B(10)	106.7 (1)	B(1)–B(5)–C(6)	106.8 (1)
B(4)–B(1)–B(5)	110.6 (1)	B(1)–B(5)–B(10)	58.5 (1)
B(4)–B(1)–B(10)	60.2 (1)	B(2)–B(5)–C(6)	55.69 (9)
B(5)–B(1)–B(10)	63.2 (1)	B(2)–B(5)–B(10)	105.3 (1)
B(1)–B(2)–B(3)	62.1 (1)	C(6)–B(5)–B(10)	113.8 (1)
B(1)–B(2)–B(5)	61.5 (1)	B(2)–C(6)–B(5)	62.1 (1)
B(1)–B(2)–C(6)	114.8 (1)	B(2)–C(6)–B(7)	63.1 (1)
B(1)–B(2)–B(7)	111.2 (1)	B(5)–C(6)–B(7)	110.0 (1)
B(3)–B(2)–B(5)	110.8 (1)	B(2)–B(7)–B(3)	58.6 (1)
B(3)–B(2)–C(6)	113.6 (1)	B(2)–B(7)–B(8)	105.0 (1)
B(3)–B(2)–B(7)	61.3 (1)	B(3)–B(7)–C(6)	107.0 (1)
B(5)–B(2)–C(6)	62.2 (1)	B(3)–B(7)–B(8)	58.0 (1)
B(5)–B(2)–B(7)	108.5 (1)	C(6)–B(7)–B(8)	114.2 (1)
C(6)–B(2)–B(7)	61.0 (1)	B(3)–B(8)–B(4)	58.1 (1)
B(1)–B(3)–B(2)	58.9 (1)	B(3)–B(8)–B(7)	58.0 (1)
B(1)–B(3)–B(4)	58.9 (1)	B(3)–B(8)–C(9)	105.7 (1)
B(1)–B(3)–B(7)	107.7 (1)	B(4)–B(8)–B(7)	104.7 (1)
B(1)–B(3)–B(8)	107.8 (1)	B(4)–B(8)–C(9)	56.4 (1)
B(2)–B(3)–B(4)	107.7 (1)	B(7)–B(8)–C(9)	111.9 (1)
B(2)–B(3)–B(7)	60.1 (1)	B(4)–C(9)–B(8)	63.3 (1)
B(2)–B(3)–B(8)	110.9 (1)	B(4)–C(9)–B(10)	63.4 (1)
B(4)–B(3)–B(7)	111.4 (1)	B(8)–C(9)–B(10)	112.5 (1)
B(4)–B(3)–B(8)	60.5 (1)	B(1)–B(10)–B(4)	58.3 (1)
B(7)–B(3)–B(8)	64.0 (1)	B(1)–B(10)–B(5)	58.3 (1)
B(1)–B(4)–B(3)	62.5 (1)	B(1)–B(10)–C(9)	106.5 (1)
B(1)–B(4)–B(8)	111.4 (1)	B(4)–B(10)–B(5)	105.2 (1)
B(1)–B(4)–C(9)	112.0 (1)	B(4)–B(10)–C(9)	56.6 (1)
B(1)–B(4)–B(10)	61.5 (1)	B(5)–B(10)–C(9)	112.8 (1)
B(3)–B(4)–B(8)	61.4 (1)		

thermal parameters for H atoms. Final atomic positional parameters are given in Table II while selected bond distances and angles appear in Tables III and IV, respectively.

Results and Discussion

The reaction of the *nido*-carborane anion $[((CH_3)_3Si)_2C_2B_4H_5]^-$ with B_5H_9 in a molar ratio of 1:1 at 75 °C in glyme produced a yellow semisolid material. A subsequent vacuum sublimation of this residue at 110 °C produced the air-stable, crystalline carborane *arachno*-$((CH_3)_3Si)C_2B_8H_{13}$ in 21% yield based upon starting anion. From the reaction mixture the neutral carborane *nido*-$((CH_3)_3Si)_2C_2B_4H_6$, the conjugate acid of the starting material, was also isolated in 46% yield.

