PROTON-SPONGE-INITIATED REACTIONS OF 6,8-DICARBA-*arachno*-NONABORANE(13) AND 6,7-DICARBA-*arachno*-NONABORANE(13) WITH METHYL PROPYNOATE: ONE-STEP SYNTHESES OF THE 6-(MeOOCCH$_2$)-5,6,7-TRICARBA-*arachno*-DECABORANE(12) AND 6-(MeOOCCH$_2$)-5,6,10-TRICARBA-*nido*-DECABORANE(10) TRICARBABORANES

Andrew E. WILLE and Larry G. SNEDDON[1]

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, U.S.A.; e-mail: [1] sneddon@a.chem.upenn.edu

Received March 12, 1997
Accepted May 15, 1997

Dedicated to Jaromir Plesek, one of the pioneers of carborane chemistry, on the occasion of his 70th birthday.

The reaction of *arachno*-6,8-$C_2B_7H_{13}$ (**1**) with methyl propynoate in the presence of only 0.1 equivalent of 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, PS) results in the one-step formation of the neutral tricarbaborane 6-(MeOOCCH$_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**). Similarly, only 0.1 equivalent of PS initiates the reaction of the isomeric *arachno*-6,7-$C_2B_7H_{13}$ (**3**) carborane with methyl propynoate to yield the new tricarbaborane, 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**). These results suggest a cyclic reaction sequence involving initial deprotonation of the starting dicarbaborane by PS, followed by reaction of the resulting anion with methyl propynoate to produce a new anion. Protonation of this second anion by another equivalent of the starting dicarbaborane then produces the final neutral tricarbaborane product and the cycle begins again. While **4** is unreactive toward NaH or KH, it readily added n-BuLi to give, following acidification with HCl–Et$_2$O, a new product tentatively identified as 6-(MeOOCCH$_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**). The proposed structures of **4** and **6** are strongly supported by *ab initio*/IGLO nuclear shielding calculations.

Key words: Tricarbaborane; Carborane; Carbon insertion; *ab initio*/IGLO calculations.

Many polyhedral borane anions have now been shown to react readily with polar acetylenes to give carbon insertion products, including di-, tri- and tetracarbon carboranes[1]. In this paper, we demonstrate that *less than equivalent amounts* of 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, PS) initiate the reactions of the neutral, isomeric dicarbaboranes, *arachno*-6,8-$C_2B_7H_{13}$ (**1**) and *arachno*-6,7-$C_2B_7H_{13}$ (**3**), with methyl propynoate to yield, respectively, the known 6-(MeOOCCH$_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**) and the new 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) tricarbaboranes.

EXPERIMENTAL

All manipulations were carried out by using standard high vacuum or inert-atmosphere techniques as described by Shriver[2].

Materials

The *arachno*-6,8-$C_2B_7H_{13}$ (ref.[3]) (**1**) and *arachno*-6,7-$C_2B_7H_{13}$ (ref.[4]) (**3**) were prepared according to literature methods. The 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, PS), hexane and methylene chloride were purchased from Aldrich and used as received. Methyl propynoate was obtained from Aldrich or Lancaster and vacuum distilled before use. Toluene, THF, 1.6 M n-BuLi in hexanes, and 1.0 M HCl in Et_2O were purchased from Aldrich and stored under N_2 until use. Oil-dispersed NaH and KH were purchased from Aldrich, washed with dry hexane under a N_2 atmosphere and then vacuum dried.

Physical Measurements

^{11}B NMR at 64.2 MHz was obtained on a Bruker AF-200 spectrometer, equipped with the appropriate decoupling accessories. ^{1}H NMR at 500.1 MHz, ^{11}B NMR at 160.5 MHz and ^{13}C NMR spectra at 125.7 MHz were obtained on a Bruker AM-500 spectrometer. All ^{11}B chemical shifts are referenced to external $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^{1}H and ^{13}C chemical shifts were measured relative to internal residual protons or carbons in the lock solvents and are referenced to Me_4Si (0.0 ppm). Two-dimensional COSY ^{11}B-^{11}B NMR experiments were performed at 64.2 MHz using the procedures described previously[5]. High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin–Elmer 1430 spectrometer.

Reaction of *arachno*-6,8-$C_2B_7H_{13}$ (**1**) with Methyl Propynoate and 0.1 Equivalent of PS: Synthesis of 6-($MeOOCCH_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**)

A 100 ml round bottom flask fitted with a vacuum stopcock was charged with **1** (0.51 g, 4.52 mmol) and PS (0.10 g, 0.47 mmol). Methyl propynoate (4 ml) was then vacuum transferred into the flask. After warming to room temperature, the solution was cooled by a water bath and stirred under vacuum for 18 h. The methyl propynoate was vacuum evaporated to leave a red oil, that was then dissolved in CH_2Cl_2. Addition of hexane resulted in precipitation of impurities that were removed by filtration. The solvent was then vacuum evaporated at 0 °C, and the remaining solid extracted with hexane and filtered through a layer of silica gel. The hexane was vacuum evaporated at 0 °C to yield a white solid identified as 6-($MeOOCCH_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**) (0.57 g, 2.90 mmol, 64.2% yield) by comparison of its ^{11}B NMR and GC/MS spectra with literature values[1b].

Reaction of **1** with Methyl Propynoate and One Equivalent of PS

In a manner similar to that above, **1** (0.24 g, 2.13 mmol), PS (0.47 g, 2.19 mmol) and methyl propynoate (5 ml) were reacted at room temperature under N_2 overnight. The ^{11}B NMR spectrum of the reaction solution showed formation of only [6-(MeOOCCH=CH)-*arachno*-6,8-$C_2B_7H_{11}$]$^-$ (**5a**, ref.[1b]).

