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Synthesis and Structural Studies of Subicosahedral Adjacent-Carbon Carboranes

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Abstract: Synthesis and structural studies, employing combined NMR, X-ray crystallographic, and ab initio/IGLO/NMR methods, of a variety of new subicosahedral carboranes with adjacent cage carbons are reported. Acetonitrile-induced cage degradation of *arachno*-4,5-$C_2B_7H_{12}^-$ gave *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) in nearly quantitative yield, which can then be protonated to give the neutral carborane *nido*-4,5-$C_2B_6H_{10}$ (**1**) in good yield. Both of these nido electron-count clusters are shown to have an arachno-type geometry, i.e. a six-membered open face. The *nido*-4,5-$C_2B_6H_{10}$ (**1**) hydroborated alkenes or alkynes which following deprotonation gave *nido*-7-R-4,5-$C_2B_6H_8^-$ (**2a**$^-$−**c**$^-$) ions. Both *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) and *nido*-4,5-$C_2B_6H_{10}$ (**1**) serve as useful precursors to other adjacent cage-carbon clusters. Thus, *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) reacted with BH_3·THF to give *arachno*-5,6-$C_2B_7H_{12}^-$ (**3**$^-$) which a single-crystal X-ray diffraction study showed is the first carborane to adopt the *n*-B_9H_{15} cage geometry. Thermal or chemical degradation of *nido*-4,5-$C_2B_6H_{10}$ (**1**) gave *closo*-2,3-$C_2B_5H_7$ (**5**) in good to moderate yields. The *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) was also found prone to lose a cage boron as evidenced by its reactions with $(\eta\text{-}C_5H_5)Co(CO)I_2$ and $(\eta^6\text{-}C_6Me_6)_2Ru_2Cl_4$ which gave *closo*-3,1,2-$(\eta\text{-}C_5H_5)CoC_2B_5H_7$ (**6**) and *closo*-3,1,2-$(\eta^6\text{-}C_6Me_6)RuC_2B_5H_7$ (**7**), respectively. NMR studies showed the *nido*-4,5-$C_2B_6H_{10}$ (**1**) was converted to *arachno*-4,5-$C_2B_6H_{11}^-$ by reaction with $LiEt_3BH$, and an alkyl derivative, *arachno*-7-CH_3-4,5-$C_2B_6H_{10}^-$ (**4**$^-$), was formed by reacting MeLi with *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) followed by protonation. The *closo*-2,3-$C_2B_5H_7$ (**5**) was also converted in high yields to the smaller nido carborane, *nido*-2,3-$C_2B_4H_8$, via reaction with TMEDA/H_2O, and to *nido*-3,4-$C_2B_5H_8^-$ (**8**$^-$) by reaction with $LiEt_3BH$.

Introduction

The small carboranes (subicosahedra) were first synthesized in the early 1960s by high temperature cage growth reactions involving boranes and acetylenes.[1] Because of the lower stability of adjacent-carbon carboranes relative to isomerization to their non-adjacent isomers, the high temperature reactions yielded predominantly non-adjacent carbon products. Likewise, the high temperature reactions typically gave low yields and complex mixtures of products that then required extensive purification. Gas-phase methods for small carborane synthesis are now giving way to solution based procedures that, because of their milder conditions, generally have much higher yields, selectivities, and easier purification, allowing the isolation of kinetic rather than thermodynamic products.[2] In this paper we report the synthesis and structural studies of a variety of new subicosahedral adjacent-carbon carboranes via selective cage degradation and insertion reactions.

Experimental Section

All manipulations were carried out using standard high vacuum or inert-atmosphere techniques as described by Shriver.[3]

Materials. THF, pentane, hexanes, and benzene were dried over Na/benzophenone and freshly distilled before use. Acetonitrile, dried over CaH_2, then P_2O_5, and methylene chloride, dried over CaH_2, were distilled before use. Acidification of 1,8-bis(dimethylamino)naphthalene (Proton Sponge) with a 1 M Et_2O solution of HCl was used to generate the hydrochloride salt. The *arachno*-4,5-$C_2B_7H_{13}$,[4] $(\eta\text{-}C_5H_5)Co(CO)I_2$,[5] and $(\eta^6\text{-}C_6Me_6)_2Ru_2Cl_4$[6] were prepared according to literature methods. All other materials were obtained from Aldrich and used as received.

Physical Measurements. ^1H NMR at 200 or 500 MHz, ^{11}B NMR at 64.2 or 160.5 MHz, and ^{13}C NMR at 50.3 or 125.7 MHz were obtained on Bruker AF-200 or Bruker AM-500 spectrometers. All ^{11}B chemical shifts are referenced to $BF_3·O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^1H and ^{13}C chemical shifts were measured relative to internal residual protons or carbons from the lock solvents and then referenced to Me_4Si (0.0 ppm). Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer and can be found in Supporting Information.

K^+*nido*-4,5-$C_2B_6H_9^-$ (1$^-$). A 100-mL three-neck round-bottom flask equipped with a vacuum stopcock, septum, sidearm addition-funnel, and stirbar was charged with 1.50 g (13.3 mmol) of freshly prepared *arachno*-4,5-$C_2B_7H_{13}$ under a N_2 atmosphere. Following the *in vacuo* addition of THF (∼50 mL), an excess of KH was slowly added via the sidearm at −50 °C until H_2 evolution had ceased. The K^+*arachno*-

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(1) See the following, and references therein: (a) Williams, R. E. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon Press: Oxford, 1970; Vol. II, pp 37−118. (b) Grimes, R. N. *Carboranes*; Academic: New York, 1970. (c) Onak, T. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic: New York, 1973; pp 349−382. (d) Onak, T. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds; Pergamon: Oxford, 1982; Chapter 5.4, pp 411−458.

(2) Štíbr, B.; Plešek, J.; Jelínek, T.; Baše, K.; Janoušek, Z.; Heřmánek, S. *Boron Chemistry*; Heřmánek, S., Ed.; World Scientific Publishing Co. PTE, Ltd.: Singapore, 1987; pp 175−206 and references therein.

(3) Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(4) (a) Heřmánek, S.; Jelínek, T.; Plešek, J.; Štíbr, B.; Fusek, J. *J. Chem. Soc., Chem. Commun.* **1987**, 927−928. (b) Štíbr, B.; Heřmánek, S.; Plešek, J. *Inorg. Synth.* **1983**, *22,* 237−239.

(5) King, R. B. *Inorg. Chem.* **1966**, *5,* 82−87.

(6) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, K. A. *Inorg. Synth.* **1982**, *21,* 74−76.

(7) Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1976**, *109,* 3480−3485.

(8) Jelínek, T.; Štíbr, B.; Heřmánek, S.; Plešek, J. *J. Chem. Soc., Chem. Commun.* **1989**, 804−805.

(9) Beck, J. S.; Quintana, W.; Sneddon, L. G. *Organometallics* **1988**, *7,* 1015−1016.

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4,5-$C_2B_7H_{12}^-$ solution was brought to room temperature and filtered, and the filtrate was transferred to a 250-mL two-neck round-bottom flask equipped with a stirbar, vacuum stopcock, and septum. Following vacuum transfer of CH_3CN (∼50 mL), the vacuum stopcock was replaced with a condenser and the solution refluxed under a N_2 atmosphere. According to ^{11}B NMR spectroscopy, the reaction was complete within 24−36 h. Any insoluble material, if formed, was removed by filtration. The volatiles were vacuum evaporated leaving K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) as a yellow solid, which according to NMR was contaminated with *N,N,N*-$Et_3B_3N_3H_3$ (δ ^{11}B 33.1 ppm).[7] Washing the solid with two 50-mL portions of benzene afforded 1.76 g (12.8 mmol, 96.6%) of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) as a pale yellow, slightly air-sensitive solid.

The Bu_4N^+ salt of *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) was prepared by addition of a THF solution of (*n*-Bu)$_4$NBr to a THF solution of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$). This mixture was then stirred at room temperature, KBr was removed by filtration, and toluene was added to the solution until cloudiness appeared. The solution was cooled at 0 °C to obtain crystals suitable for crystallographic studies. For Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ (Bu_4N^+**1**$^-$): mp 92−93 °C; elemental analyses for Bu_4N^+**1**$^-$ gave larger than normal deviations (Anal. Calcd: C, 63.51; H, 13.32, N, 4.11. Found: C, 59.73; H, 12.75; N, 4.12) but the structure of Bu_4N^+**1**$^-$ was determined crystallographically (Supporting Information Tables S2−S7), and exact mass measurements of the protonated form (**1**, see below) are consistent with the proposed formula.

***nido*-4,5-$C_2B_6H_{10}$ (1).** A 250-mL round-bottom flask fitted with a vacuum stopcock and stirbar was charged with 1.19 g (8.7 mmol) of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) under a N_2 atmosphere. Pentane (∼35 mL) was added by vacuum distillation. The pentane suspension of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) was brought to −50 °C, and an excess of HCl gas was expanded into the vacuum line and allowed to react with the solution for ∼2 h. When the HCl addition appeared complete, the solution was vacuum fractionated through a series of −20, −78, and −196 °C traps. The *nido*-4,5-$C_2B_6H_{10}$ (**1**) condensed in the −78 °C trap as an air- and temperature-sensitive, white crystalline solid in an optimized yield of 0.601 g (6.17 mmol, 70.0%). For *nido*-4,5-$C_2B_6H_{10}$ (**1**): mp ≈ −50 °C; exact mass calcd for $^{12}C_2{}^{11}B_6{}^1H_{10}$ 100.1341, found 100.1349.

PSH^+*nido*-7-(R)-4,5-$C_2B_6H_8^-$ (2a$^-$−c$^-$). In a typical reaction, a one-neck vacuum flask fitted with a stirbar was charged with ∼2 mmol of *nido*-4,5-$C_2B_6H_{10}$ (**1**) and an excess of phenyl acetylene, 2-butyne, or 1-hexene, respectively. The reaction was stirred until completion, then 1.2 equiv of Proton Sponge was added. The precipitated salt was filtered, then washed and/or recrystallized. The yields were as follows: PSH^+*nido*-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_8^-$ (**2a**$^-$) (83.2%), PSH^+*nido*-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_8^-$ (**2b**$^-$) (77.5%), PSH^+*nido*-7-(*n*-hexyl)-4,5-$C_2B_6H_8^-$ (**2c**$^-$) (41.3%). Details are given in the Supporting Information. To establish the composition of **2a**$^-$, in a separate reaction, after the formation of **2a**, *nido*-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_9$, was observed, the volatiles were then evaporated *in vacuo* and the remaining oily material dissolved in CH_2Cl_2. Exact mass measurements on **2a** confirm its composition: exact mass calcd for **2a**, $^{12}C_{10}{}^{11}B_6{}^1H_{16}$ 202.1810, found 202.1831. Furthermore, the similarity of the spectroscopic data of **2a**$^-$ with that of the X-ray characterized butenyl analog **2b**$^-$ (below) provides additional structural confirmation. In a separate experiment carried out in a 5-mm NMR tube equipped with a Teflon stopcock, *nido*-7-(octyl)-4,5-$C_2B_6H_9$ (**2d**) carboranes were generated by reaction of ∼0.1 mmol of *nido*-4,5-$C_2B_6H_{10}$ (**1**) and ∼0.7 mL of octenes (a mixture of 1- and 2-octenes) at 60 °C for 1 h. ^{11}B NMR showed only the formation of *nido*-7-(octyl)-4,5-$C_2B_6H_9$ (**2d**) carboranes.

***arachno*-5,6-$C_2B_7H_{12}^-$ (3$^-$).** A solution of BH_3·THF (1 mL of a 1.0 M THF) was slowly added via syringe to 0.12 g (0.88 mmol) of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) dissolved in ∼20 mL of THF at 0 °C. After warming to room temperature, the volatiles were removed to give 0.13 g (0.86 mmol, 97.7%) of K^+*arachno*-5,6-$C_2B_7H_{12}^-$ (**3**$^-$) as a slightly air-sensitive, pale yellow solid.

