

Transition-Metal-Promoted Reactions of Boron Hydrides. 7.¹ Platinum(II) Bromide Catalyzed Cage Growth and Dehydrocoupling Reactions of Diborane with Small Polyhedral Carboranes and Boranes: Synthesis of a New Arachno Carborane, 5,6-C₂B₆H₁₂, and the Diborane-Coupled Compounds 2:1',2'-[1,6-C₂B₄H₅][B₂H₅] and 2:1',2'-[B₅H₈][B₂H₅]

Edward W. Corcoran, Jr., and Larry G. Sneddon*

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received July 8, 1985

Abstract: Platinum dibromide has been found to promote cage growth and dehydrocoupling reactions between diborane and small, polyhedral carboranes and boranes, yielding either larger single-cage compounds or bridge-substituted diborane-polyhedral carborane/borane complexes. For the catalyzed reaction of diborane with 1,5-C₂B₃H₅, a cage growth reaction occurs to give the new arachno carborane, 5,6-C₂B₆H₁₂. For 1,6-C₂B₄H₆ and B₃H₉, cage growth reactions do not take place but instead the coupled diborane-polyhedral cage species 2:1',2'-[1,6-C₂B₄H₅][B₂H₅] and 2:1',2'-[B₅H₈][B₂H₅] are obtained.

Our previous work has shown that transition-metal catalysts can be used to promote a variety of transformations involving polyhedral boranes, including acetylene addition,²⁻⁴ olefin coupling,⁵ and dehydrodimerization^{1,6} reactions and has resulted in the development of new high yield synthetic routes to both carboranes and boron-boron coupled multicage clusters.

In the previous paper¹ in this series, we reported that platinum(II) bromide is an attractive dehydrodimerization catalyst for polyhedral boranes and carboranes, giving both high yield and high selectivity of product under mild conditions. These results suggested several other potential applications for dehydrocondensation catalysts in polyhedral boron cage chemistry. For example, if, instead of coupling two polyhedral cages, these catalysts could be used to promote a dehydrocondensation reaction between a polyhedral borane or carborane and diborane, then this might ultimately lead to a cage growth reaction. With these aims in mind, we have investigated the platinum(II) bromide promoted reactions of diborane with 1,5-C₂B₃H₅, 1,6-C₂B₄H₆, and B₃H₉, and the results of these studies are reported herein.

Experimental Section

Materials. PtBr₂ was used as received from Aldrich Chemicals. Pentaborane(9) was obtained from laboratory stock. The small closo carboranes, 1,5-C₂B₃H₅ and 1,6-C₂B₄H₆, were purchased from Chemical Systems, Inc., and were purified by vacuum line fractionation. Diborane was prepared by standard literature method.⁷ Decane was dried over and distilled from P₂O₅. All manipulations involving boranes or carboranes were carried out in vacuo.

Physical Measurements. Boron-11 NMR spectra at 115.5 MHz were obtained on a Bruker WH-360 Fourier transform spectrometer located at the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. Proton NMR spectra at 200 MHz, boron-11 NMR at 64.2 MHz, carbon-13 NMR at 50.3 MHz, and two-dimensional ¹¹B-¹¹B NMR experiments were obtained on an IBM WP-200SY Fourier transform spectrometer. Broad-band ¹¹B decoupling was accomplished by square-wave modulation of a 64.2-MHz signal which was generated by a PTS160 synthesizer driving an EN1320L broad-band amplifier with appropriate band-pass filtering. Boron-11 chemical shifts were referenced to BF₃·O(C₂H₅)₂ = 0.0 ppm with a negative sign indicating an upfield

shift. All proton and ¹³C chemical shifts were measured relative to internal residual solvent from the lock solvent (C₆D₆, 99.5%) and then referenced to Si(CH₃)₄ = 0.00 ppm, with a positive value indicating a downfield shift.