Reaction of **1** with PS

A 100 ml round bottom flask fitted with a vacuum stopcock was charged with 10 ml of a CH_2Cl_2 solution containing **1** (0.25 g, 2.22 mmol) and 10 ml of a CH_2Cl_2 solution containing PS (0.48 g,

2.24 mmol). After stirring for 15 min, the solution was concentrated to ≈5 ml by vacuum evaporation of the solvent. Hexane (20 ml) was added and the solution filtered. The remaining solid was washed with 10 ml of diethyl ether and recrystallized from CH_2Cl_2–hexane to give a white solid identified on the basis of its ^{11}B and ^1H NMR spectra, as $(PSH)^+[arachno\text{-}6,8\text{-}C_2B_7H_{12}]^-$ ($(PSH)^+$**1a**) (0.59 g, 1.80 mmol, 81.1% yield)[1].

Reaction of $(PSH)^+[arachno\text{-}6,8\text{-}C_2B_7H_{12}]^-$ ($(PSH)^+$**1a**) with Methyl Propynoate

A 100 ml round bottom flask fitted with a vacuum stopcock was charged with PSH^+**1a** (0.11 g, 0.34 mmol) and methyl propynoate (5 ml). The mixture was warmed to room temperature and stirred under N_2 for 15 min. The ^{11}B NMR spectrum of the solution then showed complete conversion to the $[6\text{-}(MeOOCCH{=}CH)\text{-}arachno\text{-}6,8\text{-}C_2B_7H_{11}]^-$ (**5a**) anion[1b].

Reaction of $[6\text{-}(MeOOCCH{=}CH)\text{-}arachno\text{-}6,8\text{-}C_2B_7H_{11}]^-$ (**5a**) with **1**

After formation of 0.34 mmol of the **5a** anion as described above, **1** (0.05 g, 0.44 mmol) was immediately added to the reaction solution. The mixture was stirred for 6 h at room temperature under N_2. A ^{11}B NMR spectrum of the solution showed formation of both **1a** (ref.[6]) and 6-($MeOOCCH_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**) (ref.[1b]).

Reaction of *arachno*-6,7-$C_2B_7H_{13}$ (**3**) with Methyl Propynoate and 0.1 Equivalent of PS: Synthesis of 6-($MeOOCCH_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**)

A 100 ml round bottom flask fitted with a vacuum stopcock was charged with **3** (0.27 g, 2.39 mmol), PS (0.05 g, 0.23 mmol) and methyl propynoate (10 ml). The mixture was then stirred at room temperature overnight. The methyl propynoate was vacuum evaporated to leave a red oil that was dissolved in a minimum amount of CH_2Cl_2. Then, hexane (10 ml) was added and the solution filtered. The solvent was vacuum evaporated from the filtrate at –50 °C and the remaining solid was extracted with hexane and filtered again. The hexane was vacuum evaporated at –50 °C to yield 6-($MeOOCCH_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) as a clear liquid (0.18 g, 0.92 mmol, 38.5% yield). IR (NaCl plates, CCl_4, cm^{-1}): 3 050 (w), 2 950 (w), 2 920 (w), 2 580 (s), 1 745 (s), 1 435 (m), 1 410 (s), 1 385 (s), 1 365 (s), 1 330 (s), 1 260 (s), 1 235 (m), 1 200 (m), 1 175 (m), 1 100 (m), 1 015 (m). Exact mass calculated for $^{12}C_6{}^{11}B_7{}^{16}O_2{}^1H_{15}$ 196.1723; found 196.1740.

Reaction of **3** with Methyl Propynoate and One Equivalent of PS

In a manner similar to that above, **3** (0.13 g, 1.15 mmol), PS (0.25 g, 1.17 mmol) and methyl propynoate (5 ml) were reacted overnight at room temperature. A ^{11}B NMR spectrum of the solution showed only unidentified cage degradation products.

Reaction of 6-($MeOOCCH_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) with n-BuLi and HCl

To a NMR tube containing a THF solution of **4** (≈10 mg, ≈0.05 mmol) was added ≈1 equivalent of n-BuLi as a 1.6 M solution in hexane. After several minutes, the ^{11}B NMR spectrum showed complete conversion to a new product. Acidification with an excess of 1.0 M HCl in Et_2O yielded a second product which, based on *ab initio*/IGLO/NMR calculations (*vide infra*), is formulated as 6-($MeOOCCH_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**).

Reaction of **4** with NaH or KH

To a NMR tube containing a THF solution of **4** (≈10 mg, ≈0.05 mmol) was added an excess of NaH. After several hours, no reaction was observed by ^{11}B NMR. A similar addition of KH also did not show any evidence of reaction.

Computational Methods

The combined *ab initio*/IGLO/NMR method, using the GAUSSIAN92 program[7], was used as described previously[8]. The geometries were fully optimized at the HF/6-31G* level (using the standard basis sets included) on a Silicon Graphics International IRIS 4D/440VGX computer. A vibrational frequency analysis was performed at the HF/3-21G level and a true minimum was found (*i.e.* possessing no imaginary frequencies). The NMR chemical shifts were calculated using the IGLO method[9] employing the following basis sets. Basis DZ: C, B, 7s3p contracted to [4111, 21]; H 3s contracted to [21]. Tables of cartesian coordinates and selected bond distances and angles of the optimized geometries are available from the authors.

