

distance of 0.95 Å. In the use of methyl groups, one hydrogen was found from the difference Fourier map and its position was idealized by assuming it was in the plane defined by R-C-H, made a 109.5° bond angle and 0.95-Å bond length. The positions of the two remaining hydrogens were then calculated. Except in the case of compound 5, the hydrogen positions and temperature factors were fixed during the remainder of the refinement.

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Supplementary Material Available: Tables of positional parameters, general temperature factors, bond distances, and bond angles for 2 and 5 (30 pages); listing of structure factor amplitudes for 2 and 5 (38 pages). Ordering information is given on any current masthead page.

Reactions of Decaborane(14) with Silylated Acetylenes. Synthesis of the New Monocarbon Carborane 9-Me₂S-7-[(Me₃Si)₂CH]-CB₁₀H₁₁

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The dimethyl sulfide promoted reactions of decaborane(14) with the silylated acetylenes, bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, have been studied and were not found to yield the expected *ortho*-carborane derivatives but instead gave either alkenyldecaborane or monocarbon carborane products. Thus, the reaction of decaborane(14) with dimethyl sulfide and bis(trimethylsilyl)acetylene produced 9-(CH₃)₂S-7-[(CH₃)₃Si]₂CH-CB₁₀H₁₁ (I) and 5-(CH₃)₂S-6-[(CH₃)₃Si]₂C=CH-B₁₀H₁₁ (II) while the analogous reaction with (trimethylsilyl)propyne yielded 5-(CH₃)₂S-6-[(CH₃)₃Si(CH₃)C=CH]-B₁₀H₁₁ (III). A single-crystal X-ray determination of III demonstrated that compounds II and III result from acetylene hydroboration reactions and have structures based on a decaborane(14) geometry with a dimethyl sulfide bound to the 5-boron and an alkenyl group bound to the 6-boron on the open face. Crystal data for III: space group $P\bar{1}$; $Z = 4$; $a = 16.406$ (4) Å, $b = 16.677$ (5) Å, $c = 8.627$ (2) Å, $\alpha = 100.67$ (2)°, $\beta = 97.78$ (2)°, $\gamma = 118.23$ (2)°, $V = 1974.9$ Å³; $R = 0.077$ and $R_w = 0.103$ for the 5208 reflections having $F_o^2 > 3\sigma(F_o^2)$. The data obtained for compound I indicate that it is an unusual monocarbon carborane resulting from the insertion of only one of the acetylenic carbons of the bis(trimethylsilyl)acetylene into the cage structure. The cluster geometry is based on an icosahedron missing one vertex, with an exopolyhedral bis(trimethylsilyl)methyl group bonded to the cage carbon. The reaction of I with either NaH, LiEt₃BH, Na, or (η^5 -C₅H₅)₂Co results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the 2-((CH₃)₃Si)₂CH-CB₁₀H₁₀⁻ anion. A single-crystal X-ray determination of the cobaltocenium salt VI established that the compound has a closo structure based on an octadecahedron, with the cage carbon occupying the four-coordinate 2-position in the structure. Crystal data for VI: space group $P2_1/n$; $Z = 4$; $a = 12.260$ (1) Å, $b = 17.252$ (3) Å, $c = 13.701$ (3) Å, $\beta = 107.94$ (1)°; $V = 2757.0$ Å³; $R = 0.058$ and $R_w = 0.068$ for the 3061 reflections having $F_o^2 > 3\sigma(F_o^2)$. Thermolysis of I at toluene reflux yielded as the major product 6-(CH₃)₂S-2-[(CH₃)₃Si]₂CH-CB₁₀H₉ (VII) while thermolysis of I in the solid phase gave VII and small amounts of 6-(CH₃)₂S-4-OH-2-[(CH₃)₃Si]₂CH-CB₁₀H₈ (VIII). Compounds VII and VIII are isoelectronic with VI, and single-crystal X-ray determinations confirmed that VII and VIII have similar octadecahedral structures. Crystal data for VII: space group $P\bar{1}$; $Z = 2$; $a = 8.834$ (3) Å, $b = 19.211$ (2) Å, $c = 6.998$ (1) Å, $\alpha = 96.20$ (1)°, $\beta = 109.63$ (2)°, $\gamma = 91.91$ (2)°; $V = 1108.9$ Å³; $R = 0.067$ and $R_w = 0.081$ for the 2864 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for VIII: space group $P\bar{1}$; $Z = 4$; $a = 13.729$ (1) Å, $b = 16.345$ (2) Å, $c = 10.880$ (1) Å, $\alpha = 96.62$ (1)°, $\beta = 93.45$ (1)°, $\gamma = 74.47$ (1)°; $V = 2335.4$ Å³; $R = 0.065$ and $R_w = 0.078$ for the 5623 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction of decaborane(14) with an alkyne in the presence of dimethyl sulfide is a well-established route to *ortho*-carborane 1,2-C₂B₁₀H₁₂ and its alkyl derivatives.¹

Previous studies² have suggested that this reaction involves the initial formation of bis(dimethyl sulfide)decaborane(12), which can then dissociate a dimethyl sulfide, yielding a reactive B₁₀H₁₂SMe₂ species. Further reaction of this B₁₀H₁₂SMe₂ intermediate with the alkyne then leads to the direct insertion of the two-carbon acetylenic unit into the cage along with dissociation of the remaining SMe₂ and H₂ loss to yield the final product.

We have now investigated the dimethyl sulfide promoted reactions of decaborane(14) with two silylated acetylenes, bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, and report that, in contrast to the results discussed above,

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(2) Hill, W. E.; Johnson, F. A.; Novak, R. W. *Inorg. Chem.* 1975, 14, 1244-49.

these reactions do not result in the formation of *ortho*-carborane derivatives. Instead, hydroboration of the acetylene, accompanied by silyl group migration is observed in both cases to yield as major products 5-(dimethyl sulfide)-6-alkenyldecaborane(14) compounds. An additional product, apparently resulting from the insertion of a single carbon of the acetylenic unit into the decaborane cage, was also isolated in good yields in the bis(trimethylsilyl)acetylene reaction and was identified as the new monocarbon carborane, 9-Me₂S-7-[(Me₃Si)₂CH]-CB₁₀H₁₁. The synthesis, characterization, and preliminary investigations of the chemistry of these unique alkenyldecaborane and monocarbon carborane compounds are described below.

Experimental Section

Materials. Bis(trimethylsilyl)acetylene was purchased from Strem Chemicals and used as received. Decaborane(14) was obtained from laboratory stock and recrystallized twice from heptane before use. Lithium triethylborohydride, dimethyl sulfide, sodium, sodium hydride, and cobaltocene were purchased from Aldrich Chemicals and used as received. (Trimethylsilyl)propyne was purchased from Petrarch Systems and used as received. All reaction solvents were reagent grade and purified and dried by literature methods.

Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). Analytical thin-layer chromatography was conducted on 0.25 mm (5 × 10 cm) silica gel F-254 plates (Merck).

Physical Measurements. The 64.2-MHz boron-11 spectra were obtained on a Bruker WP-200SP Fourier transform spectrometer. Boron-11 spectra at 115.5 MHz were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. All boron-11 chemical shifts were referenced to BF₃·O(C₂H₅)₂ = 0.0 ppm with a negative sign indicating an upfield shift. Proton NMR spectra at 200 and 250 MHz were obtained on Bruker WP-200SP and Bruker WM-250 Fourier transform spectrometers, respectively. All proton chemical shifts were referenced to internal residual solvent from the lock solvents used (99.5% C₆D₆, 99.8% CDCl₃, and 99.0% CD₂Cl₂) and then referenced to tetramethylsilane = 0.0 ppm with positive values indicating downfield shifts.

Low-resolution EI mass spectra were obtained on a Perkin-Elmer Hitachi RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. Low-resolution CI mass spectra and all high-resolution mass spectra were obtained on a VG 7070-H mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer.

Elemental analyses were performed by Schwarzkopf Labs, Inc. All melting points are uncorrected.

Reaction of Decaborane(14) with Bis(trimethylsilyl)acetylene. A dry 250-mL, three-neck flask, fitted with a magnetic stir bar, septum, gas inlet, and a condenser connected to a mercury bubbler, was charged with 4.697 g (38.5 mmol) of twice recrystallized B₁₀H₁₄ and 75 mL of dry benzene. The system was flushed with argon for several minutes, and 77 mmol, or 5.9 mL, of dimethyl sulfide, (CH₃)₂S, was syringed into the flask. The contents of the flask were refluxed, with stirring, for 6 h. The resulting yellow solution was cooled to room temperature, and 7.659 g (45 mmol) of bis(trimethylsilyl)acetylene was added through the condenser, followed by 20 mL of dry benzene. The system was closed and flushed with argon. The contents of the flask were heated at a gentle reflux for 14 h. The system was cooled to room temperature, and the gas inlet and condenser were replaced with a stopper and a vacuum adapter. Dimethyl sulfide and benzene were pulled off of the reaction mixture, with caution, under vacuum. The flask was opened to argon and refitted with the condenser and bubbler. The septum was replaced with a dropping funnel containing 75 mL of methanol.

