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A Simple High-Yield Sulfur-Insertion Reaction: Synthesis and Structural Characterizations of New 11-Vertex *arachno*-Dithiaborane Clusters

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The reaction of *nido*-6-$SB_9H_{10}^-$ with elemental sulfur results in sulfur insertion into the *nido*-SB_9 cage framework to produce the new *arachno*-dithiaborane cluster anion, *arachno*-2,3-$S_2B_9H_{10}^-$ ($\mathbf{1}^-$). A single crystal X-ray study has confirmed that, consistent with its formal arachno skeletal-electron count, the anion adopts a structure that may be derived from a 13-vertex closo-deltahedron by removal of two vertices. Crystal data for $PSH^+\mathbf{1}^-$: a = 9.294(1) Å, b = 12.236(1) Å, c = 19.479(3) Å, β = 100.02(1)°, V = 2181.3(8) Å^3, and Z = 4 in the monoclinic space group $P2_1/c$. The two sulfur atoms adopt nonadjacent three-coordinate positions on the open six-membered face of the cage. In the solid state, a single bridge hydrogen was located at the B8−B11 edge; however, in solution, the NMR spectra indicate C_s cage symmetry suggesting that the bridging hydrogen is interconverting between positions at the B8−B11 and B9−B11 edges. The spectroscopic data indicate that, upon reaction of *arachno*-2,3-$S_2B_9H_{10}^-$ ($\mathbf{1}^-$) with concentrated H_2SO_4 in CH_2Cl_2, protonation occurs at one of the cage sulfur sites to give *arachno*-2-H-2,3-$S_2B_9H_{10}$ (**1**). Thermolysis of **1** in refluxing toluene results in dehydrogenation and formation of the previously known compound *nido*-7,9-$S_2B_9H_9$. Deprotonation of **1** with Proton Sponge regenerates $\mathbf{1}^-$. $\mathbf{1}^-$ also reacts with CH_3I or CH_2I_2 to give *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**) and *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ (**3**), respectively. A single crystal X-ray structure determination of **2** confirmed that the methyl is bound to a sulfur atom and thus provides additional support for the structure proposed for **1**. Crystal data for **2**: a = 7.733(1) Å, b = 10.043(3) Å, c = 13.630(2) Å, β = 101.84(1)°, V = 1036.0(6) Å^3, and Z = 4 in the monoclinic space group $P2_1/c$. In contrast to the structure observed for $\mathbf{1}^-$, in **2** the methylated sulfur adopts only a two-coordinate position bridging a boron−boron edge, while the other sulfur is in a three-coordinate position similar to those observed in $\mathbf{1}^-$. The similarity of the NMR spectra of **1**, **2**, and **3** suggest that **1** and **3** adopt cage structures similar to that confirmed for **2**. Thus, either alkylation or protonation of $\mathbf{1}^-$ results in not only substitution at sulfur, but alters the nature of the sulfur-cage bonding interactions. The reaction of **2** with Proton Sponge results in the removal of the bridge hydrogen to yield the *arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ ($\mathbf{2}^-$) anion.

Introduction

An area of continuing importance in polyhedral boron chemistry is the development of new efficient synthetic methods by which atom-insertion reactions leading to expanded-cage or hybrid clusters may be accomplished. Of particular interest to our two groups has been the synthesis and properties of dithiaborane clusters,[3] since the incorporation of electron-rich sulfur atoms into a borane cage framework results in clusters which often exhibit unique structures intermediate those found for electron-precise and electron-deficient systems. In this paper we report a new, surprisingly simple, sulfur-insertion reaction that has allowed the production of a variety of previously unknown *arachno*-S_2B_9 cluster systems.

Experimental Section

All manipulations were carried out by using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[4]

Materials. The *nido*-6-SB_9H_{11} was prepared as previously reported.[5] Proton Sponge (PS), 1,8-bis(dimethylamino)naphthalene, methyl iodide, and diiodomethane were purchased from Aldrich and used as received. Methylene chloride was dried by distillation over P_2O_5 and freshly distilled from molecular sieves before use. Pentane, hexane, toluene, THF, and diethyl ether were dried with sodium benzophenone and freshly distilled before use. Sulfur, $MgSO_4$, and sulfuric acid were purchased from Fisher and used as received. Oil-dispersed potassium

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hydride was obtained from Aldrich, washed with dry hexane under a nitrogen atmosphere, and then vacuum dried.

Physical Measurements. ^1H NMR spectra at 200.1 MHz and ^{11}B NMR at 64.2 MHz were obtained on a Bruker AF-200 spectrometer, equipped with the appropriate decoupling accessories. ^{11}B NMR at 160.5 MHz and ^1H NMR spectra at 500.1 MHz were obtained on a Bruker AM-500 spectrometer or a Varian XL-500 spectrometer. All ^{11}B chemical shifts were referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^1H chemical shifts were measured relative to internal residual protons in the lock solvents and then referenced to Me_4Si (0.0 ppm). Microanalysis was performed at Robertson Microlit, Madison, NJ. High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1430 infrared spectrophotometer. Diffuse reflectance IR spectra (DRIFT) were obtained on a Perkin-Elmer 7770 Fourier transform spectrophotometer equipped with the appropriate diffuse reflectance attachment. Melting points were obtained on a standard melting point apparatus and are uncorrected.

***arachno*-2,3-$S_2B_9H_{10}^-$ (1^-).** To a 250 mL round bottom flask was added a solution of 3.12 g (22.0 mmol) of *nido*-6-SB_9H_{11} dissolved in 50 mL of CH_2Cl_2 and 1.0 g (31.2 mmol) of elemental sulfur. This solution was then stirred and maintained at −15 °C while a solution containing 4.7 g of Proton Sponge (22.0 mmol) dissolved in 10 mL of CH_2Cl_2 was added dropwise over 10 min. The resulting reaction was slightly exothermic, and the mixture turned from colorless to yellow. The mixture was stirred at ambient temperature for an additional 24 h, and then silica gel (ca. 10 g) was added and the CH_2Cl_2 evaporated using a rotary evaporator. The solid residue was placed onto a dry silica gel column, which was then eluted with a mixture of CH_2Cl_2−hexane (1:1, v/v). Evaporation of this fraction to dryness and recrystallization from a concentrated CH_2Cl_2 solution by addition of a 2-fold volume of hexane gave 3.96 g (10.2 mmol, 47% yield) of PSH^+*arachno*-2,3-$S_2B_9H_{10}^-$ (PSH^+1^-) as yellow crystals. TLC (silica gel/CH_2Cl_2): R_f 0.15. For PSH^+1^-. IR (KBr pellet, cm^{-1}): 3060 (w), 3000 (w), 2960 (w), 2520 (vs), 1460 (m), 1390 (m), 1270 (m), 1225 (m), 1190 (m), 1165 (m), 1100 (m), 1030 (s), 1020 (s, sh), 930 (w), 830 (m), 765 (s), 610 (m), 595 (w), 470 (w). Anal. Calcd: C, 43.47; H, 7.56; N, 7.24; B, 25.15; S, 16.58. Found: C, 43.51; H, 7.69; N, 7.17; B, 24.76; S, 15.95.

