An Improved Synthesis of *arachno*-4-CB_8H_{14} and Crystallographic and ab Initio/IGLO/NMR Investigations of the Solid State and Solution Structures of the *arachno*-4-$CB_8H_{13}^-$ Anion

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An improved synthetic route for the monocarbaborane *arachno*-4-CB_8H_{14}, as well as the first definitive confirmation of the structure of its conjugate anion, *arachno*-4-$CB_8H_{13}^-$ are reported. Thus, the reaction of the *nido*-7,9-$C_2B_{10}H_{13}^-$ anion and Me_2S with the addition of concentrated hydrochloric acid has been found to give the 9-Me_2S-μ-6,9-[(HO)BCH_2]-*arachno*-6-CB_9H_{11} zwitterion, in 58% yield. Further treatment of this intermediate species with a mixture of hexane and water results in the hydrolytic elimination of one CH and two BH vertices to give *arachno*-4-CB_8H_{14} in a typical yield of 75% (45% based on the starting *o*-carborane). The structure of the *arachno*-4-$CB_8H_{13}^-$ conjugate anion was determined by both a single-crystal X-ray study and ab initio/IGLO/NMR calculations. The X-ray study confirms that in the solid state the anion has a 9-vertex arachno cage-geometry of C_1 symmetry with endo-hydrogens on C4 and B8 and adjacent bridge hydrogens at the B5−B6 and B6−B7 edges. This structure is also supported by the ab initio calculations which find that this configuration is the lowest in energy among those investigated. However, the IGLO calculated ^{11}B NMR chemical shifts for this structure do not match the reported room temperature solution ^{11}B NMR data for *arachno*-4-$CB_8H_{13}^-$. Instead, the experimental spectra indicate a C_s symmetry cage-structure containing three bridge hydrogens on the open face, suggesting the anion is fluxional in solution at room temperature. Good agreement between the experimental and calculated ^{11}B NMR chemical shifts was obtained by assuming a simple fluxional process involving rapid simultaneous migration of two hydrogens between bridge and endo positions and one hydrogen between two bridging positions. Averaging the IGLO calculated chemical shift values for the borons in the static structure that become equivalent in the fluxional process is found to give good agreement with the room temperature experimental ^{11}B NMR spectrum.

Introduction

The *arachno*-4-CB_8H_{14} and the corresponding M^+*arachno*-4-$CB_8H_{13}^-$ salts (M = K, Li, or NMe_4) were first reported in 1976[3] and 1981;[4,5] however, the lack of efficient synthetic routes to these clusters has inhibited investigations of their chemical and structural properties. In this paper we report a new simple method for the synthesis of *arachno*-4-CB_8H_{14} based on a regiospecific cluster degradation of the readily available starting material *o*-carborane. In addition, we also report the first definitive determination of the structure of its *arachno*-4-$CB_8H_{13}^-$ conjugate anion.

Experimental Section

All manipulations were carried out by using standard high vacuum or inert-atmosphere techniques as described by Shriver.[6]

Materials. The starting *closo*-1,2-$C_2B_{10}H_{12}$, *o*-carborane, was supplied by Katchem, p.l.c., and sublimed before use. The Me_2S, Me_4NCl, and Proton Sponge, 1,8-bis(dimethylamino)naphthalene, were purchased from Aldrich and used as received. The solvents were purchased from Aldrich, with tetrahydrofuran (THF) dried over Na/benzophenone and hexane dried over CaH_2 and both freshly distilled before use. Diethyl ether was stored under N_2 until use.

Physical Measurements. The ^{11}B NMR spectra were obtained either at 64.2 MHz on a Bruker AF-200 spectrometer, at 96.3 MHz on a Bruker AF-300, or at 160.5 MHz on a Varian XL-500, equipped with the appropriate decoupling and low temperature accessories. The ^{1}H NMR spectra were obtained at 300 MHz on a Bruker AF-300 or at 500 MHz on a Varian XL-500. The ^{11}B−^{11}B 2-D COSY NMR experiments were performed as described elsewhere.[7]