Methanol was added dropwise to the gummy solids in the flask. After all the methanol had been added, the mixture was stirred overnight at room temperature. The solution was cooled to salt water-ice bath temperature (-5 °C), achieving precipitation of

a yellow solid which was filtered with a coarse frit. The filtrate was then cooled again to -5 °C, and precipitation was coaxed by the dropwise addition of water. The solid was filtered off and the filtrate recooled again to isolate all of the remaining product. When a yellow gelatinous material began to precipitate, all of the remaining product had been recovered. The two isolated products were recrystallized from methylene chloride. The white powder isolated was I, 9-(CH₃)₂S-7-[(CH₃)₃Si]₂CH-CB₁₀H₁₁ [3.749 g (10.6 mmol); 27.5% based on B₁₀H₁₄; mp 147–148 °C]; exact mass measurement calcd for ¹²C₁₀¹H₃₆¹¹B₁₀³²S²⁸Si₂ 354.3030, found 354.3003. Anal. Calcd: C, 33.87; H, 10.24; B, 31.18; S, 9.03; Si, 15.80. Found: C, 32.45; H, 9.94; B, 29.27; S, 8.98; Si, 13.74. The yellow solid was II, the hydroboration product, 5-(CH₃)₂S-6-[(CH₃)₃Si]₂C=CH-B₁₀H₁₁ [2.851 g (8.0 mmol); 20.9% based on B₁₀H₁₄; mp 110–112 °C]; exact mass measurement calcd for ¹²C₁₀¹H₃₆¹¹B₁₀³²S²⁸Si₂ 354.3030, found 354.302.

Reaction of Decaborane(14) with (Trimethylsilyl)propyne. In a greaseless 250-mL round-bottom flask equipped with a high vacuum stopcock adapter were placed 1.0 g (8.2 mmol) of twice recrystallized B₁₀H₁₄, 50 mL of dry benzene, and 1.2 mL of dimethyl sulfide. The flask was cooled to -196 °C and evacuated. The solution was then heated at 80 °C for 6 h, with periodic removal of H₂. The flask was cooled to -196 °C, degassed, and opened to the air and 0.92 g (8.2 mmol) of (trimethylsilyl)propyne syringed into the flask. Heating at 80 °C in vacuo was then continued for an additional 16 h. The flask was attached to the vacuum line, and its contents were pumped out until a gummy yellow solid was obtained. The solid was dissolved in 25 mL of methanol and stirred at room temperature for 6 h. The solution was cooled by using a salt water-ice bath (-5 °C), and 50 mL of water added dropwise, resulting in the precipitation of a yellow solid which was filtered. This solid was purified by preparative TLC (benzene eluant, R_f 0.25) and repeated washings of the product with cold pentane. The isolated yellow powder was compound III, 5-(CH₃)₂S-6-[(CH₃)₃Si](CH₃)C=CH-B₁₀H₁₁ [0.503 g (1.7 mmol); 20.9% based on B₁₀H₁₄; mp 104–106 °C]; exact mass measurement calcd for ¹²C₉¹H₃₀¹¹B₁₀³²S²⁸Si 296.277, found 296.277.

Attempted Thermolysis of 5-(CH₃)₂S-6-[(CH₃)₃Si]₂C=CH-B₁₀H₁₁ (II). In a 250-mL, three-neck round-bottom flask were placed 0.2500 g (0.71 mmol) of II and 50 mL of dry mesitylene. The flask was then equipped with a reflux condenser, a N₂ gas inlet, and a septum. The solution was flushed with N₂ and heated at 160 °C for 24 h. Analysis of the reaction solution by TLC and ¹¹B NMR revealed only unreacted II.

Syntheses of [2-((CH₃)₃Si)₂CH]-CB₁₀H₁₀]. (A) In a typical reaction, 1.7 mmol of 9-(CH₃)₂S-7-[(CH₃)₃Si]₂CH-CB₁₀H₁₁ (I) and 5.2 mmol of NaH in a 50% mineral oil dispersion were placed in a 100-mL round-bottom flask with a vacuum filtering attachment and degassed. Then 50 mL of dry THF was condensed into the flask and the mixture stirred for 26 h at room temperature. The evolved hydrogen gas (1.56 mmol) was measured with a Toepler pump. The mixture was filtered, and a saturated CsCl solution was added to the filtrate. The precipitate was filtered and identified as Cs⁺[2-((CH₃)₃Si)₂CH-CB₁₀H₁₀]⁻ (IV) [0.615 g (1.4 mmol); 85% based on I; 93% based on evolved H₂; white; mp 265 °C dec]. Anal. Calcd for [(CH₃)₄N]⁺[2-((CH₃)₃Si)₂CH-CB₁₀H₁₀]⁻: C, 39.41; H, 11.31; N, 3.83; Si, 15.31. Found: C, 39.67; H, 11.49; N, 1.26; Si, 15.80.

(B) In a 50-mL, two-neck round-bottom flask with a magnetic stirrer were placed 0.35 g (1.0 mmol) of I and 10 mL of dry THF. The flask was then attached to a pressure-equalizing dropping funnel containing 1.0 mL of a 1.0 M solution of LiBEt₃H (Super-Hydride) in THF. The system was degassed at -196 °C and then warmed to -40 °C. The Super-Hydride solution was added slowly to the solution and was stirred for 1 h at -40 °C. The THF was then removed in vacuo, leaving a white solid which was identified as Li⁺[2-((CH₃)₃Si)₂CH-CB₁₀H₁₀]⁻ (V) by comparison of its ¹¹B NMR to that of IV [0.247 g (0.83 mmol), 83% based on I].

(C) In a 50-mL round-bottom flask under an atmosphere of N₂ were placed 0.2500 g (0.71 mmol) of I and 0.2300 g (10.0 mmol) of Na metal. The flask was cooled to -196 °C and evacuated. Dry THF was added and the flask heated at 90 °C for 18 h. A solid precipitated from the THF solution which was filtered along with the unreacted Na. The THF solution was evaporated to dryness, giving 0.19 g (0.61 mmol, 86%) of Na⁺[2-((CH₃)₃Si)₂CH-CB₁₀H₁₀]⁻

which was characterized by ^{11}B NMR.

(D) In a 250-mL round-bottom flask were placed 0.2500 g (0.71 mmol) of I and 0.1341 g (0.71 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$. The flask was evacuated, and 150 mL of dry THF was condensed in. The mixture was stirred for 3 h at -20°C , after which the solution turned yellow, and a brown precipitate was observed. The solution was filtered, the precipitate was discarded, and the filtrate was evaporated to dryness. A yellow solid was obtained which was extracted with methylene chloride. The yellow solid was identified as $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+[2\text{-}((\text{CH}_3)_3\text{Si})_2\text{CH}]^-\text{CB}_{10}\text{H}_{10}]^-$ (VI) [0.20 g (0.40 mmol), 58% based on I; yellow; mp 212°C dec]. Characterization was achieved by ^{11}B and ^1H NMR and by single-crystal X-ray analysis.

Thermolysis of 9-(CH₃)₂S-7-[(CH₃)₃Si]₂CH-CB₁₀H₁₁ (I).
(A) In a 250-mL 3-neck flask, fitted with a condenser, gas inlet, and septum, was placed 0.7107 g or 2.0 mmol of I. The system was flushed with nitrogen and 100 mL of toluene was added. The solution was then heated to reflux. After $5\frac{1}{2}$ h, most of the carborane I had reacted according to TLC, and the solution was cooled to room temperature. The solution was concentrated on a rotary evaporator and separated by preparative TLC. The plates were developed in 3:1 benzene-hexane, and the reaction mixture was separated into seven bands. The bands including the base line were scrapped, ground, and eluted with methylene chloride or ethyl acetate.

The major product isolated was 6-(CH₃)₂S-2-[(CH₃)₃Si]₂CH-CB₁₀H₉ (VII) [*R_f* 0.46; 0.075 g (0.21 mmol); 10.6% based on I; mp (sub) 107°C ; white]; exact mass measurement calcd for $^{12}\text{C}_{10}^{1}\text{H}_{34}^{11}\text{B}_{10}^{32}\text{S}^{28}\text{Si}_2$ 352.2874, found 352.2861. The remaining bands were obtained in insufficient amounts to allow characterization; however, spectral data for these compounds, as well as for compounds obtained from thermolyses performed in mesitylene solvent, suggest that these compounds may be fused carboranes or double hydroboration products with the general formula $(\text{Me}_3\text{Si})_2\text{C}_2\text{H}_2\text{B}_2\text{H}_{22}2\text{SMe}_2$.

