Preparation of Some *nido*-Dicarbanonaborane(11)'s and *nido*-Dicarbadecaborane(12)'s[1,2]

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Abstract: Octaborane(12) reacts with acetylene in diethyl ether to give a 65% yield of a mixture of *nido*-dicarbanonaborane(11), $B_7C_2H_{11}$, and *nido*-dicarbadecaborane(12), $B_8C_2H_{12}$, members of the $B_nC_2H_{n+4}$ series of carboranes. Boron-11 nmr spectra suggest that $B_7C_2H_{11}$ is the first example of a carborane containing an integral $-BH_2$ group. The reaction of B_8H_{12} with 2-butyne in diethyl ether produces $B_7C_2H_9(CH_3)_2$ and $B_8C_2H_{10}(CH_3)_2$ in 78% yield. Boron-11 and pmr evidence suggests that $B_7C_2H_9(CH_3)_2$ differs in structure from $B_7C_2H_{11}$ and contains its "extra" hydrogens in two distinct bridging locations. $B_8C_2H_{12}$ and $B_8C_2H_{10}(CH_3)_2$ appear to be in the decaborane(14) geometry, carbon atoms occupying the 5,6 positions. One minor product of this reaction is a new 2,3 isomer of *closo*-$B_5C_2H_5(CH_3)_2$. Reactions of B_8H_{12} with other acetylenes are mentioned. Reactions of *n*-nonaborane(15) with C_2H_2 and with 2-butyne are discussed.

The members of the $B_nC_2H_{n+4}$ series of nido carboranes for $n = 4$[3] and $n = 9$[4] have proven to be precursors to numerous interesting and, in some cases, potentially commercially useful compounds. Pyrolysis of $B_4C_2H_8$ generates the closo carboranes 1,5-$B_3C_2H_5$, 1,6-$B_4C_2H_6$, and 2,4-$B_5C_2H_7$,[5] the latter of which has been incorporated into siloxane polymers to decrease thermal depolymerization.[6] Pyrolyses and oxidative degradations of 7,8-$B_9C_2H_{13}$ have generated the nido and closo carboranes 2,3-$B_9C_2H_{11}$, 1,3-$B_7C_2H_{13}$, 1,7-$B_6C_2H_8$, 1,6-$B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, and 1,10-$B_8C_2H_{10}$.[7] Numerous "expanded" cage transition metal complexes have been made from dianions of these carboranes.[8] Recently, polyhedra containing non-transition row metallic heteroatoms have been synthesized directly from the nido carboranes themselves, *e.g.*, $(CH_3)_2AlB_9C_2H_{12}$,[9] $CH_3GaB_4C_2H_6$,[10] and $(\pi\text{-}C_2B_4H_6)Fe(CO)_3$.[11]

To a large degree, the aforementioned chemistry developed because the precursors to the nido carboranes are the thermally stable and easily made boranes B_5H_9 and $B_{10}H_{14}$. Because we had synthetic routes to the less stable B_8 and B_9 hydrides,[12,13] we investigated low-temperature routes to nido carboranes from these boranes. This paper details the preparation of the new B_7C_2 and B_8C_2 nido carboranes containing vicinal carbon atoms produced in the reactions of alkynes with B_8H_{12}, $B_8H_{12}\cdot O(C_2H_5)_2$, $B_8H_{12}\cdot THF$, and *n*-B_9H_{15}.

Experimental Section

Preparation of Starting Materials. All manipulations involved in this investigation involved standard high vacuum techniques described elsewhere.[14]

Acetylene (Matheson) was passed through a −112° trap to remove acetone. Deuterioacetylene was generated from D_2O and CaC_2 and purified through a −112° trap. Propyne (Matheson) was passed through a −95° trap (vp at −63° = 83 mm). 2-Butyne (Columbia Chemicals) was distilled through −63° into a −95° trap (vp at 0° = 245 mm). 3-Hexyne (Farchan) was passed through −30° to a −63° trap (vp at 20° = 72.5 mm). 1,4-Dichloro-2-butyne and 1,4-dibromo-2-butyne (Columbia) were distilled before use. Disilylacetylene of laboratory stock[15] was purified by passage from a −45° into a −95° trap (vp at 0° = 145 mm). Diphenylacetylene (K & K) was used without further purification.

Octaborane(12) was generated from the rapid decomposition of *i*-B_9H_{15} in *n*-pentane solution at −30°.[12] *n*-Nonaborane(15) was prepared in the hot-cold, flow-quench reaction of B_5H_9 with B_2H_6[13] and purified on a high-vacuum low-temperature distillation column.[16] 2,4-Dicarbaheptaborane(7) and 2,4-dimethyldicarbaheptaborane(7) were prepared by literature methods,[5] purified by preparative vpc, and identified by their characteristic ^{11}B nmr spectra.[17]

Spectroscopic Techniques. The ^{11}B nuclear magnetic resonance spectra were obtained on Varian Associates HA-60-IL, HA-100, and HR-220 high-resolution spectrometers operating at 19.3, 32.1, and 70.6 MHz, respectively. Proton-decoupled 70.6-MHz ^{11}B nmr spectra were obtained by simultaneously irradiating hydrogen nuclei at 220 MHz using a home-built, white-noise, wide-band decoupler. Proton magnetic resonance spectra were obtained on the HA-100 and HR-220 spectrometers at 100 and 220 MHz, respectively. Chemical shifts for ^{11}B and ^1H spectra were measured relative to external samples of $BF_3\cdot O(C_2H_5)_2$ and TMS, respectively. All ^{11}B coupling constants are reported from frequency swept spectra at 51.7 kG (70.6 MHz).

Mass spectra were obtained with Consolidated Electrodynamics Corp. Model 21-620, Varian Model CH-7, and Associated Electrical Industries Model MS-9 mass spectrometers using room temperature gas inlets. Exact mass measurements were made on the latter instrument by measuring mass ratios to known peaks of perfluorotributylamine.

Infrared spectra were recorded on Perkin-Elmer Model 137 prism and 621 grating spectrophotometers.

Analytical Techniques. Analytical and preparative vpc were performed on a F & M Model 700 gas chromatograph using thermal

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conductivity and gas density balance detectors. Diisodecyl phthalate (30%) (1/4 in. × 10 ft) and 30% Silicone Fluid SF-96 (1/8 in. × 10 ft and 3/8 in. × 10 ft) on NAW firebrick columns were pretreated with B_5H_9 and B_2H_6 before use. Preparative fractions were collected in liquid N_2 cooled traps.

Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of B_8H_{12} and Acetylene. In a typical preparation, 0.740 g of B_8H_{12} (7.51 mmol) was distilled into a removable 200-ml tared trap containing ~9 cm^3 of diethyl ether (6 g). Octaborane(12) was always distilled directly into the reaction vessel from a $-23°$ trap to eliminate $B_{10}H_{14}$ and minimize decomposition. The trap was sealed, removed from the vacuum line, warmed to form $B_8H_{12}\cdot O(C_2H_5)_2$, and weighed. After refreezing, 10.00 mmol of C_2H_2 was condensed into the trap. The trap was then sealed, removed from the line, and allowed to warm slowly to room temperature in a shielded wire cage.[18] As the ether melted, the $B_8H_{12}\cdot O(C_2H_5)_2$ went into solution, but no bubbling was observed. The clear solution yellowed slightly in 30 min and was a deep orange hue after 16 hr, at which time the trap was cooled to $-196°$.

The more volatile products were identified by their infrared and mass spectra. Hydrogen (0.314 mmol) was removed and measured with a Toepler pump. Traces of diborane, ethane, and acetylene stopped at $-196°$; 1.145 mmol of ethane and acetylene stopped at $-157°$. When longer reaction times were employed, more ethane was generated and less acetylene was recovered. The bulk of the ether stopped at $-112°$, while the main products were retained at $-78°$.