RESULTS AND DISCUSSION

Su *et al.*[1] reported that the [*arachno*-6,8-$C_2B_7H_{12}]^-$ (**1a**) dicarbaboranyl anion readily reacts with methyl propynoate in THF solution to yield, following protonation, the tricarbaborane 6-(MeOOCCH$_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**). As outlined in Fig. 1, the reaction was proposed to proceed by a mechanism involving initial nucleophilic attack of

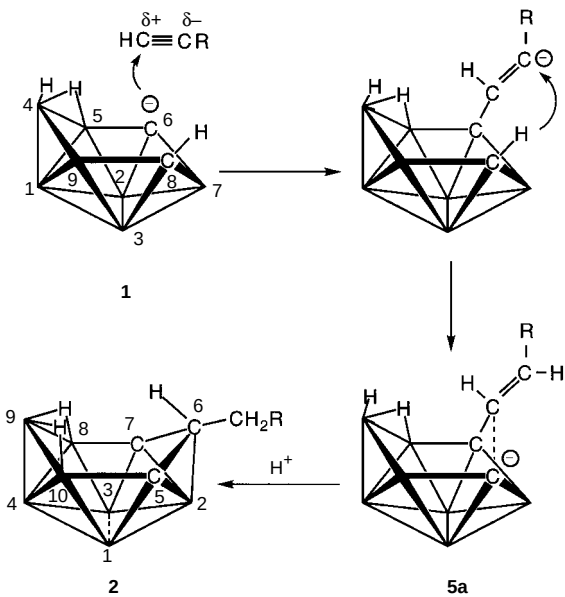


FIG. 1
Previously proposed[1] reaction pathway for the reaction of methyl propynoate with [*arachno*-6,8-$C_2B_7H_{12}]^-$ (**1a**)

the **1a** anion at the terminal acetylenic carbon to form an intermediate [6-(MeOOCCH=CH)-*arachno*-6,8-$C_2B_7H_{11}]^-$ (**5a**) anion which, upon acidification, rearranged to the final tricarbaborane product **2**. Starting from *arachno*-6,8-$C_2B_7H_{13}$ (**1**), the actual synthetic procedure required three separate steps: (i) the initial synthesis of the **1a** anion (Eq. (*1*)); (ii) reaction of **1a** with methyl propynoate (Eq. (*2*)) to form **5a**; and (iii) the protonation of the **5a** anion to form the final product **2** (Eq. (*3*)).

$$\underset{\mathbf{1}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{13}} + NaH \rightarrow \underset{\mathbf{1a}}{Na^+[\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{12}]^-} + H_2 \qquad (1)$$

$$\mathbf{1a} + MeOOCC{\equiv}CH \rightarrow \underset{\mathbf{5a}}{[6\text{-}(MeOOCCH{=}CH)\text{-}\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{11}]^-} \qquad (2)$$

$$\mathbf{5a} + H^+ \rightarrow \underset{\mathbf{2}}{6\text{-}(MeOOCCH_2)\text{-}\textit{arachno}\text{-}5,6,7\text{-}C_3B_7H_{12}} \qquad (3)$$

We have now discovered that the synthesis of **2** can be accomplished in a one-step process which does not require either the THF solvent or the prior synthesis of the **1a** anion. Thus, the reaction of **1** with excess methyl propynoate and only 0.1 equivalent of PS resulted in the direct formation of **2** (Eq. (*4*)).

$$\underset{\mathbf{1}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{13}} + MeOOCC{\equiv}CH \xrightarrow{0.1\ \text{eq. PS}} \underset{\mathbf{2}}{(MeOOCCH_2)\text{-}\textit{arachno}\text{-}5,6,7\text{-}C_3B_7H_{12}} \qquad (4)$$

Obviously, the reaction sequence involved in Eq. (*4*) has to be similar to the process outlined in Eqs (*1*)–(*3*), but because PS is required in less than equivalent amounts and the neutral carborane is obtained directly without a separate acidification step, a cyclic or catalytic mechanism is required. A chain reaction sequence consistent with the experimental results is presented in Fig. 2. The sequence begins with the 0.1 equivalent of PS reacting with **1** to yield a corresponding amount of **1a**. This anion can then react, as previously outlined in Fig. 1, with methyl propynoate to form the intermediate **5a** anion. If this anion is next protonated by an additional equivalent of **1**, then equal amounts of the neutral tricarbaborane product **2** and the **1a** anion are generated. The cycle would then continue until all of **1** is used.

Strong support for the above mechanism comes from individual studies of each of the proposed reaction steps. Thus, in a separate experiment, PS was found to readily deprotonate **1** to form **1a** (Eq. (*5*)).

$$\underset{\mathbf{1}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{13}} + PS \rightarrow (PSH)^+[\underset{\mathbf{1a}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{12}}]^- \qquad (5)$$

Likewise, an isolated sample of ((PSH)$^+$**1a**) was found to react with methyl propynoate to give the **5a** anion (Eq. (*6*), ref.[1]).

$$((PSH)^+\mathbf{1a}) + MeOOCC{\equiv}CH \rightarrow (PSH)^+[\underset{\mathbf{5a}}{6\text{-}(MeOOCCH{=}CH)\text{-}\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{11}}]^- \qquad (6)$$

Since the final product of the reaction in Eq. (*4*) is the *neutral* tricarbaborane, the intermediate **5a** anion must be protonated during the reaction. The only available proton source is unreacted starting compound **1** and it is therefore necessary to have some **1** present in solution for the reaction to go to completion. Indeed, when the reaction of **1** with methyl propynoate was carried out (Eq. (*7*)) in the presence of 1.0 equivalent of PS, instead of the 0.1 equivalent in Eq. (*4*), the reaction stopped with the formation of the **5a** anion, since under that condition there was no neutral **1** available for the protonation reaction.

$$\underset{\mathbf{1}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{13}} + MeOOCC{\equiv}CH \xrightarrow{\text{1.0 eq. PS}} \underset{\mathbf{5a}}{[6\text{-}(MeOOCCH{=}CH)\text{-}\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{11}]^-} \qquad (7)$$

The key feature which enables the protonation step essential to the cyclic reaction sequence is that **1** is a stronger acid than **2**. This was shown to be true in a separate