(B) In a 17-mm o.d. glass tube, sealed at one end and with an O-ring joint at the other, was placed 0.3439 g or 0.975 mmol of I. The tube was evacuated and then heated with an oil bath at 100°C while pumping through a -196°C trap. After 1 h, no apparent change and no gas evolution were noticed. The temperature was slowly increased until it reached 140°C , at which temperature a liquid started to condense in the -196°C trap and noncondensable gas evolution was noticed. After 1 h, the tube contained a yellow viscous liquid at the base and sublimed white solid on the walls above the heating zone. No more gas evolution or condensable liquid evolved from the reaction. The tube was removed from the high-vacuum line, cooled to room temperature, and then opened to the air. The yellow liquid hardened into a glassy yellow solid which was extracted with methylene chloride. The material condensed in the -196°C trap was identified by IR as $(\text{CH}_3)_2\text{S}$ (0.317 mmol; 32.5% based on I). The extracted solution was separated by preparative TLC using a 1:1 benzene-hexane solution. Six bands were obtained from the TLC plates, which were scrapped and eluted with methylene chloride or ethyl acetate. The major product was identified as compound VII by ^{11}B NMR [39.2 mg (0.11 mmol); 11.42% based on I]. The band at *R_f* 0.0 was redeveloped by using 3:1 benzene-hexane, giving three bands. The band at *R_f* 0.16 was identified as 6-(CH₃)₂S-4-OH-2-[(CH₃)₃Si]₂CH-CB₁₀H₈ (VIII) [2.9 mg (0.007 mmol); 0.8% based on I; mp $143\text{--}144^\circ\text{C}$]. The remaining bands were present in insufficient amounts to allow characterization.

Crystallographic Data for 5-(CH₃)₂S-6-[(CH₃)₃Si]₂CH-CB₁₀H₁₁ (III), [Cp₂Co]⁺[2-((CH₃)₃Si)₂CH-CB₁₀H₁₀]⁻ (VI), 6-(CH₃)₂S-2-[(CH₃)₃Si]₂CH-CB₁₀H₉ (VII), and 6-(CH₃)₂S-4-OH-2-[(CH₃)₃Si]₂CH-CB₁₀H₈ (VIII). Single crystals of III and VI were grown overnight by slow evaporation in air of methylene chloride/heptane solutions and a benzene/heptane solution for compounds VII and VIII. In each case, a suitable size crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 20–25 accurately centered reflections. See Table IV for crystal data.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo K α or Cu K α radiation from a highly oriented graphite-crystal monochromator. The raw intensities

Table I. ^{11}B NMR Data

compd	δ (J, Hz)	relative intensities
I ^{a,b}	-1.52 (139) B5, -5.05 (173) B2 or B3, -6.70 (171) B2 or B3, -8.62 (154) B8 and B11, -20.42 B9, -21.03 (129) B10, -24.84 (147) B1, -28.20 (145) B4 or B6, -29.51 (149) B4 or B6	1:1:1:2:1:1:1:1:1
II ^{a,b}	31.10, 4.80 (124), -0.57, -3.53 (128), -4.74 (150), -10.75 (130), -23.01 (126), -40.20 (133)	1:2:1:2:1:1:1:1
III ^{b,c}	30.10, 3.19 (137), -2.43, -4.11, ^d -6.64, ^d -11.23, ^d -24.03 (150), -41.71 (151)	1:3:1:1:1:1:1:1
IV ^{a,e}	-6.23 (133), -11.07 (120), -12.09 (140)	1:5:4
V ^{a,e}	-6.84 (157), -11.56 (130)	1:9
VI ^{b,c}	-6.23, ^d -11.06 (100)	1:9
VII ^{a,f}	-5.46, -6.10, ^d -11.94 (155), -17.09 (150)	1:2:4:3
VIII ^{b,c}	9.1, -6.5, ^d -11.4, ^d -14.1 (~135), -15.8 (~109), -23.0 (148)	1:3:1:2:2:1

^a 115.5 MHz. ^b CH₂Cl₂ solvent. ^c 64.2 MHz. ^d Coupling constants could not be reliably measured because of overlapping peaks. ^e - (CD₃)₂CO. ^f CDCl₃ solvent.

Table II. ^1H NMR Data

compd	δ (rel area, assign)
I ^{a,b}	2.62 (3, CH ₃ S), 2.64 (3, CH ₃ S), 0.93 (1, CH), 0.10 (18, (CH ₃) ₃ Si), -2.23 (1, BHB), ^c -3.28 (1, BHB) ^c
II ^{a,d}	7.97 (1, HC=C), 1.57 (3, CH ₃ S), 1.49 (3, CH ₃ S), 0.20 (9, (CH ₃) ₃ Si), -0.02 (9, (CH ₃) ₃ Si), -2.27 (1, BHB), -2.56 (1, BHB), -2.74 (1, BHB)
III ^{a,d}	6.93 (1, HC=C), 1.96 (3, CH ₃), 1.59 (3, CH ₃ S), 1.50 (3, CH ₃ S), -0.10 (9, (CH ₃) ₃ Si), -2.31 (1, BHB), -2.47 (1, BHB), -2.82 (1, BHB)
IV ^{b,e}	1.70 (1, CH), 0.13 (18, (CH ₃) ₃ Si)
VI ^{b,f}	4.80 (10, C ₅ H ₅), 1.65 (1, CH), 0.49 (18, (CH ₃) ₃ Si)
VII ^{a,b}	2.58 (6, (CH ₃) ₂ S), 1.87 (1, CH), 0.14 (18, (CH ₃) ₃ Si)
VIII ^{a,b}	2.45 (1, OH), 1.72 (1, CH), 1.20 (6, (CH ₃) ₂ S), 0.37 (18, (CH ₃) ₃ Si)

^a C₆D₆ solvent. ^b 250 MHz. ^c Bridge hydrogen shifts determined on ^{11}B -spin-decoupled spectrum at 200 MHz. ^d 200 MHz. ^e - (CD₃)₂CO solvent. ^f CD₂Cl₂ solvent.

Table III. IR Data (cm⁻¹)

I ^a	3004 (sh), 2920 (s), 2876 (m), 2842 (sh), 2570 (sh), 2520 (s), 1420 (s), 1340 (w), 1255 (sh), 1240 (s), 1100 (m), 1030 (s), 1000 (s), 993 (m), 938 (m), 858 (sh), 840 (vs, br), 765 (s, br), 690 (sh), 680 (m), 620 (m), 515 (m)
II ^a	2950 (m), 2940 (sh), 2540 (sh), 2510 (s), 1550 (sh), 1475 (m), 1420 (m), 1375 (s), 1240 (s), 1230 (s), 1096 (m), 1080 (m), 1026 (m), 980 (m), 930 (m), 900 (sh), 890 (sh), 860 (sh), 830 (s, br), 750 (m, br), 670 (m), 626 (m)
III ^b	2550 (s), 1525 (m), 1270 (m), 1255 (m), 1130 (w), 1100 (w), 1050 (m), 1025 (m), 960 (m, br), 930 (w), 850 (s, br), 830 (sh), 770 (m), 740 (m)
IV ^a	2950 (m), 2900 (sh), 2510 (s), 2350 (sh), 1600 (w), 1550 (w), 1410 (m), 1250 (s), 1080 (s), 1020 (s), 870 (sh), 830 (s, br), 680 (m), 630 (m)
VI ^a	2940 (m), 2880 (m), 2580 (sh), 2530 (s), 1430 (m), 1270 (sh), 1260 (m), 1110 (w), 1050 (sh), 1040 (m), 1010 (m), 1000 (w), 950 (w), 895 (sh), 860 (s), 780 (w), 700 (sh), 670 (sh), 650 (m), 640 (sh)
VII ^a	3020 (sh), 2950 (sh), 2940 (m), 2900 (sh), 2870 (w, sh), 2850 (w, sh), 2600 (sh), 2530 (s), 1440 (m), 1340 (m), 1260 (sh), 1250 (s), 1030 (sh), 1005 (m), 870 (sh), 840 (s), 680 (m), 630 (m)
VIII ^a	3565 (s), 2925 (m), 2875 (m), 2825 (w), 2605 (m), 2535 (sh), 2495 (s), 1425 (m), 1300 (m), 1250 (s), 1230 (sh), 1170 (m), 1070 (m), 1030 (w), 990 (m), 950 (w), 870 (sh), 840 (s, br), 770 (sh), 680 (m), 650 (sh), 630 (m)

^a KBr pellet. ^b Nujol mull.

were corrected for Lorentz and polarization effects by using the Enraf-Nonius program START.

Solution and Refinement of the Structure. All calculations were performed on either PDP 11/60 or VAX 750 computers using

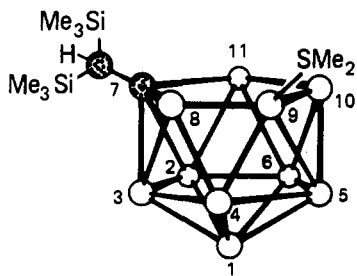


Figure 1. Cage skeletal structure of 9-Me₂S-7-[(Me₃Si)₂CH]-B₁₀H₁₁ (I) Terminal and bridging hydrogens are not shown.