The latter products were placed on a low-temperature fractional distillation column.[16] A very small amount of crystals and liquid distilled off between -80 and $-50°$. Mass spectra and ^{11}B nmr spectra suggested this fraction was a mixture of B_6H_{10} and the parent 2,3-$B_5C_2H_7$. The major products, $B_7C_2H_{11}$ and $B_8C_2H_{12}$, sublimed from the column between -30 and $+15°$ and were weighed together in a tared trap. Single passes up the column provided little resolution of these compounds except to remove the impurities of lower volatility (mainly n-$B_{18}H_{22}$), a step which greatly speeded subsequent transfers. ^{11}B nmr spectra of the 0.6075 g of crystals collected indicated the mixture was ~40% $B_7C_2H_{11}$ and ~60% $B_8C_2H_{12}$ (total yield ~65% based on B_8H_{12} consumed). These percentages varied only slightly for other runs of the same reaction. Some low-volatility white crystals were sublimed out of the remaining yellow oil by heating the reaction trap to $+150°$. Boron-11 nmr spectra and single-crystal X-ray diffraction patterns identified these crystals as n-$B_{18}H_{22}$.[19,20] Mass balance: 0.74 g B_8H_{12} + 0.260 g C_2H_2 = 1.00 g reactants; 0.027 g C_2H_2 and C_2H_6 + 0.608 g $B_7C_2H_{11}$ and $B_8C_2H_{12}$ + 0.396 g yellow oil = 1.031 g products.

The reaction of B_8H_{12} and C_2H_2 in the absence of diethyl ether also gave $B_7C_2H_{11}$ and $B_8C_2H_{12}$, only in much lower yield (~5%). In addition, more H_2 was formed, and larger quantities of B_2H_6, C_2H_6, C_3H_8, and C_4H_{10} were found. The B_8H_{12} decomposed significantly as the vessel was warmed to room temperature and the principal product was a bubbly, nonvolatile, foul-smelling, orange goo.

Larger Preparation and Separation of $B_7C_2H_{11}$ and $B_8C_2H_{12}$. Octaborane(12) (1.433 g, 14.5 mmol) and 20.6 mmol of acetylene in 20 cm^3 of diethyl ether were allowed to react as above except the trap was left open to a manometer and manifold of the vacuum line to monitor the $H_2 + C_2H_2$ pressure (total volume ~600 ml). The pressure rose to ~700 mm after the $B_8H_{12}\cdot O(C_2H_5)_2$ melted and went into solution and dropped to ~500 mm as the reaction proceeded. After 72 hr, 4.98 mmol of H_2 was pumped away. Fractionation of the volatile products gave 1.59 mmol of unreacted C_2H_2, 0.0115 g of n-$B_{18}H_{22}$, and 0.904 g of a mixture of $B_7C_2H_{11}$ and $B_8C_2H_{12}$ (50% conversion based on B_8H_{12}).

The $B_7C_2H_{11}$–$B_8C_2H_{12}$ mixture was quickly (6–8 hr) sublimed up a low-temperature column to remove the last traces of ether, B_6H_{10}, and n-$B_{18}H_{22}$. A series of very slow fractionations was then begun (3–6 days each) to slowly sublime the more volatile $B_8C_2H_{12}$ away from the $B_7C_2H_{11}$. $B_8C_2H_{12}$ could be sublimed from the column between -45 and 0°, while the bulk of the $B_7C_2H_{11}$ (and some $B_8C_2H_{12}$) sublimed off between -10 and $+10°$. The composition of fractions was continuously monitored by their 70.6-MHz ^{11}B nmr spectra in n-pentane. Fractions with higher percentages of $B_8C_2H_{12}$ (or $B_7C_2H_{11}$) were kept apart and combined for subsequent sublimations. Those fractions containing <70% $B_8C_2H_{12}$ (or $B_7C_2H_{11}$) were recombined for subsequent sublimations. Three successive sublimations were sufficient to obtain $B_8C_2H_{12}$ of >95% purity; however, at least nine successive sublimations were needed to produce $B_7C_2H_{11}$ of similar purity. At this point, the fractions were roughly ~0.3 g (>95%) $B_8C_2H_{12}$, ~0.3 g (>70%) $B_8C_2H_{12}$, ~0.3 g (>80%) $B_7C_2H_{11}$, and ~0.1 g (>98%) $B_7C_2H_{11}$.

Numerous attempts were made to separate $B_7C_2H_{11}$ and $B_8C_2H_{12}$ by other techniques. Low-temperature, high-vacuum fractional recrystallization in n-pentane affords a slight enrichment of $B_8C_2H_{12}$ in the filtrate; however, hundreds of recrystallizations would have had to be performed to produce enough $B_7C_2H_{11}$ of sufficient purity for characterization. Both column and thin-layer chromatography were also explored as possible separation methods. Some success was realized by eluting $B_8C_2H_{12}$ on predried cellulose powder with n-pentane–diethyl ether mixtures, but $B_7C_2H_{11}$ hydrolyzed badly from the residual water in the cellulose. No resolution at all was obtained on alumina or silica gel tlc plates with a wide range of solvents. Although $B_8C_2H_{12}$ passed unchanged through all of the heretofore mentioned vpc columns at 150°, $B_7C_2H_{11}$ decomposed completely under these conditions, giving a mixture of closo carboranes.[21]

Reaction of n-B_9H_{15} and Acetylene. n-Nonaborane(15) (0.128 g, 1.14 mmol) and 1.73 mmol of C_2H_2 were condensed into a tared trap and allowed to warm to room temperature. No evidence of a reaction was seen. The mobile clear liquid slowly yellowed into a thick syrup over a 4 day period. At this time, the volatile materials were 1.53 mmol of H_2 and 0.050 g of some white crystals. No acetylene was present. A 70.6-MHz ^{11}B nmr spectra of these crystals in ether solution showed resonances for $B_8C_2H_{12}$, $B_9C_2H_{13}$,[22] and $B_{10}H_{14}$. This solution was then injected into a 1/4 in. × 6 ft SE-30 on firebrick column operating at 130°, connected to a Varian CH-7 mass spectrometer. The three major eluates were identified as 2,3-$B_9C_2H_{11}$ (~40%), $B_8C_2H_{12}$ (~40%), and $B_{10}H_{14}$ (~10%). An independent experiment showed that the 2,3-$B_9C_2H_{11}$ actually arose from thermal decomposition of 7,8-$B_9C_2H_{13}$ in the heated vpc inlet. Three additional minor eluates with parent masses at m/e = 136, 146, and 150 could not be conclusively identified; however, the mass spectra of the center component closely resembled that of 1,2-$B_{10}C_2H_{12}$.

Reaction of B_8H_{12} and 2-Butyne. In a typical preparation, 0.593 g of B_8H_{12} (5.84 mmol) was allowed to react with 6.73 mmol of 2-butyne in a shielded trap containing 10 ml of diethyl ether. As the vessel warmed to room temperature, the $B_8H_{12}\cdot O(C_2H_5)_2$ went into solution slowly with no bubbling. The solution yellowed slightly in 15 min and was deep orange after 17 hr. At the time, the trap was frozen down and 0.216 mmol of H_2 was measured. Fractional distillation of the volatile products produced 0.400 mmol of ethane and a trace of diborane (passing $-112°$), 0.050 mmol of unreacted 2-butyne (passing $-95°$), and excess diethyl ether. Traces of ether in the 2-butyne were removed with BF_3. The major products stopped at $-78°$ and were separated on a low-temperature fractionation column. B_6H_{10} (0.152 mmol) (2.6% yield) and 0.088 mmol of 2,3-$B_5C_2H_5(CH_3)_2$ (1.5% yield) distilled from the column between -80 and $-40°$. Their separation is described below. Pure $B_7C_2H_9(CH_3)_2$ (0.255 g, 29% yield) distilled off between -31 and $-7°$, and pure $B_8C_2H_{10}(CH_3)_2$ (0.088 g, 10% yield) distilled between $+3$ and $+11°$. Two additional fractionations of the material distilling between -7 and $+3°$ raised the yields to 58 and 20%, respectively. The overall conversion of B_8H_{12} to carboranes was 80%.

Larger Preparation and Separation of $B_7C_2H_9(CH_3)_2$ and $B_8C_2H_{10}(CH_3)_2$. 2-Butyne (12.91 mmol) was added to 1.264 g of B_8H_{12} (12.81 mmol) in 10 cm^3 of ether as described above. After 16 hr the volatile products were distilled into a $-78°$ trap to remove H_2, ethane, unreacted 2-butyne, and excess ether. After pumping overnight, ~2 cm^3 of clear liquid was distilled up a low-temperature column. A clear liquid (0.29 mmol) distilled off between -80 and $-25°$ and was further purified by preparative vpc (see below). ^{11}B nmr spectra showed the fraction subliming off between -25 and $+1°$ to be >90% $B_7C_2H_9(CH_3)_2$. At these temperatures, crystals were present on the upper half of the column while the liquid

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(18) No B_8H_{12}–acetylene reaction has ever exploded in this laboratory even though the boron/carbon ratio was nearly always the 4:1 required for B_4C formation.