Two-dimensional ¹¹B-¹¹B NMR experiments⁸ were conducted as follows: a 64.2-MHz ¹¹B shift correlated COSY experiment was performed with *N*-type selection parameters. The sweep width in the *F*₂ direction was 10000 and in the *F*₁ direction, 5000. A total of 128 increments (increment size of 0.1 ms) was collected, each slice having 512 *F*₂ data points. The data were zero-filled once in the *F*₁ direction and subjected to 2D Fourier transformation with sine-bell apodization in both domains. A total of 160 scans was taken for each increment with a recycle time of 0.1 s (Table I).

High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer interfaced to a Kratos DS50-S data system. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer.

5,6-C₂B₆H₁₂.⁹ A reaction flask containing 0.37 g of PtBr₂ (1.1 mmol) was evacuated and charged with 5.7 mmol of 1,5-C₂B₃H₅, 10.0 mmol of B₂H₆, and ~4 mmol of dried hexanes (distilled from P₂O₅). The mixture was stirred at room temperature for 48 h with periodic removal of hydrogen. The volatiles were then fractionated through a -30, -78, -196 °C trap series, with the 5,6-C₂B₆H₁₂ (~1 mmol) stopping in the -78 °C trap: exact mass for ¹²C₂¹¹B₆¹H₁₂ calcd 102.1500, found 102.1507; IR (~3-cm cell pressure) 2580 (s), 2510 (m), 2540 (w), 1140 (w), 995 cm⁻¹ (m).

The carborane, when heated to 65 °C, slowly converted to C₂B₆H₁₀,¹⁰ as indicated by ¹¹B NMR. The conversion was about 75% complete after 4 h.

2:1',2'-[1,6-C₂B₄H₅][B₂H₅].¹¹ A 0.37-g sample of PtBr₂ (1.1 mmol) was allowed to react with 2.8 mmol of 1,6-C₂B₄H₆, 5.3 mmol of B₂H₆,

(8) (a) Bax, A. "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; Delft University Press: Delft, Holland, 1982. (b) Finster, D. C.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 400-401. (c) Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29-37.

(9) Numbering was taken from the full name of this compound: 2*H*,4*H*-(2,8- μ H),(4,10- μ H)-5,6-dicarba-1,7-didebor[*C*₃₀-(1*v*⁶3*v*⁴33)- Δ ¹⁶-closo]decaborane(12); for rules describing this nomenclature, see: (a) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1981**, *20*, 1333-1341. (b) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2228-2235. (c) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2236-2245. (d) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1984**, *23*, 4132-4143.

(10) Gotcher, A. J.; Ditter, J. F.; Williams, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 7514-7516.

(11) The full name for this compound is 1,6-dicarba-2'*H*,3'*H*-(2',3'- μ H)[(6*v*)[*O*_h-(141)- Δ ⁸-closo]-2-commo-1'-(3*v*)[*T*_h-(13)- Δ ⁴-closo(-1*v*)⁴]octaborane(10); we prefer the shorter version, 2-[diboran(6)-*u*-yl]-closo-1,6-dicarbahexaborane(6); rules describing this nomenclature are contained in ref 9 of this paper.

(1) For part 6, see: Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793-7800.

(2) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857-2858.

(3) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955-3962.

(4) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506-514.

(5) Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693-1694.

(6) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

(7) Norman, A. D.; Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 15-19.