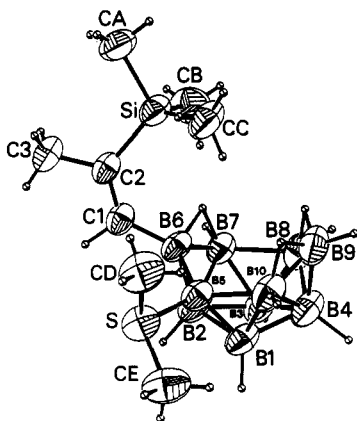


Figure 2. ORTEP drawing of the molecular structure of 5-Me₂S-6-[(Me₃Si)(Me)C=CH]-B₁₀H₁₁ (III).

the Enraf-Nonius structure packages.³ The full-matrix least-squares refinement was based on F , and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The scattering factors for non-hydrogen atoms were taken from Cromer and Waber⁴ and those for hydrogen atoms from Stewart.⁵ The effects of anomalous dispersion were included in F_c by using Cromer and Ibers⁶ values for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

For compound VI, a three-dimensional Patterson synthesis gave the coordinates of the cobalt atom. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinement followed by a difference Fourier synthesis resulted in the location of the cage hydrogens and some of the hydrogens in the trimethylsilyl groups and cyclopentadienyl rings. The remaining hydrogens were calculated and included (but not refined) in the structure factor calculations. Final refinements included numerical absorption corrections along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms.

For compounds III, VII and VIII, direct methods, using 11/82 version of Multan, yielded the location of all the cage atoms, along with the trimethylsilyl and dimethyl sulfide groups. Anisotropic refinement followed by difference Fourier syntheses resulted in the location of the cage hydrogens, the vinyl hydrogen in compound III, and some of the hydrogens of the trimethylsilyl and dimethyl sulfide groups. The remaining hydrogens were calculated and included (but not refined) in the structure factor calculations. As in the case of compound VI, final refinements included an-

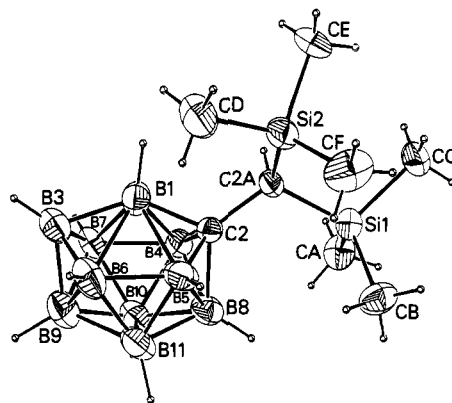


Figure 3. ORTEP drawing of the molecular structure of the *closo*-2-(Me₃Si)₂CH-CB₁₀H₁₀⁻ anion (VI).

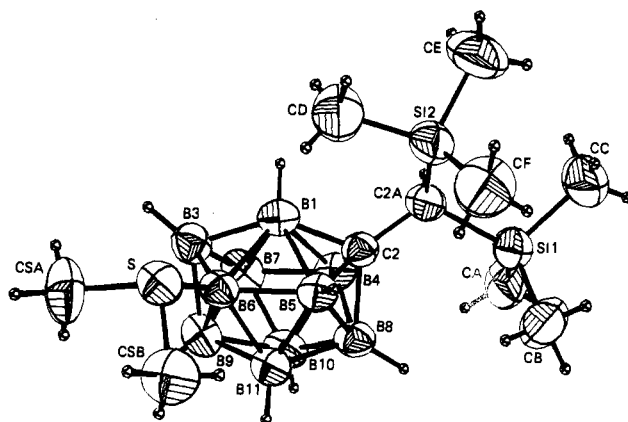


Figure 4. ORTEP drawing of the molecular structure of *closo*-6-Me₂S-2-(Me₃Si)₂CH-CB₁₀H₉ (VII).

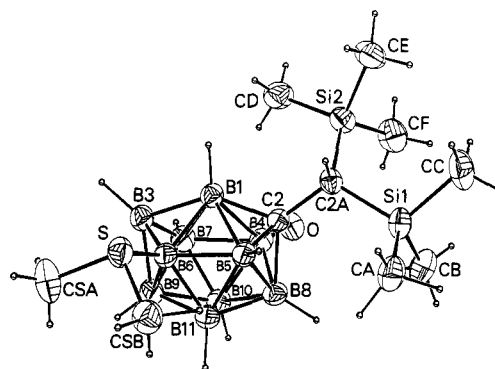


Figure 5. ORTEP drawing of the molecular structure of *closo*-6-Me₂S-4-OH-2-(Me₃Si)₂CH-CB₁₀H₈ (VIII).

isotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms.

Final positional parameters are given in Tables V-VIII. Intramolecular bond distances are presented in Tables IX and X. Figures 2, 3, 4, and 5 give ORTEP views of III, VI, VII, and VIII, respectively.

Results

The reaction of decaborane(14) and dimethyl sulfide for 6 h followed by further reaction with bis(trimethylsilyl)acetylene at benzene reflux for 12 h resulted in the isolation of two air-stable compounds. Compound II was a yellow solid which precipitated from methanol on cooling, while I was a white powder obtained when dropwise addition of water coaxed its precipitation from cold methanol

(3) B. A. Frenz and Assoc. Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland.

(4) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(5) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175-87.

(6) Cromer, D. T.; Ibers, J. A. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table IV. Data Collection and Structure Refinement Information for 5-(CH₃)₂S-6-[(CH₃)₃SiCH₂C=CH]-B₁₀H₁₁ (III), [Cp₂Co]⁺[2-((CH₃)₃Si)₂CH]-CB₁₀H₁₀⁻ (VI), 6-(CH₃)₂S-2-[(CH₃)₃Si)₂CH]-CB₁₀H₉ (VII), and 6-(CH₃)₂S-4-OH-2-[(CH₃)₃Si)₂CH]-CB₁₀H₈ (VIII)

	III	VI	VII	VIII
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	16.406 (4)	12.260 (1)	8.834 (3)	13.729 (1)
<i>b</i> , Å	16.677 (5)	17.252 (3)	19.211 (2)	16.345 (2)
<i>c</i> , Å	8.627 (2)	13.701 (3)	6.998 (1)	10.880 (1)
α , deg	100.67 (2)		96.20 (1)	96.62 (1)
β , deg	97.78 (2)	107.94 (1)	109.63 (2)	93.45 (1)
γ , deg	118.23 (2)		91.91 (2)	74.47 (1)
<i>V</i> , Å ³	1974.9	2757.0	1108.9	2335.4
<i>Z</i>	4	4	2	4
ρ (calcd), g cm ⁻³	0.991	1.153	1.050	1.043
cryst dimens, mm	0.35 × 0.30 × 0.20	0.32 × 0.28 × 0.10	0.24 × 0.20 × 0.08	0.25 × 0.20 × 0.22
mol formula	C ₈ H ₃₀ B ₁₀ SSi	C ₁₈ H ₃₉ B ₁₀ CoSi ₂	C ₁₀ H ₃₄ B ₁₀ SSi ₂	C ₂₅ H ₃₄ B ₁₀ OSSi ₂
mol wt	294.59	478.73	350.73	366.73
λ	Cu K α , 1.541 84 Å	Mo K α , 0.717 03 Å	Mo K α , 0.717 03 Å	Cu K α , 1.541 84 Å
scanning range, deg	0° ≤ 2 θ ≤ 45°	0° ≤ 2 θ ≤ 55°	0° ≤ 2 θ ≤ 55°	0° ≤ 2 θ ≤ 140°
scan mode	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
$\pm h, \pm k, \pm l$	±20, -20, ±10	+15, +22, ±17	+11, ±25, ±9	±16, +19, ±13
no. of measd <i>I</i> 's	7756	6834	5402	9198
no. of <i>F</i> _o ² > 3 σ (<i>F</i> _o ²)	5208	3061	2864	5623
no. of variables	361	313	238	487
abs coeff (μ), cm ⁻¹	18.33	7.11	2.37	21.52
trans coeff, %	55.6	89.1		89.8 (empirical)
max, min, %	64.0, 41.9	94.4, 81.5		99.7, 81.6
<i>R</i>	0.077	0.058	0.067	0.065
<i>R</i> _w	0.103	0.068	0.081	0.078