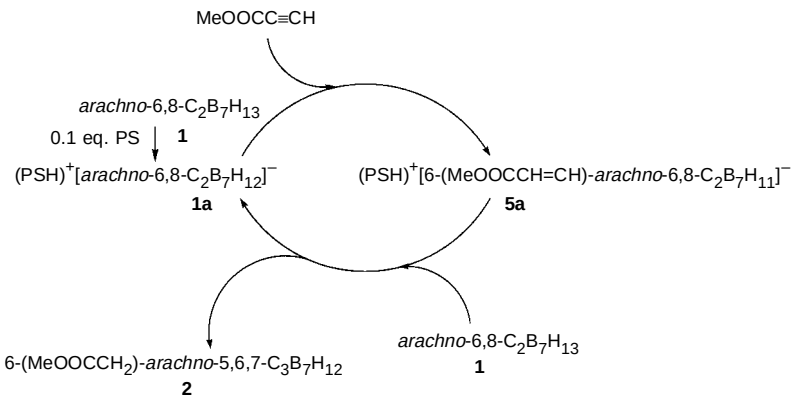


FIG. 2
Proposed cyclic reaction sequence for the reaction of *arachno*-6,8-$C_2B_7H_{13}$ (**1**) with methyl propynoate and 0.1 equivalent of PS

experiment, where it was found that the addition of **1** to a solution of the **5a** anion, produced both neutral **2** and the **1a** anion (Eq. (*8*)).

$$\underset{\mathbf{5a}}{(PSH)^{+}[6\text{-}(MeOOCCH{=}CH)\text{-}\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{11}]^{-}} + \underset{\mathbf{1}}{\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{13}} \rightarrow$$

$$\underset{\mathbf{2}}{6\text{-}(MeOOCCH_2)\text{-}\textit{arachno}\text{-}5,6,7\text{-}C_3B_7H_{12}} + \underset{\mathbf{1a}}{(PSH)^{+}[\textit{arachno}\text{-}6,8\text{-}C_2B_7H_{12}]^{-}} \qquad (8)$$

Thus, the studies discussed above of the individual steps proposed in Fig. 2 demonstrated that each step can, in fact, occur and thus, strongly support the overall mechanism.

The one-step synthetic method gives the 6-(MeOOCCH$_2$)-*arachno*-5,6,7-$C_3B_7H_{12}$ (**2**) product in slightly higher yields (≈64%) than in the earlier[1] three-step process (57%), but, more importantly, has the advantages that it (i) is a one-pot reaction; (ii) does not use a solvent; (iii) does not require stoichiometric amounts of the deprotonating agent; and (iv) yields the neutral carborane directly in excellent purity. These differences suggested that these procedures might also prove beneficial for carbon insertion reactions involving other polyhedral boranes, especially systems that had proven unsuccessful using the earlier conditions. For example, unlike the reaction with [*arachno*-6,8-$C_2B_7H_{12}]^-$ (**1a**) in Eq. (*2*), the reaction of stoichiometric amounts of [*arachno*-6,7-$C_2B_7H_{12}]^-$ (**3a**) anion with methyl propynoate does not result in carbon insertion, but rather only decomposition (Eq. (*9*), ref.[10]).

$$\underset{\mathbf{3a}}{[\textit{arachno}\text{-}6,7\text{-}C_2B_7H_{12}]^{-}} + MeOOCC{\equiv}CH \rightarrow \text{decomposition} \qquad (9)$$

A similar difference in reactivity of the these two isomeric dicarbaborane anions was previously found for their reactions with acetonitrile, where reaction with **1a** results in carbon insertion to form [*nido*-6-Me-5,6,9-$C_3B_7H_9]^-$ (ref.[11]), whereas the reaction with **3a** results in loss of BH_3, to form [*nido*-4,5-$C_2B_6H_9]^-$ and MeCN·BH_3 (ref.[12]). Thus, **3a** appears to be much more susceptible to degradation reactions than its isomer **1a**. The mild conditions of the PS-initiated reactions, which would allow the *in situ* generation and reaction of the [*arachno*-6,7-$C_2B_7H_{12}]^-$ (**3a**) anion in the absence of basic solvents, would appear to enhance the possibility of observing a carbon insertion product.

Indeed, unlike the reaction carried out under stoichiometric conditions (Eq. (*9*)) where only degradation was observed, the reaction of *arachno*-6,7-$C_2B_7H_{13}$ (**3**) with excess methyl propynoate and only 0.1 equivalent of PS resulted in carbon insertion to form a new tricarbaborane 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) in 38.5% yield (Eq. (*10*)).

$$\underset{\mathbf{3}}{\textit{arachno}\text{-}6,7\text{-}C_2B_7H_{13}} + MeOOCC{\equiv}CH \xrightarrow{0.1\ \text{eq. PS}} \underset{\mathbf{4}}{6\text{-}(MeOOCCH_2)\text{-}\textit{nido}\text{-}5,6,10\text{-}C_3B_7H_{10}} + H_2 \qquad (10)$$

The proposed composition was initially established by exact mass measurements and then further confirmed by *ab initio*/IGLO/NMR studies (*vide infra*). In contrast to the reaction of *arachno*-6,8-$C_2B_7H_{13}$ (**1**) with methyl propynoate, which yields the *arachno*-cage product **2** (Eq. (*4*)), the reaction with *arachno*-6,7-$C_2B_7H_{13}$ (**3**) gave the *nido*-tricarbaborane, 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**), containing two fewer hydrogens. Compound **4** is isoelectronic with the known tricarbaborane, 6-Me-*nido*-5,6,9-$C_3B_7H_{10}$ (**7**) (Fig. 3a, ref.[11]) and should have a similar structure based on an 11-vertex *closo* polyhedron missing one vertex. The ^{11}B NMR spectrum of **4** (Fig. 4) shows seven unique boron resonances, indicating C_1 cage symmetry, but at shifts different from those found for **7**, indicating that it must have a different arrangement of the skeletal atoms. The ^{1}H NMR spectrum shows the presence of two cage CH groups, at 4.06 and 2.79 ppm, and one bridge hydrogen at –3.01 ppm. The ^{13}C NMR spectrum shows, in addition to the three carbons of the side chain, a singlet at 112.1 ppm and doublets at 59.0 and 37.4 ppm that may be assigned to the CR and two CH cage-carbon resonances, respectively.