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Table I. Additional $B_7C_2H_9RR'$-$B_8C_2H_{10}RR'$ Preparations

Alkyne	RC≡CR′ (mmol)	B_8H_{12} (mmol)	Total yield (g)	%	Relative percentage of $B_7C_2H_9RR'$	Relative percentage of $B_8C_2H_{10}RR'$
C_2D_2	11.40	7.83	Estimated from C_2D_2 consumed	~50	35	65
$HC{\equiv}CCH_3$	2.66	1.93	Estimated from liquid volume	~50	55	45
$C_2H_5C{\equiv}CC_2H_5$	2.19	1.79	0.655	37	40	60
$CH_2ClC{\equiv}CCH_2Cl$	12.25	2.31	0.449	86	30	70
$CH_2BrC{\equiv}CCH_2Br$	6.92	1.86	0.367	64	>95	Not observed
$SiH_3C{\equiv}CSiH_3$	1.85	1.66	0.318	1	~50	~50
$(C_6H_5)C{\equiv}C(C_6H_5)$	6.46	1.87	See text	?	>95	Not observed

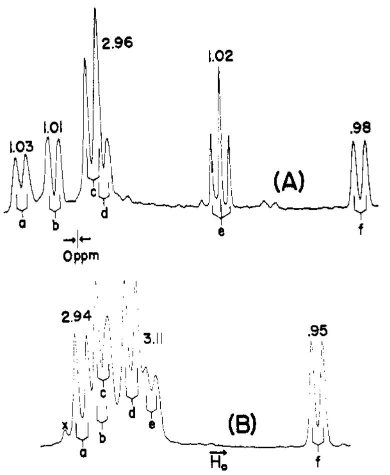

Figure 1. (A) The 70.6-MHz ^{11}B nmr spectrum of $B_7C_2H_{11}$ in *n*-pentane. Chemical shifts (ppm relative to external $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (Hz) are: (a) −10.4, 150; (b) −4.7, 160; (c) +3.0, ~160; (d) +5.2, ~150; (e) +28.3, 125; and (f) +55.4, 160. (B) The 70.6-MHz ^{11}B nmr of neat $B_7C_2H_9(CH_3)_2$. Chemical shifts and coupling constants are: (a) 0, 170; (b) +3.7, ~150; (c) +4.4, ~150; (d) +10.1, ~155; (e) +13.9, 135; and (f) +46.7, 148. Integrated areas are given above the peaks.

carboranes refluxed in the lower half. The remaining liquid (~1 cm³) distilling off between +1 and +11° was >90% $B_8C_2H_{10}(CH_3)_2$. Fractionation of the >90% $B_7C_2H_9(CH_3)_2$ afforded ~6 mmol of pure $B_7C_2H_9(CH_3)_2$ (exited −24 to −5°) to −5°) and ~1 mmol of impure $B_8C_2H_{10}(CH_3)_2$ (exited −2 to 0°). Fractionation of the >90% $B_8C_2H_{10}(CH_3)_2$ afforded ~1 mmol of impure $B_7C_2H_9(CH_3)_2$ (exited −5 to +2°) and ~2 mmol of pure $B_8C_2H_{10}(CH_3)_2$ (exited +2 to +7°). A fourth fractionation on the two combined impure fractions brought the yields to ~7.5 mmol of $B_7C_2H_9(CH_3)_2$ and ~2.5 mmol of $B_8C_2H_{10}(CH_3)_2$. Total yield from B_8H_{12} was ~80%. The 3:1 predominance of $B_7C_2H_9(CH_3)_2$ occurred in all B_8H_{12}–2-butyne reactions.

Anal. Calcd for $B_7C_2H_9(CH_3)_2$: C, 34.60; H, 10.89; B, 54.51. Found: C, 31.56; H, 11.28; B, 52.28. Calcd for $B_8C_2H_{10}(CH_3)_2$: C, 31.89; H, 10.70; B, 54.71. Found: C, 31.64, 31.26; H, 10.82, 11.55; B, 56.72, 56.72.

Purification of 2,3-$B_5C_2H_5(CH_3)_2$. The −80 to −25° fraction from above was passed through a 1/4 in. × 10 ft diisodecyl phthalate on firebrick column operating at 72°. Relative retention times for diethyl ether, B_6H_{10}, and 2,3-$B_5C_2H_5(CH_3)_2$ were 1.00, 1.92, and 3.20, respectively. B_6H_{10} (0.1505 mmol) and 2,3-$B_5C_2H_5(CH_3)_2$ (0.0905 mmol) were recovered from this reaction.

Reaction of $B_8H_{12} \cdot$THF and 2-Butyne. Two milliliters of THF was distilled from $LiAlH_4$ into a tared "U" trap with an nmr tube affixed to the bottom. After weighing, 0.205 g of B_8H_{12} (2.08 mmol) was distilled in. Upon warming, $B_8H_{12} \cdot$THF formed and went into solution. After a second weighing and cooling 2.75 mmol of 2-butyne was condensed in the vessel, which was then warmed to room temperature for 20 min. No bubbling was seen, but the solution turned yellow. H_2 (0.073 mmol) was present at this time. After 1 cm³ of THF and unreacted 2-butyne was distilled away, the remaining liquid was sealed in the nmr tube. A 70.6-MHz ^{11}B nmr spectra showed this liquid to contain a 2:2:1 mixture of $B_7C_2H_9(CH_3)_2$, $B_8C_2H_{10}(CH_3)_2$, and unreacted $B_8H_{12} \cdot$THF. No attempt was made to separate the products.

Reaction of *n*-B_9H_{15} and 2-Butyne. *n*-B_9H_{15} (0.205 g, 1.68 mmol), 3.60 mmol of 2-butyne, and 2 cm³ of *n*-pentane were sealed in a 250-ml bulb and allowed to warm to room temperature. A clear solution formed first but turned faint yellow after 18 hr. Measured H_2 was 0.228 mmol. Approximately 0.2 cm³ of liquid less volatile than *n*-pentane was pumped from the bulb and partially separated by low-temperature fractionation. B_6H_{10} and $B_8C_2H_{10}(CH_3)_2$ were identified by their ^{11}B nmr spectra. A crystalline material of much lower volatility which decomposed slowly displayed ^{11}B nmr resonances that could be attributed to 7,8-$B_9C_2H_{11}(CH_3)_2$. It was estimated from liquid volumes that the latter two carboranes accounted for ~60% of the *n*-B_9H_{15} consumed.

Preparation of Other $B_7C_2H_9RR'$ and $B_8C_2H_{10}RR'$ Species. These species were generated in experiments similar to those described above, *i.e.*, always using $B_8H_{12} \cdot O(C_2H_5)_2$ and a slight excess of the alkyne. The products from the reaction with C_2D_2 were white crystals, while clear liquids resulted from the reactions involving propyne, 3-hexyne, 1,4-dichloro-2-butyne, and disilylacetylene. The material obtained from the 1,4-dibromo-2-butyne reaction was a thick brown oil. The $B_7C_2H_9(C_6H_5)_2$ obtained from the tolan reaction was an unstable white solid which decomposed to a yellow-brown oil in 20–30 min. The products of the propyne and 3-hexyne reactions were partially resolved by low-temperature fractionation, but no other separations were attempted. The results of these B_8H_{12}–alkyne reactions are given in Table I.

Results and Discussion

$B_7C_2H_{11}$. *nido*-Dicarbanonaborane(11) is a sweet-smelling, air and moisture sensitive, white crystalline solid of volatility similar to decaborane(14). No hydrogen buildup, color changes, or differences in ^{11}B nmr signals have been noted on sealed samples at 25° for several days. $B_7C_2H_{11}$ yellows upon melting (~90°) and decomposes (~150°) to a mixture of 5,6-$B_8C_2H_{12}$, 1,2-$B_8C_2H_{10}$, 1,6-$B_8C_2H_{10}$, and minor amounts of other known $B_nC_2H_{n+2}$ closo carboranes.[21] Attempts to obtain mass spectra of $B_7C_2H_{11}$ at low ionization voltages on conventional mass spectrometers result in spectra of pyrolysis products. $B_7C_2H_{11}$ is soluble in all common dry nonpolar organic solvents. Although formally isoelectronic with the Lewis acid B_9H_{13}, the compound does not show a similar tendency to complex with diethyl ether or THF.