Synthesis of 9-Me_2S-μ-6,9-[(HO)BCH_2]-*arachno*-6-CB_9H_{11} (2) and *arachno*-4-CB_8H_{14} (3). A solution of *o*-carborane (14.6 g, 100 mmol) in 150 mL of THF was treated with naphthalene (0.5 g) and finely cut sodium metal (5 g, 217 mmol), and the mixture was stirred at ambient temperature for 4 h. The dark green solution thus formed was maintained at 0 °C and treated with 100 mL of 20% aqueous NaCl. The THF layer was separated and poured into a solution of Me_4NCl (13.2 g, 120 mmol) in 50 mL of water. The THF was removed in vacuo, and the precipitated Me_4N^+ salts were isolated by suction filtration followed by washing with ∼100 mL of water and drying in vacuo. The mixture of the Me_4N^+ salts of two isomeric *nido*-$C_2B_{10}H_{13}^-$ anions thus obtained was stirred with 100 mL of Me_2S and 100 mL of concentrated hydrochloric acid at room temperature for 24 h. The two-layer mixture was filtered with suction and the Me_2S layer (upper) evaporated and dried in vacuo for 6 h to obtain 13.0 g (58 mmol, 58% based on the starting *o*-carborane and 77% on the *nido*-7,9-$C_2B_{10}H_{13}^-$ anion) of a white compound which was identified as 9-Me_2S-μ-6,9-[(HO)BCH_2]-*arachno*-6-CB_9H_{11} (**2**) by NMR spectroscopy. For **2**: mp

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Table 1. Crystallographic Data Collection and Structure Refinement Information for PSH^+*arachno*-4-$CB_8H_{13}^-$.

formula: $C_{15}B_8H_{32}N_2$	$F(000) = 1408$
fw 326.92	radiation: Cu Kα ($\lambda = 1.541\,84$ Å)
space group: $P2_1/c$ (No. 14)	θ range: 2.0−60.0°
$Z = 8$	scan mode: $\omega-2\theta$
cell constants:	*h*, *k*, *l* collcd: ±12, −30, +16
$a = 11.137(3)$ Å	no. of reflcns measd: 6572
$b = 27.175(4)$ Å	no. of unique reflcns: 6138
$c = 14.631(2)$ Å	no. of reflcns used in refinement:
$\beta = 111.16(1)°$	4642 ($F^2 > 3.0\sigma$)
$V = 4129(3)$ Å^3	no. of params: 556
$\mu = 3.72$ cm^{-1}	data/param ratio: 8.3
crystal size:	R_1: 0.044
0.18 × 0.40 × 0.40 mm	R_2: 0.061
$D_{calc} = 1.052$ g/cm^3	

102 °C dec. Anal. Calcd C, 21.40; H, 8.98. Found: C, 20.15; H, 9.30. The parent ion for this compound was not observed in its mass spectrum, but instead peaks attributed to a decomposition product, $(C_2B_{10}H_{11})_2O$, were found: mass calcd for $(^{12}C_2{}^{11}B_{10}{}^1H_{11})_2{}^{16}O$, 306; found, 306 (4%), 300 (50%).

Compound **2** (13.0 g, 58 mmol) was then stirred with 100 mL of hexane and 100 mL of water for 24 h at ambient temperature. The hexane layer was separated and the hexane removed by evaporation to leave a white solid which was then sublimed in vacuo at ∼50 °C (bath) to give 5 g (44 mmol, 75% based on the starting **2** and 45% based on the *o*-carborane used) of *arachno*-4-CB_8H_{14} (**3**), which was identified by comparison of its ^{11}B NMR spectrum with that of an authentic sample.[3,4,5]

Synthesis of PSH^+*arachno*-4-$CB_8H_{13}^-$ (3^-). The PSH^+*arachno*-4-$CB_8H_{13}^-$ salt was obtained by slowly adding 0.65 g (3.03 mmol) of Proton Sponge dissolved in 10 mL of diethyl ether to a 100 mL round bottom flask containing 0.32 g (2.84 mmol) of *arachno*-4-CB_8H_{14} dissolved in 10 mL of diethyl ether. The solution was stirred for 15 min, and then the resulting precipitate was removed by filtration and washed with 10 mL of diethyl ether. This solid was dissolved in 10 mL of CH_2Cl_2 and filtered. The product was crystallized by addition of hexane to the CH_2Cl_2 solution, then the solvent was removed via cannula. Washing the remaining solid with additional hexane and drying in vacuo yielded 0.71 g (2.17 mmol, 76.4% yield) of PSH^+*arachno*-4-$CB_8H_{13}^-$ as an off-white solid.

Crystallographic Data. Single crystals of PSH^+*arachno*-4-$CB_8H_{13}^-$ were grown by slow evaporation of a CH_2Cl_2/hexane solution. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections.

Collection and Refinement of the Data. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Cu Kα radiation using the $\omega-2\theta$ scan technique. Three standard reflections measured every 3500 s of X-ray exposure showed an intensity decay of 2.2% decay 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.