Table I. ^{11}B , ^1H , and ^{13}C NMR Data

compound	nucleus	δ^a (J(Hz) assignment)	rel areas
5,6- $\text{C}_2\text{B}_6\text{H}_{12}$	$^{11}\text{B}^b$	7.8 (d, 179, B_9), -10.6 (d, 160, B_3), -17.6 (t, 134, $\text{B}_{2,4}$, $J_{\text{B-H}\mu} = 28$), -29.5 (d, 160, $\text{B}_{8,10}$), $J_{\text{B-H}\mu} = 39$	1:1:2:2
	$^1\text{H}^c$	3.56 (q, $\text{B}_9\text{-H}$, $J = 168$), 2.62 (q, $\text{B}_3\text{-H}$, $J = 157$), 2.17 (q, $\text{B}_{8,10}\text{-H}$, $J = 146$), 1.42 (q, $\text{B}_{2,4}\text{(c or a)-H}$, $J = 146$), 0.74 (s, C-H), 0.06 (q, $\text{B}_{2,4}\text{(a or e)-H}$, $J = 146$), -2.61 (s, $\text{H}\mu$)	1:1:2:2:2:2:2
	$^{13}\text{C}^d$	-10.40 ($\text{C}_{5,6}$)	
2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5]	$^{11}\text{B}^{b,e}$	-3.9 (t, 154, $\text{B}_{1,2}$, $J_{\text{B-B}} = 23$), -12.6 (d, 202, $\text{B}_{3,5}$), -16.0 (d, 128, B_4), -23.7 (s, B_2)	2:2:1:1
	$^1\text{H}^{c,f}$	2.30 (s, C-H), -1.50 (s, $\text{H}\mu$)	
2:1',2'-[B_3H_8][B_2H_5]	$^{11}\text{B}^{b,g}$	-1.5 (t, 128, $\text{B}_{1,2}$, $J_{\text{B-B}} = 26$), -10.9 (d, 161, $\text{B}_{3,5}$, $J_{\text{B-B}} = 18$), ~ -11 (s, B_2), $^h -12.0$ (d, 161, B_4 , $J_{\text{B-B}} = 19$), -50.5 (d, 193, B_1)	2:2:1:1:1
	$^1\text{H}^{c,f}$	-2.75 (s, $\text{H}\mu$)	

^a Key: s = singlet, d = doublet, t = triplet, q = quartet; all shifts are in ppm. ^b Boron-11 NMR at 64.2 MHz, run at 7 °C, dried C_6D_6 as the lock solvent. ^c Proton NMR at 200 MHz, run at 7 °C, dried C_6D_6 as the lock solvent. ^d Carbon-13 NMR at 50.3 MHz, run at 7 °C, dried C_6D_6 as the lock solvent; ^1H decoupled. ^e Resonance attributed to 2:1'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5] appeared in the spectrum at 24.8 (q, B_1 , $J_{\text{B-B}} = 94$). ^f Terminal B-H protons not resolved. ^g Resonance attributed to 2:1'-[B_3H_8][B_2H_5] appeared in the spectrum at 31.4 (q, B_1 , $J_{\text{B-B}} = 93$). ^h Resonance obscured by $\text{B}_{3,5}$ and B_4 resonances.

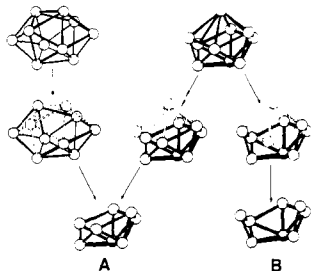


Figure 1. Derivation of eight-vertex arachno cage structures from closo ten-vertex polyhedrons.

and ~ 3 mmol of dried decane at room temperature, in vacuo, with periodic removal of hydrogen. After 48 h, the mixture was fractionated through a -60 , -95 , -196 °C trap series, with about 0.5 mmol of 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5] being retained in the -95 °C trap. The reaction consumed 0.7 mmol of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ and 0.8 mmol of B_2H_6 ; exact mass for $^{12}\text{C}_2^{11}\text{B}_6^1\text{H}_{10}$ calcd 100.1343, found 100.1327. Moderate heating of the coupled compound (40 °C) for 1 h totally decomposed it to 1,6- $\text{C}_2\text{B}_4\text{H}_6$ and B_2H_6 according to the ^{11}B NMR spectrum.

2:1',2'-[B_3H_8][B_2H_5].¹² In a typical reaction, 0.35 g of PtBr_2 powder (1.0 mmol) was stirred with 2.0 mmol of B_3H_9 , 10.0 mmol of B_2H_6 , and ~ 3 mmol of dried decane at room temperature, in vacuo, with periodic removal of hydrogen. After 48 h, the mixture was separated by vacuum-line fractionation through a -45 , -78 , -196 °C trap series. About 0.1 mmol of 2:1',2'-[B_3H_8][B_2H_5] was isolated in the -78 °C fraction, while 0.1 mmol of B_3H_9 and 0.4 mmol of B_2H_6 were consumed by the reaction: exact mass for $^{11}\text{B}_7^1\text{H}_{13}$ calcd 90.1669, found 90.1671; IR (~ 3 -cm cell pressure, slow sample decomposition) 2600 (s), 2550 (m), 2500 (m), 1850 (w), 1580 (s), 1490 (w), 1400 (w), 1260 (w), 1170 (s), 1149 (w), 1089 (s), 905 (w), 819 cm^{-1} (m).