***arachno*-2-H-2,3-$S_2B_9H_{10}$ (1).** In a 100 mL round bottom flask was added 0.71 g (1.83 mmol) of PSH^+1^- dissolved in 30 mL of CH_2Cl_2, and the solution was cooled at 0 °C. To this solution was added dropwise 5 mL of concentrated H_2SO_4, and the mixture was stirred for 1 h. The CH_2Cl_2 layer was separated and the H_2SO_4 layer extracted twice with CH_2Cl_2. The CH_2Cl_2 layers were combined, dried over $MgSO_4$, and then filtered. Vacuum evaporation of the CH_2Cl_2 left a yellow solid. Recrystallization from CH_2Cl_2/hexane afforded 0.24 g (1.38 mmol, 75.8% crude yield) of *arachno*-2-H-2,3-$S_2B_9H_{10}$ (**1**). Sublimation in vacuo at 50 °C was used to further purify samples for spectroscopic characterization. For **1**, Mp: ~120 °C dec. DRIFT (KBr, cm^{-1}): 2565 (vs), 2480 (s), 1455 (m), 1200 (w), 1025 (m), 1005 (s), 780 (m), 690 (w), 640 (w), 555 (w). Exact mass: calcd for $^{32}S_2{}^{11}B_9{}^1H_9$ (M − 2H) 172.0983, found 172.0991.

Thermolysis of 1. A 1.07 g (2.77 mmol) sample of 1^- was used to synthesize **1**, which was then dissolved in 10 mL of toluene in a 100 mL round bottom flask. The solution was refluxed for 2 h. The toluene was vacuum-evaporated at −20 °C, and the remaining solid was dissolved in CH_2Cl_2 and passed down a short column of silica gel. The fractions containing the product were combined, and the CH_2Cl_2 was vacuum-evaporated at −20 °C. The product was recrystallized from pentane at −78 °C to give 0.17 g (1.00 mmol, 36.1% yield) of material that was identified as *nido*-7,9-$S_2B_9H_9$ by comparison of its mass spectral and ^{11}B NMR data with literature values.[3g,q]

***arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (2).** In a 100 mL round bottom flask was added 1.06 g (2.75 mmol) of PSH^+1^- dissolved in 50 mL of CH_2Cl_2. To the reaction solution was then added via syringe 2.0 mL (32 mmol) of methyl iodide. The reaction mixture was stirred at room temperature overnight. The reaction solution was filtered, and the CH_2Cl_2 was vacuum-evaporated at −20 °C. The remaining solid was extracted with hexane. The hexane solution was then filtered and the hexane vacuum-evaporated at −20 °C. Vacuum sublimation at room temperature gave 0.28 g (1.50 mmol, 55% yield) of *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**). Mp: 47−48 °C. DRIFT (KBr, cm^{-1}): 2955 (w), 2575 (vs), 2545 (vs), 2345 (m), 1415 (m), 1310 (m), 1260 (m), 1090 (m), 1035 (s), 1005 (s), 795 (m), 680 (m), 555 (m). Exact mass: calcd for $^{12}C^{32}S_2{}^{11}B_9{}^1H_{12}$ (M − H) 187.1218, found 187.1223.

***arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ (2^-).** In a 50 mL round bottom flask was added 0.12 g (0.64 mmol) of **2** dissolved in 5 mL of diethyl ether. To this solution was added 0.16 g (0.75 mmol) of Proton Sponge in 5 mL of diethyl ether. After the solution was stirred for 30 min at room temperature, the resulting yellow precipitate was removed and washed with additional diethyl ether. The precipitate was then dissolved in CH_2Cl_2 and recrystallized by addition of hexane to afford 0.18 g (0.45 mmol, 70% yield) of PSH^+*arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ (PSH^+2^-). DRIFT (KBr, cm^{-1}): 3055 (m), 3015 (m), 2930 (m), 2845 (m), 2575 (s), 2515 (vs), 2475 (vs), 2360 (s), 1470 (m), 1305 (m), 1275 (m), 1220 (m), 1185 (m), 1055 (m), 1020 (m), 830 (m), 775 (m), 615 (m), 490 (m). Anal. Calcd: C, 44.95; H, 7.79; N, 6.99; B, 24.27; S, 16.00. Found: C, 44.96; H, 7.80; N, 6.90; B, 24.11; S, 15.87.

Attempted Reaction of 2^- with CH_3I. In a 100 mL round bottom flask was added 0.04 g (0.21 mmol) of **2** dissolved in 5 mL of CH_2Cl_2, and 0.05 g (0.23 mmol) of PS was added. Then, 0.3 mL (4.8 mmol) of CH_3I was added and the solution stirred for several days. NMR analysis of the solution showed no evidence of reaction.

***arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ (3).** In a 100 mL round bottom flask was added 1.21 g (3.13 mmol) of 1^- dissolved in 20 mL of CH_2Cl_2, and 2.5 mL (31 mmol) of CH_2I_2 was added. The solution was refluxed overnight. The volatiles were then vacuum-evaporated to give an oily solid. The product was extracted from the oil with hexane and the hexane then vacuum-evaporated to give a white solid. The product was recrystallized from pentane at −78 °C to give 0.17 g (0.54 mmol, 17.3% yield) of *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ (**3**). Mp: 33−35 °C. DRIFT (KBr, cm^{-1}): 3035 (s), 2965 (s), 2565 (vs), 1375 (m), 1140 (s), 1080 (w), 1020 (s), 1005 (s), 785 (m), 690 (m), 565 (m). Exact mass: calcd for $^{12}C^{32}S_2{}^{11}B_9{}^1H_{11}{}^{127}I$ (M − H) 313.0184, found 313.0176.

Attempted Reaction of 3 with KH or Proton Sponge. In a 100 mL round bottom flask was added 0.06 g (0.19 mmol) of **3** dissolved in 5 mL of THF. The solution was maintained at −78 °C, and 0.01 g (0.25 mmol) of KH was slowly added. Upon slow warming to room temperature, hydrogen evolution occurred, but the resulting product decomposed too rapidly to allow isolation and characterization. A reaction with Proton Sponge gave similar results.