Solution and Refinement of the Structure. The calculations were performed on a DEC MicroVAX 3100 computer using the Enraf-Nonius Molen structure package. The structure was solved by direct methods (SIR88). Refinement was by full-matrix least squares techniques based on *F* to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. 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 were not refined.

Crystal and refinement data are given in Table 1. Refined positional parameters are given in Table 2. Selected intramolecular bond distances are presented in Table 3.

Computational Methods. The combined ab initio/IGLO/NMR method, using the GAUSSIAN92 program,[8] was used as described previously.[9] The geometry was fully optimized at the HF/6-31G* level within the specified symmetry constraints (using the standard basis sets included) on a Silicon Graphics International IRIS 4D/440VGX computer. A vibrational frequency analysis at the HF/6-31G* level determined that the optimized structure possessed no imaginary

Table 2. Refined Positional Parameters for PSH^+*arachno*-4-$CB_8H_{13}^-$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
C4	0.1665(2)	0.05990(8)	1.2913(2)	5.23(5)
B1	0.0785(2)	0.09511(9)	1.3376(2)	4.21(5)
B2	0.1788(2)	0.12055(9)	1.4511(2)	4.10(5)
B3	0.1321(2)	0.15597(9)	1.3410(2)	4.12(5)
B5	0.2140(2)	0.06011(9)	1.4160(2)	4.74(6)
B6	0.3333(2)	0.10293(9)	1.4844(2)	4.42(6)
B7	0.2886(2)	0.16166(9)	1.4249(2)	4.39(6)
B8	0.2523(2)	0.1624(1)	1.2914(2)	4.87(6)
B9	0.1190(2)	0.1192(1)	1.2420(2)	4.76(6)
C10	0.1406(2)	0.06975(7)	0.8034(1)	3.51(4)
C11	0.1224(2)	0.02635(7)	0.8437(1)	4.45(5)
C12	0.1243(2)	0.02462(8)	0.9398(2)	5.06(5)
C13	0.1455(2)	0.06604(8)	0.9940(1)	4.86(5)
C14	0.1667(2)	0.11161(8)	0.9566(1)	3.97(4)
C15	0.1890(2)	0.15504(9)	1.0139(1)	4.82(5)
C16	0.2068(2)	0.19876(8)	0.9772(1)	5.01(5)
C17	0.2063(2)	0.20222(8)	0.8813(1)	4.42(5)
C18	0.1858(2)	0.16136(7)	0.8242(1)	3.41(4)
C19	0.1645(2)	0.11424(7)	0.8585(1)	3.29(4)
C22	0.3149(2)	0.17756(9)	0.7226(1)	4.92(5)
C23	0.0870(2)	0.19980(8)	0.6621(1)	4.50(5)
C24	0.2418(2)	0.04177(9)	0.6909(2)	5.68(6)
C25	0.0113(2)	0.05729(8)	0.6299(1)	5.00(5)
N20	0.1859(1)	0.16525(6)	0.7240(1)	3.45(3)
N21	0.1372(1)	0.07159(5)	0.7026(1)	3.61(3)
C4′	−0.2207(2)	0.06728(8)	0.8337(2)	5.21(5)
B1′	−0.3550(2)	0.10013(8)	0.8088(2)	3.85(5)
B2′	−0.3155(2)	0.15908(8)	0.8637(2)	3.66(5)
B3′	−0.3480(2)	0.15008(8)	0.7363(2)	3.59(5)
B5′	−0.2201(2)	0.10664(9)	0.9237(2)	4.33(5)
B6′	−0.1575(2)	0.16743(9)	0.9257(2)	4.29(6)
B7′	−0.2250(2)	0.19027(9)	0.8025(2)	3.88(5)
B8′	−0.2118(2)	0.1499(1)	0.7050(2)	4.47(6)
B9′	−0.2936(2)	0.09344(9)	0.7156(2)	4.23(5)
C10′	0.5851(2)	0.13022(7)	1.1625(1)	3.49(4)
C11′	0.5381(2)	0.11025(8)	1.0710(1)	4.60(5)
C12′	0.4821(2)	0.06331(8)	1.0563(2)	5.18(6)
C13′	0.4743(2)	0.03737(7)	1.1328(2)	4.80(5)
C14′	0.5233(2)	0.05623(7)	1.2292(1)	3.90(4)
C15′	0.5180(2)	0.02889(7)	1.3096(2)	4.62(5)
C16′	0.5695(2)	0.04646(7)	1.4025(1)	4.65(5)
C17′	0.6266(2)	0.09306(7)	1.4203(1)	4.12(5)
C18′	0.6313(2)	0.12133(6)	1.3444(1)	3.32(4)
C19′	0.5812(2)	0.10392(6)	1.2457(1)	3.21(4)
C22′	0.8243(2)	0.17082(8)	1.4239(1)	4.95(5)
C23′	0.6125(2)	0.20375(8)	1.4031(1)	4.81(5)
C24′	0.7588(2)	0.18246(9)	1.1540(2)	6.42(6)
C25′	0.5474(3)	0.21719(9)	1.1254(2)	6.81(7)
N20′	0.6863(1)	0.17092(5)	1.3626(1)	3.32(3)
N21′	0.6413(1)	0.17966(6)	1.1777(1)	3.70(4)
H1	−0.020(2)	0.0823(7)	1.326(1)	4.9(4)*
H2	0.137(2)	0.1283(7)	1.509(1)	5.9(5)*
H3	0.066(2)	0.1876(8)	1.329(1)	6.7(5)*
H4a	0.118(2)	0.0272(8)	1.252(1)	7.1(6)*
H4b	0.252(2)	0.069(1)	1.276(2)	9.9(8)*
H5	0.203(2)	0.0254(8)	1.454(1)	6.7(5)*
H6	0.389(2)	0.0986(7)	1.559(1)	5.2(5)*
H7	0.324(2)	0.1948(7)	1.473(1)	5.4(5)*
H8a	0.245(2)	0.1997(8)	1.255(1)	6.2(5)*
H8b	0.332(2)	0.1404(8)	1.288(1)	6.5(5)*
H9	0.045(2)	0.1221(7)	1.170(1)	5.8(5)*
H56	0.337(2)	0.0684(9)	1.441(2)	9.4(7)*
H67	0.389(2)	0.1239(7)	1.447(1)	6.3(5)*
H1′	−0.441(2)	0.0806(7)	0.811(1)	4.7(4)*
H2′	−0.387(2)	0.1767(6)	0.890(1)	4.7(4)*
H3′	−0.434(1)	0.1662(6)	0.685(1)	4.2(4)*
H4a′	−0.234(2)	0.0267(9)	0.843(2)	8.6(7)*
H4b′	−0.133(2)	0.076(1)	0.826(2)	11.3(8)*
H5′	−0.223(2)	0.0904(7)	0.991(1)	5.7(5)*
H6′	−0.128(2)	0.1915(7)	0.989(1)	5.4(5)*
H7′	−0.233(2)	0.2301(7)	0.799(1)	5.4(5)*
H8a′	−0.112(2)	0.1373(7)	0.741(1)	5.6(5)*
H8b′	−0.234(2)	0.1679(7)	0.632(1)	5.4(5)*
H9′	−0.340(2)	0.0680(7)	0.657(1)	5.8(5)*
H56′	−0.109(2)	0.1320(8)	0.944(2)	8.2(6)*
H67′	−0.109(2)	0.1748(8)	0.873(1)	7.5(6)*