The PSH^+*arachno*-5,6-$C_2B_7H_{12}^-$ salt (PSH^+**3**$^-$) was prepared by addition of ∼10 mL of a CH_2Cl_2 solution of PSH^+Cl^- (0.22 g, 0.88 mmol) to a ∼10 mL THF solution of K^+*arachno*-5,6-$C_2B_7H_{12}^-$ (**3**$^-$) (0.12 g, 0.79 mmol), followed by ∼10 mL of Et_2O. Filtration removed the KCl, and addition of heptane then precipitated the PSH^+**3**$^-$. The structure of PSH^+**3**$^-$ was established crystallographically with suitable single crystals obtained by cooling a CH_2Cl_2/Et_2O/heptane solution of PSH^+**3**$^-$ at −25 °C.

NMR Study of Reaction of 1 with $LiEt_3BH$. A 25-mL two-neck round-bottom flask equipped with a stirbar, vacuum stopcock, and rubber septum was attached to the vacuum line and 0.15 g (1.52 mmol) of *nido*-4,5-$C_2B_6H_{10}$ (**1**) followed by ∼10 mL of CH_2Cl_2 were vacuum transferred into the flask. The flask was maintained at −30 °C, and under nitrogen, ∼1 equiv (1.6 mL) of a 1.0 M THF solution of $LiEt_3BH$ was added via syringe. When brought to room temperature, a ^{11}B NMR spectrum (see Supporting Information) of the solution showed the *arachno*-4,5-$C_2B_6H_{11}^-$ [8] (∼60%) and *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) (∼40%) ions.

NMR Study of Reaction of 1$^-$ with Methyllithium. To a THF solution of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) in a NMR tube equipped with a rubber septum was added a slight excess of a 1.4 M Et_2O solution of CH_3Li at 0 °C. The solution was heated at 40 °C for 1 h until its ^{11}B NMR spectrum showed the formation of *arachno*-7-CH_3-$C_2B_6H_9^{2-}$ (**4**$^{2-}$), then ∼1 equiv of PSH^+Cl^- was added to form *arachno*-7-CH_3-4,5-$C_2B_6H_{10}^-$ (**4**$^-$) as shown by ^{11}B NMR (see Supporting Information).

***closo*-2,3-$C_2B_5H_7$ (5) via Thermal Degradation.** A 0.70-g (7.07 mmol) sample of *nido*-4,5-$C_2B_6H_{10}$ (**1**) was slowly passed (by keeping it at −22 °C) through a 350 °C "hot tube" reactor (a 15 in. Pyrex glass tube of 1 in. diameter) connected to a vacuum line. The condensable products were collected in a −196 °C trap, then fractionated through a 0, −45, −78, and −196 °C series of traps. According to ^{11}B NMR, the −78 °C trap contained a 5:1 mixture of *closo*-2,3-$C_2B_5H_7$ (**5**) and *closo*-1,7-$C_2B_6H_8$, but they could not be further separated using vacuum fractionation. Based on this ratio the estimated yield of *closo*-2,3-$C_2B_5H_7$ (**5**) was 0.33 g (3.8 mmol, 54%). The −196 °C trap contained *closo*-2,4-$C_2B_5H_7$ and B_2H_6. Refractionation of this material gave 0.04 g (0.47 mmol, 6.6%) of *closo*-2,4-$C_2B_5H_7$ in a −100 °C trap. The 0 and −45 °C traps contained small amounts of larger closo carboranes (1,6-$C_2B_7H_9$, 1,6-$C_2B_8H_{10}$, *m*-$C_2B_{10}H_{12}$) as shown by ^{11}B NMR and mass spectroscopy.

***closo*-2,3-$C_2B_5H_7$ (5) via Thermolysis of 2b.** Dry dodecane (∼15 mL) was placed in a 50-mL vacuum flask equipped with a stirbar, then 0.15 g (1.52 mmol) of *nido*-4,5-$C_2B_6H_{10}$ (**1**) and a ∼5-fold excess of 2-butyne were vacuum transferred to the flask. The solution was heated at 50 °C for 1 h at which point a ^{11}B NMR spectrum showed complete formation of *nido*-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_9$ (**2b**). The solution was heated further at 110 °C for 1.5 h, and a ^{11}B NMR spectrum of this solution showed the presence of *closo*-2,3-$C_2B_5H_7$ (**5**) and a broad resonance (65 ppm) in the region typically found for alkyl boranes. This solution was then fractionated through a −20, −50, −78, and −196 °C series of traps. An unoptimized yield of 0.045 g (0.53 mmol, 34.9%) of *closo*-2,3-$C_2B_5H_7$ (**5**) was isolated in the −78 °C trap. Exact mass calcd for $^{12}C_2{}^{11}B_5{}^1H_7$ 86.1013, found 86.1011. A small amount of *closo*-1-(butenyl)-2,3-$C_2B_5H_6$ condensed in the −50 °C trap together with dodecane.

***closo*-3,1,2-(η-C_5H_5)$CoC_2B_5H_7$ (6) and *closo*-3,1,2-(η^6-C_6Me_6)-$RuC_2B_5H_7$ (7).** In separate reactions, CH_2Cl_2 solutions of (η-C_5H_5)Co(CO)I_2 (0.684 g) and (η^6-C_6Me_6)$_2Ru_2Cl_4$ (0.342 g) were added dropwise to 1.53 and 1.02 mmol of K^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$), respectively, dissolved in ∼20 mL of THF. After stirring overnight, the mixtures were filtered and separated by column chromatography to give *closo*-3,1,2-(η-C_5H_5)$CoC_2B_5H_7$ (**6**) (20 mg, 6.2% yield) and *closo*-3,1,2-(η^6-C_6Me_6)$RuC_2B_5H_7$ (**7**) (56 mg, 20.5% yield). For the dark red-orange colored *closo*-3,1,2-(η-C_5H_5)$CoC_2B_5H_7$ (**6**): mp 124−7 °C; exact mass calcd for $^{12}C_7{}^{11}B_5{}^{59}Co{}^1H_{12}$ 210.0736, found 210.0742; Anal. Calcd: C, 40.20; H, 5.78. Found: C, 39.92; H, 5.70. For the yellow solid *closo*-3,1,2-(η^6-C_6Me_6)$RuC_2B_5H_7$ (**7**): mp 150 °C dec; exact mass calcd for $^{12}C_{14}{}^{11}B_5{}^{101}Ru{}^1H_{25}$ 350.1465, found 350.1455. Anal. Calcd: C, 48.25; H, 7.23. Found: C, 47.97; H, 7.32.

NMR Study of Reaction of 5 with $LiEt_3BH$. To a NMR tube equipped with a Teflon stopcock was vacuum transferred ∼0.1 mmol of *closo*-2,3-$C_2B_5H_7$ (**5**) and ∼0.7 mL of THF, then via syringe an excess of a 1.0 M THF solution of $LiEt_3BH$ was added. A ^{11}B NMR spectrum (see Supporting Information) showed complete conversion to *nido*-3,4-$C_2B_5H_8^-$ (**8**$^-$), as evidenced by comparison with the literature values[9] for *nido*-3,4-$Et_2C_2B_5H_6^-$ and the ab initio/IGLO calculated shifts.

***nido*-2,3-$C_2B_4H_8$.** A 25-mL two-neck round-bottom flask equipped with a stirbar, vacuum stopcock, and septum was charged with ~10 mL of dodecane and ~2 mL of tetramethylethylenediamine (TMEDA). Following the vacuum transfer of ~2 mmol of *closo*-2,3-$C_2B_5H_7$ (**5**) (measured by gas volume), the solution was brought to room temperature. A ^{11}B NMR spectrum (Table 1) then showed complete formation of a TMEDA adduct, presumably *nido*-6-(TMEDA)-3,4-$C_2B_5H_7$ (**9**). The solution was then maintained at ~15 °C and ~0.5 mL of degassed H_2O was added by syringe. The solution was stirred vigorously while the volatiles were continuously vacuum fractionated through −78 and −196 °C traps. After ~3 h, 0.012 g (0.154 mmol, 77.0%) of *nido*-2,3-$C_2B_4H_8$ had been trapped at −196 °C. The product was characterized by comparison of its spectroscopic data with literature values.[10]

X-ray Crystallographic Studies. Details of the collection, solution, and refinement of the crystallographic data for PSH^+**2b**$^-$ and PSH^+**3**$^-$ are in the Supporting Information. The structural determination of PSH^+**1**$^-$ is described in the earlier communication[11] and in the Supporting Information.

Computational Methods. The details of the methods employed have been given elsewhere.[12] The NMR chemical shifts were calculated using the IGLO method[13,14] employing Huzinaga Gaussian lobe functions[15] with specific basic sets described previously.[12] B_2H_6 is the primary reference for the ^{11}B NMR chemical shifts and the δ values were converted to the $BF_3 \cdot O(C_2H_5)_2$ scale using the experimental value of $\delta(B_2H_6) = 16.6$ ppm.[16] ^{13}C shifts are referenced to the experimental standard, tetramethylsilane (TMS). Because of the satisfactory agreement between the calculated and experimental values, the IGLO calculated ^{13}C NMR data have been included in Table 2; however, it should be noted that previous studies[17,18] indicate the levels of theory employed in this study may not always be suitable for the accurate calculation of cage carbons in carboranes. Comparisons of the calculated and available experimental ^1H NMR data have not been included because ^1H shifts currently cannot be accurately calculated.[19]

The GIAO-MP2 electron correlated chemical shift calculation as implemented by J. Gauss[20] was carried out using the ACESII program package[21] employing the tzp Ahlrichs basis set[22] for C and B, which includes one set of d polarization functions. H is described by a double-ζ basis set.

Results and Discussion

The new carborane anion *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) was prepared in high yields, as described in the Experimental Section, from the acetonitrile-induced cage degradation reaction of the conjugate anion of *arachno*-4,5-$C_2B_7H_{13}$:

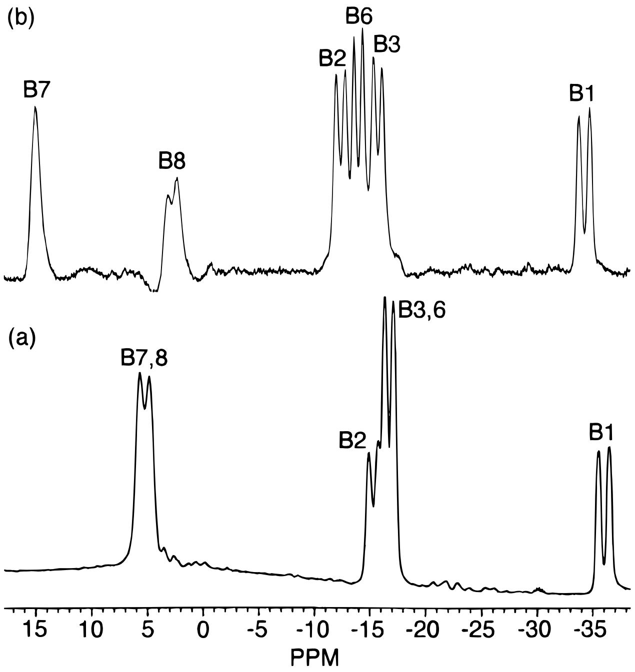

Figure 1. Proton spin-decoupled 160.5-MHz ^{11}B NMR spectra of (a) *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) and (b) *nido*-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_8^-$ ($\mathbf{2a}^-$).

$$\textit{arachno}\text{-}4,5\text{-}C_2B_7H_{12}^- + CH_3CN \xrightarrow{\Delta} \underset{\mathbf{1}^-}{\textit{nido}\text{-}4,5\text{-}C_2B_6H_9^-} + 1/3\ Et_3B_3N_3H_3 \quad (1)$$

The cage degradation observed in this reaction is different than the reaction of CH_3CN with the isomeric *arachno*-6,8-$C_2B_7H_{12}^-$ anion, which results in the monocarbon cage insertion product *nido*-6-CH_3-5,6,9-$C_3B_7H_9^-$.[23] This difference in reactivity is probably a consequence of the fact that the 4,5-isomer contains two BH_2 groups while the 6,8-isomer has a single BH_2.[24] The CH_3CN appears to cause the base-induced cleavage of BH_3 from one of the BH_2 groups of the 4,5-isomer with subsequent rearrangement of the resulting $CH_3CN{\bullet}BH_3$ adduct to 1,3,5-$Et_3B_3N_3H_3$.[25]

The ^{11}B NMR spectrum of $\mathbf{1}^-$ (Figure 1a) shows four doublet resonances in 2:1:2:1 ratios, indicating the presence of a cage mirror plane, with each boron containing one terminal hydrogen. The ^1H NMR spectrum of $\mathbf{1}^-$ is likewise consistent with C_s cage symmetry, showing four B−H_t, one C−H, and a bridge-hydrogen resonances in ratios of 2:2:2:1:1:1. The ^{13}C NMR spectrum of $\mathbf{1}^-$ shows a single resonance at 108.4 ppm (Table 1).