Computational Methods. The structure of 1^- was investigated by the combined ab initio/IGLO/NMR method using the GAUSSIAN92 program,[6] as described previously.[7] The calculations were performed on a Silicon Graphics International IRIS 4D/440VGX computer or an IBM RS/6000 Model 580 computer. The calculations were performed at the DZ//6-31G* level using the following basis sets. Basis DZ: C, B 7s3p contracted to [4111, 21]; H 3s contracted to [21]; S 10s6p contracted to [511111, 3111].

Crystallographic Data for *arachno*-2,3-$S_2B_9H_{10}^-PSH^+$ (PSH^+1^-) and *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (2). Single crystals were grown by slowly cooling CH_2Cl_2/hexane solutions at 0 °C.

Collection and Refinement of the Data. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu Kα radiation and using the $\omega-2\theta$ scan technique. Three standard reflections measured every 3500 s of X-ray exposure showed no significant decay for PSH^+1^- and an intensity decay of 2.8% for **2** over the course of data collection. A linear decay correction was applied. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

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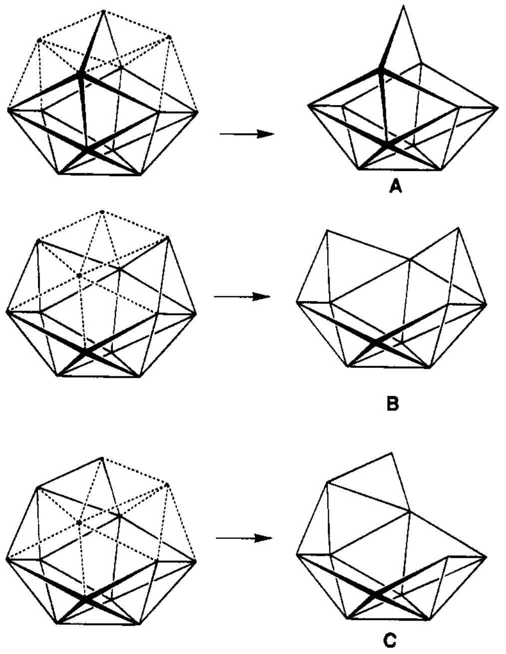

Figure 1. Derivation of 11-vertex arachno geometries A, B, and C from a 13-vertex closo-deltahedron.

Solution and Refinement of the Structure. X-ray data were processed, and the structures were solved and refined using the Enraf-Nonius MolEn[8a] package on a DEC MicroVAX 3100 computer. The structures were solved by direct methods (SIR88).[8b] Refinement was by full-matrix least squares techniques based on F to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. For $\mathbf{1}^-$, non-hydrogen atoms were refined anisotropically, cage hydrogens were refined isotropically, and all other hydrogen atoms were included as constant contributions to the structure factors and not refined. For **2**, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and not refined.

Results and Discussion

The reactions discussed below have resulted in the formation of a variety of new 11-vertex, 28 skeletal-electron *arachno*-dithiaborane clusters. According to simple skeletal electron counting rules,[9] such arachno clusters should adopt cage geometries derived by removal of two vertices from a 13-vertex closo-deltahedron as shown in Figure 1.[10] A number of isoelectronic 11-vertex clusters have previously been isolated and shown to adopt three different geometries depending upon which two vertices are removed from the parent closo-deltahedron. Thus, structural determinations of *arachno*-(PPh_2)-$B_{10}H_{12}^-$ [11] and the tetracarbaborane *arachno*-Br-$(CH_3)_4$-$C_4B_7H_8$[12] and the spectroscopic characterizations of other *arachno*-$R_4C_4B_7H_9$ tetracarbaboranes[12,13] and the azacarbaborane *arachno*-Bu^t-$NC_2B_8H_{12}$[14] have shown that these compounds adopt structures based on geometry A in Figure 1, which is formed, as indicated, by the removal of two nonadjacent five-coordinate vertices. On the other hand, the azaborane *arachno*-$NB_{10}H_{13}(N_3)^-$ [15] has been proposed to adopt a structure based on geometry B, which is formed by removal of adjacent six-coordinate and four-coordinate vertices. Removal of adjacent six-coordinate and five-coordinate vertices yields geometry C, and this cage structure has been proposed for *arachno*-$B_{10}H_{12}(N_3)(NH_2)$[15] and *arachno*-$C_2NB_8H_{13}$[16] as well as a number of metallaboranes.[17] As discussed below, structural studies of $\mathbf{1}^-$ and **2** have demonstrated that they adopt structures based on geometries B and C, respectively.

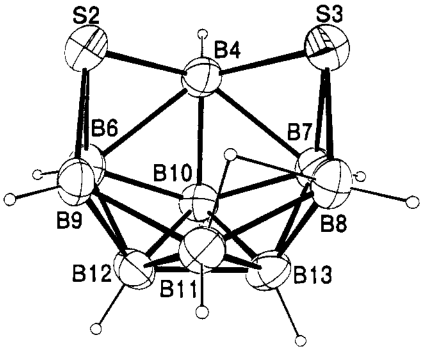

Figure 2. ORTEP drawing of the anion structure of *arachno*-2,3-$S_2B_9H_{10}^-$ ($\mathbf{1}^-$).

The reaction (eq 1) of PSH^+*nido*-6-$SB_9H_{10}^-$ with elemental sulfur in CH_2Cl_2 was found to give the new *arachno*-dithiaborane anion *arachno*-2,3-$S_2B_9H_{10}^-$ ($\mathbf{1}^-$) in excellent yield.

$$PSH^+\textit{nido}\text{-}6\text{-}SB_9H_{10}^- + {}^1/_8S_8 \rightarrow PSH^+\textit{arachno}\text{-}2,3\text{-}S_2B_9H_{10}^- \quad (1)$$

The compound is isolated as an air stable yellow solid. A single crystal X-ray structural determination of $\mathbf{1}^-$, as shown in the ORTEP drawing in Figure 2, established that the anion has a cage geometry based on structure B in Figure 1. Thus, the removal of the adjacent four- and six-coordinate vertices in the parent closo-deltahedron has generated an arachno structure with a puckered six-membered open face. As mentioned above, a similar cage structure has been proposed, based on the spectroscopic data, for the azaborane *arachno*-$NB_{10}H_{13}(N_3)^-$,[15] but the crystallographic determination of $\mathbf{1}^-$ provides the first confirmation of this geometry for an 11-vertex arachno cage system. In $\mathbf{1}^-$, the two sulfur atoms occupy nonadjacent positions on the open face, with the S2−S3 distance 3.136(1) Å being clearly nonbonding. Also located on the open face is a single bridging hydrogen at the B8−B11 edge. Both sulfur atoms are bonded to three borons, and the sulfur−boron distances (~1.90−1.99 Å), as well as the boron−boron bond