Table V. Positional Parameters and Their Estimated Standard Deviations for 5-(CH₃)₂S-6-[(CH₃)₃SiCH₂C=CH]-B₁₀H₁₁ (III)

atom	<i>x</i>	<i>y</i>	<i>z</i>
Si	0.06643 (7)	0.15843 (7)	0.8098 (1)
S	0.45441 (7)	0.41285 (7)	1.1124 (1)
C1	0.2196 (2)	0.3393 (2)	1.0101 (4)
C2	0.1473 (2)	0.2908 (2)	0.8738 (4)
C3	0.1294 (3)	0.3449 (3)	0.7629 (4)
CA	0.1384 (3)	0.0989 (3)	0.8175 (5)
CB	-0.0075 (3)	0.1197 (3)	0.5964 (5)
CC	-0.0152 (3)	0.1230 (4)	0.9456 (6)
CD	0.5730 (3)	0.4457 (4)	1.2118 (6)
CE	0.4336 (3)	0.3349 (3)	0.9217 (5)
B1	0.4012 (3)	0.3378 (3)	1.4132 (5)
B2	0.3161 (3)	0.3685 (3)	1.3528 (5)
B3	0.2933 (3)	0.2916 (3)	1.4742 (5)
B4	0.3470 (4)	0.2221 (3)	1.4453 (6)
B5	0.3678 (3)	0.3298 (3)	1.2109 (5)
B6	0.2567 (3)	0.3058 (3)	1.1466 (5)
B7	0.2025 (3)	0.2689 (3)	1.3050 (5)
B8	0.2235 (4)	0.1708 (3)	1.3832 (6)
B9	0.2860 (4)	0.1305 (3)	1.2692 (6)
B10	0.3836 (3)	0.2357 (3)	1.2593 (6)
Si'	0.66399 (9)	0.07297 (8)	0.3033 (1)
S'	0.90281 (9)	0.46855 (8)	0.6165 (1)
C1'	0.8412 (2)	0.2349 (2)	0.4925 (4)
C2'	0.7960 (2)	0.1613 (2)	0.3582 (4)
C3'	0.8516 (3)	0.1463 (3)	0.2412 (5)
CA'	0.5967 (3)	0.1362 (4)	0.3118 (6)
CB'	0.6286 (4)	-0.0047 (4)	0.0922 (7)
CC'	0.6348 (5)	-0.0019 (4)	0.4416 (7)
CD'	0.9258 (4)	0.5796 (3)	0.7273 (7)
CE'	0.8259 (4)	0.4475 (4)	0.4321 (6)
B1'	0.8258 (3)	0.4069 (3)	0.9117 (6)
B2'	0.8705 (3)	0.3330 (3)	0.8411 (5)
B3'	0.7911 (4)	0.3003 (4)	0.9675 (5)
B4'	0.7111 (4)	0.3430 (4)	0.9482 (6)
B5'	0.8221 (3)	0.3763 (3)	0.7072 (5)
B6'	0.8078 (3)	0.2700 (3)	0.6368 (5)
B7'	0.7776 (3)	0.2162 (3)	0.7953 (6)
B8'	0.6725 (4)	0.2234 (4)	0.8815 (7)
B9'	0.6205 (3)	0.2756 (4)	0.7755 (8)
B10'	0.7202 (3)	0.3789 (3)	0.7616 (6)

Table VI. Positional Parameters and Their Estimated Standard Deviations for [(η^5 -C₅H₅)₂Co]⁺[2-((CH₃)₃Si)₂CH]-CB₁₀H₁₀⁻ (VI)

atom	<i>x</i>	<i>y</i>	<i>z</i>
Co	0.22656 (5)	0.00177 (4)	0.22060 (4)
Si1	0.7137 (1)	0.38210 (9)	0.1850 (1)
Si2	0.36642 (1)	0.21222 (9)	0.0929 (1)
CA	0.7383 (6)	0.4429 (3)	0.3001 (5)
CB	0.6232 (5)	0.4410 (3)	0.0780 (4)
CC	0.8569 (5)	0.3718 (4)	0.1667 (5)
CD	0.8134 (4)	0.1731 (3)	0.1358 (4)
CE	0.5618 (4)	0.1303 (3)	0.0711 (4)
CF	0.6351 (5)	0.2587 (4)	-0.0356 (4)
C2A	0.6364 (3)	0.2863 (3)	0.1851 (3)
C2	0.6408 (4)	0.2542 (2)	0.2910 (3)
C11	0.2428 (6)	0.0079 (4)	0.3694 (4)
C12	0.1319 (5)	-0.0014 (4)	0.3147 (5)
C13	0.1008 (5)	0.0586 (4)	0.2510 (5)
C14	0.1902 (6)	0.1075 (3)	0.2633 (4)
C15	0.2804 (5)	0.0746 (4)	0.3383 (5)
C21	0.2508 (7)	0.0072 (4)	0.0852 (4)
C22	0.3523 (5)	-0.0132 (4)	0.1584 (5)
C23	0.3292 (5)	-0.0811 (4)	0.1967 (4)
C24	0.2224 (5)	-0.1014 (4)	0.1538 (5)
C25	0.1739 (6)	-0.0465 (5)	0.0841 (5)
B1	0.5900 (5)	0.3025 (4)	0.3707 (4)
B3	0.5895 (6)	0.2982 (4)	0.4948 (4)
B4	0.5387 (5)	0.2028 (3)	0.3082 (4)
B5	0.7506 (5)	0.2560 (4)	0.3882 (5)
B6	0.7217 (6)	0.2783 (5)	0.5081 (5)
B7	0.5066 (5)	0.2272 (4)	0.4267 (4)
B8	0.6820 (5)	0.1659 (3)	0.3411 (4)
B9	0.6342 (6)	0.2044 (4)	0.5310 (4)
B10	0.5956 (5)	0.1467 (3)	0.4216 (5)
B11	0.7391 (5)	0.1828 (4)	0.4741 (5)

Similar reaction of decaborane(14) and dimethyl sulfide with (trimethylsilyl)propyne gave only one product, III, which was shown, as discussed below, to be structurally related to compound II.

Chemical analysis and/or exact mass determination established that both I and II have the same molecular formula, (Me₃Si)₂C₂B₁₀H₁₂(SMe₂); however, the fragmentation patterns observed in their mass spectra clearly indicated structural differences. Both compounds show parent ions consistent with the proposed formulas, but I has a major fragment at *m/e* 204, corresponding to a loss

solutions. Both I and II could be further purified by preparative thin-layer chromatography and were isolated in 27.5% and 20.9% yields, respectively.

Table VII. Positional Parameters and Their Estimated Standard Deviations for 6-(CH₃)₂S-2-[(CH₃)₃Si]₂CH-CB₁₀H₉ (VII)

atom	x	y	z
S	0.2930 (1)	0.13876 (5)	0.2682 (2)
Si1	1.0302 (2)	0.32481 (7)	0.8211 (2)
Si2	0.6869 (2)	0.37717 (6)	0.5723 (2)
B1	0.6680 (5)	0.2081 (2)	0.2620 (7)
B3	0.5668 (6)	0.1328 (3)	0.1004 (7)
B4	0.8823 (5)	0.1816 (2)	0.4096 (7)
B5	0.6356 (5)	0.1971 (2)	0.5326 (7)
B6	0.5156 (5)	0.1383 (2)	0.3054 (7)
B7	0.7621 (6)	0.1214 (3)	0.1867 (7)
B8	0.8266 (5)	0.1629 (2)	0.6220 (7)
B9	0.6297 (5)	0.0678 (2)	0.2617 (7)
B10	0.8259 (5)	0.0947 (2)	0.4320 (7)
B11	0.6532 (5)	0.1054 (2)	0.5154 (7)
CSA	0.1996 (6)	0.0726 (3)	0.0592 (9)
CSB	0.2700 (5)	0.0981 (3)	0.4748 (8)
C2	0.7835 (4)	0.2350 (2)	0.4995 (5)
C2A	0.8452 (4)	0.3118 (2)	0.5780 (6)
CA	1.1980 (5)	0.2722 (3)	0.7961 (8)
CB	0.9876 (6)	0.3040 (3)	1.0521 (7)
CC	1.1128 (7)	0.4173 (3)	0.8689 (9)
CD	0.4885 (6)	0.3530 (3)	0.3699 (8)
CE	0.7564 (7)	0.4612 (3)	0.513 (1)
CF	0.6456 (7)	0.3935 (3)	0.8146 (9)

of a Me₄Si unit, while II showed a fragment at *m/e* 183, corresponding to loss of a (Me₃Si)₂C₂H- group. Both compounds also showed large peaks at *m/e* 73 and 62, attributed to Me₃Si and Me₂S.

Both the ¹¹B and ¹H NMR spectra of I indicate that the compound lacks a plane of symmetry. The ¹¹B NMR spectrum at 115.5 MHz contains nine resonances, one being of intensity 2, with the singlet at -20.4 ppm assigned to a dimethyl sulfide substituted boron. The fact that the remaining resonances are all doublets indicates that the organosilicon group cannot be bonded to a boron in a terminal fashion and suggests that there has been carbon insertion into the cage. This conclusion was confirmed by an X-ray structural study of I, which was carried out on a twinned crystal.⁷ Because of the twinning, the structure could not be refined anisotropically and, therefore, reliable calculation of bond distances and angles was not possible. However, the locations of all heavy atoms were determined, and the structure was refined to *R* = 0.18 and *R_w* = 0.24. The results of this investigation are consistent with the structure shown diagrammatically in Figure 1.