A $C_2B_6H_9^-$ carborane is an 8-vertex, 20-skeletal-electron, nido-cluster system and, on the basis of skeletal electron counting rules,[26] would be expected to adopt an open-cage structure based on a tricapped trigonal prism missing one high-coordinated vertex (Figure 2a). However, the only structurally characterized 8-vertex nido-cluster with this geometry is *nido*-

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[10] Onak, T.; Drake, R. P.; Dunks, G. B. *Inorg. Chem.* **1964**, *3*, 1686−1690.

[11] Kang, S. O.; Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 6248−6249.

[12] Bausch, J. W.; Rizzo, R. C.; Sneddon, L. G.; Wille, A. E.; Williams, R. E. *Inorg. Chem.* **1996**, *35*, 131−135.

[13] See: Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: Berlin, 1990; Vol. 23, pp 165−262 and references therein.

[14] For examples of the IGLO method applied to boron compounds, see footnote 17 in: Diaz, M.; Jaballas, J.; Tran, D.; Lee, H.; Arias, J.; Onak, T. *Inorg. Chem.* **1996**, *35*, 4536−4540.

[15] Huzinaga, S., *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

[16] Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533−1535.

[17] Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477−491.

[18] (a) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385−12390. (b) Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1766−1768.

[19] Bühl, M.; Schleyer, P. v. R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds., Wiley: New York, 1991; Chapter 4, pp 113−142.

[20] (a) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614−620. (b) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629−3643.

[21] ACESII: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1992**, *26*, 879−894.

[22] Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577.

[23] (a) Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339−2347. (b) Kang, S. O.; Sneddon, L. G. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 195−213.

[24] The structures of the *arachno*-4,5-$C_2B_7H_{12}$- and *arachno*-6,8-$C_2B_7H_{12}^-$ anions, and a possible mechanism for the formation of *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$), will be discussed in a subsequent paper. Bausch, J. W., Sneddon, L. G., unpublished results.

[25] Emeléus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614−2617.

Table 1. NMR Data

compd	nucleus	δ (multiplicity, assignment, J (Hz))
nido-4,5-$C_2B_6H_9^-$ (**1**$^-$)	^{11}B[a]	5.0 (d, B7,8, J_{BH} 135), −15.0 (d, B2, J_{BH} 129), −16.8 (d, B3,6, J_{BH} 124), −36.1 (d, B1, J_{BH} 157, J_{BB} 20)
	^{11}B−^{11}B[b]	crosspeaks: B7,8-B2; B7,8-B3,6; B2-B1; B2-B3,6
	^{1}H{^{11}B}[c]	5.5 (C4,5H), 3.9 (B7,8H), 2.1 (B3,6H), 0.8 (B2H), −0.3 (B1H), −6.3 (BHB)
	^{13}C[d]	108.4 (br, C4,5)
nido-4,5-$C_2B_6H_{10}$ (**1**)	^{11}B[e]	7.8 (br, B7,8), −7.3 (d, B1, J_{BH} 176), −12.4 (d, B3,6, J_{BH} 143), −26.6 (d, B2, J_{BH} 146)
	^{11}B−^{11}B[f]	crosspeaks: B7,8-B3,6; B7,8-B2; B1-B3,6; B1-B2; B3,6-B2
	^{1}H(^{11}B)[g]	6.2 (C4,5H), 3.0 (m, B7,8H), 2.6 (B3,6H), 2.0 (B1H), 1.2 (B2H), −3.4 (br, BHB)
	^{13}C[h]	120.0 (br, C4,5)
nido-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_8^-$ (**2a**$^-$)	^{11}B[i]	15.5 (br, B7), 3.2 (d, B8, J_{BH} 142), −12.1 (d, B2, J_{BH} 131), −13.7 (d, B6, J_{BH} 125), −15.5 (d, B3, J_{BH} 122), −34.1 (d, B1, J_{BH} 151)
	^{1}H{^{11}B}[j,k]	7.5−7.0 (Ph, ═C−H), 6.6 (d, ═C−H, J_{HH} 18), 5.7 (CH), 5.65 (CH), 3.6 (BH), 2.0 (BH), 1.9 (BH), 1.2 (BH), −0.3 (BH), −4.8 (B−H−B)
nido-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_8^-$ (**2b**$^-$)	^{11}B[l]	17.2 (B7), −1.0 (br, B8), −13.4 (d, B2, J_{BH} 146), −15.8 (d, B6, J_{BH} 156), −17.8 (d, B3, J_{BHH} 141), −36.4 (d, B1, J_{BH} 143)
nido-7-(*n*-hexyl)-4,5-$C_2B_6H_8^-$ (**2c**$^-$)	^{11}B[l]	19.1 (br, B7), −1.3 (br, B8), −13.0 (d, B2, J_{BH} 153), −15.7 (d, B6, J_{BH} 161), −18.1 (d, B3, J_{BH} 139), −36.3 (d, B1, J_{BH} 140)
nido-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_9$ (**2a**)	^{11}B[m]	40.2 (br, B7), −8.4 (d, B6, J_{BH} 141), −13.3 (d, B1, $J_{BH} \approx 130$), −16.9 (d, B3, J_{BH} 156), −23.0 (d, B8, $J_{BH} \approx 160$), −25.3 (d, B2, J_{BH} 145)
nido-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_9$ (**2b**)	^{11}B[n]	43.8 (s, B7), −8.2 (d, B6, J_{BH} 140), −13.7 (d, B1, J_{BH} 176), −16.6 (d, B3, J_{BH} 154), −23.3 (d, B8, J_{BH} 153), −24.7 (d, B2, J_{BH} 144)
	^{11}B−^{11}B[o]	crosspeaks: B1-B2; B1-B3; B1-B6; B2-B3; B2-B6; B2-B8; B3-B8; B6-B7
nido-7-(*n*-hexyl)-4,5-$C_2B_6H_9$ (**2c**)	^{11}B[p]	49.2 (s, B7), −6.4 (d, B6, J_{BH} 138), −11.7 (d, B1, J_{BH} 181), −16.3 (d, B3, J_{BH} 142), −21.4 (d, B8, J_{BH} 176), −24.2 (d, B2, J_{BH} 158)
nido-7-(octyl)-4,5-$C_2B_6H_9$ (**2d**)	^{11}B[q]	49.2 (s, B7), −6.4 (d, B6, J_{BH} 142), −12.0 (d, B1, J_{BH} 182), −16.4 (d, B3, J_{BH} 147), −21.4 (d, B8, J_{BH} 156), −24.4 (d, B2, J_{BH} 154)
arachno-5,6-$C_2B_7H_{12}^-$ (**3**$^-$)	^{11}B[r]	-1.4 (d, B1, J_{BH} 126), −7.7 (t, B9, J_{BH} 115), −9.6 (d, B4,7, J_{BH} 129), −43.5 (d, B3,8, J_{BH} 118), −44.7 (d, B2, J_{BH} 157)
	^{11}B−^{11}B[s]	crosspeaks: B1-B2; B1-B3,8; B1-B4,7; B3,8-B4,7
	^{1}H{^{11}B}[t]	5.5 (C5,6H), 2.5 (B4,7H), 2.3 (m, *exo*-B9H, br), 2.1 (s, B1H), 0.7 (t, *endo*-B9H, J_{HH} 6), 0.1 (B3,8H), −0.7 (B2H), −1.4 (BHB)
	^{13}C[u]	116.2 (br, C5,6)
arachno-7-CH_3-4,5-$C_2B_6H_{10}^-$ (**4**$^-$)	^{11}B[v]	6.6 (d, B6, J_{BH} 128), 3.4 (d, B3, J_{BH} 146), −20.2 (d, B2, J_{BH} 141), −31.6 (d, B7, J_{BH} 99), −37.9 (t, B8, J_{BH} 107), −57.7 (d, B1, J_{BH} 170)
	^{11}B−^{11}B[w]	crosspeaks: B1-B2; B1-B3; B1-B6; B2-B3; B2-B6; B2-B7; B2-B8; B3-B8; B6-B7
arachno-7-CH_3-4,5-$C_2B_6H_9^{2-}$ (**4**$^{2-}$)	^{11}B[x]	-3.0 (br, B6), −9.6 (br, overlap, B2,B3), −31.5 (br, B7), −45.3 (t, B8, $J_{BH} \approx 90$), −58.9 (d, B1, $J_{BH} \approx 120$)
closo-2,3-$C_2B_5H_7$ (**5**)	^{11}B[e]	6.9 (d, B4,6, J_{BH} 172), 3.1 (d, B5, J_{BH} 157), −17.9 (d, B1,7, J_{BH} 176)
	^{1}H{^{11}B}[y]	6.9 (C2,3H), 4.4 (B4,6H), 3.9 (B5H), −0.1 (B1,7H)
	^{13}C[z]	93.8 (br, C2,3)
closo-1-(butenyl)-2,3-$C_2B_5H_6$	^{11}B[aa]	6.9 (d, B4,6, J_{BH} 154), 2.9 (d, B5, J_{BH} 160), −6.8 (s, B1), −25.0 (d, B7, J_{BH} 180)
closo-3,1,2-CpCo$C_2B_5H_7$ (**6**)	^{11}B[f]	67.2 (d, J_{BH} 156), 18.2 (d, J_{BH} 166), −1.3 (d, J_{BH} 177), −8.2 (d, J_{BH} 155)
	^{1}H{^{11}B}[bb]	9.4 (BH), 6.4 (CH), 5.3 (C_5H_5), 4.3 (BH), 2.8 (BH), 0.7 (BH)
	^{13}C[cc]	86.1 (C_5H_5), 66.8 (cage C, br)
closo-3,1,2-(η^6-C_6Me_6)Ru$C_2B_5H_7$ (**7**)	^{11}B[f]	57.7 (d, 148), 13.7 (d, 153), −2.6 (d, 172), −11.8 (d, 134)
	^{1}H[bb]	7.4 (BH), 5.1 (CH), 4.2 (BH), 2.7 (BH), 0.5 (BH) (one peak obscured)
	^{13}C[cc]	102.6 (s, Me_6C_6), 60.4 (br, cage C), 17.4 (s, Me_6C_6)
nido-3,4-$C_2B_5H_8^-$ (**8**$^-$)	^{11}B[x]	21.4 (d, B2, J_{BH} 128), 18.9 (t, B6, J_{BH} 116), 1.1 (d, B5,7, J_{BH} 110), −34.0 (d, B1, J_{BH} 158)
nido-6-(TMEDA)-3,4-$C_2B_5H_7$ (**9**)	^{11}B[o]	19.6 (d, B2, J_{BH} 132), 15.7 (d, B6, J_{BH} 139), 4.5 (d, B5,7, J_{BH} 136), −31.7 (d, B1, J_{BH} 169)

[a] 160.5 MHz in THF-d_8 (K^+ salt). [b] 64.2 MHz in THF-d_8 (K^+ salt). [c] 500 MHz in THF-d_8 (K^+ salt). [d] 50.3 MHz in THF-d_8 (K^+ salt). [e] 160.5 MHz in CD_2Cl_2. [f] 64.2 MHz in CD_2Cl_2. [g] 200 MHz in C_6D_6. [h] 50.3 MHz in C_6D_6. [i] 160.5 MHz in CD_3CN (PSH^+ salt). [j] 500 MHz in CD_3CN (PSH^+ salt). [k] Peaks for PSH^+ not included. [l] 64.2 MHz in CH_2Cl_2 (PSH^+). [m] 64.2 MHz decane. [n] 160.5 MHz in C_6D_6. [o] 64.2 MHz in C_6D_6. [p] 64.2 MHz in pentane. [q] 64.2 MHz in octenes. [r] 160.5 MHz in CD_2Cl_2 (PSH^+ salt). [s] 64.2 MHz in CD_2Cl_2 (Bu_4N^+ salt). [t] 200 MHz in CD_2Cl_2 (Bu_4N^+ salt). [u] 125.7 MHz in CD_2Cl_2 (Bu_4N^+ salt). [v] 64.2 MHz in CD_3CN. [w] 64.2 MHz in CH_2Cl_2 (PPN^+ salt). [x] 64.2 MHz in THF. [y] 500 MHz in CD_2Cl_2. [z] 125.7 MHz in C_6D_6. [aa] 64.2 MHz in dodecane. [bb] 200 MHz in CD_3CN. [cc] 125.7 MHz in CD_3CN.