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Table 1. NMR Data

compounds	nucleus	δ (multiplicity, assignment, J (Hz))
arachno-2,3-$S_2B_9H_{10}^-$ (**1**$^-$)	^{11}B[a,b]	-5.5 (d, B8,9, J_{BH} 153), -7.7 (d, B12,13, J_{BH} 137), -11.6 (d, B6,7, J_{BH} 165), -15.1 (d, B4, J_{BH} 153), -51.5 (d, B10, J_{BH} ~120), -52.0 (d, B11, J_{BH} ~120)
	^{11}B$-^{11}$B[a,b]	observed crosspeaks: B4−B10;[c] B4−B6,7; B6,7−B10;[c] B6,7−B8,9; B6,7−B12,13; B8,9−B11;[c] B8,9−B12,13; B10,11[c]−B12,13
	^{11}B (calc)[d]	-6.0 (B8,B9), -7.2 (B6,B7), -9.1 (B4), -12.9 (B12,B13), -44.7 (B11), -48.7 (B10)
	^{1}H{^{11}B-selective}[b,e]	3.21 (B4H), 2.83 (B8,9H), 2.60 (B12,13H), 2.57 (B6,7H), -0.23 (BHB), -0.45 (B10H or B11H), -0.94 (B10H or B11H)
arachno-2-H-2,3-$S_2B_9H_{10}$ (**1**)	^{11}B[a,f]	34.3 (d, B4, J_{BH} 174), 12.0 (d, B9, J_{BH} 163), 9.6 (d, B8, J_{BH} 167), 2.1 (d, B12, J_{BH} 149), -4.0 (d, B13, J_{BH} 153), -9.5 (d, B10, J_{BH} 152), -21.2 (d, B6, J_{BH} 180), -22.9 (d, B7, J_{BH} 163), -35.2 (d, B11, J_{BH} 143)
	^{11}B$-^{11}$B[a,b]	observed crosspeaks: B4−B6, B4−B7, B4−B10, B6−B9, B6−B10, B6−B12, B7−B10, B7−B13, B8−B11, B8−B13, B9−B11, B9−B12, B10−B12, B10−B13, B11−B12, B11−B13, B12−B13
	^{1}H {^{11}B-selective}[e,f]	5.32 (B4H), 3.67 (B8H), 3.58 (B9H), 3.28 (B12H), 3.13 (B13H), 3.01 (s, S2H), 2.63 (B10H), 1.48 (B7H), 1.15 (B6H), 0.72 (B11H), -0.95 (BHB)
nido-7,9-$S_2B_9H_9$	^{11}B[a,g,h]	0.7 (d, 1, J_{BH} 156), -1.0 (d, 2, J_{BH} 177), -3.7 (d, 4, J_{BH} 156), -11.8 (d, 1, J_{BH} 177), -36.9 (d, 1, J_{BH} 154)
	^{1}H {^{11}B}[e,g]	3.20 (BH), 2.93 (2, BH), 2.82 (2, BH), 2.74 (2, BH), 2.12 (2, BH)
arachno-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**)	^{11}B[a,g]	32.0 (d, B4, J_{BH} 169), 13.2 (d, B9, J_{BH} 167), 9.4 (d, B8, J_{BH} 161), 0.0 (d, B12, J_{BH} 149), -2.0 (d, B13, J_{BH} 151), -9.4 (d, B10, J_{BH} 144), -19.2 (d, B6, J_{BH} 183), -21.5 (d, B7, J_{BH} 158), -34.4 (d, B11, J_{BH} 147)
	^{11}B$-^{11}$B[a,b]	observed crosspeaks: B4−B6, B4−B7, B4−B10, B6−B9, B6−B10, B6−B12, B7−B8, B7−B10, B7−B13, B8−B11, B8−B13, B9−B11, B9−B12, B10−B12, B10−B13, B11−B12, B11−B13, B12−B13
	^{1}H {^{11}B-selective}[e,g]	5.45 (B4H), 4.10 (B9H), 3.87 (2, B8H, B12H), 3.39 (B13H), 3.31 (B10H), 1.91 (B7H), 1.32 (B6H), 1.13 (B11H), 1.03 (s, S2-CH_3), -0.87(BHB)
arachno-2,3-CH_3-$S_2B_9H_9^-$ (**2**$^-$)	^{11}B[a,i]	26.2 (d, B4, J_{BH} 169), 8.1 (d, B9, J_{BH} ~190), 4.4 (d, B8, J_{BH} ~180), -3.1 (d, B12, J_{BH} 135), -5.5 (d, B13, J_{BH} 135), -12.2 (d, B10, J_{BH} 144), -19.1 (d, B11, J_{BH} ~115), -25.5 (d, B6,7, J_{BH} ~155)
	^{11}B$-^{11}$B[a,i]	observed crosspeaks: B4−B6, B4−B7, B4−B10, B6−B10, B6−B12, B7−B10, B7−B13, B8−B11, B8−B13, B9−B11, B9−B12, B10−B12, B10−B13, B11−B12, B11−B13, B12−B13
	^{1}H {^{11}B-selective}[e,i]	4.70 (B4H), 3.23 (s, S2-CH_3), 2.54 (B9H), 2.42 (B8H), 2.39 (B12H), 2.32 (B13H), 2.19 (B10H), 1.34 (B11H), 0.99 (B6H or B7H), 0.59 (B6H or B7H)
arachno-2-CH_2I-2,3-$S_2B_9H_{10}$ (**3**)	^{11}B[a,g]	32.1 (d, B4, J_{BH} 164), 13.0 (d, B8, J_{BH} 158), 10.9 (d, B9, J_{BH} 166), -0.3 (d, B12, J_{BH} 149), -2.2 (d, B13, J_{BH} 150), -8.5 (d, B10, J_{BH} 148), -19.0 (d, B6 or B7, J_{BH} ~145), -19.7 (d, B6 or B7, J_{BH} ~145), -33.9 (d, B11, J_{BH} 149)
	^{11}B$-^{11}$B[g,j]	observed crosspeaks: B4−B6,7,[k] B4−B10, B6,7[k]−B10, B6[k]−B12, B7[k]−B13, B8−B11, B8−B13, B9−B12, B10−B12, B10−B13, B11−B12, B11−B13, B12−B13
	^{1}H {^{11}B}[e,g]	5.24 (BH), 3.72 (3, BH), 3.21 (BH), 3.07 (BH), 2.14 (d of d, S2-CH_2I), 1.65 (BH), 1.15 (BH), 1.03 (BH), -1.03 (BHB)

[a] 160.5 MHz. [b] $CDCl_3$. [c] B10 and B11 resonances overlap. [d] DZ//6-31G*, optimized asymmetric structure, values in table are the average of the two calculated shifts of the indicated resonances. [e] 500.1 MHz. [f] CD_2Cl_2. [g] C_6D_6. [h] The previously reported spectra was too overlapped to observe individual peaks, see ref 3g. [i] CD_3CN. [j] 64.2 MHz. [k] B6 and B7 resonances overlap.

distances, are in the ranges observed in other thia- and dithiaboranes.[3]

The NMR data for **1**$^-$ do not agree with the C_1 cage symmetry observed in the solid state, but instead are consistent with a C_s cage symmetry. Thus, instead of the expected nine boron resonances, only six resonances in a ratio of 2:2:2:1:1:1 are observed (Figure 3a). Likewise, in the boron-decoupled ^{1}H NMR spectrum, six terminal protons in a similar ratio were observed, along with a bridge proton resonance of intensity one at -0.94 ppm. The apparent C_s symmetry observed by NMR probably arises owing to the rapid rearrangement of the bridging proton between the B8−B11 and B9−B11 edges, giving rise to the higher symmetry. Attempts to observe a static structure by NMR experiments carried out at lower temperatures were unsuccessful down to −94 °C.