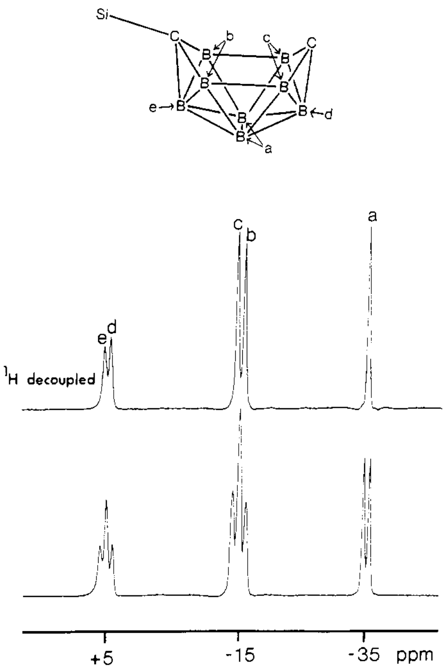

Figure 1. 160.4-MHz ^{11}B NMR spectrum of *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$.

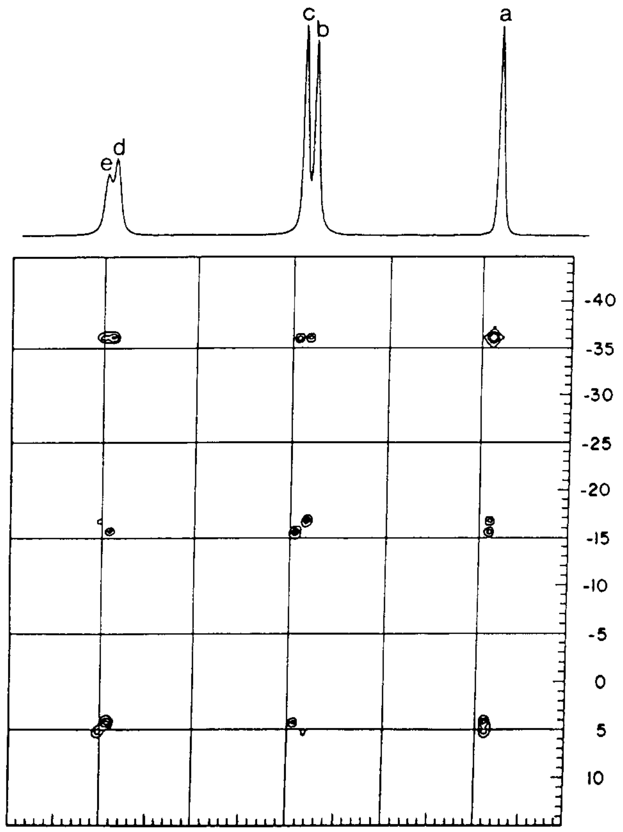

Figure 2. ^{11}B COSY experiment for *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$.

Spectra. The boron-11 NMR spectrum (Figure 1) showed five doublets at 5.73, 4.80, −15.03, −16.15, and −35.58 ppm in the relative intensity 1:1:2:2:2. The presence of five signals in the ^{11}B NMR spectrum suggests a molecule of C_s symmetry, in which both carbon atoms lie on the mirror plane. A two-dimensional ^{11}B–^{11}B COSY (Figure 2) experiment confirmed these positions. The signal labeled *a* was shown to be coupled to all of the other signals. This immediately suggests a 6,9-C_2B_8 structure since this is the only possibility in which one boron atom would be coupled to all of the others. Signal *b* is coupled to *e* and *a*; *c* is coupled to *d* and *a*. Thus *a* is assigned to the B(1,3) atoms and *b* and *c* can be assigned to the two pairs B(5,7) and B(8,10). There is

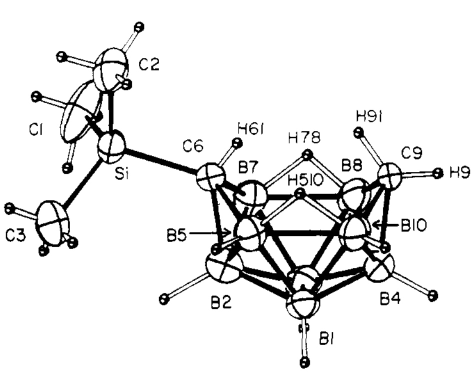

Figure 3. Molecular structure of *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$ showing the atom-numbering scheme.