Compound I is, in fact, a monocarbon carborane, 9-Me₂S-7-[(Me₃Si)₂CH]-CB₁₀H₁₁, resulting from the cage insertion of only one of the acetylenic carbons of the bis-(trimethylsilyl)acetylene. The cluster geometry is based on an icosahedron missing one vertex, with the open face of the carborane consisting of a five-membered ring containing the cage carbon in the 7-position. Bonded to the carbon is an exopolyhedral bis(trimethylsilyl)methyl group, apparently formed by migration of a trimethylsilyl group from the cage carbon atom. The dimethyl sulfide is also bound to a boron on the open face, and, while they were not located in the X-ray study, the spectroscopic data are consistent with the presence of two bridging hydrogens. Thus, the boron spin-decoupled ¹H NMR spectrum shows two resonances each of intensity 1 at shifts (-2.23 and -3.28 ppm, respectively) characteristic of boron-bridging protons. The ¹H NMR spectrum also shows a singlet resonance of

Table VIII. Positional Parameters and Their Estimated Standard Deviations for 6-(CH₃)₂S-4-OH-2-[(CH₃)₃Si]₂CH-CB₁₀H₉ (VIII)

atom	x	y	z
Si1	0.40194 (9)	0.36351 (8)	0.5567 (1)
Si2	0.35789 (9)	0.17985 (7)	0.5151 (1)
S	0.19454 (8)	0.31076 (7)	-0.02270 (9)
CA	0.3600 (3)	0.4758 (3)	0.5168 (5)
CB	0.5424 (3)	0.3310 (3)	0.5394 (5)
CC	0.3766 (4)	0.3667 (3)	0.7246 (4)
CD	0.3391 (4)	0.0960 (3)	0.3921 (4)
CE	0.2683 (4)	0.1916 (3)	0.6397 (4)
CF	0.4879 (4)	0.1391 (3)	0.5816 (5)
C2A	0.3470 (3)	0.2853 (2)	0.4505 (3)
C2	0.2452 (2)	0.3206 (2)	0.3824 (3)
CSA	0.1733 (3)	0.2071 (3)	-0.0505 (4)
CSB	0.0929 (4)	0.3717 (3)	-0.1112 (4)
B1	0.2327 (3)	0.3911 (3)	0.2809 (4)
B3	0.1379 (3)	0.4542 (3)	0.1876 (4)
B4	0.1520 (3)	0.3874 (3)	0.4433 (4)
B5	0.2205 (3)	0.2761 (3)	0.2486 (4)
B6	0.1557 (3)	0.3503 (3)	0.1423 (4)
B7	0.0909 (3)	0.4644 (3)	0.3247 (5)
B8	0.1398 (3)	0.2837 (3)	0.3720 (4)
B9	0.0372 (3)	0.4094 (3)	0.2019 (4)
B10	0.0429 (3)	0.3792 (3)	0.3526 (4)
B11	0.0859 (3)	0.2999 (3)	0.2238 (4)
O	0.1546 (2)	0.4192 (2)	0.5667 (2)
Si3	0.60071 (9)	0.14354 (8)	0.0267 (1)
Si4	0.6534 (1)	0.32407 (8)	0.0687 (1)
S'	0.82172 (7)	0.20148 (7)	-0.49254 (9)
CG	0.4616 (3)	0.1809 (3)	-0.0037 (5)
CH	0.6213 (4)	0.1367 (3)	0.1959 (4)
CI	0.6393 (3)	0.0324 (3)	-0.0499 (5)
CJ	0.5235 (4)	0.3674 (3)	0.1275 (5)
CK	0.6758 (4)	0.4093 (3)	-0.0146 (5)
CL	0.7424 (4)	0.3069 (3)	0.2037 (4)
CSC	0.8460 (4)	0.3032 (3)	-0.4714 (4)
CSD	0.9246 (4)	0.1427 (4)	-0.5843 (5)
C2A'	0.6599 (3)	0.2222 (2)	-0.0375 (3)
C2'	0.7614 (2)	0.1837 (2)	-0.1020 (3)
B1'	0.7704 (3)	0.1169 (3)	-0.2307 (4)
B3'	0.8626 (3)	0.0534 (3)	-0.3321 (5)
B4'	0.8502 (3)	0.1138 (3)	-0.0530 (4)
B5'	0.7921 (3)	0.2294 (3)	-0.2126 (4)
B6'	0.8532 (3)	0.1567 (3)	-0.3385 (4)
B7'	0.9065 (3)	0.0361 (3)	-0.1916 (5)
B8'	0.8719 (3)	0.2139 (3)	-0.0793 (4)
B9'	0.9679 (3)	0.0889 (3)	-0.2837 (5)
B10'	0.9623 (3)	0.1154 (3)	-0.1211 (5)
B11'	0.9256 (3)	0.1979 (3)	-0.2237 (4)
O'	0.8439 (2)	0.0797 (2)	0.0574 (2)

Table IX. Selected Interatomic Distances (Å) for 5-(CH₃)₂S-6-[(CH₃)₃SiCH₃C=CH]-B₁₀H₁₁ (III)^a

B1-B2	1.750 (8)	B5-B10	1.817 (8)
B1-B3	1.766 (7)	B6-B7	1.778 (6)
B1-B4	1.798 (7)	B7-B8	2.032 (9)
B1-B5	1.717 (6)	B8-B9	1.774 (9)
B1-B10	1.828 (7)	B9-B10	1.756 (6)
B2-B3	1.741 (7)	C1-C2	1.344 (4)
B2-B5	1.773 (7)	C1-B6	1.562 (6)
B2-B6	1.757 (5)	C2-Si	1.876 (3)
B2-B7	1.736 (5)	C2-C3	1.520 (6)
B3-B4	1.761 (9)	Si-CA	1.869 (6)
B3-B7	1.780 (7)	Si-CB	1.869 (4)
B4-B8	1.739 (8)	Si-CC	1.857 (6)
B4-B9	1.711 (6)	S-B5	1.887 (4)
B4-B10	1.804 (7)	S-CD	1.784 (5)
B5-B6	1.657 (6)	S-CE	1.775 (4)

^a Distances given are for only one of the two independent molecules in the unit cell.

(7) The crystal was found to be twinned along *a*. Data collection was performed by assuming *a* = 23.952 Å. However, the data were subsequently transformed to correspond to a cell with dimensions *a* = 11.976 (4) Å, *b* = 9.099 (2) Å, *c* = 20.981 (14) Å, β = 90.31°, and space group *P*2₁/*c*.

intensity 18 for the trimethylsilyl protons and an intensity one resonance at 0.93 ppm which is assigned to the methyl proton of the bis(trimethylsilyl)methyl moiety. The absence of a plane of symmetry in the cage is reflected in the

Table X. Selected Interatomic Distances (Å) for [Cp₂Co]⁺[2-(Me₃Si)₂CH]-CB₁₀H₁₁⁻ (VI), 6-Me₂S-2-(Me₃Si)₂CH-CB₁₀H₉ (VII), and 6-Me₂S-4-OH-2-(SiMe₃)₂CH-CB₁₀H₈ (VIII)^a

	VI	VII	VIII
B1-C2	1.641 (8)	1.646 (5)	1.656 (6)
B1-B3	1.704 (9)	1.747 (3)	1.775 (6)
B1-B4	1.938 (8)	1.943 (6)	2.157 (7)
B1-B5	2.070 (9)	2.040 (7)	1.923 (6)
B1-B6	2.110 (8)	1.987 (7)	1.948 (6)
B1-B7	1.950 (9)	1.985 (7)	2.045 (6)
C2-B4	1.609 (7)	1.581 (6)	1.568 (5)
C2-B5	1.575 (6)	1.570 (6)	1.610 (5)
C2-B8	1.682 (7)	1.693 (6)	1.703 (6)
C2-C2A	1.540 (6)	1.532 (5)	1.542 (4)
B3-B6	1.611 (10)	1.637 (8)	1.669 (6)
B3-B7	1.679 (9)	1.656 (7)	1.634 (7)
B3-B9	1.731 (10)	1.752 (7)	1.750 (7)
B4-B7	1.833 (9)	1.819 (6)	1.905 (7)
B4-B8	1.791 (8)	1.782 (8)	1.826 (6)
B4-B10	1.781 (8)	1.763 (7)	1.770 (6)
B5-B6	1.825 (10)	1.825 (5)	1.795 (6)
B5-B8	1.790 (8)	1.767 (6)	1.764 (6)
B5-B11	1.762 (9)	1.768 (6)	1.794 (6)
B6-B9	1.755 (11)	1.775 (7)	1.773 (6)
B6-B11	1.743 (10)	1.757 (6)	1.754 (7)
B6-S		1.895 (5)	1.894 (4)
B7-B9	1.808 (7)	1.776 (8)	1.759 (7)
B7-B10	1.781 (9)	1.757 (7)	1.754 (8)
B8-B10	1.780 (10)	1.761 (7)	1.784 (6)
B8-B11	1.763 (8)	1.751 (6)	1.751 (6)
B9-B10	1.740 (9)	1.764 (5)	1.758 (7)
B9-B11	1.738 (10)	1.784 (7)	1.774 (7)
B10-B11	1.795 (9)	1.818 (7)	1.806 (6)
Si1-CA	1.840 (6)	1.867 (5)	1.864 (5)
Si1-CB	1.847 (5)	1.858 (6)	1.873 (4)
Si1-CC	1.857 (7)	1.850 (6)	1.872 (5)
Si2-CD	1.866 (5)	1.852 (5)	1.860 (5)
Si2-CE	1.853 (6)	1.846 (6)	1.844 (5)
Si2-CF	1.866 (5)	1.848 (6)	1.864 (5)
S-CSA		1.776 (6)	1.784 (5)
S-CSB		1.781 (6)	1.783 (5)
C2A-Si1	1.905 (5)	1.908 (3)	1.900 (4)
C2A-Si2	1.901 (5)	1.903 (4)	1.902 (4)
B-O			1.384 (5)

^aDistances given are for only one of the two independent molecules in the unit cell.

fact that separate resonances are observed for each of the dimethyl sulfide methyl groups.