In addition to the known 6-R-*nido*-5,6,9-$C_3B_7H_{10}$ isomer, there are only two other potential arrangements, the 5,6,8 and the 5,6,10 isomers, of the carbon atoms in a *nido*-C_3B_7 framework, that both have the three cage-carbons in the favored low-coordinate locations on the open face and the C_1 symmetry indicated by the NMR data (Fig. 3). The structures and NMR properties of these three isomers were then investigated using

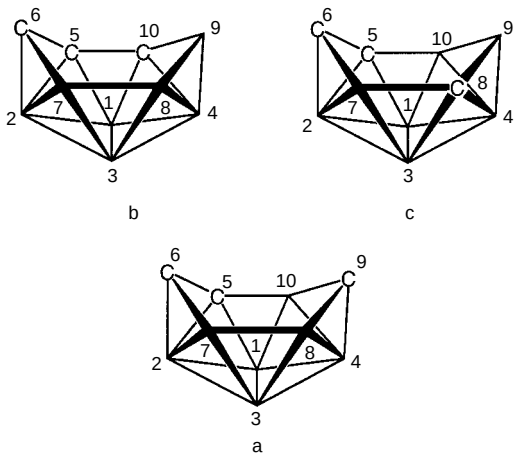


FIG. 3
Three possible structures for a C_1 symmetry *nido*-C_3B_7 framework

ab initio/IGLO/NMR calculations. In these calculations, the geometry of a proposed structure is first optimized using *ab initio* theory, then this structure is used as input for an IGLO NMR chemical shift calculation. This yields ^{11}B NMR shifts and assignments that can be compared to experimentally determined values. Such methods have now been widely employed to establish the structures of many polyhedral boron clusters[14].

Ab initio/IGLO/NMR calculations yielded the optimized structure for the *nido*-5,6,10-$C_3B_7H_{11}$ (**8**) isomer shown in Fig. 5, and the calculated ^{11}B NMR chemical shifts and assignments for this isomer are in good agreement with both the experimentally observed ^{11}B NMR chemical shifts and the assignments determined by ^{11}B-^{11}B 2-D NMR (Table I). IGLO calculations of ^{13}C NMR chemical shifts at the DZ/6-31G* level

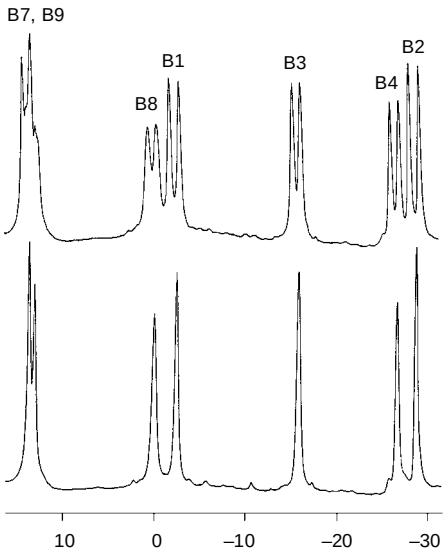


FIG. 4
^{11}B NMR spectra of 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) at 160.5 MHz; ^{1}H-coupled (top), ^{1}H-decoupled (bottom)

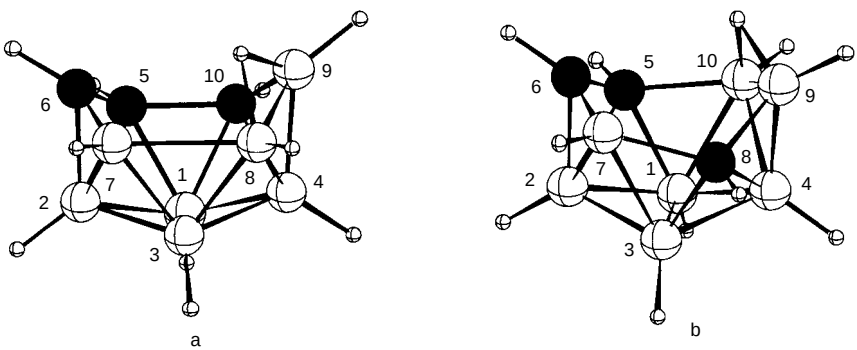


FIG. 5
Optimized structures of a *nido*-5,6,10-$C_3B_7H_{11}$ (**8**) and b *nido*-5,6,8-$C_3B_7H_{11}$ (**9**)

are generally not as accurate[15] as ^{11}B NMR chemical shift calculations; however, the ^{13}C shifts calculated for the cage-carbon resonances are consistent with the large differences found in the experimental spectrum, thereby allowing the assignments given in Table I.

The optimized structure of the *nido*-5,6,8-$C_3B_7H_{11}$ isomer (**9**) (Fig. 5b) is ≈38 kJ/mol lower in energy than the 5,6,10 isomer (**8**), but yields less satisfactory agreement with the experimental ^{11}B NMR chemical shifts (Table I). More importantly, the 5,6,8 isomer (**9**) is eliminated as a possibility because it does not contain the five-connected boron observed in the experimental ^{11}B-^{11}B 2-D NMR spectrum of **4** (Table I).