The spectral assignments given in Figure 3a and Table 1 are also supported by selective decoupling experiments and by an ab initio/IGLO NMR study. The ab initio calculations show the asymmetric geometry observed in the solid state (Figure 2) to be the lowest energy structure, but as indicated in Table 1, good correlation between the IGLO-calculated chemical shifts and the observed ^{11}B NMR spectrum (C_s symmetry) were obtained by averaging the calculated shifts of the boron atoms in the asymmetric structure that should become equivalent in the fluxional structure observed by NMR (i.e., B6/B7, B8/B9, and B12/B13).

Traditional sulfur-insertion reactions leading to the formation of thia- or dithiaborane clusters have included the reactions of boranes or carboranes with sulfur reagents, such as ammonium polysulfide,[5,18] thionitrosodimethylamine,[5,18] or $KHSO_3$.[3f] However, Holub et al.[19] recently discovered that the reaction of *arachno*-4-CB_8H_{14} with elemental sulfur in the presence of triethylamine leads to sulfur insertion and the formation of the thiacarborane *arachno*-6,9-CSB_8H_{12} in good yields. Likewise, Binder[20] has shown that a mixture of $NaBH_4$ and BH_3•THF will react directly with elemental sulfur to give a number of new thiaboranes. Consistent with these earlier results, the formation of **1**$^-$ may be envisioned to have occurred, as depicted in Figure 4, by a simple process involving (a) nucleophilic attack at sulfur by the *nido*-6-$SB_9H_{10}^-$ anion leading to sulfur ring fragmentation, (b) initial insertion of a sulfur atom across the deprotonated B8−B9 bridging position, and (c) incorporation of the sulfur in its final three-coordinate cage position. The structure of the intermediate species containing the μ_2-sulfur bridge is, in fact,

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(18) Hertler, W. R.; Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1696−1706.

(19) (a) Holub, J.; Jelinek, T.; Plešek, J.; Štíbr, B.; Heřmánek, S.; Kennedy, J. D. *J. Chem. Soc., Chem. Commun.* **1991**, 1389−1390. (b) Holub, J.; Kennedy, J. D.; Jelinek, T.; Štíbr, B. *J. Chem. Soc., Dalton Trans.* **1994**, 1317−1323.

(20) Binder, H.; Wolfer, K.; Ehmann, W.; Pfeffer, W.-P.; Peters, K.; Horn, H.; Ahlrichs, R. *Chem. Ber.* **1992**, *125*, 651−655.

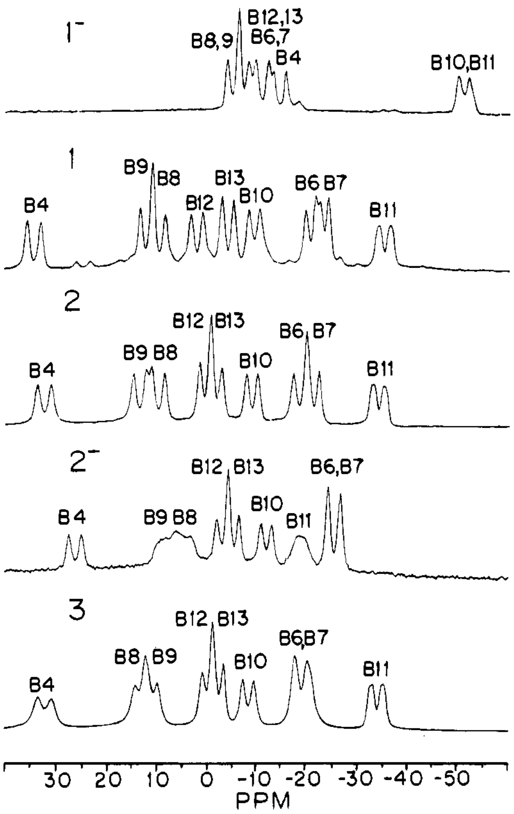

Figure 3. ^{11}B NMR spectra at 64.2 MHz of (a) *arachno*-2,3-$S_2B_9H_{10}^-$ (1^-); (b) *arachno*-2-H-2,3-$S_2B_9H_{10}$ (1); (c) *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (2); (d) *arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ (2^-); and (e) *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ (3).

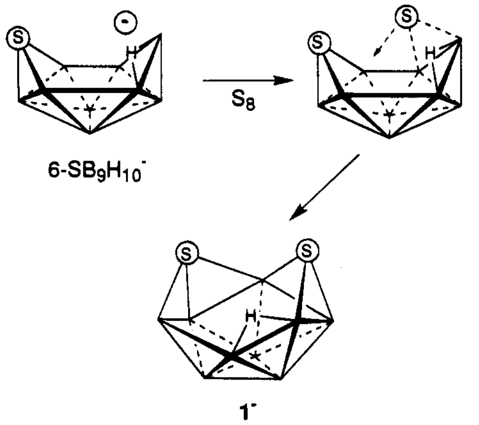

Figure 4. Possible reaction sequence leading to the formation of *arachno*-2,3-$S_2B_9H_{10}^-$ (1^-) from *nido*-6-$SB_9H_{10}^-$.