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

Table 3. Comparison of Selected Observed and Calculated Bond Distances (Å) for *arachno*-4-$CB_8H_{13}^-$

bond	obsd[a]	obsd[a]	calcd[b]
C4−B1	1.677(4)	1.655(3)	1.682
C4−B5	1.707(3)	1.694(3)	1.642
C4−B9	1.766(3)	1.770(3)	1.847
C4−H4a	1.087(20)	1.129(24)	1.074
C4−H4b	1.086(27)	1.049(30)	1.078
B1−B2	1.773(3)	1.775(3)	1.818
B1−B3	1.753(3)	1.742(3)	1.740
B1−B5	1.802(3)	1.813(3)	1.873
B1−B9	1.744(4)	1.742(4)	1.718
B2−B3	1.785(3)	1.783(3)	1.822
B2−B5	1.805(4)	1.804(3)	1.825
B2−B6	1.681(3)	1.679(3)	1.724
B2−B7	1.797(4)	1.786(4)	1.832
B3−B7	1.738(3)	1.746(3)	1.734
B3−B8	1.747(4)	1.736(4)	1.793
B3−B9	1.723(4)	1.721(3)	1.741
B5−B6	1.778(3)	1.789(4)	1.854
B5−H56	1.301(23)	1.355(23)	1.432
B6−B7	1.801(3)	1.795(3)	1.855
B6−H56	1.139(24)	1.092(22)	1.273
B6−H67	1.116(23)	1.109(25)	1.285
B7−B8	1.846(4)	1.847(4)	1.952
B7−H67	1.466(20)	1.391(18)	1.381
B8−B9	1.826(4)	1.819(4)	1.802
B8−H8a	1.133(20)	1.095(17)	1.205
B8−H8b	1.083(22)	1.118(18)	1.201