(η-C_5H_5)$_2$$Co_2SB_5H_7$.[27] Other crystallographically characterized isoelectronic clusters, such as *nido*-B_8H_{12},[28] *nido*-(η^6-C_6Me_6)-$FeMe_4C_4B_3H_3$,[29] and *nido*-(η-C_5H_5)$CoPh_4C_4B_3H_3$,[30] have structures based on a 10-vertex bicapped square antiprism missing two vertices, which is the same geometry expected for 8-vertex arachno-clusters (Figure 2b). Thus, the question of which is the preferred geometry for 8-vertex nido cages has been a longstanding problem in cluster chemistry.[26,f,31,32]

We previously communicated[11] a single-crystal X-ray study of Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) (Figure 3 and Supporting Information) that confirmed the gross arachno-type structure and this report was the first structural confirmation of this geometry for a non-metal polyhedral cage system. The C_s cage symmetry observed in the solid state is also consistent with the NMR data discussed above. The carbon atoms occupy adjacent

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(26) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210−214. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66. (c) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67−142. (d) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446−452. (e) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 11−93. (f) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177−207.

(27) Zimmerman, G. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 1102−1111.

(28) Enrione, R. E.; Boer, F. P.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1659−1666.

(29) Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1984**, *3*, 1396−1402.

(30) Zimmerman, G. J.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 3650−3655.

(31) (a) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, p 72. (b) Reference 1d, p 473.

(32) Studies of 8-vertex nido electron count carborane clusters have indicated that the 6-membered open-face geometry is usually, but not always, the preferred structure: J. W. Bausch, presentation at Loker Hydrocarbon Institute Kimbrough Symposium, Los Angeles, CA, December, 1995.

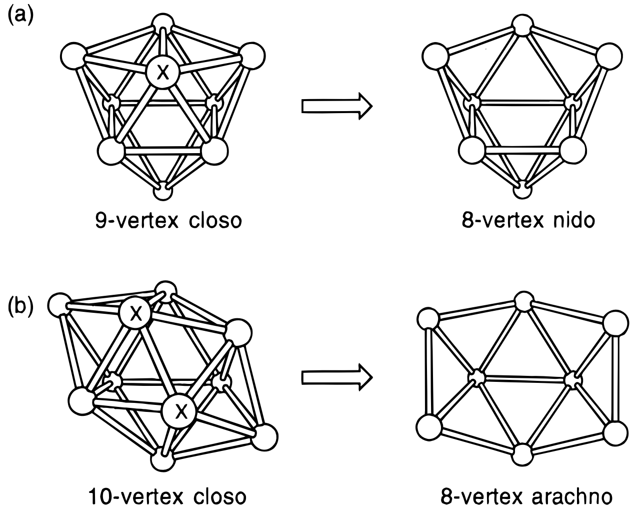


Figure 2. Derivation of open 8-vertex cage frameworks based upon geometrical systematics: (a) removal of a high-coordinated vertex from a 9-vertex tricapped trigonal prism to generate a 5-membered open-face nido geometry; (b) removal of two high-coordinated vertices from a 10-vertex bicapped square antiprism to generate a 6-membered open-face arachno geometry.

positions on the puckered 6-membered open face with the single bridge-hydrogen located at the B7−B8 edge. The 6-membered open-face geometry of **1**$^-$ is clearly demonstated by the C4−B8 distance of 2.72 Å, and the remaining cage lengths (Figure 3 caption) are within values normally found in carboranes.

The ab initio calculated structure for *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) (Supporting Information) and the IGLO calculated shifts and assignments[33] (Table 2) are likewise consistent with the crystallographically observed structure and both the experimental ^{11}B NMR chemical shifts and 2D ^{11}B−^{11}B NMR spectrum. A variety of input structures containing a 5-membered open face were employed in the calculations, but each optimized to the structure with a 6-membered open face (the C4−B8 distance is calculated to be 2.74 Å at the MP2/6-31G* level of theory).

Onak has recently reported[34] an isomer of **1**$^-$, *nido*-3,5-$C_2B_6H_9^-$, and shown with ab initio/IGLO calculations that it also has an arachno-type structure, but with the carbons located in non-adjacent positions on the 6-membered open face. The 3,5-isomer is energetically favored over **1**$^-$ by 4.5 kcal/mol (Table 3), which agrees with the empirical rules of Williams.[26e]

The neutral carborane *nido*-4,5-$C_2B_6H_{10}$ (**1**) was obtained in 70% optimized yield by protonation of a pentane suspension of **1**$^-$ with gaseous HCl at −78 °C to give a colorless, air-sensitive liquid that slowly decomposes at room temperature.

$$\underset{\mathbf{1^-}}{K^+\textit{nido}\text{-}4,5\text{-}C_2B_6H_9^-} + HCl \xrightarrow[-78\ ^\circ C]{\text{pentane}} \underset{\mathbf{1}}{\textit{nido}\text{-}4,5\text{-}C_2B_6H_{10}} + KCl \quad (2)$$

Although the ^{11}B (Figure 4a), ^{1}H, ^{13}C, and 2-D ^{11}B−^{11}B NMR spectra (Table 1) of *nido*-4,5-$C_2B_6H_{10}$ (**1**) suggest C_s symmetry, the ab initio/IGLO calculations for a C_s symmetry isomer (**1b**) showed poor agreement with the experimental data (Figure 5). Williams' empirical rules[26e] do not favor structure **1b** as it contains two bridge-hydrogens across 5-coordinated borons (B3,6). Instead, an asymmetrical arrangement of bridge-hydrogens (**1a**) would be favored. The calculations indeed show **1a** to be significantly lower in energy (28.3 kcal/mol) than **1b** (Table 3). Good agreement of the IGLO calculated ^{11}B NMR shifts of **1a** with the experimental values is obtained by averaging the shifts of the "static" structure to give the "dynamic" values (Figure 5). A fluxional process which would interconvert the two enantiomers shown below could involve rapid bridge-proton rearrangements across the B3−B8, B7−B8, and B6−B7 edges. This would account for both the apparent mirror plane of symmetry present in the NMR spectra of **1** and the broad nature of the B7−B8 resonance.

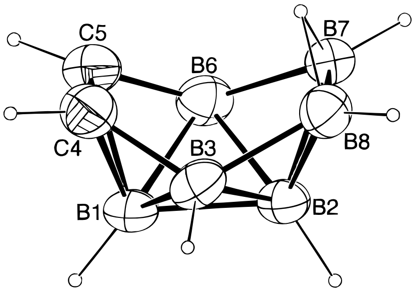


Figure 3. ORTEP drawing of the cage structure of Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$). Selected observed bond distances (Å): B1−B2, 1.749 (7); B1−B3, 1.794 (7); B1−C4, 1.687 (7); B1−C5, 1.686 (6); B1−B6, 1.805 (7); B2−B3, 1.792 (7); B2−B6, 1.833 (7); B2−B7, 1.715 (6); B2−B8, 1.710 (7); B3−C4, 1.566 (7); B3−B8, 1.699 (7); C4−C5, 1.400 (7); C5−B6, 1.562 (7); B6−B7, 1.709 (7); B7−B8, 1.666 (7); B7−H78, 1.219 (35); B8−H78, 1.294 (35).

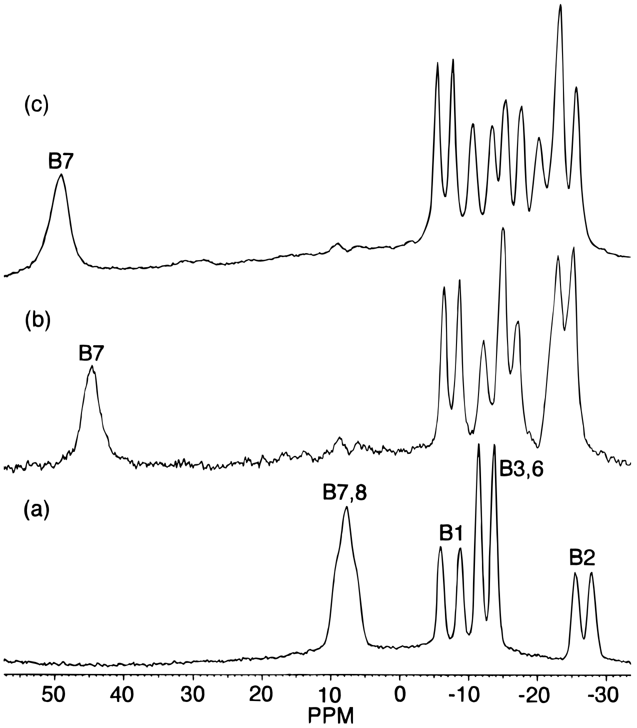
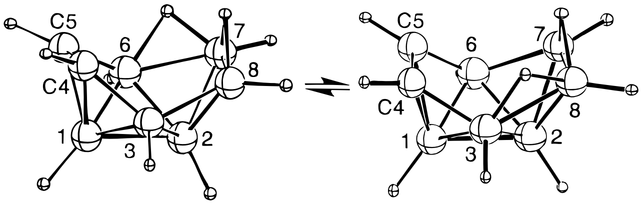


Figure 4. Proton spin-decoupled 64.2 MHz ^{11}B NMR spectra of (a) *nido*-4,5-$C_2B_6H_{10}$ (**1**); (b) *nido*-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_9$ (**2b**); and (c) *nido*-7-(octyl)-4,5-$C_2B_6H_9$ (**2d**). Complete shift assignments are given in Table 1.



This rearrangement appears to have a low-energy barrier, as

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[33] The value for B2 deviates 8 ppm from the experimental value. This larger than normal difference may arise because the computational method does not take into account solvation and counterion effects, which could be significant in these anions.

[34] Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910−3913.