Table 2. Data Collection and Structure Refinement Information for PSH^+*arachno*-2,3-$S_2B_9H_{10}^-$ (PSH^+1^-) and *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (2)

compound	PSH^+1^-	2
formula	$B_9C_{14}H_{29}S_2N_2$	$B_9CH_{13}S_2$
formula weight	386.83	186.54
crystal class	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
Z	4	4
cell constants		
a, Å	9.294(1)	7.733(1)
b, Å	12.236(1)	10.043(3)
c, Å	19.479(3)	13.630(2)
β, deg	100.02(1)	101.84(1)
V, $Å^3$	2181.3(8)	1036.0(6)
μ, cm^{-1}	21.51	39.74
crystal size, mm	0.30 × 0.30 × 0.38	0.16 × 0.18 × 0.55
D_{calc}, g/cm^3	1.178	1.196
radiation	Cu Kα (λ = 1.541 84 Å)	Cu Kα (λ = 1.541 84 Å)
θ range	2.0–65.0°	2.0–65.0°
scan mode	$\omega-2\theta$	$\omega-2\theta$
h,k,l collected	+10,+14,±22	±9,+11,−16
no. reflections measured:	4154	1956
no. unique reflections:	3697	1758
no. reflections ($F^2 > 3.0\sigma$)	3250	1439
no. parameters	289	110
data/parameter ratio	11.2	13.1
R_1	0.060	0.052
R_2	0.094	0.061

related to the structures observed for 1, 2, and 3, as discussed below

Upon reaction of 1^- with concentrated H_2SO_4 in CH_2Cl_2 (eq 2), protonation occurs and the spectroscopic data, along with the X-ray determined structure of 2 discussed below, indicate protonation occurs at the exopolyhedral position on one sulfur atom to yield *arachno*-2-H-2,3-$S_2B_9H_{10}$ (1). Thus, the SH and the single boron-bridging protons were located in the ^1H NMR spectrum (at 3.01 and −0.95 ppm, respectively), and the IR spectrum shows an absorption at 2480 cm^{-1} consistent with the presence of the SH group. In addition, both the ^1H and ^{11}B NMR (Figure 3b) spectra of 1 are consistent with a cage geometry of C_1 symmetry. Protonation at sulfur suggests that the negative charge in *arachno*-2,3-$S_2B_9H_{10}^-$ is largely localized at the sulfur atoms. Such a charge distribution is also consistent with earlier studies of the reactivity of another dithiaborane, *hypho*-$S_2B_6H_9^-$,[3k] which showed that upon its reaction with methyl iodide, only sulfur-substitution (i.e., *hypho*-2,3-$(CH_3)_2$-2,3-$S_2B_6H_8$) was observed. Furthermore, as pointed out by Williams,[10] protonation at the B9−B11 edge in 1^- is also disfavored by the fact that the resulting structure would have two hydrogens bridging six- (B8 and B9) and seven-coordinate (B11) borons. Deprotonation of 1 regenerates the original anion 1^- (eq 3).

$$PSH^+\textit{arachno}\text{-}2,3\text{-}S_2B_9H_{10}^- + {}^1\!/_2H_2SO_4 \rightarrow \textit{arachno}\text{-}2\text{-}H\text{-}2,3\text{-}S_2B_9H_{10} \quad (2)$$

$$\textit{arachno}\text{-}2\text{-}H\text{-}2,3\text{-}S_2B_9H_{10} + PS \rightarrow PSH^+\textit{arachno}\text{-}2,3\text{-}S_2B_9H_{10}^- \quad (3)$$

The thermolysis of 1 in refluxing toluene results in loss of hydrogen to produce the known 26-skeletal electron dithiaborane[3g,q] *nido*-7,9-$S_2B_9H_9$ (eq 4). The structural relationship between the 1 and *nido*-7,9-$S_2B_9H_9$ is illustrated in Figure 5. Thus, the loss of H_2 from 1 occurs by the elimination of the S-H and bridge hydrogen followed by additional skeletal rearrangements to produce the observed nido-cluster framework containing a five-membered open face.

$$\textit{arachno}\text{-}2\text{-}H\text{-}2,3\text{-}S_2B_9H_{10} \rightarrow \textit{nido}\text{-}7,9\text{-}S_2B_9H_9 + H_2 \quad (4)$$

Originally, *nido*-7,9-$S_2B_9H_9$ was isolated as one of the products, along with *nido*-7,9-$SSeB_9H_9$, from the reaction of *arachno*-$SB_9H_{12}^-$ with a mixture of potassium polysulfide/potassium-polyselenide. In contrast, our studies of preparative scale thermolytic reactions have now shown that 1 can be converted cleanly to *nido*-7,9-$S_2B_9H_9$ in reasonable isolated yields and, thus, provides the first viable synthetic route to this compound.

As in the protonation reaction, the reaction of *arachno*-2,3-$S_2B_9H_{10}^-$ with methyl iodide or diiodomethane results in addition at one sulfur atom to produce the neutral compounds

Table 3. Refined Positional Parameters for PSH^+*arachno*-2,3-$S_2B_9H_{10}^-$ (PSH^+**1**$^-$)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
S2	0.43698(9)	0.05803(6)	0.37615(4)	5.30(2)
S3	0.67248(8)	−0.12622(7)	0.37910(5)	5.61(2)
B4	0.5029(4)	−0.0560(3)	0.3183(2)	4.70(7)
B6	0.2867(4)	−0.0330(3)	0.3274(2)	5.02(7)
B7	0.5257(4)	−0.2207(3)	0.3301(2)	4.65(6)
B8	0.5547(4)	−0.2191(3)	0.4271(2)	4.57(6)
B9	0.3179(3)	−0.0337(3)	0.4236(2)	4.36(6)
B10	0.3548(4)	−0.1588(3)	0.3026(2)	4.29(6)
B11	0.3851(4)	−0.1695(3)	0.4511(2)	4.32(6)
B12	0.2551(3)	−0.1478(3)	0.3740(2)	4.49(6)
B13	0.3884(4)	−0.2518(3)	0.3755(2)	4.30(6)
C14	−0.0047(2)	−0.1996(2)	0.1218(1)	3.54(4)
C15	−0.1209(3)	−0.2459(2)	0.1455(2)	4.82(6)
C16	−0.2075(3)	−0.1841(3)	0.1823(2)	5.49(6)
C17	−0.1793(3)	−0.0768(3)	0.1947(2)	4.75(6)
C18	−0.0597(3)	−0.0248(2)	0.1716(1)	3.65(5)
C19	−0.0304(3)	0.0871(2)	0.1844(1)	4.16(5)
C20	0.0828(3)	0.1369(2)	0.1628(2)	4.54(6)
C21	0.1748(3)	0.0764(2)	0.1272(1)	4.25(5)
C22	0.1504(2)	−0.0318(2)	0.1127(1)	3.28(4)
C23	0.0309(2)	−0.0878(2)	0.1345(1)	3.14(4)
C24	0.0002(3)	−0.3007(3)	0.0146(2)	5.48(7)
C25	0.1583(4)	−0.3573(3)	0.1225(2)	5.72(7)
C26	0.2292(3)	−0.0510(2)	0.0005(1)	4.94(6)
C27	0.3990(3)	−0.0955(3)	0.1076(2)	5.21(7)
N28	0.0850(2)	−0.2645(2)	0.0822(1)	3.68(4)
N29	0.2434(2)	−0.0924(2)	0.0726(1)	3.43(4)
H4	0.539(3)	−0.022(3)	0.271(2)	7.2(9)*
H6	0.200(3)	0.002(3)	0.286(2)	9(1)*
H7	0.556(3)	−0.274(3)	0.296(2)	7.7(9)*
H8	0.618(3)	−0.279(3)	0.458(2)	6.0(7)*
H9	0.262(3)	0.001(3)	0.457(1)	5.9(7)*
H10	0.309(3)	−0.191(2)	0.249(1)	4.8(6)*
H11	0.354(3)	−0.201(3)	0.494(2)	6.7(8)*
H12	0.153(3)	−0.164(2)	0.374(1)	4.9(6)*
H13	0.349(3)	−0.331(3)	0.377(2)	6.2(8)*
H811	0.507(4)	−0.120(4)	0.469(2)	11(1)*
H28	0.176(4)	−0.181(4)	0.075(2)	10(1)*