no cross peak between *b* and *c*. This is consistant with earlier observations that coupling between nuclei bridged by a hydrogen atom is usually not observable with this technique.[30] Since *d* and *e* are coupled to *c* and *b*, respectively, they can be assigned to the B(2) and B(4) atoms. Signals *b* and *e* are broader than *c* and *d*. This broadening is attributed to the presence of the Si atom on that side of the carborane cage. These assignments are in agreement with a 6-$((CH_3)_3Si)$-6,9-$C_2B_8H_{13}$ carborane structure. The proton NMR spectrum is also in agreement with this conclusion. Three C–H protons are observed at 0.90, –0.52, and –1.55 ppm. The signal at –1.55 ppm is a doublet (J = 6 Hz) and is assigned to the axial hydrogen atom. Boron-11 decoupling resolves coupling in the signal at –0.52 ppm (septet, J = 2.4 Hz). As expected, boron-11 decoupling also indicated the presence of five terminal B–H hydrogen signals at 2.87, 2.83, 2.28, 2.26, and 0.95 ppm in a ratio of 1:1:2:2:2, a bridge hydrogen resonance at –2.74 ppm. The resonance due to the trimethylsilyl hydrogens appeared at 0.03 ppm.

The IR spectral assignments of *arachno*-$((CH_3)_3Si)C_2B_8H_{13}$ are in agreement with those of silyl and similar compounds reported in the literature.[17-21,27-34] The electron-impact (EI) mass spectrum of the *arachno*-carborane exhibits a grouping with the major cutoff at m/z 198, corresponding to the parent ion $[(^{12}CH_3)_3{}^{28}Si^{12}C_2{}^{11}B_8H_{13}]^+$, and an intense grouping with the major cutoff at m/z 183 that corresponds to the fragment (parent ion minus one methyl group) $[(^{12}CH_3)_2{}^{28}Si^{12}C_2{}^{11}B_8H_{13}]^+$. It has been observed that the most intense peaks were not in the region of the parent ion but in the region of the parent ion minus one methyl group. This phenomenon was also observed elsewhere.[36]

X-ray Structure of *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$. This *arachno*-carborane is isoelectronic with $[B_{10}H_{14}]^{2-}$, the structure of which was determined by Kendall and Lipscomb in 1973 as the bis(tetramethylammonium) salt.[37] The gross geometry of *arachno*-$[B_{10}H_{14}]^{2-}$ is like that of *nido*-$B_{10}H_{14}$, differing essentially only in the number and locations of the bridging hydrogens. The structure of *arachno*-6-$(Si(CH_3)_3)$-6,9-$C_2B_8H_{13}$ (Figure 3) resembles that of *arachno*-$[B_{10}H_{14}]^{2-}$. However, the carborane molecule has C_1 symmetry. The C(6)–C(9) distance in the carborane of 3.25 (2) Å is somewhat shorter than the B(6)–B(9) distance in $[B_{10}H_{14}]^{2-}$ of 3.39 Å. The corresponding distances in 6,9-$B_{10}H_{12}L_2$ are 3.21 Å for L = SMe_2 and 3.32 Å for L = $NCCH_3$.[37-39]

A least-squares plane through C(6), C(9), B(2), and B(4) (supplementary material) shows that the C_2B_8 framework does *not* possess C_s symmetry. The atoms C(6) and B(2) reside on opposite sides of the plane and are out of plane by about 0.5 Å each. The Si atom is also about 0.5 Å out of plane. Its C(1) and C(3) methyl carbons reside at the respective distances of 3.04 (2) and 2.82 (2) Å from the terminal hydrogen atoms H(50) and H(20) on B(5) and B(2). This is less than the sum of the van der Waals radii (3.2 Å) for a methyl group and hydrogen.[37] The H(61) and H(91) hydrogen atoms are 2.18 Å from each other, which is essentially the same distance (2.15 Å) as that between the corresponding H atoms in $[B_{10}H_{14}]^{2-}$. A least-squares plane through B(2), B(4), B(6), and B(9) in $[B_{10}H_{14}]^{2-}$ with the positional parameters of Kendal and Lipscomb[37] shows that these atoms are coplanar in the anion.

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Supplementary Material Available: Listings of anisotropic thermal parameters, exopolyhedral angles and angles involving μ-H, and least-squares planes calculations (4 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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