The nido-cage geometry observed for the carborane is consistent with skeletal electron-counting rules⁸ and is similar to that found for isoelectronic 11-vertex cage systems, such as B₁₀H₁₂CNH₃,⁹ CB₁₀H₁₃⁻,¹⁰ C₂B₉H₁₃,¹¹ B₁₁H₁₃,^{2,12} B₁₀H₁₂PC₆H₅,¹³ and B₁₀H₁₂S.¹⁴ In this regard, it should be noted that the ¹¹B NMR spectrum is, in fact, quite similar to those reported¹⁵ for B₁₀CH₁₃⁻ and B₁₀H₁₂CNMe₃, suggesting the assignments given in Table I.

Compound II, which was also isolated as a major product of the reaction of bis(trimethylsilyl)acetylene with decaborane(14), was shown by its mass spectrum to be an isomer of I; however, the spectroscopic data indicate that

it has a substantially different structure. It was also observed that the reaction of (trimethylsilyl)propyne with decaborane(14) gave a single product, III, which has a similar ¹¹B NMR spectrum to that obtained for II, suggesting that II and III are structurally related. A single-crystal X-ray structural determination carried out on compound III indicates that both compounds result from acetylene hydroboration reactions. As can be seen in Figure 2, compound III has a decaborane(14) cage geometry with a dimethyl sulfide bound to the 5-boron position and a -CH=Me(SiMe₃) group bound at the 6-position.

Tolpin has previously observed¹⁶ that B₁₀H₁₂(SMe₂)₂ will also hydroborate olefins to yield compounds analogous to II and III. For example, the product of the reaction of B₁₀H₁₂(SMe₂)₂ with cyclohexene was crystallographically determined¹⁷ to be 9-C₆H₁₁-5-Me₂S-B₁₀H₁₁. The cage structures observed for both 9-C₆H₁₁-5-Me₂S-B₁₀H₁₁ and III are quite similar to that found for the isoelectronic B₁₀H₁₃⁻ anion.¹⁸ In each of the compounds there are only three bridge hydrogens, instead of the four found in decaborane(14). In B₁₀H₁₃⁻ this results in a shortened B5-B6 distance, 1.65 Å, whereas the same bond in B₁₀H₁₄, where the hydrogen bridge is present, is 1.790 (3) Å.¹⁹ Similar shortened distances are observed for the B5-B6 borons in 9-C₆H₁₁-5-Me₂S-B₁₀H₁₁ (1.64 (1) Å) and the B5-B6 borons in III (1.657 (6) Å), suggesting an increased boron-boron single-bond character in these bonds.

The exopolyhedral organosilyl group is bound to the 6-position boron in III. The most unusual feature of this group is that it is a (Me₃Si)MeC=CH-group; that is, following the hydroboration of the (trimethylsilyl)propyne the fragment has rearranged via a trimethylsilyl migration from the α-carbon to the β-carbon of the olefinic unit. As discussed earlier, this is, in fact, one of the key steps required in the formation of the monocarbon carborane I. The ¹H NMR spectrum of III is consistent with this structure showing SiMe₃ and CH₃ resonances, along with a singlet olefinic resonance of intensity 1 at 6.93 ppm. As can be seen in Figure 2 the vinyl group is bent away from the SMe₂, toward the B7 boron. Thus, the dihedral angle between the plane of the olefin (Si, C3, C2, C1, B6) and the B6, B2, B4, B9 plane is 25.0°. The distances of closest contact between C1 and C2 and the cage atoms are C1-B7, 2.986 Å and C2-B7, 3.833 Å.

As mentioned above, the spectral data obtained for II are also consistent with its formulation as the acetylene hydroboration product: 5-Me₂S-6-(Me₃Si)₂C=CH-B₁₀H₁₁. It is important to note, the ¹H NMR spectrum of II indicates, as in the case of III, that a trimethylsilyl group migration has occurred. Thus, the ¹H NMR spectrum of II shows a singlet of intensity 1 at 7.97 ppm for the methylene proton. The low-field shift of this proton is highly indicative of the (Me₃Si)₂C=CH unit.²⁰

Synthesis of *closo*-2-(Me₃Si)₂CH-CB₁₀H₁₀⁻. The reaction of the monocarbon carborane I with either NaH, LiEt₃BH, Na, or cobaltocene results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the 2-(Me₃Si)₂CH-CB₁₀H₁₀⁻ anion. A single-crystal X-ray determination of the cobaltocenium salt (VI) established that the compound has a *closo* structure based on a oc-

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tadecahedron with the cage carbon atom occupying the four-coordinate 2-position in the structure. This structure is consistent both with the clusters $2n + 2$ skeletal electron count and with the structure proposed²¹ for the parent $\text{CB}_{10}\text{H}_{11}^-$ anion. It should be noted, however, that the ^{11}B NMR spectra of $2-(\text{Me}_3\text{Si})_2\text{CH}-\text{CB}_{10}\text{H}_{10}^-$ and $\text{CB}_{10}\text{H}_{11}^-$ indicate that these cages are fluxional in solution. Thus, on the basis of the structure shown in Figure 3, the ^{11}B NMR spectrum would be expected to show resonances in a ratio of 1:1:1:2:2:2; however, the ^{11}B NMR spectra of both anions show only three doublets in a ratio of 1:5:4. Hawthorne has previously noted²¹ this behavior in $\text{CB}_{10}\text{H}_{11}^-$ and proposed that these spectra could arise by rotation of the B1, B4, B7, B8 and B2, B5, B6, B10, B11 planes, thereby rendering the atoms in each plane equivalent.

Thermolysis of 9-Me₂S-7-(Me₃Si)₂CH-CB₁₀H₁₁. I was heated either at toluene reflux or at 140 °C in the solid phase in vacuo yielding a mixture of products which were then separated by preparative TLC. The major product of both reactions was identified as 6-Me₂S-2-(Me₃Si)₂CH-CB₁₀H₉ (VII) on the basis of a single-crystal X-ray determination, the results of which are depicted in Figure 4. The compound is, in fact, isoelectronic with the $2-(\text{Me}_3\text{Si})_2\text{CH}-\text{CB}_{10}\text{H}_{10}^-$ anion and has a similar octadecahedral structure. Selected bond lengths for both compounds are presented in Table X. Although there are small differences in the various bond lengths, the compounds are remarkably similar. The ^{11}B NMR of VII is consistent with the X-ray structure, showing four resonances in a ratio of 1:2:4:2 indicating that unlike VI, VII is not fluxional in solution.

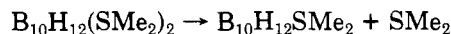
Also isolated in small amounts in the solid-phase pyrolytic reactions was the closo hydroxy-substituted compound 6-Me₂S-4-OH-2-(Me₃Si)₂CH-CB₁₀H₉ (VIII), the identity of which was also established by means of a single-crystal X-ray analysis (Figure 5). The compound has a closo-octadecahedral structure similar to those found for VI and VII. While most of the cage interatomic distances (Table X) observed for VIII are similar to those of VI and VII, the distances between B4, which has the exopolyhedral hydroxy group, and the surrounding borons B1, B7, B10 and B8 are found to be lengthened. A similar effect was previously noted in the compound 2,3-(CH₃)₂-4,7-(OH)₂-10-Br-2,3-C₂B₉H₆²² and was attributed to a cage distortion arising from the back-donation of electron density from the oxygen lone pairs of the hydroxy group into the cage framework orbitals. The boron-oxygen distance in VIII (1.384 (5) Å) is also similar to that observed for 2,3-(CH₃)₂-4,7-(OH)₂-10-Br-2,3-C₂B₉H₆²² (1.37 (1) Å). The formation of a hydroxy-substituted compound such as VIII is indeed surprising; however, the compound was formed in only trace amounts and most probably resulted from the reaction of I with water impurity under the thermolytic reaction conditions.