[a] Starred atoms were refined isotropically. $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

arachno-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**) and *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ (**3**), respectively (eqs 5 and 6).

$$PSH^+\textit{arachno}\text{-}2,3\text{-}S_2B_9H_{10}^- + CH_3I \rightarrow \textit{arachno}\text{-}2\text{-}CH_3\text{-}2,3\text{-}S_2B_9H_{10} + PSI \quad (5)$$

$$PSH^+\textit{arachno}\text{-}2,3\text{-}S_2B_9H_{10}^- + CH_2I_2 \rightarrow \textit{arachno}\text{-}2\text{-}CH_2I\text{-}2,3\text{-}S_2B_9H_{10} + PSI \quad (6)$$

Table 4. Selected Bond Distances (Å) and Angles (deg) for PSH^+*arachno*-2,3-$S_2B_9H_{10}^-$ (PSH^+**1**$^-$)

S2−S3	3.136(1)	S2−B4	1.958(4)	S2−B6	1.905(4)
S2−B9	1.922(3)	S3−B4	1.994(3)	S3−B7	1.912(3)
S3−B8	1.929(4)	B4−B6	2.067(5)	B4−B7	2.034(5)
B4−B10	1.850(5)	B4−H4	1.111(37)	B6−B9	1.845(5)
B6−B10	1.764(5)	B6−B12	1.726(5)	B6−H6	1.121(32)
B7−B8	1.861(5)	B7−B10	1.756(4)	B7−B13	1.717(5)
B7−H7	1.009(36)	B8−B11	1.824(5)	B8−B13	1.737(4)
B8−H8	1.060(30)	B8−H811	1.576(46)	B9−B11	1.823(5)
B9−B12	1.740(5)	B9−H9	0.993(32)	B10−B12	1.807(5)
B10−B13	1.805(4)	B10−H10	1.129(26)	B11−B12	1.775(4)
B11−B13	1.788(4)	B11−H11	1.007(32)	B11−H811	1.278(42)
B12−B13	1.773(5)	B12−H12	0.966(27)	B13−H13	1.033(34)

B4−S2−B6	64.7(2)	B4−S2−B9	97.2(1)
B6−S2−B9	57.6(1)	B4−S3−B7	62.7(1)
B4−S3−B8	94.9(1)	B7−S3−B8	58.0(1)
S2−B4−S3	105.0(2)	S2−B4−B6	56.4(1)
S2−B4−B7	132.6(2)	S2−B4−B10	106.3(2)
S3−B4−B6	133.4(2)	S3−B4−B7	56.7(1)
S3−B4−B10	107.1(2)	B6−B4−B7	102.1(2)
B6−B4−B10	53.2(2)	B7−B4−B10	53.5(2)
S2−B6−B4	58.9(1)	S2−B6−B9	61.6(1)
S2−B6−B10	112.3(2)	B4−B6−B9	95.9(2)
B4−B6−B10	57.1(2)	S3−B7−B4	60.6(1)
S3−B7−B8	61.5(1)	S3−B7−B10	114.9(2)
B4−B7−B8	95.7(2)	B4−B7−B10	57.9(2)
S3−B8−B11	121.1(2)	S3−B8−H811	92.1(16)
S2−B9−B11	118.5(2)	B4−B10−B6	69.7(2)
B4−B10−B7	68.6(2)	B8−B11−B9	119.7(2)
B8−B11−H811	57.9(20)	B9−B11−H811	83.7(20)
B8−H811−B11	78.7(23)		

Table 5. Refined Positional Parameters for *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
S2	0.4290(1)	0.8193(1)	0.07092(8)	4.18(2)
S3	0.7775(1)	0.9310(1)	0.20069(8)	4.07(2)
B4	0.7899(5)	0.8068(5)	0.1005(3)	3.66(9)
B6	0.5997(5)	0.6752(4)	0.0749(3)	3.41(8)
B7	0.9282(5)	0.7749(5)	0.2252(4)	3.93(9)
B8	0.7712(6)	0.8143(5)	0.3086(3)	3.73(9)
B9	0.4432(6)	0.6818(5)	0.1674(4)	4.02(9)
B10	0.8199(5)	0.6482(5)	0.1459(3)	3.71(9)
B11	0.5976(5)	0.6836(4)	0.2937(3)	2.99(8)
B12	0.6335(6)	0.5831(4)	0.1909(3)	3.45(9)
B13	0.8149(5)	0.6502(5)	0.2781(3)	3.61(9)
C1	0.2407(6)	0.7588(6)	−0.0198(4)	5.8(1)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

A single crystal X-ray structural determination, the results of which are shown in Figure 6, established that **2** has a gross cage geometry related to that found for **1**$^-$, but with significant differences in regards to the coordination of the methyl−sulfur unit to the cage. In **1**$^-$, both sulfurs are bound to three cage borons, but in **2** the methyl-substituted S2 sulfur now occupies an endo-bridging position bound to only the two borons at the B6−B9 edge. A similar type of bridging CH_3−S bonding configuration was previously observed in *hypho*-2,3-$(CH_3)_2$-2,3-$S_2B_6H_8$.[3k] In **2**, the S2−B9 (1.894(5) Å) and S2−B6 (1.952(4) Å) distances are similar to those observed for **1**$^-$, S2−B9 (1.922(3) Å), and S2−B6 (1.905(4) Å). However, the S2−B4 distance in **2** (2.740(4) Å) is now considerably lengthened compared to S2−B4 in **1**$^-$ (1.958(4) Å) and is clearly nonbonding, thereby producing a cage framework with an open seven-membered face. Thus, substitution at the sulfur has altered the nature of the sulfur-cage bonding, and the cluster framework in **2** may now be described as based on geometry C in Figure 1. A similar interconversion of C and B type structures was previously proposed by Paetzold in the deprotonation of *arachno*-$B_{10}H_{12}(N_3)(NH_2)$ (C-type) to *arachno*-$NB_{10}H_{13}(N_3)^-$ (B-type).[15]

Alternatively, rather than considering **2** as an 11-vertex arachno cluster with the CH_3S unit as part of the cage framework, **2** might be described as only a 10-vertex cluster containing a boron−boron bridging CH_3S group. Then, depending on whether the CH_3S is considered to function as a one-electron, one-orbital donor (like a bridging proton) or a three-electron, two-orbital donor[10,21] to the cage, the compound could be viewed as either a 10-vertex μ_2-(CH_3S)-*nido*-SB_9H_{10} or a μ_2-(CH_3S)-*arachno*-SB_9H_{10} cluster, respectively.