The molecular structure of $B_7C_2H_{11}$ is of major interest since the 70.6-MHz ^{11}B nmr spectrum (Figure 1A) clearly shows a $-BH_2$ triplet at +28.3 ppm (J = 125 Hz). $B_7C_2H_{11}$ thus represents the first example of a carborane containing a $-BH_2$ group. Integral $-BH_2$ units are normally found only in the lower boron hydrides (B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{12}, B_8H_{18}, and *n*-B_9H_{15}[23]), borane anions (*e.g.*, $B_3H_8^-$), and certain borane adducts (*e.g.*, $B_4H_8 \cdot CO$,[23] $B_8H_{12} \cdot CH_3CN$,[24]

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[23] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[24] J. Dobson and R. Schaeffer, *Inorg. Chem.*, 7, 402 (1968).

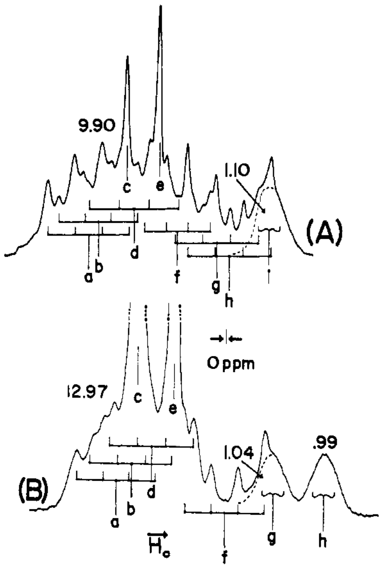

Figure 2. (A) The 220-MHz pmr spectrum of $B_7C_2H_{11}$ in CS_2. Chemical shifts (ppm relative to external TMS) and coupling constants (Hz) are: (a) −3.72, 155; (b) −3.54, 150; (c) −2.81; (d) −2.62, ~170; (e) −1.95; (f) ~−1.5, ~125; (g) −0.45, 157; (h) −0.15, 157; and (i) +0.87. (B) The 220-MHz pmr spectrum of neat $B_7C_2H_9(CH_3)_2$. Chemical shifts and coupling constants are: (a) −3.02, ~150; (b) −2.78, ~160; (c) −2.32; (d) −1.78, ~160; (e) −1.28; (f) 0, 150; (g) +1.17; and (h) +2.56. Integrated areas are given above the peaks.

and $B_9H_{13}\cdot CH_3CN$[23]). Until now, all nido carboranes contained "excess" hydrogens in bridging positions (*e.g.*, 7,8-$B_9C_2H_{13}$[22]) or as methylene protons (*e.g.*, 1,3-$B_7C_2H_{13}$[7]).

In addition to the $-BH_2$ triplet, the ^{11}B nmr spectra requires at least five additional magnetically distinct boron environments. The 220-MHz pmr spectrum (Figure 2A) also points to a molecule of low symmetry; two separate C–H signals (c and e) and at least six B–H terminal resonances are apparent. Only one bridge pmr resonance (i) of relative intensity 1 is present. The infrared spectrum (Table II) also supports a molecule of low symmetry since 18 cage vibrations are observed below 1200 cm^{-1}. Other bands characteristic of $B_nC_2H_{n+4}$ nido carboranes (and other related compounds) are noted at 1500–1600 (asymmetric B–H–B stretch), 1875–2300 (symmetric B–H–B stretch), 2500–2600 (terminal B–H stretch), and 2980–3060 cm^{-1} (cage ≫ C–H stretch).[4,22,25–27]

One possible "open" structure for $B_7C_2H_{11}$ is shown in Figure 3. This nine-particle icosahedral fragment and the placement of bridge and $-BH_2$ protons are based on crystallographic data for $B_9H_{13}\cdot C_3HCN$[23] and CsB_9H_{14}.[28] The placement of vicinal carbon atoms at positions 4 and 5 is suggested from the products obtained by pyrolyzing $B_7H_2C_{11}$[21] and from a mechanism for the B_8H_{12}–acetylene reaction (see below). We hasten to point out that nothing in our spectroscopic data precludes the possibility of a nonicosahedral geometry, and a X-ray crystal study is needed. To date, no suitable single crystals of $B_7C_2H_{11}$ have been grown.

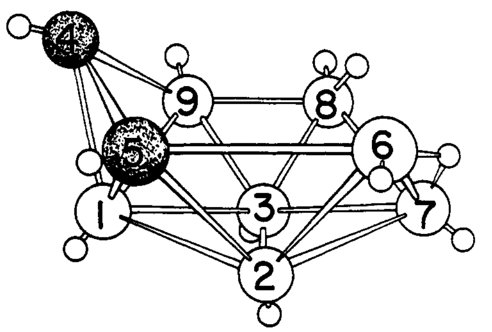

Figure 3. Possible structure for $B_7C_2H_{11}$. As drawn, this molecule represents one enantiomorph of a *d,l* pair. Note that varying placement of the bridge and/or $-BH_2$ protons is possible.

Table II. Infrared Spectra (cm^{-1})

$B_7C_2H_{11}$[a]	3048 (w), 2982 (w), 2585 (s, sh), 2505 (s), 2460 (s), 2340 (w), 1880 (vw), 1535 (m, b), 1460 (m, b), 1410 (m), 1300 (vw), 1230 (w), 1170 (m), 1125 (m), 1092 (w), 1065 (vw), 1038 (w), 1006 (w, sh), 992 (m, sh), 980 (s), 960 (w), 950 (m), 925 (m), 887 (m), 863 (m), 843 (w), 825 (w), 792 (w), 750 (w), 702 (vw)
$B_7C_2H_9(CH_3)_2$[b,c]	2965 (w), 2935 (m), 2870 (w), 2575 (vs, b), 2470 (w, sh), 1900 (w, b), 1511 (w), 1455 (m), 1444 (m, sh), 1382 (m), 1371 (m), 1168 (m), 1139 (w, sh), 1061 (vw), 1015 (w), 1000 (m), 974 (w), 945 (vw), 923 (w), 918 (w), 894 (w), 970 (w), 865 (vw, sh), 793 (vw), 762 (vw), 710 (w), 672 (vw), 640 (vw), 611 (vw)
5,6-$B_8C_2H_{12}$[a,d,e]	3060 (w), 2565 (s, b), 1950 (w), 1875 (w), 1535 (s, b), 1470 (s, b), 1300 (m), 1227 (w), 1106 (w), 1088 (m), 1055 (vw, sh), 1047 (w), 1004 (s), 995 (s), 968 (vw), 938 (m), 928 (m), 907 (vw), 892 (m), 854 (m), 841 (vw), 831 (vw), 782 (m, b), 778 (m, sh), 740 (vw), 730 (vw), 704 (w), 670 (w)
5,6-$B_8C_2H_{10}(CH_3)_2$[b,c]	2990 (w), 2973 (w), 2935 (w), 2871 (w), 2575 (s, b), 1968 (vw, sh), 1895 (w), 1545 (m), 1457 (m), 1443 (m, sh), 1388 (w), 1371 (w), 1287 (w), 1118 (vw), 1095 (vw), 1063 (w), 1018 (m), 994 (w), 949 (w), 940 (w, s), 908 (vw), 893 (vw), 870 (w), 842 (vw), 828 (w), 796 (w), 731 (vw), 718 (w), 661 (w), 625 (vw)
2,3-$B_5C_2H_5(CH_3)_2$[f]	2935 (s, b), 2865 (s), 2800 (vw), 2667 (vw), 2607 (s), 1454 (s), 1375 (w), 1260 (w), 1087 (w), 1030 (vw), 960 (vw), 895 (w), 850 (w), 810 (vw), 675 (vw)

[a] Thin film on Irtran-2 window at −196° (ref 14c, p 95). [b] Liquid film, KBr plates. [c] Liquid film, AgBr plates. [d] Nujol mull. [e] CS_2 solution in 0.1-mm liquid KBr cell *vs.* CS_2. [f] In a 5-cm KBr gas cell.