It should be noted that the same *nido*-5,6,10-C_3B_7 cage structure established for **4** was previously proposed for another compound. Stibr *et al.*[16] proposed a tricarbaborane with a 5,6,10-Me_3-*nido*-5,6,10-$C_3B_7H_8$ (**10**) structure as one of the products of the reaction of **3** and acetylene. However, it was later determined that this compound was, in fact, an isomeric tetracarbaborane having a 6,11-Me_2-*arachno*-5,6,10,11-$C_4B_7H_{11}$ (**11**)

TABLE I
NMR Data (δ in ppm)

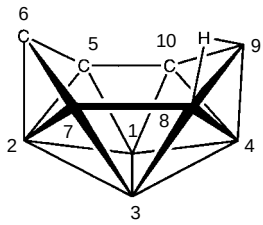
Compound	Nucleus	δ (multiplicity, *J*(Hz), assignment)
4	^{11}B[a,b]	14.1 (d, *J*(B,H) = 147, B7 or B9), 13.5 (d, *J*(B,H) ≈ 170, B7 or B9), 0.4 (d, *J*(B,H) = 150, B8), –2.0 (d, *J*(B,H) = 170, B1), –15.4 (d, *J*(B,H) = 145, B3), –26.3 (d, *J*(B,H) = 164, B4), –28.5 (d, *J*(B,H) = 175, B2)
	^{11}B (calc)[c]	20.2 B7, 12.6 B9, 4.1 B8, –1.5 B1, –17.5 B3, –24.0 B4, –33.7 B2
	^{11}B-^{11}B[d,e]	observed crosspeaks: B1-B2, B1-B3, B1-B4, B2-B3, B2-B7 (or B9)[f], B3-B4, B3-B7 (or B9)[f], B3-B8, B4-B7 (or B9)[f], B4-B8
	^{1}H[b,g]	4.06 (1, CH), 3.89 (1, BH), 3.74 (1, BH), 3.62 (s, CH_3), 3.39 (1, BH), 3.16 (d, *J*(H,H) = 16, CH_2), 3.04 (1, BH), 2.79 (1, CH), 2.09 (1, BH), 1.43 (1, BH), 1.22 (1, BH), –3.01 (1, BHB)
	^{13}C[b,h]	171.3 (s, COO), 112.1 (s, br, C6), 59.0 (d, *J*(C,H) = 179, C5), 52.1 (q, *J*(C,H) = 147, CH_3), 40.7 (t, *J*(C,H) = 131, CH_2), 37.4 (d, br, *J*(C,H) = 179, C10)
	^{13}C (calc)[c]	90.6 C6, 48.9 C5, 27.8 C10
9	^{11}B (calc)[i]	18.0 B9, 7.2 B1, 3.8 B3, 1.4 B7, –7.4 B10, –33.0 B4, –40.4 B2
	^{11}B[e,j]	5.7 (d, *J*(B,H) ≈ 140), –1.8 (d, *J*(B,H) obscured), –3.5 (d, *J*(B,H) =
6		154, –6.5 (d, *J*(B,H) obscured), –18.7 (d, *J*(B,H) = 161), –22.2 (t, *J*(B,H) ≈ 115), –49.2 (d, *J*(B,H) = 146
	^{11}B (calc)[k]	1.2 B7, –1.4 B4, –3.5 B8, –11.0 B2, –20.0 B1, –21.3 B9, –54.4 B3

[a] 160.5 MHz; [b] CD_2Cl_2; [c] calculation on the parent *nido*-5,6,10-$C_3B_7H_{11}$ (**8**) at the DZ/6-31G* level; [d] C_6D_6; [e] 64.2 MHz; [f] the B7 and B9 resonances are overlapped; [g] 500.1 MHz; [h] 125.7 MHz; [i] calculation on *nido*-5,6,8-$C_3B_7H_{11}$ (**9**) at the DZ/6-31G* level; [j] d_8-THF; [k] calculation on the parent *arachno*-5,6,10-$C_3B_7H_{13}$ (**13**) at the DZ/6-31G* level.

structure[17]. In agreement with the latter interpretation, the ^{11}B NMR chemical shifts reported for Stibr's compound are very different from those of **4**, but are in good agreement with *ab initio*/IGLO calculated values for the parent *arachno*-5,6,10,11-$C_4B_7H_{13}$ (**12**) compound (Table II and Fig. 6).

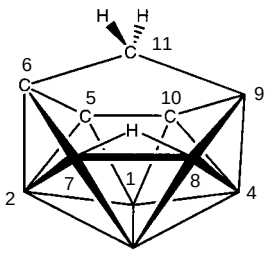
The formation of **4** can be envisioned to occur, as shown in Fig. 7, by a sequence similar to that proposed in Fig. 1 for the reaction with the **1a** anion. Nucleophilic attack of the *in situ* formed **3a** anion at the terminal acetylenic carbon, followed by hydroboration and carbon insertion along the C6–B5–B4 edges leads in a straightforward manner to the adjacent-carbon 5,6,10-isomer with the side chain at the C6 carbon. However, in contrast to the reaction with **1**, the reaction with **3** also involves loss of 1 mol of H_2 during the insertion.

As was the case for the reaction with **1**, PS was required in less than stoichiometric amounts in the reaction of **3** with methyl propynoate, and a neutral carborane product **4** was obtained without an acidificaton step. These observations again indicate a cyclic mechanism analogous to that shown in Fig. 2, where unconsumed **3** serves as a source of protons. Again, the key feature enabling the cyclic reaction sequence is that the



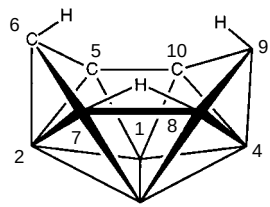
nido-5,6,10-$C_3B_7H_{11}$

8



arachno-5,6,10,11-$C_4B_7H_{13}$

12



arachno-5,6,10-$C_3B_7H_{13}$

13

FIG. 6

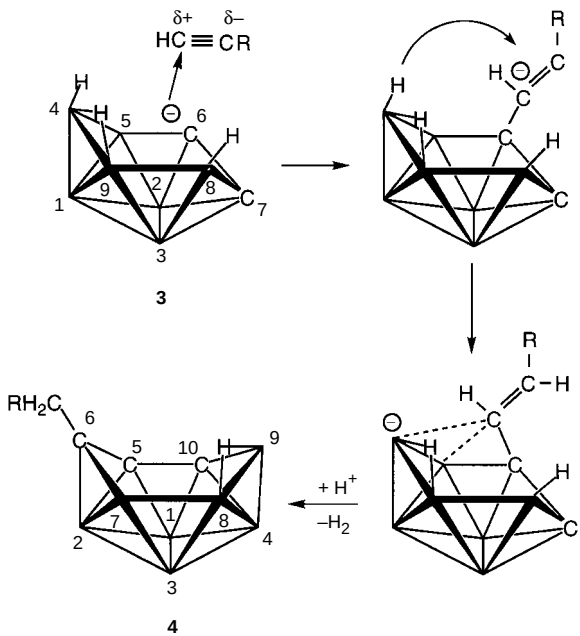
Structures of *nido*-5,6,10-$C_3B_7H_{11}$ (**8**), *arachno*-5,6,10,11-$C_4B_7H_{13}$ (**12**) and *arachno*-5,6,10-$C_3B_7H_{13}$ (**13**)