As in the case of **1**, **2** was found to deprotonate upon reaction with Proton Sponge (eq 7), but since there is a methyl, rather than a hydrogen, on the S2 sulfur in **2**, the single bridging

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[21] Williams, R. E. Private communication.

Table 6. Selected Bond Distances (Å) and Angles (deg) for *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**)

S2—S3	3.114(1)	S2—B4	2.740(4)	S2—B6	1.952(4)
S2—B9	1.894(5)	S2—C1	1.811(4)	S3—B4	1.866(5)
S3—B7	1.940(5)	S3—B8	1.889(5)	B4—B6	1.956(6)
B4—B7	1.840(6)	B4—B10	1.708(6)	B6—B9	1.920(7)
B6—B10	1.798(5)	B6—B12	1.804(6)	B7—B8	1.868(7)
B7—B10	1.766(6)	B7—B13	1.766(7)	B8—B11	1.858(6)
B8—B13	1.749(6)	B9—B12	1.748(6)	B9—B11	1.883(6)
B10—B12	1.801(6)	B10—B13	1.811(7)	B11—B12	1.794(6)
B11—B13	1.768(6)	B12—B13	1.775(6)		

B6—S2—B9	59.9(2)	B6—S2—C1	102.4(2)
B9—S2—C1	98.8(2)	B9—S2—B4	87.3(2)
B6—S2—B4	45.5(2)	B4—S3—B7	57.8(2)
B4—S3—B8	99.7(2)	B7—S3—B8	58.4(2)
S2—B4—S3	82.7(2)	S3—B4—B6	115.7(3)
S2—B6—B4	89.1(2)	S2—B6—B9	58.6(2)
B4—B6—B9	114.3(3)	S3—B8—B11	119.1(2)
B7—B8—B11	109.2(3)	S2—B9—B6	61.6(2)
S2—B9—B11	124.3(3)	B6—B9—B11	103.5(3)
B8—B11—B9	114.5(3)		

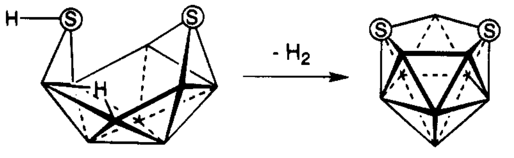
hydrogen is removed to produce *arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ ($\mathbf{2}^-$).

$$arachno\text{-}2\text{-}CH_3\text{-}2,3\text{-}S_2B_9H_{10} + PS \rightarrow PSH^+ arachno\text{-}2\text{-}CH_3\text{-}2,3\text{-}S_2B_9H_9^- \quad (7)$$

The spectral data for $\mathbf{2}^-$ are quite different than those observed for $\mathbf{1}^-$ and are consistent with the proposed structure in Figure 7. In $\mathbf{2}^-$, the resonance assigned to the bridge hydrogen in the ^1H NMR spectrum of **2** is absent. The ^{11}B NMR spectrum of $\mathbf{2}^-$ (Figure 3d) is similar to that observed for **1**, **2**, and **3**, indicating that all four compounds have similar structures containing a two-coordinate sulfur framework atom which has an exopolyhedral substituent (i.e., **1**, S-H; **2**, S-CH_3; $\mathbf{2}^-$, S-CH_3; **3**, S-CH_2I).

$\mathbf{2}^-$ could be readily protonated with HCl/Et_2O to regenerate **2**, but showed no reactivity toward methyl iodide. Therefore, attempts to generate a dimethylated derivative (i.e., *arachno*-2,3-$(CH_3)_2$-2,3-$S_2B_9H_9$) were unsuccessful. Likewise, attempts to incorporate a sulfur—sulfur bridging methylene (i.e., *arachno*-$\mu_{2,3}$-CH_2-2,3-$S_2B_9H_9$) by the KH or Proton Sponge-induced elimination of HI from *arachno*-2-CH_2I-2,3-$S_2B_9H_{10}$ were unsuccessful. With both reagents, deprotonation of **3** occurred, but the resulting products were too unstable to allow characterization.

In conclusion, the results discussed above have demonstrated a simple high-yield synthetic strategy for sulfur cluster-insertion reactions based on the nucleophilic attack of a polyhedral borane anion on elemental sulfur, as well as the synthesis and structural characterizations of a series of, until now, relatively rare 11-vertex arachno cage systems. Work is now in progress investigating both the generality of this synthetic strategy and the chemistry of these unique cage systems.



1 7,9-$S_2B_9H_9$

Figure 5. Conversion of *arachno*-2-H-2,3-$S_2B_9H_{10}$ (**1**) to *nido*-7,9-$S_2B_9H_9$.

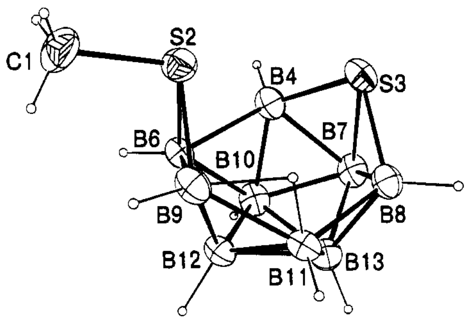
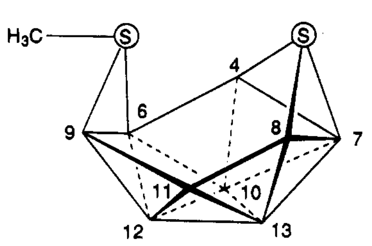


Figure 6. ORTEP drawing of the structure of *arachno*-2-CH_3-2,3-$S_2B_9H_{10}$ (**2**).



$\mathbf{2}^-$

Figure 7. Proposed stucture of *arachno*-2-CH_3-2,3-$S_2B_9H_9^-$ ($\mathbf{2}^-$).

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Supplementary Material Available: Tables listing refined thermal parameters, bond distances, bond angles, calculated atom positions, and least squares planes (15 pages). Ordering information is given on any current masthead page.