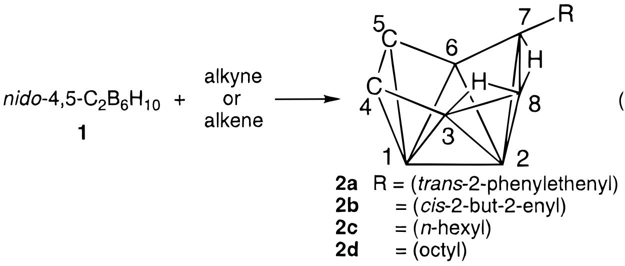
Table 2. IGLO Data

optimized structure	IGLO calculated NMR data (II′/MP2/6-31G*)
nido-4,5-$C_2B_6H_9^-$ (**1**$^-$)	^{11}B: 7.1 (B7,8), −7.2 (B2), −19.5 (B3,6), −37.8 (B1) ^{13}C: 112.0 (C3,4)
nido-4,5-$C_2B_6H_{10}$ (**1a**)	^{11}B: 37.3 (B8), −6.8 (B1), −9.8 (B3), −13.1 (B7), −19.1 (B6), −22.9 (B2) ^{13}C: 160.4 (C4), 94.4 (C5)
nido-4,5-$C_2B_6H_{10}$ (**1b**)	^{11}B: 34.4 (B1), 25.7 (B7,8), −2.5 (B3,6), −22.3 (B2) ^{13}C: 139.7 (C4,5)
nido-7-CH_3-4,5-$C_2B_6H_8^-$ (**2e**$^-$)	^{11}B: 16.9 (B7), 4.0 (B8), −5.0 (B2), −18.4 (B6), −21.0 (B3), −37.8 (B1) ^{13}C: 114.2 (C5), 110.5 (C4), −0.9 (Me)
nido-7-CH_3-4,5-$C_2B_6H_9$ (**2e**)	^{11}B: 50.6 (B7), −7.6 (B1), −8.7 (B6), −16.8 (B8), −19.2 (B3), −21.6 (B2) ^{13}C: 159.6 (C5), 91.0 (C4), 1.3 (Me)
nido-8-CH_3-4,5-$C_2B_6H_9$ (**2f**)	^{11}B: 34.9 (B7), −0.9 (B8), −1.0 (B1), −11.7 (B6), −19.0 (B3), −20.3 (B2) ^{13}C: 162.4 (C4), 96.1 (C5), −8.3 (Me)
arachno-5,6-$C_2B_7H_{12}^-$ (**3**$^-$)	^{11}B: 2.0 (B1), −8.2 (B9), −8.8 (B4,7), −44.8 (B3,8), −48.5 (B2) ^{13}C: 114.2 (C5,6)
arachno-5,6-$C_2B_7H_{13}$ (**3a**)	^{11}B: 30.9 (B7), 28.1 (B4), 20.6 (B9), 17.1 (B8), −12.7 (B1), −17.1 (B2), −21.1 (B3) ^{13}C: 109.7 (C6), 11.7 (C5)
arachno-5,6-$C_2B_7H_{13}$ (**3b**)	^{11}B: 15.4 (B1), −3.2 (B2), −8.6 (B9), −9.0 (B7), −18.5 (B8), −29.7 (B3), −30.1 (B4) ^{13}C: 150.4 (C6), 125.8 (C5)
arachno-7-CH_3-4,5-$C_2B_6H_9^{2-}$ (**4**$^{2-}$)	^{11}B: −3.1 (B6), −4.4 (B2), −7.4 (B3), −35.6 (B7), −45.5 (B8), −62.0 (B1) ^{13}C: 96.0 (C5), 92.9 (C4), 8.9 (Me)
arachno-7-CH_3-4,5-$C_2B_6H_{10}^-$ (**4**$^-$)	^{11}B: 9.6 (B6), 6.8 (B3), −21.2 (B2), −30.5 (B7), −36.4 (B8), −59.5 (B1) ^{13}C: 92.7 (C5), 91.8 (C4), 2.5 (Me)
closo-2,3-$C_2B_5H_7$ (**5**)	^{11}B: 8.1 (B4,6), 1.0 (B5), −17.5 (B1,7) ^{13}C: 87.0 (C2,3)
closo-1-CH_3-2,3-$C_2B_5H_6$	^{11}B: 9.0 (B4,6), −0.4 (B5), −7.0 (B1), −23.9 (B7) ^{13}C: 87.2 (C2,3), −8.6 (Me)
nido-3,4-$C_2B_5H_8^-$ (**8**$^-$)	^{11}B: 23.5 (B2), 22.7 (B6), 3.2 (B5,7), −36.6 (B1) ^{13}C: 109.3 (C3,4)
nido-6-NH_3-3,4-$C_2B_5H_7$	^{11}B: 25.2 (B2), 9.8 (B6), 0.1 (B5,7), −30.9 (B1) ^{13}C: 125.8 (C3,4)

^{11}B and ^{1}H NMR studies of **1** to −90 °C were unable to sufficiently slow down this process to allow observation of a static asymmetrical structure.

The NMR spectra for the carbons-apart isomer, *nido*-3,6-$C_2B_6H_{10}$,[35,36] of **1** were originally interpreted as consistent with either static-arachno or fluxional-nido structures. However, an ab initio/IGLO/NMR study[37] strongly favors a static structure. The 3,6-isomer is energetically favored by 22.5 kcal/mol over **1** (Table 3).

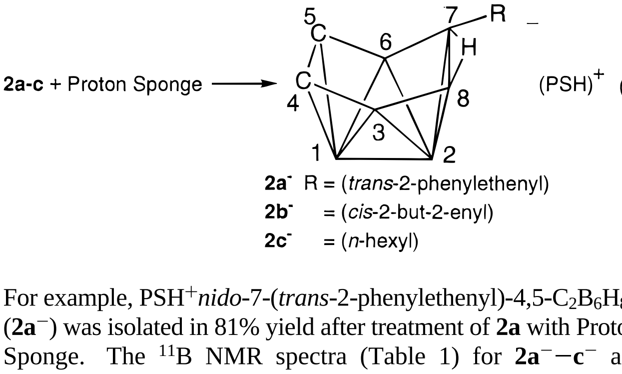
The *nido*-4,5-$C_2B_6H_{10}$ (**1**) was found[38] to readily hydroborate under mild conditions a variety of alkynes and alkenes, including phenyl acetylene, 2-butyne, 1-hexene, and octenes, to give exopolyhedral alkenyl or alkyl B7-substituted *nido*-$C_2B_6H_9$ (**2a**−**d**) species:



(3)

The ^{11}B NMR spectra for **2a**−**d** (see Figure 4 for spectra of **2b** and **2d**) contain resonances at chemical shifts expected for a "static" *nido*-4,5-$C_2B_6H_{10}$ (Figure 5), with five doublets and one downfield singlet of equal intensity. The chemical shifts of the substituted B7 borons are sensitive to their exopolyhedral substituents, with those of the olefinic derivatives, **2a** and **2b**, coming at slightly higher field (40.2 and 43.8 ppm) than those of the saturated derivatives, **2c** and **2d** (49.2 and 49.2 ppm). The IGLO calculated ^{11}B shifts for the model compound *nido*-7-CH_3-4,5-$C_2B_6H_9$ (**2e**, Figure 6) correlate well with the experimental data for **2a**−**d**. Other structures also having the C_1 symmetry which were not excluded by the experimental data were also computationally investigated. The *nido*-8-CH_3-4,5-$C_2B_6H_9$ (**2f**) isomer is calculated to be only 2.2 kcal/mol higher in energy than the 7-Me isomer **2e** (Table 3). However, the IGLO ^{11}B calculated shifts (Table 2) for **2f** correlate poorly with the experimental values for **2a**−**d**.

As discussed above, the ab initio/IGLO calculations and their experimental ^{11}B NMR spectra are consistent with the structures proposed for **2a**−**d**, but the compounds proved to be too thermally unstable to allow complete isolation and characterization. However, treatment of **2a**−**c** with Proton Sponge resulted in deprotonation to form stable alkyl or alkenyl B7-substituted *nido*-4,5-$C_2B_6H_8^-$ ions (**2a**$^-$−**c**$^-$) in moderate to high yields:



(4)

For example, PSH$^+$*nido*-7-(*trans*-2-phenylethenyl)-4,5-$C_2B_6H_8^-$ (**2a**$^-$) was isolated in 81% yield after treatment of **2a** with Proton Sponge. The ^{11}B NMR spectra (Table 1) for **2a**$^-$−**c**$^-$ are similar, with each containing one singlet and five doublet resonances in equal ratios, indicating C_1 cage symmetry (see Figure 1b for the spectrum of **2a**$^-$). The resonances also occur

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[35] Gotcher, A. J.; Ditter, J. F.; Williams, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 7514−6.

[36] Reilly, T. J.; Burg, A. B. *Inorg. Chem.* **1974**, *12*, 1250.

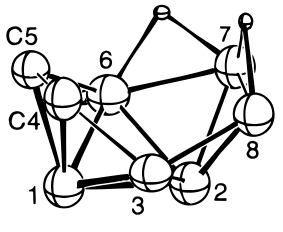
[37] Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v. R.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3060−3062.

[38] Presented in part at the Eighth International Meeting of Boron Chemistry, Knoxville, TN, July, 1993. See: Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, 1994; pp 224−227.

Table 3. Absolute (-au) and Relative (kcal/mol) Energies of Carboranes Calculated in This Study

optimized structure	sym	6-31G*//6-31G*	ZPE (NEV)[a]	E_{rel}[b]	MP2/6-31G*//MP2/6-31G*	E_{rel}[c]
nido-4,5-$C_2B_6H_9^-$ (**1**$^-$)	C_s	229.06624	81.58 (0)	9.5	229.93727	4.5
nido-3,5-$C_2B_6H_9^-$	C_1	229.08139	81.54 (0)	0.0	229.94434	0.0
nido-4,5-$C_2B_6H_{10}$ (**1a**)	C_1	229.58307	89.58 (0)	33.3	230.45050	22.5
nido-4,5-$C_2B_6H_{10}$ (**1b**)	C_s	229.54192	88.31 (0)	56.0	230.40348	50.8
nido-3,6-$C_2B_6H_{10}$[d]	C_{2v}	229.63438	90.58 (0)	0.0	230.48772	0.0
nido-7-CH_3-4,5-$C_2B_6H_8^-$ (**2e**$^-$)	C_1	268.10894	100.54 (0)		269.11481	
nido-7-CH_3-4,5-$C_2B_6H_9$ (**2e**)	C_1	268.62980	108.50 (0)	0.0	269.63637	0.0
nido-8-CH_3-4,5-$C_2B_6H_9$ (**2f**)	C_1	268.62760	108.66 (0)	1.5	269.63304	2.2
arachno-5,6-$C_2B_7H_{12}^-$ (**3**$^-$)	C_s	255.47820	103.43 (0)		256.46771	
arachno-5,6-$C_2B_7H_{13}$ (**3a**)	C_1	255.97924	112.58 (0)	15.9	256.95331	20.7
arachno-5,6-$C_2B_7H_{13}$ (**3b**)	C_1	255.95692	111.32 (0)	28.7	256.94044	27.7
arachno-4,5-$C_2B_7H_{13}$	C_1	256.00663	114.08 (0)	0.0	256.98849	0.0
arachno-7-CH_3-4,5-$C_2B_6H_9^{2-}$ (**4**$^{2-}$)	C_1	268.51614	103.67 (0)		269.54414	
arachno-7-CH_3-4,5-$C_2B_6H_{10}^-$ (**4**$^-$)	C_1	269.25029	113.51 (0)		270.26844	
closo-2,3-$C_2B_5H_7$ (**5**)	C_{2v}	203.21493	67.24 (0)		203.95708	
closo-1-CH_3-2,3-$C_2B_5H_6$	C_s	242.26088	86.04 (0)		243.14204	
nido-3,4-$C_2B_5H_8^-$ (**8**$^-$)	C_s	203.79929	71.92 (0)		204.56006	
nido-6-NH_3-3,4-$C_2B_5H_7$	C_s	259.39771	94.70 (0)		260.32430	

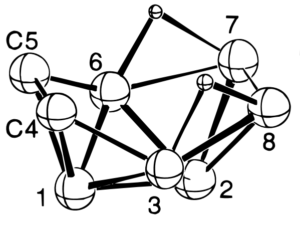
[a] Zero-point energy and number of imaginary frequencies in parentheses. [b] Relative energy at the 6-31G*//6-31G* + ZPE (6-31G*) level; the zero-point energies have been scaled by 0.89 as recommended.[13] [c] Relative energy at the MP2/6-31G*//MP2/6-31G* + ZPE (6-31G*) level; the zero-point energies have been scaled by 0.89 as recommended.[13] [d] Reference 35.



IGLO data (II'//MP2/6-31G*)

"static"		"dynamic"		Exp't
B1	-6.8	B1	-6.8	-7.3
B2	-22.9	B2	-22.9	-26.6
B3	-9.8	> B3,6	-14.4	-12.4
B6	-19.1			
B7	-13.1	> B7,8	12.1	7.8
B8	37.3			

nido-4,5-$C_2B_6H_{10}$ (**1a**)



IGLO data (II'//MP2/6-31G*)

		Exp't
B1	34.4	-7.3
B2	-22.3	-26.6
B3,6	-2.5	-12.4
B7,8	25.7	7.8

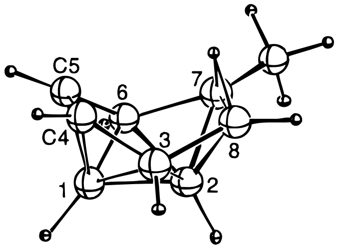
nido-4,5-$C_2B_6H_{10}$ (**1b**)

Figure 5. Calculated structures and IGLO ^{11}B NMR data for *nido*-4,5-$C_2B_6H_{10}$ (**1**): MP2(FULL)/6-31G* optimized geometries for the asymmetric (**1a**) and symmetric (**1b**) isomers and comparison with the experimental data.

at shifts similar to those of *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) with the exception that the substituted-B7 resonances are shifted to lower field. Strong support for the proposed structures **2a**$^-$−**c**$^-$ also comes from the good agreement (Figure 6) of the ab initio/IGLO calculated shifts on model compound *nido*-7-CH_3-4,5-$C_2B_6H_9^-$ (**2e**$^-$) with the experimental data for **2a**$^-$−**c**$^-$.