TABLE II

Comparisons of the *ab initio*/IGLO calculated[a] ^{11}B NMR chemical shifts (in ppm) of *nido*-5,6,10-$C_3B_7H_{11}$ (**8**), *arachno*-5,6,10,11-$C_4B_7H_{13}$ (**12**) and *arachno*-5,6,10-$C_3B_7H_{13}$ (**13**) with the experimental values for 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**), 6,11-Me$_2$-*arachno*-5,6,10,11-$C_4B_7H_{11}$ (**11**) and 6-(MeOOCCH$_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**)

8		**12**		**13**	
calc (assignment)	exp **4**	calc (assignment)	exp **11**	calc (assignment)	exp **6**
20.2 (B7)	14.1	8.0 (B7)	4.30	1.2 (B7)	5.7
12.6 (B9)	13.5	0.5 (B8)	2.82	–1.4 (B4)	–1.8
4.1 (B8)	0.4	0.3 (B4)	–0.44	–3.5 (B8)	–3.5
–1.5 (B1)	–2.0	–5.8 (B2)	–6.05	–11.0 (B2)	–6.5
–17.5 (B3)	–15.4	–11.1 (B9)	–10.27	–20.0 (B1)	–18.7
–24.0 (B4)	–26.3	–13.4 (B1)	–10.27	–21.3 (B9)	–22.2
–33.7 (B2)	–28.5	–45.0 (B3)	–40.74	–54.4 (B3)	–49.2

[a] Calculations at DZ/6-31G* level; [b] experimental values for **11** from refs[16,17].



3 **4**

FIG. 7

Proposed reaction pathway for the reaction of methyl propynoate with [*arachno*-6,7-$C_2B_7H_{12}$]$^-$ (**3a**)

starting carborane **3** must be a stronger acid than the 6-(MeOOCCH$_2$)-*nido*-5,6,10-$C_3B_7H_{10}$ (**4**) product.

Although unreactive toward either NaH or KH, a NMR study showed that **4** readily adds n-BuLi to give, following acidification with HCl–Et_2O, a new product tentatively formulated as the neutral 6-(MeOOCCH$_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**) tricarbaborane (Eq. (*11*)).

$$\underset{\mathbf{4}}{\text{6-(MeOOCCH}_2\text{)-}\textit{nido}\text{-5,6,10-C}_3\text{B}_7\text{H}_{10}} \xrightarrow[\text{2. HCl}]{\text{1. n-BuLi}} \underset{\mathbf{6}}{\text{6-(MeOOCCH}_2\text{)-Bu-}\textit{arachno}\text{-5,6,10-C}_3\text{B}_7\text{H}_{11}} \qquad (11)$$

The compound was not isolated in sufficient amounts and purity to allow complete characterization. However, a cluster of 6-(MeOOCCH$_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**) composition would be a 10-vertex *arachno* (*n* + 3 electron pairs) electronic system and, therefore, be predicted to have a gross cage geometry similar to that of the isoelectronic compound **2**. The ^{11}B NMR chemical shifts of the two compounds are very different, suggesting an alternative arrangement of the cage-carbon atoms.

Ab initio calculations on the isoelectronic parent molecule, *arachno*-5,6,10-$C_3B_7H_{13}$ (**13**), yielded the structure shown in Fig. 8. The IGLO calculated chemical shifts (Table II) for this optimized structure are, in fact, in surprisingly good agreement with the experimentally observed ^{11}B NMR chemical shifts of the proposed 6-(MeOOCCH$_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**) compound, even though the calculation employed hydrogen atoms in place of the butyl and MeOOCCH$_2$ substituents. It is also significant that the calculation correctly predicts the B9 boron (BH_2 group) resonance to appear at a shift (–21.3 ppm) nearly identical to that found for the triplet resonance (–22.2 ppm)

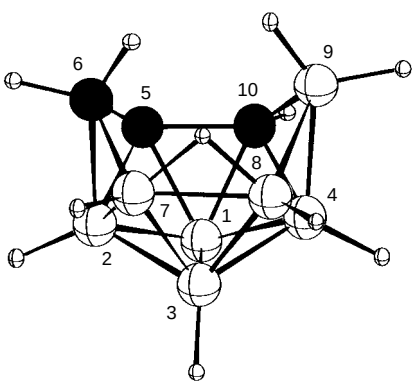


FIG. 8
Optimized structure of *arachno*-5,6,10-$C_3B_7H_{13}$ (**13**)

observed in the experimental spectrum. The presence of *endo*-substituents at the B9 and C6 positions, as well as the bridging hydrogen at the B5-B10 edge, are consistent with the structural features observed in other isoelectronic clusters including, [*arachno*-$B_{10}H_{14}]^{2-}$ (ref.[18]) and *arachno*-6,9-$C_2B_8H_{14}$ (ref.[19]). Although the exact position of attachment of the exopolyhedral butyl group in **6** is unproven, the fact that the remaining resonances in the ^{11}B NMR spectrum of the compound all appear to show doublet coupling to exopolyhedral hydrogens, indicates that the butyl group must be attached to one of the cage carbons. As shown in Fig. 6, the proposed structure is also very similar to that established for 6,11-Me_2-*arachno*-5,6,10,11-$C_4B_7H_{11}$ (**11**, ref.[17]). In the latter compound, the methylene bridges the 6,9-positions at the endo sites on these cage atoms. As shown in Table II, the ^{11}B NMR chemical shifts, as well as their IGLO predicted assignments, for **6** and **11** are again quite similar providing additional strong support for the proposed 6-($MeOOCCH_2$)-Bu-*arachno*-5,6,10-$C_3B_7H_{11}$ (**6**) structure.