$B_7C_2H_9(CH_3)_2$. Dimethyldicarbanonaborane(11) is an air sensitive, clear liquid (mp −9°, Stock method) of moderate thermal stability at 20°. It is more stable than $B_7C_2H_{11}$; sealed samples have remained unchanged at room temperature for several months. A sample of neat $B_7C_2H_9(CH_3)_2$ was shown by ^{11}B nmr spectra to be <5% decomposed after 5 days at 80°; however, a similar sample that was held at 150° for 12 hr showed no resonances attributable to $B_7C_2H_9(CH_3)_2$. Under the latter conditions 2,3-$B_5C_2H_5(CH_3)_2$ (*vide infra*), 5,6-$B_8C_2H_{10}(CH_3)_2$, 1,2-$B_8C_2H_{10}(CH_3)_2$, and a mixture of known closo carboranes are formed.[21]

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(25) T. Onak, D. Marynick, P. Mattschei, and G. Dunks, *Inorg. Chem.*, 7, 1754 (1968).

(26) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, Jr., and T. Onak, *ibid.*, 7, 216 (1968).

(27) D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

(28) N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Commun.*, 505 (1970).

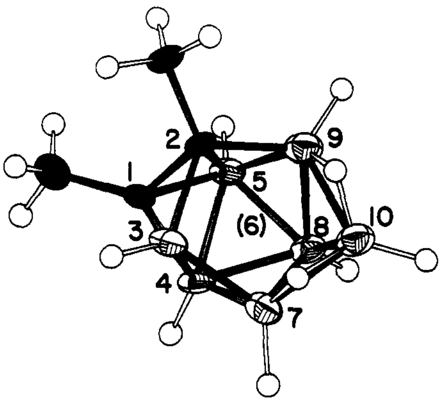

Figure 4. Crystal structure of *nido*-1,2-$B_7C_2H_9(CH_3)_2$ from ref 31. The molecule is numbered to be consistent with other known bicapped Archimedian antiprismatic structures. Here the molecule is missing position 6. The enantiomorph shown is paired with the other *d,l* form in the crystalline state.

Even using a cold inlet, the mass spectrum at 70 eV contained intense B_6C_4 and B_7C_4 and weaker B_8C_4 and B_9C_4 envelopes. At 40 eV, the B_7C_4 envelope predominated with a maximum at *m/e* 137 and a cutoff at *m/e* 140, corresponding to the $^{11}B_7{}^{12}C_4{}^1H_{15}{}^+$ ion. At 40 eV, the relative intensities were characteristic of other known nido carboranes.[29] The molecular weight was determined to be 140 (calcd for $B_7C_4H_{15}$: 138.8) by freezing point depression in cyclohexane.

The infrared spectrum (Table II) suggests the presence of B–H and B–H–B groups. Two structurally nonequivalent C–CH_3 groups are noted by the double set of bands in the regions for C–CH_3 asymmetric stretch (1440–1460 cm^{-1}) and C–CH_3 symmetric stretch (1370–1390 cm^{-1}).[30] Lack of absorption between 3000 and 3060 cm^{-1} and at 1320 and 1250–1280 cm^{-1} diminishes the possibilities for $\gg$C–H and B–CH_3 units, respectively.[30] The 18 weak cage vibrations observed between 611 and 1168 cm^{-1} suggest a molecule of low symmetry. Degradation in propionic acid with Pd catalyst yields 96% *n*-butane, providing chemical evidence that the cage carbon atoms are vicinal in $B_7C_2H_9(CH_3)_2$.

The apparent 1:1:1:2:1:1 pattern in the 70.6-MHz ^{11}B nmr spectrum (Figure 1B) is strikingly different from that for $B_7C_2H_{11}$ (Figure 1A), but it too requires at least six magnetically nonequivalent boron environments. White noise proton decoupling experiments at 70.6 MHz and comparison ^{11}B nmr spectra at 32.1 MHz support the above group of doublets and eliminate any possibility of a –BH_2 group. The 220-MHz pmr spectrum (Figure 2B) contains two methyl resonances (c and e), only one sharp apical quartet (f), and *two* distinct bridge resonances (g and h). These nmr spectra suggest that a structural difference exists between $B_7C_2H_{11}$ and $B_7C_2H_9(CH_3)_2$. It is surprising that more than one structure might be required for the $B_7C_2H_9RR'$ carborane family, especially considering that the structural differences might arise only from sublet steric or electronic effects of substituting –CH_3 for H.

Table III. Partial Mass Spectra of $B_8C_2H_{10}R_2$ Species at 70 eV

m/e	$I/I_0[B_8C_2H_{12}]$	*m/e*	I/I_0-$[B_8C_2H_{10}(CH_3)_2]$
80	8.1	110	28.0
81	14.2	111	31.0
82	5.0	112	36.0
83	7.7	113	53.0
84	3.1	114	47.0
85	3.1	115	16.6
86	3.5	116	17.0
87	4.2	117	24.0
88	6.9	118	23.0
89	8.1	119	10.5
90	12.3	120	7.5
91	10.4	121	5.8
92	9.6	122	5.4
93	6.6	123	8.5
94	4.6	124	10.1
95	3.1	125	14.9
96	5.4	126	12.5
97	1.9	127	8.8
98	4.6	128	7.1
99	8.1	129	7.5
100	13.1	130	9.5
101	11.9	131	11.9
102	10.8	132	12.2
103	13.4	133	12.9
104	15.8	134	8.5
105	12.7	135	8.5
106	11.1	136	10.5
107	7.3	137	12.5
108	11.5	138	8.5
109	10.8	139	6.4
110	8.5	140	7.5
111	11.5	141	12.9
112	19.3	142	20.0
113	15.8	143	30.0
114	21.5	144	46.0
115	25.8	145	64.0
116	33.5	146	90.0
117	50.0	147	100.0
118	86.6	148	85.0
119	100.0	149	63.0
120	80.8	150	51.0
121	44.3	151	36.0
122	32.7	152	20.0
123	29.2	153	2.0 (P + 1)
124	20.8	154	0.85 (P + 2)
125	3.1 (P + 1)		
126	2.7 (P + 2)		

Originally, we incorrectly proposed an "open" structure for $B_7C_2H_9(CH_3)_2$ (see ref 1), *i.e.*, an icosahedral fragment like that pictured for $B_7C_2H_{11}$ (see Figure 3), but with C–CH_3 groups and with both extra nonmethyl hydrogens in bridging positions. Recently, Huffman and Streib have shown the crystal structure of $B_7C_2H_9(CH_3)_2$ (Figure 4) to be intermediate between geometries normally associated with either open or closed carboranes.[31] They envision the molecule as a bicapped Archimedian antiprism from which one beltline boron atom has been removed to expose a B_4C face. We note that the B_3C_2 closed end of $B_7C_2H_9(CH_3)_2$ closely parallels the structure of the known closo carborane 1,2-$B_8C_2H_8(CH_3)_2$,[21] while the remaining four borons (and two bridging hydrogens) resemble the nido geometry for the B(2,5,6,7) atoms in $B_{10}H_{14}$.[23] This structure also agrees with the predictions of Williams[32] regarding carborane geometries. Here, the most highly coordinated vertex [B(6)] of *closo*-1,2-$B_8C_2H_8(CH_3)_2$ has been removed to generate

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[29] R. E. Williams in "Progress in Boron Chemistry," Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, Elmsford, N. Y., 1967, pp 81–90.

[30] R. N. Grimes, *J. Organometal. Chem.*, **8**, 45 (1967).

[31] J. C. Huffman and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 665 (1972).

[32] R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).