The structure of PSH$^+$**2b**$^-$ was further confirmed by a crystallographic study, but because of the poor quality of the diffraction data, a satisfactory refinement could not be obtained. Thus, while the gross cage geometry and *syn* hydroboration of 2-butyne were confirmed, the bond distances and angles are unreliable. Details of the structural determination and an ORTEP plot of PSH$^+$**2b**$^-$ are given in the Supporting Information.

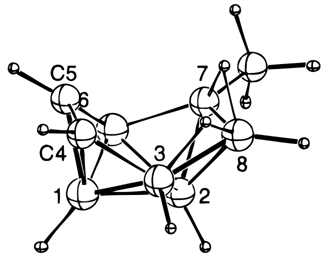
Both *nido*-4,5-$C_2B_6H_{10}$ (**1**) and its conjugate anion, *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$), were found to be useful precursors to smaller and larger cage systems. The *nido*-4,5-$C_2B_6H_9^-$ (**1**$^-$) readily



IGLO data (II'//MP2/6-31G*)

		Exp't		
	2e$^-$	**2a**$^-$	**2b**$^-$	**2c**$^-$
B1	-37.8	-34.1	-36.4	-36.3
B2	-5.0	-12.1	-13.4	-13.0
B3	-21.0	-15.5	-17.8	-18.1
B6	-18.4	-13.7	-15.8	-15.7
B7	16.9	15.5	17.2	19.1
B8	4.0	3.2	-1.0	-1.3

nido-7-CH_3-4,5-$C_2B_6H_8^-$ (**2e**$^-$)



IGLO data (II'//MP2/6-31G*)

		Exp't		
	2e	**2a**	**2b**	**2c**
B1	-7.6	-13.3	-13.7	-11.7
B2	-21.6	-25.3	-24.7	-24.2
B3	-19.2	-16.9	-16.6	-16.3
B6	-8.7	-8.4	-8.2	-6.4
B7	50.6	40.2	43.8	49.2
B8	-16.8	-23.0	-23.3	-21.4

nido-7-CH_3-4,5-$C_2B_6H_9$ (**2e**)

Figure 6. (a) Calculated structure and IGLO ^{11}B NMR data for *nido*-7-CH_3-4,5-$C_2B_6H_8^-$ (**2e**$^-$): MP2(FULL)/6-31G* optimized geometry and comparison with the experimental data for **2a**$^-$−**c**$^-$. (b) Calculated structure and IGLO ^{11}B NMR data for *nido*-7-CH_3-4,5-$C_2B_6H_9$ (**2e**): MP2(FULL)/6-31G* optimized geometries and comparison with the experimental data for **2a**−**c**.

underwent cage expansion by the addition of BH_3·THF to a THF solution of **1**$^-$ giving the new carborane anion K$^+$*arachno*-5,6-$C_2B_7H_{12}^-$ (**3**$^-$) in essentially quantitative yield.[39] A $C_2B_7H_{12}^-$ carborane is a 9-vertex, 24 skeletal electron, arachno-cluster system and, on the basis of skeletal electron counting rules,[26] would be expected to adopt a structure based on a octadecahedron missing two vertices. Two frameworks generated using this method are shown in Figure 7: the "iso" arachno structure with a 6-membered open face, found for *iso*-B_9H_{15},[40] and the

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(39) For examples of cage expansion by the addition of BH_3 to borane anions, see: (a) Geanangel, R. A.; Shore, S. G. *J. Am. Chem. Soc.* **1967**, *89*, 6771−6772. (b) Remmel, R. J.; Johnson, H. D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395−5403. (c) Geanangel, R. A.; Johnson, H. D., II; Shore, S. G. *Inorg. Chem.* **1971**, *10*, 2363−2364.

(40) (a) Dobson, J.; Keller, P. C.; Schaeffer, R. *J. Am. Chem. Soc.* **1965**, *87*, 3522−3523. (b) Dobson, J.; Keller, P. C.; Schaeffer, R. *Inorg. Chem.* **1968**, *7*, 399−402.

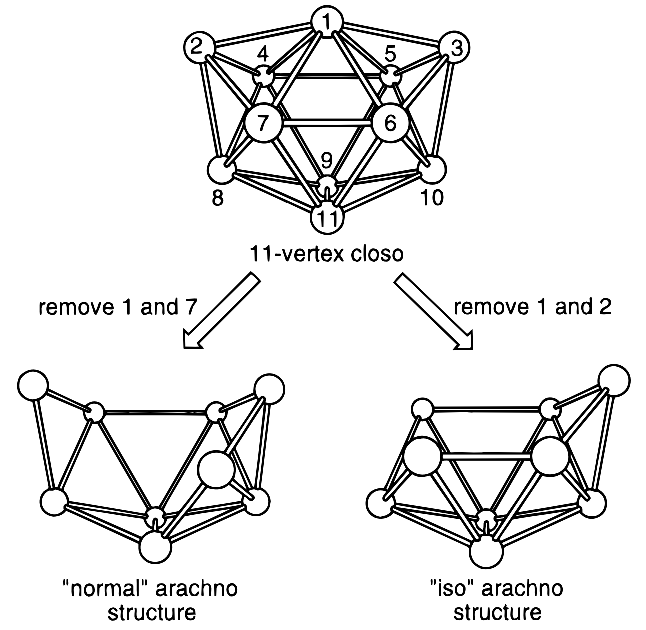


Figure 7. Derivation of 9-vertex arachno cage frameworks based upon geometrical systematics: removal of six- and five-coordinated vertices (1 and 7) from an octadecahedron to generate a 7-membered open-face "normal" arachno structure and removal of six- and four-coordinated vertices (1 and 2) to generate the 6-membered open-face "iso" arachno structure.

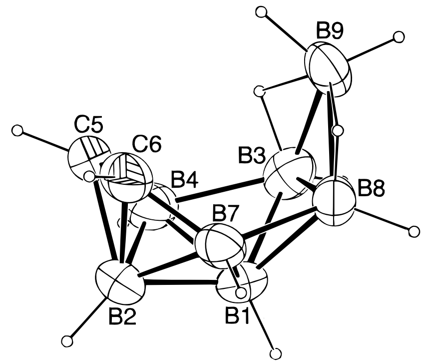
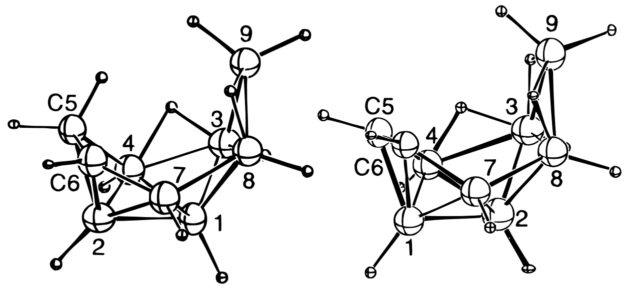


Figure 8. ORTEP drawing of the cage structure of $(PSH)^+$*arachno*-5,6-$C_2B_7H_{12}^-$ ($\mathbf{3}^-$). Selected observed bond distances (Å): B1−B2, 1.678 (6); B1−B3, 1.791 (6); B1−B4, 1.776 (5); B1−B7, 1.755 (5); B1−B8, 1.767 (5); B2−B4, 1.801 (7); B2−B7, 1.764 (5); B3−B4, 1.862 (6); B3−B8, 1.747 (5); B3−B9, 1.807 (6); C5−B2, 1.698 (6); C5−B4, 1.513 (6); C5−C6, 1.430 (5); C6−B2, 1.701 (6); C6−B7, 1.520 (5); B7−B8, 1.864 (6); B8−B9, 1.815 (6); B3−H39, 1.155(28); B8−H89, 1.172 (30); B9−H39, 1.379 (23); B9−H89, 1.501 (30); B9−H9a, 1.066 (27); B9−H9b, 1.224 (25).

less common "normal" arachno structure with a 7-membered open-face, found for *n*-B_9H_{15}.[41] The NMR data for $\mathbf{3}^-$ (Table 1), which indicate C_s cage symmetry with equivalent cage carbon atoms, strongly support the "normal" arachno 9-vertex framework.

A single-crystal X-ray diffraction study of the $PSH^+\mathbf{3}^-$ salt (Figure 8 and Supporting Information) shows that *arachno*-5,6-$C_2B_7H_{12}^-$ ($\mathbf{3}^-$) does in fact have a "normal" arachno-framework, with the carbon atoms (C5,6) occupying low-coordinated adjacent positions on the 7-membered open face. Consistent with the triplet resonance observed in the ^{11}B NMR spectrum (Table 1), the unique boron (B9) on the open face (formally from the BH_3·THF) is a BH_2 with two bridge-hydrogens, similar to that found in *n*-B_9H_{15}.[41] A comparison of the geometries for $\mathbf{3}^-$ and *n*-B_9H_{15} showed that they are similar when allowances are made for the different cage lengths found in $\mathbf{3}^-$ due to the presence of the cage carbons. The ab initio calculated structure for $\mathbf{3}^-$ (Supporting Information) and the IGLO calculated chemical shifts and assignments (Table 2) are likewise consistent with the crystallographically observed structure and both the experimental ^{11}B NMR chemical shifts and 2D $^{11}B-^{11}B$ NMR spectrum.



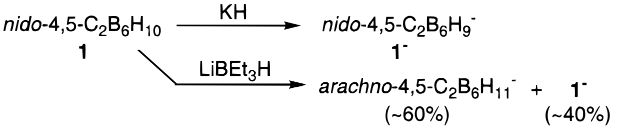
arachno-5,6-$C_2B_7H_{13}$ (**3a**) *arachno*-5,6-$C_2B_7H_{13}$ (**3b**)

Figure 9. Calculated structures and IGLO ^{11}B NMR data for *arachno*-5,6-$C_2B_7H_{13}$ (**3**): MP2(FULL)/6-31G* optimized geometries for **3a** and **3b**.

The $\mathbf{3}^-$ anion is the third isomer of this carborane anion to be reported. The two previous isomers,[24] *arachno*-4,5-$C_2B_7H_{12}^-$ and *arachno*-6,8-$C_2B_7H_{12}^-$, have structures based upon *iso*-B_9H_{15},[40] but this new isomer *arachno*-5,6-$C_2B_7H_{12}^-$ ($\mathbf{3}^-$) is the first reported carborane analog of *n*-B_9H_{15}.[41] The only other reported analog of *n*-B_9H_{15} is a ruthenaborane, *arachno*-(η^6-C_6Me_6)RuB_8H_{14}.[42] Many attempts were made to protonate $\mathbf{3}^-$, with the desired product being the unknown *arachno*-5,6-$C_2B_7H_{13}$ (**3**) carborane having a *n*-B_9H_{15} structure. In NMR tube experiments, when either the Bu_4N^+ or PSH^+ salt of $\mathbf{3}^-$ was dissolved in CH_2Cl_2 and treated with HCl·Et_2O or concentrated H_2SO_4 at −78 °C and slowly warmed to room temperature, the only identifiable product was *arachno*-4,5-$C_2B_7H_{13}$.[4]

The results of ab initio calculations indicate two possible structures for *arachno*-5,6-$C_2B_7H_{13}$ (**3a** and **3b**) (Figure 9) that retain the *n*-B_9H_{15} framework, with **3a** 8.0 kcal/mol more stable than **3b** (Table 3). However, **3a** is 20.7 kcal/mol less stable than the "iso" framework isomer *arachno*-4,5-$C_2B_7H_{13}$.[43] It may be that "normal" **3a** or **3b** is initially formed by the protonation of $\mathbf{3}^-$, but quickly isomerizes to the more stable *arachno*-4,5-$C_2B_7H_{13}$ "iso" isomer. Attempts to locate computationally an isomer similar to **3a**, but with B3−B4 bridge-hydrogen moved to the B3−B9 edge, failed; this geometry optimized to isomer **3a**.