[a] The unit cell contained two independent molecules. [b] HF/6-31G*.

frequencies. A single point calculation, carried out at the MP2(FULL)/6-31G* level using the HF/6-31G* optimized geometry, gave a relative energy of −243.82794 au. The zero point energy (ZPE), determined at the HF/6-31G* and scaled by 0.89 as recommended,[10] is 96.65 kcal/mol. The NMR chemical shifts were calculated using the HF/6-31G* optimized geometry as input for the IGLO program employing the following basis sets. Basis DZ: C, B, 7s3p contracted to [4111, 21]; H 3s contracted to [21].

Results and Discussion

One of our groups has previously demonstrated that the *nido*-7,9-$C_2B_{10}H_{13}^-$ anion[11] (structure **1** in Figure 1) is a versatile starting material for the syntheses of a range of important types of intermediate-sized carboranes. These syntheses are based on a regiospecific dismantling of the *nido*-7,9-$C_2B_{10}H_{13}^-$ cage with reaction conditions that can be controlled to yield specific smaller-cage products, ranging from the dicarbaboranes *nido*-7,8-$C_2B_9H_{12}^-$ and *nido*-5,6-$C_2B_8H_{12}$,[12] to monocarbaboranes, including 6-L-*arachno*-4-CB_8H_{12},[13] *arachno*-4-CB_7H_{13}[13] and *closo*-1-$CB_7H_8^-$.[14] As discussed below, it has now been found

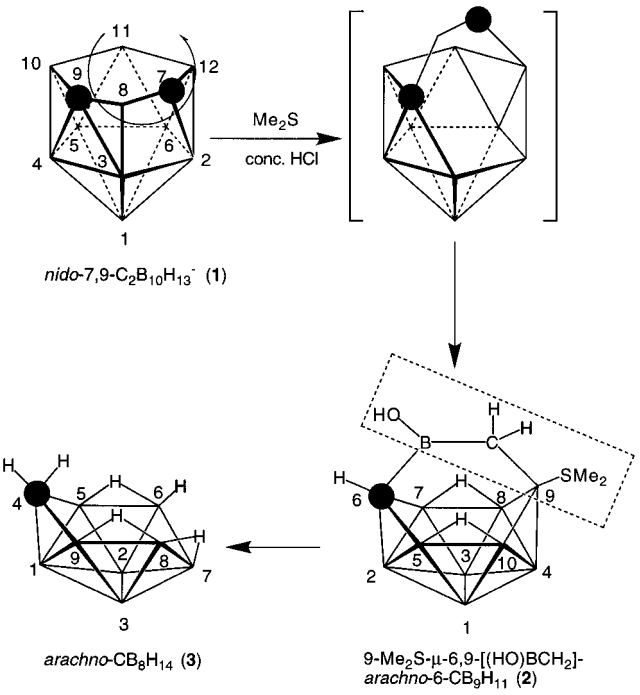

Figure 1. Possible reaction sequence to form *arachno*-4-CB_8H_{14}.

that under different conditions, this degradation reaction can be employed as a convenient and efficient synthetic route to the *arachno*-4-CB_8H_{14} monocarbaborane.

As outlined in Figure 1, the room temperature reaction between the tetramethylammonium salt of anion **1** (generated from the reaction between *o*-carborane and metallic sodium) and dimethyl sulfide in the presence of concentrated hydrochloric acid generated a moderately stable, zwitterionic monocarbaborane 9-Me_2S-μ-6,9-[(HO)BCH_2]-*arachno*-6-CB_9H_{11} (**2**) in 77% yield (58% based on the starting *o*-carborane), according to the stoichiometry in eq 1. The composition of **2** is consistent

$$\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{13}^- + H_3O^+ + Me_2S \rightarrow 9\text{-}Me_2S\text{-}\mu\text{-}6,9\text{-}[(HO)BCH_2]\text{-}\textit{arachno}\text{-}6\text{-}CB_9H_{11} + H_2 \quad (1)$$