In conclusion, we are now attempting to expand the scope of these new Proton-Sponge-initiated carbon insertion reactions to include a variety of polyhedral borane, carborane and heteroborane clusters. These studies along with the results of further chemical investigations of the new tricarbaboranes discussed herein will be presented in future publications.

We thank the National Science Foundation for the support of this research.

REFERENCES

1. a) Su K., Barnum B. A., Carroll P. J., Sneddon L. G.: J. Am. Chem. Soc. *114*, 2730 (1992); b) Su K., Carroll P. J., Sneddon L. G.: J. Am. Chem. Soc. *115*, 10004 (1993).
2. Shriver D. F., Drezdzon M. A.: *Manipulation of Air Sensitive Compounds*, 2nd ed. Wiley, New York 1986.
3. Garrett P. M., George T. A., Hawthorne M. F.: Inorg. Chem. *8*, 2008 (1969).
4. Stibr B., Plesek J., Hermanek S.: Inorg. Synth. 22, 237 (1983); Hermanek S., Jelinek T., Plesek J., Stibr B., Fusek J.: J. Chem. Soc., Chem. Commun. *1987*, 927.
5. Kang S. O., Carroll P. J., Sneddon L. G.: Organometallics *7*, 772 (1988).
6. Tebbe F. N., Garrett P. M., Hawthorne M. F.: J. Am. Chem. Soc. *90*, 869 (1968).
7. Frisch M. J., Trucks G. W., Schlegel H. B., Gill P. M. W., Johnson B. G., Wong M. W., Foresman J. B., Robb M. A., Head-Gordon M., Replogle E. S., Gomperts R., Andres J. L., Raghavachari K., Binkley J. S., Gonzalez C., Martin R. L., Fox D. J., Defrees D. J., Baker J., Stewart J. J. P., Pople J. A.: *Gaussian 92/DFT*, Revision F.2. Gaussian, Inc., Pittsburgh (PA) 1993.
8. Keller W., Barnum B. A., Bausch J. W., Sneddon L. G.: Inorg. Chem. *32*, 5058 (1993).
9. Kutzelnigg W., Fleischer U., Schindler M. in: *NMR Principles and Progress* (P. Diehl, E. Fluck, H. Gunther, R. Kosfeld and J. Seelig, Eds), Vol.23, p. 165 and references therein. Springer, Berlin 1990.
10. Su K.: Unpublished results.
11. Kang S. O., Furst G. T., Sneddon L. G.: Inorg. Chem. *28*, 2339 (1989).

12. Kang S. O., Bausch J. W., Carroll P. J., Sneddon L. G.: J. Am. Chem. Soc. *114*, 6248 (1992); Bausch J. W., Matoka D. J., Carroll P. J., Sneddon L. G.: J. Am. Chem. Soc. *118*, 11423 (1996).
13. Williams R. E.: Inorg. Chem. *10*, 210 (1971); Wade K.: Adv. Inorg. Chem. Radiochem. *18*, 1 (1976); Williams R. E.: Adv. Inorg. Chem. Radiochem. *18*, 67 (1976); Rudolph R. W.: Acc. Chem. Res. *9*, 446 (1976); Williams R. E.: Chem. Rev. *92*, 177 (1992); Bausch J. W., Rizzo R. C., Sneddon L. G., Wille A. E., Williams R. E.: Inorg. Chem. *35*, 131 (1996).
14. For examples see: Buhl M., Schleyer P. v. R. in: *Electron Deficient Boron and Carbon Clusters* (G. A. Olah, K. Wade and R. E. Williams, Eds) p. 113. Wiley, New York 1991; references in footnote[17] in: Diaz M., Jaballas J., Tran D., Lee H., Arias J., Onak T.: Inorg. Chem. *35*, 4536 (1996).
15. Buhl M., Schleyer P. v. R.: J. Am. Chem. Soc. *114*, 477 (1992); Schleyer P. v. R., Gauss J., Buhl M., Greatrex R., Fox M. A.: J. Chem. Soc., Chem. Commun. *1993*, 1766; Buhl M., Gauss J., Hofmann M., Schleyer P. v. R.: J. Am. Chem. Soc. *115*, 12385 (1993); Diaz M., Jaballas J., Arias J., Lee H., Onak T.: J. Am. Chem. Soc. *118*, 4405 (1996).
16. Stibr B., Jelinek T., Janousek Z., Hermanek S., Drdakova E., Plzak Z., Plesek J.: J. Chem. Soc., Chem. Commun. *1987*, 1106; Stibr B., Jelinek T., Drdakova E., Hermanek S., Plesek J.: Polyhedron *7*, 669 (1988).
17. Stibr B.: Chem. Rev. *92*, 225 (1992).
18. Kendall D. S., Lipscomb W. N.: Inorg. Chem. *12*, 546 (1973).
19. Stibr B., Plesek J., Hermanek S.: Collect. Czech. Chem. Commun. *39*, 1805 (1974); Stibr B., Janousek Z., Plesek J., Jelinek T., Hermanek S.: J. Chem. Soc., Chem. Commun. *1985*, 1365; Janousek Z., Plesek J., Hermanek S., Stibr B.: Polyhedron *4*, 1797 (1985); Stibr B., Janousek Z., Plesek J., Jelinek T., Hermanek S.: Collect. Czech. Chem. Commun. *52*, 103 (1987).