NMR studies of the reaction of sodium or potassium hydride with *nido*-4,5-$C_2B_6H_{10}$ (**1**) showed the formation of *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$). However, when $LiBEt_3H$ was employed, the major product (∼60%) was the known[8] *arachno*-4,5-$C_2B_6H_{11}^-$, arising from hydride addition to the cage, along with *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) (∼40%).



(5)

An NMR study of the reaction of a THF solution of K^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) with ∼1 equiv of a 1.4 M Et_2O solution of CH_3Li showed evidence of the initial formation of *arachno*-7-

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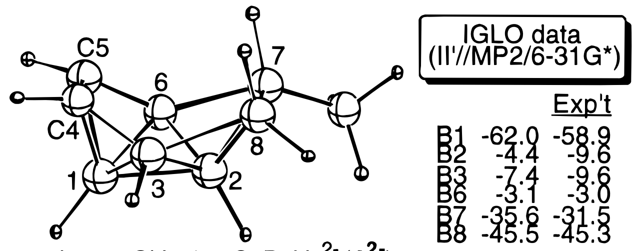
[41] Dickerson, R. E.; Wheatley, P. J.; Howell, P. A.; Lipscomb, W. N. *J. Chem. Phys.* **1957**, *27*, 200−209.

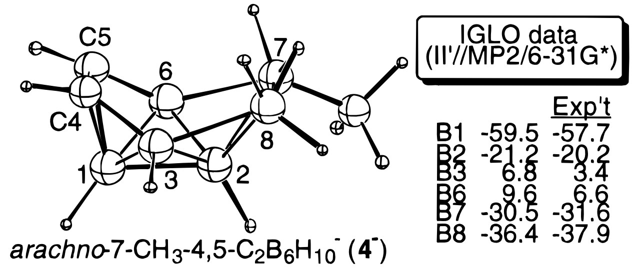
[42] Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Organomet. Chem.* **1986**, *315*, C1-C4.

[43] The optimized structure for *arachno*-4,5-$C_2B_7H_{13}$ at HF/6-31G* has been reported: McKee, M. L. *Inorg. Chem.* **1994**, *33*, 6213−6218.



		Exp't
B1	-62.0	-58.9
B2	-4.4	-9.6
B3	-7.4	-9.6
B6	-3.1	-3.0
B7	-35.6	-31.5
B8	-45.5	-45.3

arachno-7-CH_3-4,5-$C_2B_6H_9^{2-}$ ($\mathbf{4}^{2-}$)



		Exp't
B1	-59.5	-57.7
B2	-21.2	-20.2
B3	6.8	3.4
B6	9.6	6.6
B7	-30.5	-31.6
B8	-36.4	-37.9

arachno-7-CH_3-4,5-$C_2B_6H_{10}^-$ ($\mathbf{4}^-$)

Figure 10. Calculated structures and IGLO ^{11}B NMR data for *arachno*-7-CH_3-4,5-$C_2B_6H_9^{2-}$ ($\mathbf{4}^{2-}$) and *arachno*-7-CH_3-4,5-$C_2B_6H_{10}^{2-}$ ($\mathbf{4}^-$): MP2(FULL)/6-31G* optimized geometries and comparison with the experimental data.

CH_3-4,5-$C_2B_6H_9^{2-}$ ($\mathbf{4}^{2-}$), which following protonation with PSH^+Cl^- gave *arachno*-7-CH_3-4,5-$C_2B_6H_{10}^-$ ($\mathbf{4}^-$):

$$\begin{tikzcd} \underset{\mathbf{1^-}}{nido\text{-}4,5\text{-}C_2B_6H_9^-} \arrow[r, "CH_3Li"] & \underset{\mathbf{4^{2-}}}{arachno\text{-}7\text{-}CH_3\text{-}4,5\text{-}C_2B_6H_9^{2-}} \arrow[d, "PSH^+Cl^-"] \\ & \underset{\mathbf{4^-}}{arachno\text{-}7\text{-}CH_3\text{-}4,5\text{-}C_2B_6H_{10}^-} \end{tikzcd} \qquad (6)$$

The structure of the final product ($\mathbf{4}^-$) is strongly supported by its ^{11}B NMR spectrum (Table 1), which shows six resonances (C_1 symmetry) in similar chemical shift regions as the parent *arachno*-4,5-$C_2B_6H_{11}^-$. The 2-D $^{11}B-^{11}B$ NMR spectrum of the $PPN^+\mathbf{4}^-$ showed the expected crosspeaks, except B7−B8. The ^{11}B NMR spectrum for the initial product ($\mathbf{4}^{2-}$) contains five resonances in ratios of 1:2:1:1:1, with overlap of two peaks likely. In the proton-coupled ^{11}B NMR spectrum, the three downfield resonances are broad, but the two upfield resonances, at −37.9 and −57.7 ppm, are a triplet and a doublet, respectively (Table 1). The likely structure for $\mathbf{4}^{2-}$ is similar to $\mathbf{4}^-$, but without the bridge-proton. The ab initio/IGLO calculations for *arachno*-7-CH_3-4,5-$C_2B_6H_{10}^-$ ($\mathbf{4}^-$) and *arachno*-7-CH_3-4,5-$C_2B_6H_9^{2-}$ ($\mathbf{4}^{2-}$) (Figure 10) are in good agreement with the experimental values.

Vacuum thermolysis of *nido*-4,5-$C_2B_6H_{10}$ (**1**), through a hot tube heated at 350 °C, resulted in loss of BH_3 and the production of *closo*-2,3-$C_2B_5H_7$ (**5**).

$$\underset{\mathbf{1}}{nido\text{-}4,5\text{-}C_2B_6H_{10}} \xrightarrow[\text{flow system}]{350\ °C} \underset{\mathbf{5}}{closo\text{-}2,3\text{-}C_2B_5H_7} + 1/2\ B_2H_6 \qquad (7)$$

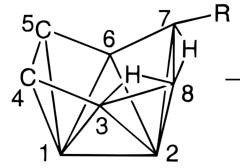
The *closo*-2,3-$C_2B_5H_7$ (**5**) was isolated in a −78 °C trap in ~65% yield. Smaller amounts of other closo carboranes (*closo*-2,4-$C_2B_5H_7$[44] and *closo*-1,7-$C_2B_6H_8$[45]) were also produced, with the *closo*-1,7-$C_2B_6H_8$ not separable from the *closo*-2,3-$C_2B_5H_7$ (**5**) by vacuum fractionations. According to the integration of the ^{11}B NMR signals, the ratios of *closo*-2,3-$C_2B_5H_7$ (**5**), *closo*-2,4-$C_2B_5H_7$, and *closo*-1,7-$C_2B_6H_8$ were approximately 10:1:2.

Table 4. ^{11}B NMR Data for *closo*-2,3-$C_2B_5H_7$ and Alkyl Derivatives

compd	B4,6	B5	B1,7
calcd[a] for *closo*-2,3-$C_2B_5H_7$	6.7	3.1	−17.4
closo-2,3-$C_2B_5H_7$ (**5**)	6.9	3.1	−17.9
closo-2,3-$Me_2C_2B_5H_5$[b]	10.6	5.2	−12.1
closo-2,3-$Et_2C_2B_5H_5$[c]	7.0	2.5	−14.2
"*closo*-2,3-$C_2B_5H_7$" (1973)[d]	−2 (2)	15 (1)	−25 (2)

[a] GIAO-MP2 method. [b] Reference 44. [c] Reference 45. [d] Reference 46.

The *closo*-2,3-$C_2B_5H_7$ (**5**) was also produced by moderate temperature thermolysis of solutions of the hydroborated intermediates **2a**−**c**:



$$\xrightarrow{\Delta} \underset{\mathbf{5}}{closo\text{-}2,3\text{-}C_2B_5H_7} + \text{"}RBH_2\text{"} \qquad (8)$$

2a R = (*trans*-2-phenylethenyl)
2b = (*cis*-2-but-2-enyl)
2c = (*n*-hexyl)

For example, thermal degradation of *nido*-7-(*cis*-2-but-2-enyl)-4,5-$C_2B_6H_9$ (**2b**) was accomplished by heating at 110 °C in dodecane solution. A ^{11}B NMR spectrum of this solution showed the presence of *closo*-2,3-$C_2B_5H_7$ (**5**), as well as a broad resonance (~65 ppm) in the range typically found for alkyl boranes, which is consistent with the loss of a "RBH_2" unit. Vacuum fractionation gave *closo*-2,3-$C_2B_5H_7$ (**5**) in an unoptimized yield of 34.9% in a −78 °C trap as a low-melting, volatile, air-sensitive solid and is thermally stable at room temperature. The *closo*-2,3-$C_2B_5H_7$ made in this way is, according to NMR and mass spectrometry, of higher purity than that produced by the gas phase flow system. By careful choice of reagents and optimization of the isolation procedure, this solution phase method may ultimately give higher yields of *closo*-2,3-$C_2B_5H_7$ (**5**) than the gas-phase method.

The *closo*-2,3-$C_2B_5H_7$ (**5**) carborane was one of the few remaining parent adjacent-carbon closo carboranes to be isolated and unambiguously characterized. The first alkyl substituted adjacent-carbon *closo*-C_2B_5- system, *closo*-2,3-$Me_2C_2B_5H_5$, was isolated in low yield by Schaeffer in 1971[46] from the gas phase reaction of octaborane and 2-butyne. Beck has reported[47] the synthesis of *closo*-2,3-$Et_2C_2B_5H_5$ and its ^{11}B NMR data are consistent with those for *closo*-2,3-$Me_2C_2B_5H_5$ (Table 4). In 1973,[48] Schaeffer also reported isolation of a small amount of impure material from the octaborane/2-butyne reaction which mass spectroscopy indicated was of the formula $C_2B_5H_7$. The ^{11}B NMR spectrum contained three resonances at 15, −2, and −25 ppm, in 1:2:2 ratios, which were tentatively assigned to *closo*-2,3-$C_2B_5H_7$. However, these resonances are significantly different (Table 4) than those of the alkyl derivatives discussed above, as well as those for compound **5**. Thus, ab initio/IGLO studies were undertaken to confirm the structural assignment of **5**.

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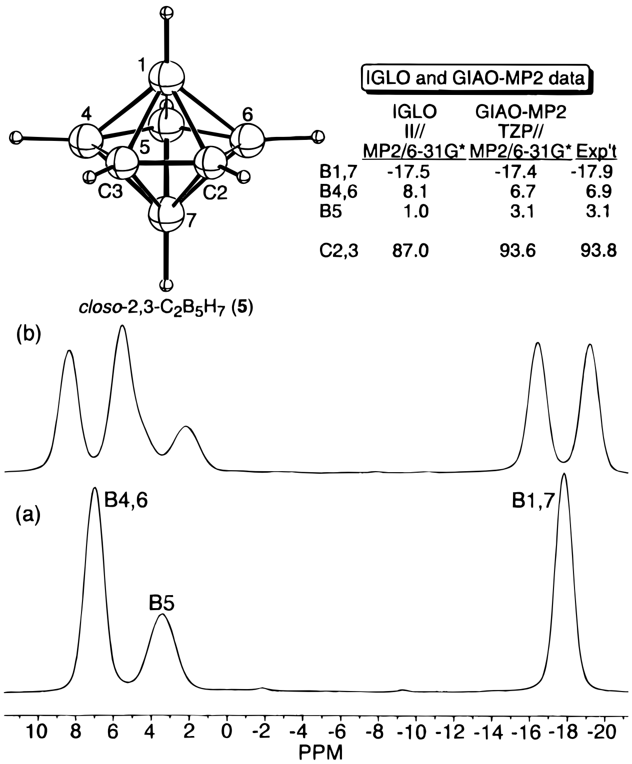
[44] (a) Williams, R. E.; Good, C. D.; Shapiro, I. *Abstracts*; 140th Meeting of the American Chemical Society, Chicago, IL, Sept 1961; p 14N. (b) Onak, T. P.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3378−3380.