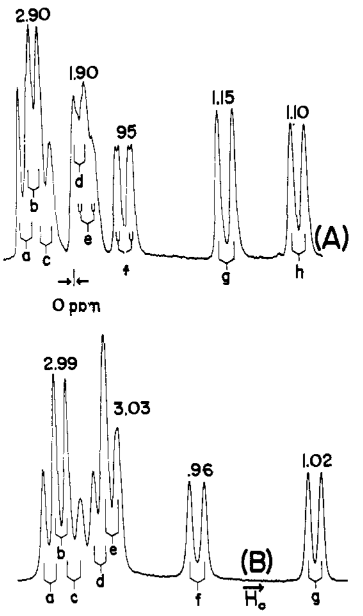

Figure 5. (A) The 70.6-MHz ^{11}B nmr spectrum of $B_8C_2H_{12}$ in *n*-pentane. Chemical shifts (ppm relative to external $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (Hz) are: (a) −8.0, 160; (b) −6.7, 155; (c) −4.8, ~150; (d) +1.3, 135; (e) +2.3, 170; (f) +8.7, 158; (g) +25.6, 180; and (h) +37.7, 158. Bridge proton splitting on peaks e and f is ~30 and 35 Hz, respectively. (B) The 70.6-MHz ^{11}B nmr spectrum of neat $B_8C_2H_{10}(CH_3)_2$. Chemical shifts and coupling constants are: (a) −4.9, 150; (b) −2.8, 140; (c) −0.7, 170; (d) +3.7, ~140; (e) +5.7, ~150; (f) +20.2, 175; and (g) +39.9, 150. Integrated areas are given above the peaks.

the *nido*-1,2-$B_7C_2H_9(CH_3)_2$ geometry. Rudolph and Pretzer[33] have deduced the same geometry by noting the 22 framework electrons of *nido*-1,2-$B_7C_2H_9(CH_3)_2$ place it in the $2n + 4$ series ($n = 9$) of nido carboranes.[34]

$B_8C_2H_{12}$. Dicarbadecaborane(12) is a white, crystalline solid (mp 92°, sealed tube) with a repugnant odor like the lower boron hydrides. It possesses moderate stability toward air and moisture, especially when in the crystalline state. Samples in sealed tubes have been stored at room temperature for over 1 year with no apparent decomposition.

Mass spectra of $B_8C_2H_{12}$ (see Table III) are characteristic of open-cage carboranes.[29] An exact mass matching experiment gave 124.16818 (calcd for $^{11}B_8{}^{12}C_2{}^1H_{12}{}^+$: 124.16835). The infrared spectrum (Table II) suggests the presence of C–H, B–H, and B–H–B units (*vide supra*). The 20 cage vibrations below 1200 cm^{-1} and eight distinct B–H doublets in the 70.6-MHz ^{11}B nmr spectrum (Figure 5A) strongly suggest a molecule of C_s symmetry. White noise proton decoupling experiments at 70.6 MHz, comparison spectra at 32.1 MHz, and a series of partially relaxed Fourier transform ^{11}B nmr spectra[35] at 70.6 MHz all show

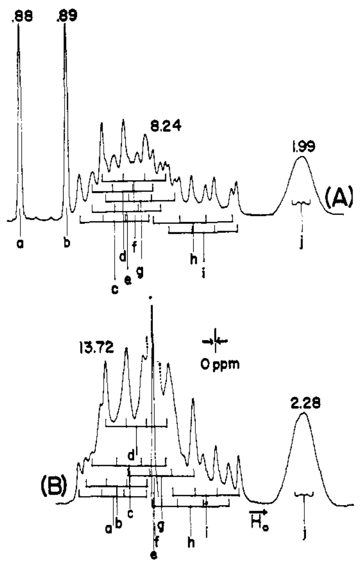

Figure 6. (A) The 220-MHz pmr spectrum of $B_8C_2H_{12}$ in CS_2. Chemical shifts (ppm relative to external TMS) and coupling constants (Hz) are: (a) −6.15; (b) −4.64; (c) −3.16, 158; (d) −2.88, 140; (e) −2.76, 157; (f) −2.53, 147; (g) −2.32, 157; (h) −0.71, 180; (i) −0.39, 155; and (j) +2.60. (B) The 220-MHz pmr spectrum of neat $B_8C_2H_{10}(CH_3)_2$. Chemical shifts and coupling constants are: (a) −3.30, 155; (b) −3.20, 140; (c) −2.8, ~170; (d) −2.55, ~140; (e) −2.05; (f) −2.00; (g) −1.8, ~150; (h) −0.89, 175; (i) −0.48, 150; and (j) +2.59. Integrated areas are given above the peaks.

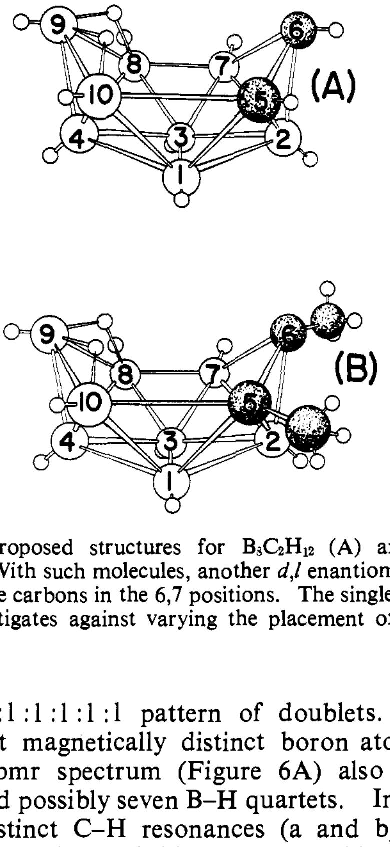

Figure 7. Proposed structures for $B_8C_2H_{12}$ (A) and $B_8C_2H_{10}$-$(CH_3)_2$ (B). With such molecules, another *d,l* enantiomorph would exist with cage carbons in the 6,7 positions. The single bridge pmr resonance mitigates against varying the placement of the bridge hydrogens.

this 1:1:1:1:1:1:1:1 pattern of doublets. This requires eight magnetically distinct boron atoms. The 220-MHz pmr spectrum (Figure 6A) also shows at least six and possibly seven B–H quartets. In addition, the two distinct C–H resonances (a and b) are well resolved, but only *one* bridge resonance (j) of intensity 2 is apparent. The doublets at higher field in Figure 5A (g and h) and the quartets at higher field in Figure 6A (h and i) are indicative of two distinct apical B–H groups (positions 2 and 4). A $B_8C_2H_{12}$ structure (Figure 7A) based on the isoelectronic species decaborane(14) is in complete accord with the above observations.

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(33) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972).

(34) At present, we are unable to say whether the same generalizations hold true for the parent species, $B_7C_2H_{11}$. If they do, a structure like that in Figure 4 might be expected. However, exceptions to these rules are already known in the cases of 1,3-$B_7C_2H_{13}$ and *i*-B_9H_{15}, both of which are generated by removing the *least* coordinated vertex from the *nido*-$B_8C_2H_{12}$ or $B_{10}H_{14}$ framework, respectively. Removing the least coordinated vertex of *closo*-1,2-$B_8C_2H_{10}$ [*i.e.*, B(10)] would generate a third possible $B_7C_2H_{11}$ structure, *i.e.*, a monocapped Archemedian antiprism with a four-boron face containing a bridge proton and a $-BH_2$ group.

(35) A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, 94, 2445 (1972).

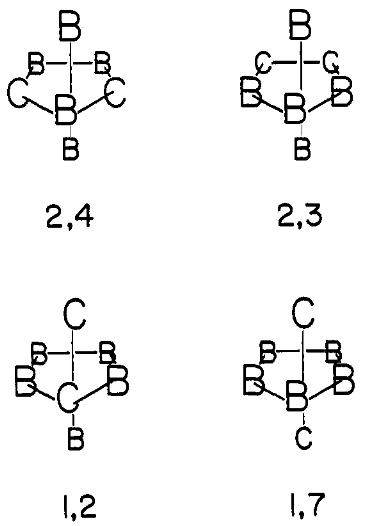

Figure 8. Skeletal isomers of $B_5C_2H_7$.

This species, 5,6-$B_8C_2H_{12}$, and another new dicarbadecaborane(12) containing nonadjacent carbon atoms, 5,7-$B_8C_2H_{12}$,[36] represent the first case of skeletal isomers in nido carboranes.

The characterization of 5,6-$B_8C_2H_{12}$ is of particular importance because it can be converted in high yield to 1,2-$B_8C_2H_{10}$ (and subsequently to 1,6- or 1,10-$B_8C_2H_{10}$) by pyrolysis.[21] Since 5,6-$B_8C_2H_{12}$ is now available in high yield from *i*-B_9H_{15}[37] and easily separated from its major contaminant (7,8-$B_9C_2H_{13}$) by utilizing their varying rates of hydrolysis in water, a non-dicarbadodecarborane(12) route now exists to the B_8 carboranes.