Moderate heating of the compound (40 °C) for 2 h caused sample decomposition to B_2H_6 and B_3H_9 , as seen in the ^{11}B NMR. Decomposition was complete after 3 h.

Results

The reaction of 1,5- $\text{C}_2\text{B}_3\text{H}_5$ with B_2H_6 in the presence of platinum(II) bromide was carried out in vacuo at room temperature for 48 h with periodic removal of evolved hydrogen. Vacuum-line fractionation of the reaction mixture resulted in the isolation of one product in reasonable purity stopping in a -78 °C trap. Williams¹⁰ and Burg¹³ independently studied the thermally initiated reaction of B_2H_6 with 1,5- $\text{C}_2\text{B}_3\text{H}_5$ and isolated from that reaction the carborane $\text{C}_2\text{B}_6\text{H}_{10}$. Exact mass measurements on the compound produced in the platinum(II) bromide promoted reaction are, however, consistent with the formula, $\text{C}_2\text{B}_6\text{H}_{12}$, and the spectroscopic data for the compound are substantially different than that reported for $\text{C}_2\text{B}_6\text{H}_{10}$.

A carborane of the formula $\text{C}_2\text{B}_6\text{H}_{12}$ would be an example of a $n + 3$ arachno skeletal-electron system (8 cage atoms and 11

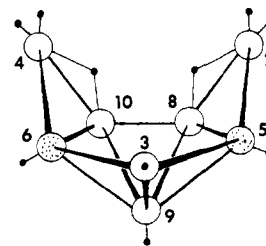


Figure 2. Proposed structure for 5,6- $\text{C}_2\text{B}_6\text{H}_{12}$.

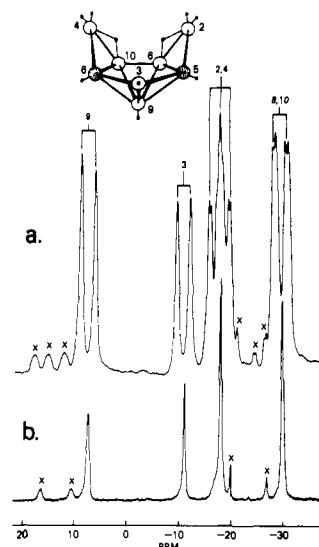


Figure 3. ^{11}B NMR spectrum (64.2 MHz) of 5,6- $\text{C}_2\text{B}_6\text{H}_{12}$: (a) proton spin-coupled; (b) proton spin-decoupled. X indicates impurity.

skeletal-electron pairs) and would be expected to adopt an open-cage geometry based on a regular polyhedron missing two vertices. The only previously reported examples of eight-vertex arachno cage systems are B_8H_{14} and $\text{B}_8\text{H}_{12}\text{L}^{14}$ ($\text{L} = \text{CH}_3\text{CN}$, NEt_3 , or Et_2O). These compounds have not yet been structurally characterized; however, from the spectroscopic data,^{14,15} they are proposed to have structures based on a bicapped square-antiprism missing two adjacent five-coordinate vertices, as shown in Figure 1 (structure A). It should be noted that this type of structure has also been found for eight-vertex $n + 2$ skeletal-electron systems. For example, this structure has been confirmed by means of single-crystal X-ray studies for B_8H_{12} ,¹⁶ ($\eta\text{-C}_5\text{H}_5$)Co(Ph) $_4\text{C}_4\text{B}_3\text{H}_3$,¹⁷ and ($\eta\text{-C}_6\text{Me}_6$)Fe(Me) $_4\text{C}_4\text{B}_3\text{H}_3$ ¹⁸ and proposed,