with the hydrolytic expulsion of the C7 and B8 vertices on the open face of **1**, followed by the formation of a −B(OH)−CH_2− bridge between the cage C6 and B9 positions of the newly formed 10-vertex arachno monocarbaborane framework. In this respect, **2** can be regarded as a bridged derivative of the earlier reported 9-L-*arachno*-6-CB_9H_{13} monocarbaborane zwitterions[4,15] or as an endo-6,9-bridging derivative of the *arachno*-6-$CB_9H_{14}^-$ anion.[16] Consistent with its proposed C_s symmetry, the ^{11}B NMR spectrum of **2** (Table 4) consists of one low-field singlet (assigned to the sp^2 BOH unit) and a set of 1(d):1(d):1(s):2(d):2(d):2(d) resonances (reading upfield) that are similar to those found for the above 10-vertex arachno monocarbaboranes.[15,16] The ^{1}H NMR spectrum of **2** consists of one broad low-field and three sharper singlets, together with one broader high-field singlet, at δ (^{1}H) 8.30, 2.60, 1.44, 0.41, and −4.21 ppm that are attributed to the resonances of the BOH (bridge), Me_2S, C6H, CH_2 (bridge), and B5−H−B10/B7−H−B8 protons, respectively.

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Table 4. NMR Data for **2** in $(CD_3)_2CO$

compound	nucleus	δ (multiplicity, assignment, J (Hz))
9-Me_2S-μ-6,9-[(HO)BCH_2]-*arachno*-6-CB_9H_{11} (**2**)	^{11}B[a]	47.5 [s, B(OH, bridge)], 5.7 (d, B4, J_{BH} 132), −5.6 (d, B2, J_{BH} 160), −7.6 (s, B9),−10.6 (d, B5,7, J_{BH} 147/30[b]), −22.4 (d, B8,10, J_{BH} 133/43[b]), −33.2 (d, B1,3, J_{BH} 145)
	$^{11}B-^{11}B$	cross-peaks: B4−B9; B4−B8,10; B4−B1,3; B5,7−B8,10;[c] B5,7−B1,3; B9−B8,10
	^{1}H	8.30 (s, br, 1 H, BO*H* bridge), 2.60 (s, 6H, S*Me*$_2$), 1.44 (s, 1 H C6*H*), 0.41 (s, 2 H, CH_2 bridge), −4.21 (s, br, 2 H, μH5,7/8,10)

[a] Assignments determined by $^{11}B\{^{1}H(broadband)\}$ measurements and 2-D $^{11}B-^{11}B$ COSY NMR spectroscopy and by comparison of the ^{11}B NMR patterns with those of the structurally related arachno compounds 9-Me_2S-*arachno*-6-CB_9H_{13} and *arachno*-6-$CB_9H_{14}^-$. [b] Additional μH splitting. [c] Weak cross-peaks.

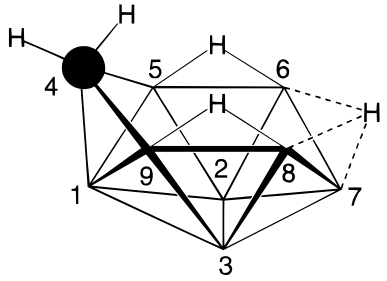

Figure 2. Previously proposed C_s symmetry structure of *arachno*-4-$CB_8H_{13}^-$.

Intermediate **2** can then be converted into *arachno*-4-CB_8H_{14} (**3**) in 75% yield (45% based on the *o*-carborane used), by treatment with water at room temperature for 24 h, as shown in eq 2. The formation of **3** is in agreement with the hydrolytic removal of the triatomic B(OH)−CH_2−B9 section from **2** (dotted area in Figure 1).

$$\underset{\mathbf{2}}{\textit{arachno}\text{-9-}Me_2S\text{-}\mu\text{-6,9-[(HO)}BCH_2\text{]-6-}CB_9H_{11}} + 4H_2O \rightarrow \underset{\mathbf{3}}{\textit{arachno}\text{-4-}CB_8H_{14}} + CH_3B(OH)_2 + B(OH)_3 + SMe_2 \quad (2)$$

The new route to *arachno*-4-CB_8H_{14} is much less complicated than the multistep methods that have previously been reported.[3,4] Furthermore, this route employs the commercially available *o*-carborane as a starting material and the product can be essentially obtained in one reaction. This reaction now promises to open the way for extensive investigations of the properties of the *arachno*-4-CB_8H_{14} monocarbaborane.

Definitive structural determinations of neither *arachno*-4-CB_8H_{14} nor *arachno*-4-$CB_8H_{13}^-$ have been previously reported. Williams[17] had proposed and McKee[18] recently confirmed using ab initio calculations that *arachno*-4-CB_8H_{14} should have a C_1 symmetry cage framework, even though the solution NMR data[3] indicate a more symmetrical structure. Likewise, the room temperature ^{11}B and ^{1}H NMR spectra, as well as a 2-D NMR study[5] of the *arachno*-4-$CB_8H_{13}^-$ anion suggest that in solution the anion also has a C_s cage symmetry, such as shown in the structure in Figure 2. However, Williams[17] has proposed that these spectra are the result of a rapid interconversion between two enantiomeric C_1 structures. We have now confirmed the C_1 structures proposed by Williams by both a single-crystal X-ray determination and ab initio/IGLO/NMR computational methods as described below.