$B_8C_2H_{10}(CH_3)_2$. Dimethyldicarbadecaborane(12) is a thermally stable, clear liquid (mp +3°, Stock method), unreactive in air or water for several hours. Samples in sealed tubes have been kept without decomposition for up to 2 years. The mass spectrum (see Table III) is characteristic of known nido carboranes[29] with the most intense peak (m/e = 147) down several mass units from the parent ion. An exact mass matching experiment for the parent ion gave m/e = 152.20042 (calcd for ${}^{11}B_8{}^{12}C_4{}^1H_{16}{}^+$: 152.19965). The molecular weight was determined as 151 (calcd for $B_8C_4H_{16}$: 150.6) by vapor density measurements. The infrared spectrum (Table II) implies the presence of B–H–B and two C–CH_3 groups, the absence of $\gt$C–H and B–CH_3 groups,[30] and a general lack of symmetry. A 39% yield of *n*-butane from the propionic acid–Pd catalyst degradation of $B_8C_2H_{10}(CH_3)_2$ supports the presence of vicinal carbon atoms.

Both the ^{11}B and ^1H nmr spectra of $B_8C_2H_{10}(CH_3)_2$ imply that it is isostructural with $B_8C_2H_{12}$. The former (Figure 5B) is similar to that of $B_8C_2H_{12}$ (Figure 5A); and the apparent 1:1:1:1:2:1:1 pattern of doublets requires at least seven magnetically distinct borons. The latter (Figure 6B) is similar to the pmr of $B_8C_2H_{12}$ (Figure 6A), in that it contains two distinct –CH_3 signals (e and f), only one B–H–B resonance of intensity two (j), a series of overlapped B–H quartets (a, b, c, d, and g), and two sharp B–H quartets (h and i). The chemical shifts of these last two quartets suggest they arise from protons attached to the two different apical borons in this molecule. The two corresponding ^{11}B nmr doublets (f and g) are seen in Figure 5B. This evidence suggests the structure of $B_8C_2H_{10}(CH_3)_2$ (Figure 7B) is the expected dimethyl C-substituted $B_8C_2H_{12}$ species. Both structures are based on a 2640 styx formulation[23] predicted for the known $B_{10}H_{12}{}^{2-}$ ion.[38]

Table IV. Partial Mass Spectra of Dimethyldicarbaheptaborane(7) Isomers at 70 eV

m/e	I/I_0-[2,4-$B_5C_2H_5(CH_3)_2$]	I/I_0-[2,3-$B_5C_2H_5(CH_3)_2$]
80	7.4	4.9
81	10.4	6.2
82	14.3	6.6
83	42.2	7.4
84	18.7	5.6
85	10.0	4.9
86	6.9	2.6
87	5.6	3.1
88	3.0	0.5
89	3.5	0.7
90	3.9	1.3
91	10.4	2.2
92	7.4	3.3
93	6.9	4.4
94	7.8	5.1
95	11.7	7.7
96	16.1	10.5
97	18.7	11.6
98	23.9	7.9
99	11.7	6.3
100	6.9	2.3
101	7.8	1.7
102	5.7	1.1
103	5.7	1.3
104	6.5	1.5
105	3.0	1.4
106	4.8	2.1
107	6.5	4.5
108	15.2	10.1
109	36.1	28.8
110	64.4	54.3
111	76.1	66.3
112	71.8	68.5
113	100.0	100.0
114	77.8	78.3
115	6.0 (P + 1)	6.1 (P + 1)
116		1.2 (P + 2)

2,3-$B_5C_2H_5(CH_3)_2$. *closo*-2,3-Dimethyldicarbaheptaborane(7) was recognized as a new B_5C_2 isomer when its mass spectrum did not match that of the known 2,4-$B_5C_2H_5(CH_3)_2$ species (see Table IV).[5,17] The mass spectra of this new liquid did resemble those of known closo carboranes.[29] An exact mass match for the parent ion gave m/e 114.13246 (calcd for ${}^{11}B_5{}^{12}C_4{}^1H_{11}{}^+$: 114.13261). The infrared spectrum (Table II) suggested only B–H units and one type of C–CH_3 group in a molecule of high symmetry. The 70.6-MHz ^{11}B nmr spectrum consisted of doublets at δ −10.6 (J = 150 Hz), −5.2 (J = 150 Hz), and +12.1 ppm (J = 170 Hz) in relative intensity 2:1:2. Of the four possible $B_5C_2H_7$ isomers (see Figure 8), only the 1,2; 2,3; and 2,4 isomers were consistent with this ^{11}B nmr spectrum. The known 2,4 isomer,[39] prepared as in

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[36] P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 1265 (1971). The 5,7 numbering refers to Figure 7.

[37] R. Schaeffer and E. Walter, to be submitted for publication.

[38] P. H. Wilks and J. C. Carter, *J. Amer. Chem. Soc.*, **88**, 3441 (1966).

[39] Under the nomenclature rules adopted by IUPAC [*Pure Appl. Chem.*, **30**, 681 (1972)] the heteratoms in $B_5C_2H_7$ receive the lowest numbers (see Figure 8).

ref 5, was not considered because its 70.6-MHz ^{11}B nmr spectrum displayed doublets at δ -8.5 (J = 178 Hz), -5.9 (J = 169 Hz), and $+17.3$ ppm (J = 178 Hz) in relative intensity 1:2:2. The single methyl resonance at δ -0.67 ppm in the 100-MHz pmr spectrum was evidence against a 1,2 isomer, which might be expected to contain two distinct methyl pmr resonances. We concluded that this liquid was a new 2,3 cage isomer of $B_5C_2H_5(CH_3)_2$.

2,3-$B_5C_2H_7$. Mass spectra of the diethyl ether recovered from the B_8H_{12} and acetylene reactions showed that it contained a very small amount of a boron containing material of like volatility. After distilling away the bulk of the ether, a small amount of material contaminated with B_6H_{10} gave mass envelopes of *m/e* 86 and a 19.3-MHz ^{11}B nmr spectra of 2:2:1 doublets[40] as expected for a parent 2,3-$B_5C_2H_7$ species. Lack of more material prohibited further characterization.

Other $B_7C_2H_9RR'$ and $B_8C_2H_{10}RR'$ Species. In attempts to produce crystals more suited for X-ray structure determinations, the nido carboranes listed in Table I were synthesized. Except for the B_8H_{12}–diphenylacetylene reaction, the ^{11}B nmr spectra of the products of every reaction displayed resonances characteristic of both B_7C_2 and B_8C_2 cages; however, only $B_7C_2H_{10}CH_3$ and $B_7C_2H_9D_2$ showed the -BH_2 triplet characteristic of the $B_7C_2H_{11}$ structure. All of the $B_8C_2H_{10}RR'$ ^{11}B nmr spectra were similar to those shown for $B_8C_2H_{12}$ and $B_8C_2H_{10}(CH_3)_2$. As R became larger, the $B_7C_2H_9RR'$ species predominated, but the thermal stability of both carboranes decreased markedly.

Formation of B_7C_2 and B_8C_2 Frameworks. It is perhaps interesting to speculate on a mechanism by which nido carboranes form from octaborane(12), especially in view of the fact that both B_7C_2 and B_8C_2 skeletons have been characterized as products of a single reaction system.

Since the strong Lewis acid behavior of B_8H_{12} is well documented,[24] one might envision first the addition of the alkyne (acting as a weak Lewis base) above B(8) (Figure 9A) to form a $B_8H_{12}C_2R_2$ species (Figure 9B). Such an intermediate can be envisioned as a B_8H_{12}·ligand compound with a filled molecular orbital of the triple bond in C_2R_2 donating to the vacant orbital speculated to be on a 3421 B_8H_{12}·fragment.[24] Deuterium labeling and kinetic studies of the gas-phase tetraborane(10)–acetylene reaction[41] provide evidence for a similar Lewis acid–acetylene addition intermediate $B_4H_8C_2H_2$. Formation of a $B_9H_{13}C_2H_2$ intermediate, may likewise be of importance in isononaborane(15)–acetylene reactions.[37] Note that it is also possible to envision these intermediates as members of the $B_nC_2H_{n+6}$ series of arachno carboranes.[33,42]