In both of the pyrolytic reactions several additional bands were isolated in quantities insufficient to allow complete characterization. Mass spectral analysis, however, suggests that these compounds may in fact be larger fused-cage systems.

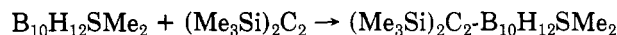
Discussion

The results presented above have demonstrated that the dimethyl sulfide promoted reactions of decaborane(14) with the silylated acetylenes bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne do not result in alkyne in-

sertion reactions but rather yield alkenyldecaborane products and, in the case of bis(trimethylsilyl)acetylene, a monocarbon carborane. The initial reaction sequence leading to the formation of these compounds is undoubtedly related to the reaction mechanism² involved in the formation of *ortho*-carborane. For example, as in the synthesis of 1,2-C₂B₁₀H₁₂, the first step probably involves the dissociation of one of the dimethyl sulfide ligands from B₁₀H₁₂(SMe₂)₂.



The resulting B₁₀H₁₂SMe₂ fragment is electrophilic and would readily form an adduct with an acetylene, such as bis(trimethylsilyl)acetylene.



The acetylene adduct could then react further in one of two ways: (1) the second dimethyl sulfide could dissociate, followed by acetylene insertion and hydrogen loss to yield the *ortho*-carborane derivative 1,2-(Me₃Si)₂C₂B₁₀H₁₀ or (2) hydroboration of the acetylene could occur by the 6-position B-H group to yield an alkenyldecaborane product. Whether reaction (1) or (2) is favored should depend on the relative ability of the bound acetylene to undergo hydroboration.

In general, it has been observed that electron-rich olefins and acetylenes hydroborate much more readily than those containing electron-withdrawing groups.²³ Since the Si-C bond in a silylated acetylene should be polarized,²⁴ the acetylenic carbon is slightly negative and should show enhanced reactivity toward electrophilic attacks like hydroboration.²⁵

The initial hydroboration products of the reactions of bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne with B₁₀H₁₂(SMe₂)₂ would be expected to be 9-Me₂S-6-(Me₃SiC(H)=C(SiMe₃))-B₁₀H₁₂ and 9-Me₂S-6-(CH₃)C(H)=C(SiMe₃)-B₁₀H₁₂, respectively; however, the actual alkenyl products obtained were 5-Me₂S-6-((Me₃Si)₂C=CH)-B₁₀H₁₂ and 5-Me₂S-6-(Me₃Si(CH₃)C=CH)-B₁₀H₁₂. Thus, two rearrangements have occurred in both systems. First, in each compound a trimethylsilyl group has migrated from the α- to the β-carbon of the olefinic group. Such a migration may have been induced by the steric repulsion between a Me₃Si group on the α-carbon and the decaborane cage. It should be noted that a similar Me₃Si migrations between olefinic carbons have been observed in other organoboron compounds.²⁶ A second rearrangement which has taken place in these compounds has involved the migration of the Me₂S group from the 9-position to the 5-position. As mentioned earlier, Tolpin^{16,17} has previously studied the hydroboration of cyclohexene by B₁₀H₁₂(SMe₂)₂ and found 9-C₆H₁₁-5-Me₂S-B₁₀H₁₂ to be the major product. The formation of this product also involves a Me₂S migration, but the reasons for the differences in the Me₂S substitution preferences in these

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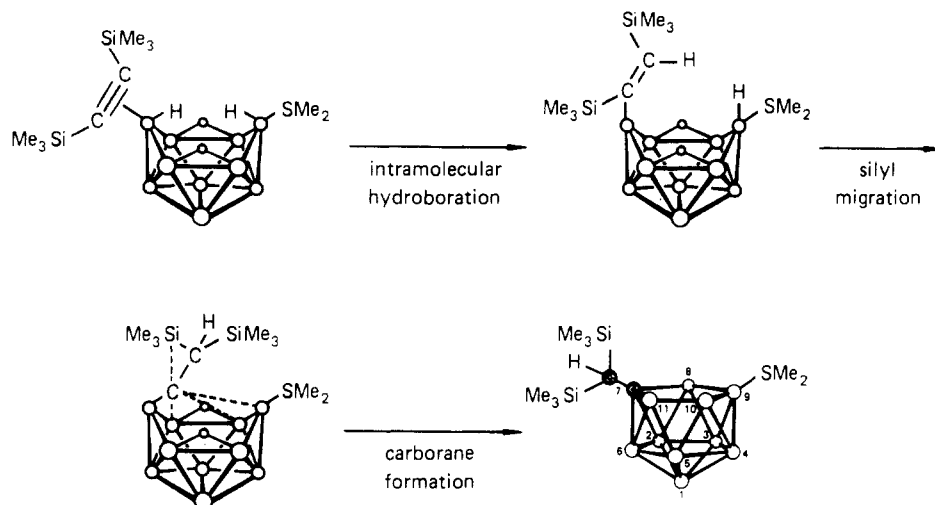
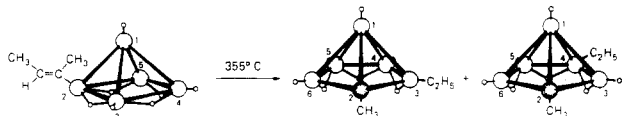


Figure 6. Possible reaction sequence leading to the formation of 9-Me₂S-7-[(Me₃Si)₂CH]-B₁₀H₁₁.

systems is not readily apparent.

We have previously shown²⁷ that small cage alkenylboranes, such as alkenylpentaboranes, can be converted in high yields to monocarbon carboranes. For example, the thermolysis of 2-butenylpentaborane gives monocarbon carboranes based on the 2-CB₅H₉ cage system in ~90% yields.



We proposed that this one carbon insertion reaction proceeds via an intramolecular hydroboration reaction in which an adjacent cage B-H group adds to the olefinic bond, leading to insertion of the α -carbon into the cage. These observations suggested that the alkenyldecaborane compound II might, in fact, be the precursor to the monocarbon carborane I. Thermolysis of II did not, however, yield compound I. It may be instead that the proposed initial hydroboration product 9-Me₂S-6-(Me₃SiC(H)=CSiMe₃)-B₁₀H₁₂ is the precursor to II. Thus, once formed the compound could either rearrange, as discussed above, to form 5-Me₂S-6-((Me₃Si)₂C=CH)-B₁₀H₁₂ or, as shown in Figure 6, undergo silyl group migration and α -carbon insertion to yield I. Such a difference in reactivity of different substituted-decaborane isomers is not unprecedented. For example, as mentioned earlier, the species 6-Me₂S-B₁₀H₁₂ is the proposed intermediate in the *ortho*-carborane synthesis; however, the isomer of this compound 5-Me₂S-B₁₀H₁₂ can be prepared and has been found to be unreactive toward alkynes.^{2,28}

Other ten-boron nido-monocarbon carboranes, such as R₃NCB₁₀H₁₂ and CB₁₀H₁₃⁻, have previously been syn-

thesized by the reactions of decaborane(14) with, for example, cyanide^{9,29} or alkyl isocyanides.^{15,29} Compound I is unusual, however, in that under appropriate conditions both the two bridging hydrogens and the boron-coordinated dimethyl sulfide group are reactive. Thus, deprotonation (with NaH or LiBEt₃H) or reduction (with Na or (η -C₅H₅)₂Co) results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the previously known *closo*-RCB₁₀H₁₀⁻ anion. Under thermolytic conditions, only hydrogen loss is observed and again cage closure occurs to give the isoelectronic neutral *closo* system RCB₁₀H₉SMe₂. Thus, the compound appears to have a number of different modes of reactivity. One aspect of particular interest is that I could function as an η^5 six-electron ligand with different formal oxidation states. For example, both of the nido ten-vertex cage anions RCB₁₀H₉SMe₂²⁻ and RCB₁₀H₁₀³⁻ are possible, and indeed we have now synthesized a wide variety of transition-metal sandwich complexes in which the carborane ligand exhibits these different formal oxidation states. These studies will be the subject of a forthcoming publication.

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Registry No. I, 105335-10-2; II, 105371-62-8; III, 105335-11-3; IV, 105335-12-4; VI, 105309-49-7; VII, 105335-13-5; VIII, 105399-70-0; [(CH₃)₄N]⁺[2-((CH₃)₃Si)₂CH]-CB₁₀H₁₀]⁻, 105309-50-0; Na⁺[2-((CH₃)₃Si)₂CH]-CB₁₀H₁₀]⁻, 105309-51-1; (CH₃)₂S, 75-18-3; decaborane(14), 17702-41-9; bis(trimethylsilyl)acetylene, 14630-40-1; (trimethylsilyl)propyne, 6224-41-5; cobaltocene, 1277-43-6.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen atom coordinates, least-squares planes, bond distances, and bond angles for compounds III, VI, VII, and VIII (53 pages); listings of observed and calculated structure factor amplitudes for III, VI, VII, and VIII (46 pages). Ordering information is given on any current masthead page.

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