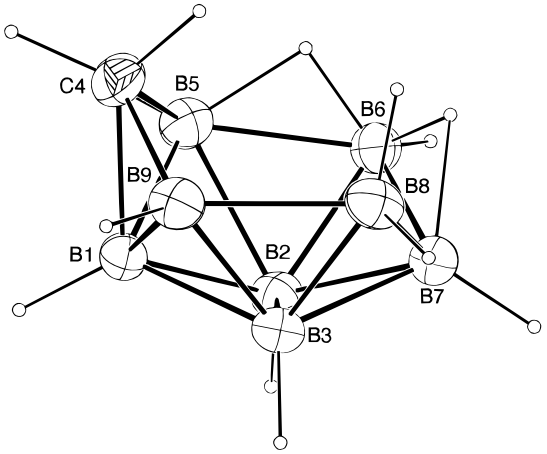

Figure 3. ORTEP drawing of the molecular structure of *arachno*-4-$CB_8H_{13}^-$.

Deprotonation of *arachno*-4-CB_8H_{14} with Proton Sponge was found to yield an air-stable, crystalline PSH^+*arachno*-4-$CB_8H_{13}^-$ salt that was suitable for a single crystal X-ray structural determination. The salt crystallized in space group $P2_1/c$ with $Z = 8$; therefore, there are two independent molecules in the unit cell. Selected bond distances for both molecules are given in Table 3 and an ORTEP drawing for one anion is presented in Figure 3. The gross cage geometry observed for the anion is typical of those found for other nine-vertex arachno clusters, including, for example, *arachno*-$B_9H_{14}^-$,[19] *arachno*-4,5-$C_2B_7H_{13}$,[20] and *arachno*-4,6-$C_2B_7H_{13}$.[21] However, the cage is found to have the C_1 symmetry predicted by Williams,[17] rather than the C_s symmetry suggested by the NMR data. Thus, rather than having a symmetric arrangement of bridging hydrogens, there is, in addition to the CH_2 group, one BH_2 (B8), and two bridge-hydrogens located at the adjacent B5−B6 and B6−B7 edges. Accordingly, B5−B6 (1.778(3) and 1.789(4) Å) and B6−B7 (1.801(3) and 1.795(3) Å) are shorter than in the corresponding unbridged B7−B8 (1.846(4) and 1.847(4) Å) and B8−B9 (1.826(4) and 1.819(4) Å) edges. The remaining intracage bond distances and angles are all within normal ranges.

The crystallographic structure is also supported by ab initio calculations at the HF/6-31G* level. Initially a symmetric structure similar to that shown in Figure 2 was used as input, but the optimization yielded the C_1 symmetry structure shown in Figure 4, where the bridge and endo hydrogen atoms are

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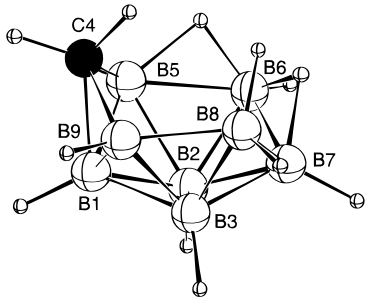

Figure 4. Optimized C_1 structure of *arachno*-4-$CB_8H_{13}^-$.

Table 5. Comparison of Calculated and Experimental ^{11}B NMR shifts for *arachno*-4-$CB_8H_{13}^-$

calcd[a]	calcd,[b] av	exptl[c]	diff[d]
10.1 (B9) −4.9 (B5)	2.6	4.0 (B5, B9)	1.4
3.4 (B7)	3.4	−3.9 (B7)	7.3
−17.0 (B1)	−17.0	−21.5 (B1)	4.5
−9.9 (B3) −54.5 (B2)	−32.2	−30.4 (B2, B3)	1.8
−24.6 (B6) −42.3 (B8)	−33.5	−35.2 (B6, B8)	1.7

[a] DZ//6-31G*. [b] Averaged values that become equivalent [c] From ref 5; assignments based on 2-D $^{11}B-^{11}B$ NMR data. [d] Difference between calculated and experimental chemical shifts.

located at the same positions as those in the crystallographic determination. A similar result was obtained when the atomic coordinates of the X-ray determined structure were used as input and there is good agreement between the values of the bond distances and angles in the optimized and X-ray structures (Table 3). When the ab initio calculation was constrained to give only structures possessing a mirror plane of symmetry, then the resulting optimized structure at the HF/6-31G* level was found to possess two imaginary frequencies and to be at higher energy than the structure in Figure 4. Likewise, further optimization of this symmetric structure, with the symmetry constraints released, yielded the C_1 structure.