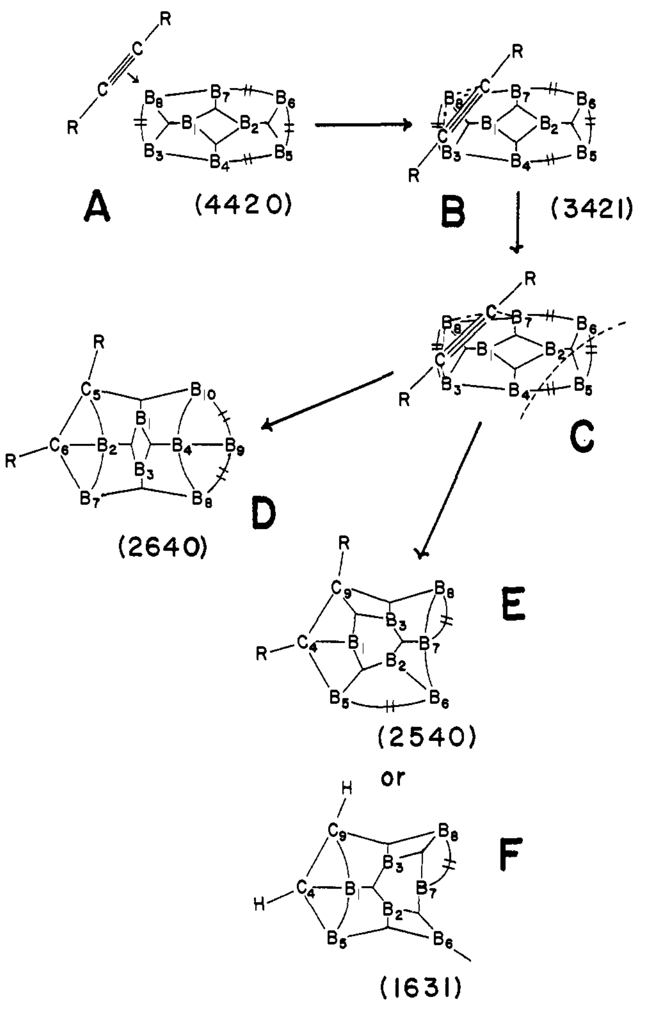

Figure 9. One possible mechanism for *nido*-$B_7C_2H_9R_2$ and *nido*-$B_8C_2H_{10}R_2$ formation involving (A) RC≡CR attack on octaborane(12), (B) formation of a $B_8H_{12}C_2R_2$ intermediate with B_8H_{12}·ligand geometry, (C) formation of C–B(3) and C–B(7) bonds, followed by (D) formation of C–B(6) bond, H_2 loss, and cage closure to $B_8C_2H_{10}R_2$, or (E) formation of C–B(6) bond, BH_3 loss, and cage closure to an *open* $B_7C_2H_9R_2$. The numbers in parentheses refer to *styx* formulations[23] for the species shown. (F) shows one possible 1631 *styx* formulation for a *nido*-$B_7C_2H_{11}$. All terminal hydrogens have been omitted for clarity. The correct numbering for Figures 9E and 9F is shown in Figure 4.

Formation of the $B_8C_2H_{10}R_2$ nido carborane is then easily explained by formation of C–B(3) and C–B(7) bonds (Figure 9C), loss of H_2, and closure of the cage with a C–B(6) bond (not depicted) to a decaborane(14)-like molecule (Figure 9D). The electron delocalization possible in the numerous resonance forms of a $B_{10}H_{14}$ basket arrangement of cage atoms undoubtably accounts for much of the thermal and hydrolytic stability of $B_8C_2H_{12}$.

Formation of the *open* $B_7C_2H_9R_2$ would also result from forming these same three bonds, loss of BH_3 at the other (B(5)) end of the intermediate (dotted line in Figure 9C), and closure to a nine particle fragment (Figure 9E or 9F).[43] Diborane(6) was found in some reactions, however, not the stoichiometric amount required to account for all the $B_7C_2H_9R_2$ generated. It is interesting to note that the nature of R may impart subtle steric and electronic effects upon any intermediate and, hence, determine its propensity to

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(40) Chemical shifts (ppm relative to $BF_3·O(C_2H_5)_2$) and coupling constants (Hz) were approximately: -15 (140), $+2$ (155), and $+25$ (160). A 70.6-MHz ^{11}B nmr spectrum of the known 2,4-$B_5C_2H_7$ displayed doublets at -6.6 (185), -3.5 (175), and -22.0 (180) in 1:2:2 relative intensity.

(41) D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 387 (1971).

(42) The arachno classification given in ref 33 ($2n + 6$ skeletal electrons) is based on a eight boron framework containing 22 electrons, *i.e.*, two electrons from each proton + one electron from each bridging hydrogen + two electrons donated by the ligand, in this case, acetylene.

(43) Removal of boron atoms other than B(5), *e.g.*, B(4), B(6), or B(7), results in a beltline B_7C_2 species containing one boron with insufficient connectivity. Such structures are also inconsistent with the moderate thermal stability of $B_7C_2H_9R_2$ species.

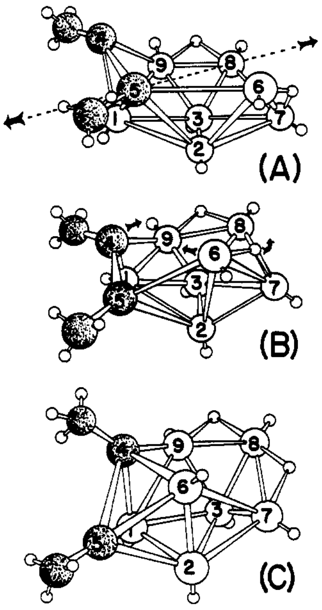

Figure 10. Probable mechanism for 1,2-$B_7C_2H_9(CH_3)_2$ formation by deformation of *nido*-$B_7C_2H_9(CH_3)_2$ geometry (A, Figure 9E) to form apical carbon site (B), followed by bridge proton migration and C(4)–B(6) bond formation to proven partially closed structure (C). The correct numbering for structure C is shown in Figure 4.

lose H_2 or BH_3. This would be consistent with the invariant *relative* yields of B_7C_2 and B_8C_2 species with a given acetylene but differing ratios of products for different acetylenes.

The X-ray crystal structure of $B_7C_2H_9(CH_3)_2$[31] and the similarity of ^{11}B nmr spectra for larger R-substituted B_7C_2 species imply that further closing of the $B_7C_2H_9R_2$ cage has occurred.[44] Again, we are unable to ascertain whether steric and electronic effects of R are responsible, but we note that the further closing involves only minimal distortion of the molecule (see Figure 10). In fact, B(1), B(2), and B(3) remain immobile throughout the closure. To effect closure of the open $B_7C_2H_9(CH_3)_2$ (Figure 10A), one merely pulls on C(5) and B(8) to elongate the molecule, thus bringing C(4) and B(6) together (Figure 10B). Migration of one bridge hydrogen and formation of a C(4)–B(6) bond gives the proven[31] $B_7C_2H_9(CH_3)_2$ structure (Figure 10C).

No evidence exists to suggest that fragments such as $B_7H_9\cdot$ are required as intermediates; all of the B_8H_{12} compounds employed as reactants are stable in the general temperature range for reactions (*ca.* −30 to 0°). The chemical and X-ray evidence for vicinal carbon atoms and spectral evidence for similar carbon placement in B_7C_2 and B_8C_2 fragments suggest that major skeletal rearrangements have not occurred.

The reaction of *n*-B_9H_{15} and acetylene might proceed through C_2H_2 attack on the B(5,6,7,8) side of the molecule (the end resembling B_8H_{12}; see Figure 1, ref 35), hydrogen loss and formation of a $B_9H_{13}C_2H_2$ intermediate, followed by additional hydrogen loss with cage closure to 7,8-$B_9C_2H_{13}$ or followed by B(3)H_3 loss to 5,6-$B_8C_2H_{12}$. It is doubtful that B_8H_{12} is involved as intermediate in this reaction, because no $B_7C_2H_{11}$ was noted among the products.

Nomenclature. All boron nomenclature and numbering in this paper conforms to the rules adopted by the IUPAC in July, 1971.[39] In many cases the numbering may be different from that used in the references cited.

Acknowledgments. We gratefully acknowledge the support of the National Science Foundation through Grant No. GP24266X and the Indiana University Foundation for a graduate fellowship to R. R. R. We are also indebted to Mr. A. O. Clouse and Mr. T. Roseberry for assistance in obtaining the ^{11}B nmr spectra and to Mr. J. C. Huffman and Dr. William E. Streib for preliminary communication of the X-ray crystal structure data.

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[44] The ^{11}B nmr spectra of $B_7C_2H_{11}$, $B_7C_2H_9D_2$, and $B_7C_2H_{10}CH_3$ are all compatible with the open 1631 structure shown in Figure 9F and probably have not closed up further.