[45] Williams, R. E.; Gerhart, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513−3515.

[46] Rietz, R. R.; Schaeffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 1263−1265.

[47] (a) Beck, J. S.; Kahn, A. P.; Sneddon, L. G. *Organometallics* **1986**, *5*, 2552−2553. (b) Beck, J. S.; Sneddon, L. G. *Inorg. Chem.* **1990**, *29*, 295−302.

[48] Rietz, R. R.; Schaeffer, R. *J. Am. Chem. Soc.* **1973**, *95*, 6254−6262.



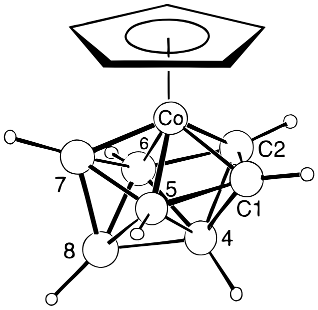
	IGLO II// MP2/6-31G*	GIAO-MP2 TZP// MP2/6-31G*	Exp't
B1,7	-17.5	-17.4	-17.9
B4,6	8.1	6.7	6.9
B5	1.0	3.1	3.1
C2,3	87.0	93.6	93.8

Figure 11. Calculated structure and IGLO and GIAO-MP2 ^{11}B NMR data for *closo*-2,3-$C_2B_5H_7$ (**5**) together with 64.2-MHz ^{11}B NMR spectra: (a) proton spin-decoupled and (b) proton spin-coupled.

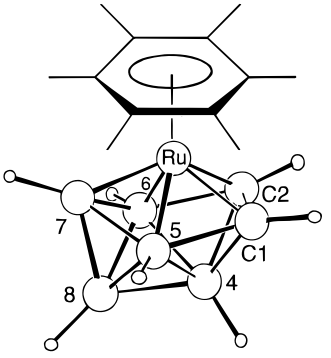
Ab initio calculations[49] show that only two isomers of $C_2B_5H_7$ are energetically favored: *closo*-2,3-$C_2B_5H_7$ and *closo*-2,4-$C_2B_5H_7$. Calculations by Schleyer et al.[16] for *closo*-2,4-$C_2B_5H_7$ agree very well with the experimental data for that isomer. Our ab initio/IGLO calculated ^{11}B NMR shifts for *closo*-2,3-$C_2B_5H_7$ (Figure 11) of 8.1, 1.0, and −17.5 ppm are in excellent agreement with the experimental values observed for **5** of 6.9, 3.1, and −17.9 ppm, respectively.[50] GIAO-MP2 NMR chemical shift calculations[51] on *closo*-2,3-$C_2B_5H_7$ (**5**) (Figure 11) likewise gave even better results (Table 4): each boron and carbon shift is within 0.5 ppm of the experimental value! On the other hand, the ^{11}B chemical shifts assigned by Schaeffer to his proposed *closo*-2,3-$C_2B_5H_7$ (15, −2, −25 ppm) correlate poorly with the IGLO and GIAO-MP2 calculated values. Thus, we conclude, based on the comparisons in Table 4, that compound **5** reported herein, and not the product reported by Schaeffer, is definitively characterized as *closo*-2,3-$C_2B_5H_7$.[52]

In the thermal degradation of **2b**, a small amount of an additional compound was also formed, which according to the ^{11}B NMR and GC-MS data combined with ab initio/IGLO theoretical calculations is *closo*-1-(butenyl)-2,3-$C_2B_5H_6$. Its ^{11}B NMR spectrum indicated B1 substitution with the shifts of the observed four resonances (Table 1) in good agreement with the ab initio IGLO calculated shifts (Table 2) of the model compound *closo*-1-CH_3-2,3-$C_2B_5H_6$. It should also be noted that there appears to be a significant "anti-podal" effect[53] of the R group at B1 upon B7, since the B7 shift (−25.0 ppm) is over 8 ppm upfield from B7 in *closo*-2,3-$C_2B_5H_7$ (−17.9 ppm).

The *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) anion, like the neutral *nido*-4,5-$C_2B_6H_{10}$ (**1**), is also prone to loss of a cage boron, as exemplified by its reactions with transition metal complexes. For example, separate reactions of K^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) with CpCo(CO)I_2 and (η^6-$C_6Me_6)_2Ru_2Cl_4$ gave *closo*-3,1,2-(η-C_5H_5)-Co$C_2B_5H_7$ (**6**) and *closo*-3,1,2-(η^6-C_6Me_6)Ru$C_2B_5H_7$ (**7**), respectively.



closo-3,1,2-(η-C_5H_5)Co$C_2B_5H_7$
6



closo-3,1,2-(η^6-C_6Me_6)Ru$C_2B_5H_7$
7

The compositions of **6** and **7** were established by elemental analyses and exact mass measurements. Their ^{11}B NMR spectra (Table 1), which each show four doublets in 1:2:1:1 ratios, are nearly identical to those found for the previously structurally characterized *closo*-1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)Co$C_2B_5H_5$.[54]

NMR studies also showed that *closo*-2,3-$C_2B_5H_7$ (**5**) readily undergoes cage expansion and degradation reactions. For example, reaction with $LiEt_3BH$ gave *nido*-3,4-$C_2B_5H_8^-$ ($\mathbf{8}^-$):

$$\underset{\mathbf{5}}{closo\text{-}2,3\text{-}C_2B_5H_7} + Li^+BEt_3H^- \longrightarrow \underset{\mathbf{8}^-}{Li^+nido\text{-}3,4\text{-}C_2B_5H_8^-} \quad (9)$$

This $\mathbf{8}^-$ ion is the parent derivative of the known *nido*-3,4-$Et_2C_2B_5H_6^-$, made in similar fashion by cage opening of *closo*-2,3-$Et_2C_2B_5H_5$ with hydride ion.[9] The ab initio optimized structure for $\mathbf{8}^-$ (with C_s symmetry, Supporting Information) contains a 5-membered open face with a BH_2 unit, similar to the crystallographically determined *nido*-3,4-$Et_2C_2B_5H_6^-$.[9] The spectrum for $\mathbf{8}^-$ is similar to that of *nido*-3,4-$Et_2C_2B_5H_6^-$, but the B1 resonance in the Et_2 derivative appears significantly further downfield at −21.3 ppm. The ^{11}B NMR spectra and assignments (Table 1) of $\mathbf{8}^-$ and *nido*-3,4-$Et_2C_2B_5H_6^-$ [55] correlate well with the IGLO calculated results and demonstrate that ethyl substituents do indeed cause a downfield shift of the B1 resonance.

Grimes has previously shown that *closo*-1-M-2,3-$R_2C_2B_4H_4$ metallacarboranes are easily "decapitated" by treatment with wet TMEDA to give *nido*-1-M-2,3-$R_2C_2B_3H_5$ complexes.[56] An

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[49] See: McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317−5321 and references therein.

[50] In ref 38, the figure showing the comparison of the IGLO calculated values for **5** versus the experimental values was mislabeled. The assignments for B5 and B4,6 were accidentally reversed.

[51] For examples applied to carboranes, see ref 17.

[52] Recently, Greatrex and Fox observed that the ^{11}B NMR data reported by Grimes in 1971 for a compound believed at that time to be *closo*-$C_3B_5H_7$ closely matches the data reported herein for *closo*-2,3-$C_2B_5H_7$. See: Fox, M. A.; Greatrex, R. *J. Chem. Soc., Dalton Trans.* **1994**, 3197−3198. Thompson, M. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 6677−6679.

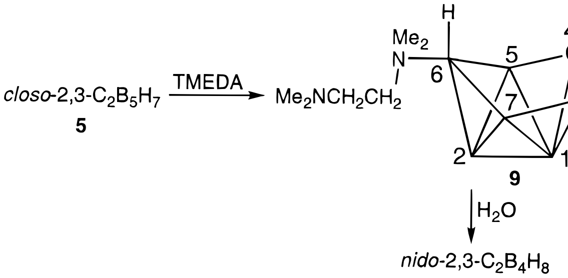
[53] Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Heřmánek, S. *Inorg. Chem.* **1991**, *30*, 3107−3111 and references therein.

[54] Zimmerman, G. J.; Sneddon, L. G. *Acta Crystallogr* **1983**, *C39*, 856−858.

[55] The II//MP2/6-31G* calculation of *nido*-3,4-$Et_2C_2B_5H_6^-$ (C_s symmetry) gives ^{11}B NMR chemical shifts in satisfactory agreement with the experimental values:[9] assignment (cald, obsd), B1 (-29.8, −21.3), B2 (21.0, 24.1), B5,7 (1.4, 4.8), B6 (20.5, 19.3). Bausch, J. W., Sneddon, L. G., unpublished results.

[56] (a) Grimes, R. N. *Pure Appl. Chem.* **1991**, *63*, 369−372. (b) Grimes, R. N. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds., Wiley: New York, 1991; Chapter 11, pp 261−285.

analogous reaction of **4** with excess TMEDA, then H_2O, gave *nido*-2,3-$C_2B_4H_8$[10] in 77% yield.



(10)

When the progress of the reaction was monitored by ^{11}B NMR spectroscopy, the formation of an initial TMEDA adduct was observed. The addition of 2 electrons to the cage, provided by the TMEDA, should result in cage opening to give a nido 7-vertex structure, *nido*-6-exo-(TMEDA)-3,4-$C_2B_5H_7$ (**9**). In support of this proposed structure, the ^{11}B NMR spectrum (Table 1) of **9** contains four doublets in a 1:1:2:1 ratio, similar to the isoelectronic $\mathbf{8}^-$ ion, and the previously structurally characterized *nido*-3,4-$Et_2C_2B_5H_6^-$,[47b] *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$,[47b] and *nido*-6-(Me_3P^+-CH_2)-3,4-$Et_2C_2B_5H_5^-$.[57] Further support for the structure of **9** comes from ab initio/IGLO calculations (Table 2) on *nido*-6-NH_3-3,4-$C_2B_5H_7$, which showed satisfactory agreement with the experimental values (Table 1).

In summary, simple methods for the synthesis of a variety of adjacent carbon carboranes in moderate to high yields have been developed via cage degradation and expansion reactions. Of special significance are (1) the first isolation and characterization of the parent *closo*-2,3-$C_2B_5H_7$ (**5**) carborane, (2) the structural confirmations of arachno-type geometries for *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) and *nido*-4,5-$C_2B_6H_{10}$ (**1**), and (3) the synthesis and structural confirmation of the "normal" *n*-B_9H_{15} structure for *arachno*-5,6-$C_2B_7H_{12}^-$ ($\mathbf{3}^-$).

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Supporting Information Available: Details of the preparation of $PSH^+\mathbf{2a}^-$, $PSH^+\mathbf{2b}^-$, and $PSH^+\mathbf{2c}^-$; tables listing infrared data (S1); details of structural determination of $Bu_4N^+\mathbf{1}^-$ (S2-S7), $PSH^+\mathbf{2b}^-$ (S8-S12), and $PSH^+\mathbf{3}^-$ (S13-S18), Cartesian coordinates of the optimized geometries (S19), and comparison of calculated and experimental geometries for *nido*-3,4-$Et_2C_2B_5H_6^-$ (S20); figures showing comparison of calculated and experimental geometries for $\mathbf{1}^-$ (S1) and $\mathbf{3}^-$ (S2), optimized geometry for $\mathbf{8}^-$ (S3), ORTEP for $PSH^+\mathbf{2b}^-$ (S4), ^{11}B NMR spectra of *nido*-4,5-$C_2B_6H_{10}$ (**1**) with $LiEt_3BH$ (S5), *nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$) with MeLi (S6) followed by PSH^+Cl^- (S7), and *closo*-2,3-$C_2B_5H_7$ (**5**) with $LiEt_3BH$ (S8) (40 pages). See any current masthead page for ordering and Internet access instructions.

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(57) Su, K.; Fazen, P. J.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 2715−2718.