The ^{11}B NMR chemical shifts for the optimized structure were calculated using the HF/6-31G* optimized geometry as input for the IGLO program, but the calculated values are substantially different than those observed experimentally, as shown in Table 5. Additionally, even though a BH_2 group is both observed by X-ray crystallography and predicted by the ab initio calculations, the triplet coupling expected for a BH_2 unit is not observed for any resonance in the experimental ^{11}B NMR spectrum. Given the proposed fluxional behavior of *arachno*-4-$CB_8H_{13}^-$ in solution, the disagreement between the observed chemical shifts and coupling pattern with those of a calculated "static" structure is not surprising. Good agreement between the experimental and calculated ^{11}B NMR spectra, however, was obtained by assuming a simple fluxional process involving the simultaneous rapid migration of two hydrogens between the two bridge and endo positions (B5−B6 and B6; B8 and B8−B9) and one hydrogen between two other bridging positions (B6−B7 and B7−B8). Such a process can be envisioned to occur by the individual steps depicted in Figure 5. Averaging the IGLO calculated chemical shift values[22] for those borons (B2 and B3; B5 and B9; and B6 and B8) in the static structure that become equivalent in the fluxional process, is found to give good

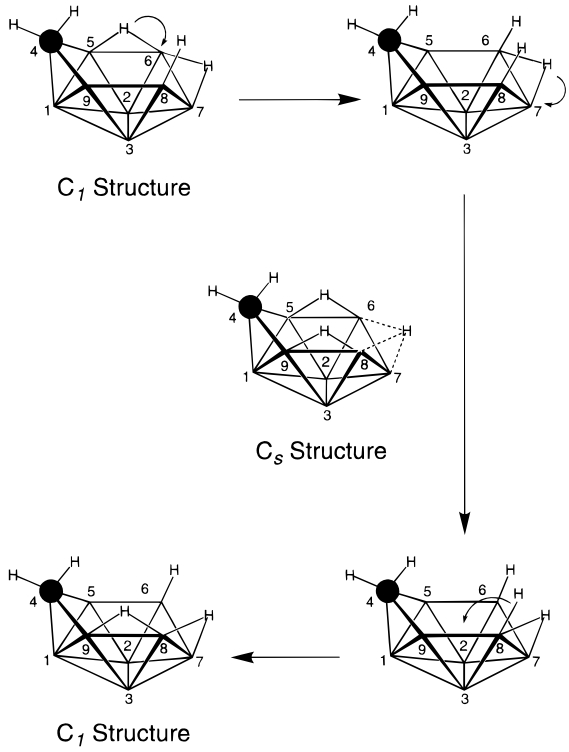

Figure 5. Proposed interconversion between the enantiomeric forms of *arachno*-4-$CB_8H_{13}^-$.

agreement with the room temperature experimental ^{11}B NMR spectrum.[23]

Low temperature NMR studies of *arachno*-4-$CB_8H_{13}^-$ were also carried out in an attempt to observe the ^{11}B NMR spectrum of the static structure. At −100 °C in CD_2Cl_2, broadening of all the peaks was observed. Most importantly, the two peaks attributed to the B2−B3 and B6−B8 boron pairs at −30.4 and −35.2 ppm disappeared and new broad resonances were observed near −15 ppm and between −40 and −50 ppm. These resonances are near the predicted IGLO values for B3 (−9.9), B8 (−42.3) and B2 (−54.5) in the static structure. The peak at 4.0 ppm which is attributed to the B5 and B9 borons would also be predicted to be replaced by new peaks at 10.1 and −4.9 ppm, but these were not observed, only significant broadening of the 4.0 ppm peak. Clearly, although the observed spectral changes are consistent with a slowing of the fluxional process to approach the static structure, the slow exchange limit was not reached at the limit (−100 °C) of our low temperature experiment.

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Supporting Information Available: Tables listing refined thermal parameters, bond distances, bond angles and calculated atom positions, and Cartesian coordinates for the optimized structure at the HF/6-31G* level (11 pages). Ordering information is given on any current masthead page.

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