(12) Full name for this compound: 2'H,3'H-(2',3'- μH), (2,3- μH), (2,5- μH), (3,4- μH), (4,5- μH)[(5 ν)] $[\text{O}_h\text{-}(141)\text{-}\Delta^8\text{-closo}(-1\nu)^6\text{-}2\text{-commo-}1'\text{-}(3\nu)\text{[}T_r(13)\text{-}\Delta^4\text{-closo}(-1\nu)^4\text{]heptaborane}](13)$; we prefer the shorter version, 2-[diboran(6)- μ -yl]-nido-pentaborane(9); rules describing this nomenclature are contained in ref 9 of this paper.

(13) Reilly, T. J.; Burg, A. B. *Inorg. Chem.* **1974**, *13*, 1250.

(14) Dobson, J.; Schaeffer, R. *Inorg. Chem.* **1968**, *7*, 402-408.

(15) Moody, D. C.; Schaeffer, R. *Inorg. Chem.* **1976**, *15*, 233-236.

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

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

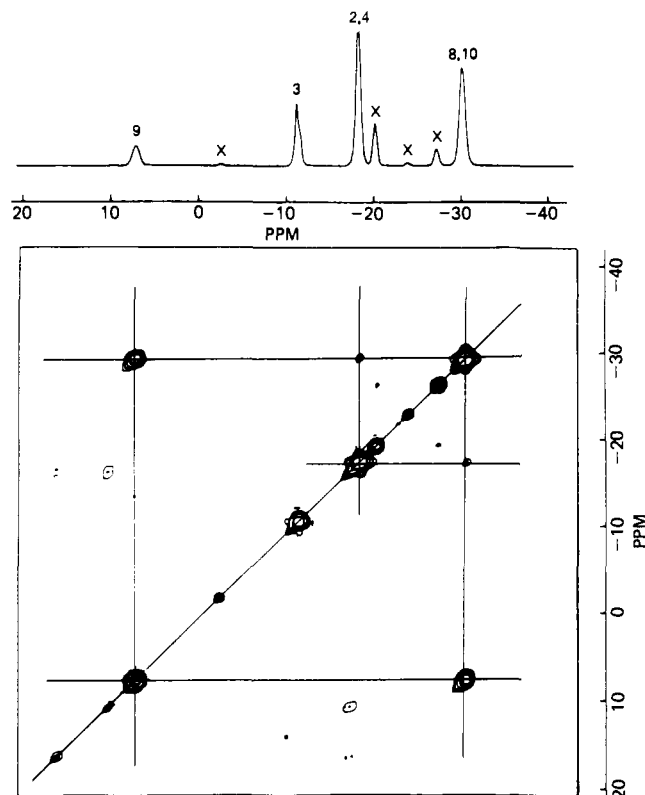


Figure 4. Two-dimensional proton spin-decoupled ^{11}B NMR spectrum (64.2 MHz) of $5,6\text{-C}_2\text{B}_6\text{H}_{12}$. X indicates impurity.

again based on the spectroscopic data, for $\text{Me}_4\text{C}_4\text{B}_4\text{H}_4^{19}$ and $\text{C}_2\text{B}_6\text{H}_{10}$.¹⁰ Thus, both eight-vertex arachno and nido cage systems appear to favor this structure. The spectroscopic data for the new carborane $5,6\text{-C}_2\text{B}_6\text{H}_{12}$ is, however, inconsistent with this type of geometry and favors instead the structure shown in Figure 2. This structure cannot be derived from a bicapped square-antiprism, but can be generated in a straightforward manner from the alternate close C_{3v} polyhedron shown in Figure 1 by the removal of the six-coordinate and one five-coordinate vertices (structure B). A similar type of structure has, in fact, been established²⁰ for the ferraborane $[\text{N}(\eta\text{-C}_4\text{H}_9)_4]^+[\text{Fe}(\text{CO})_4\text{B}_7\text{H}_{12}]^-$.

Supporting the proposed structure, the ^{11}B NMR spectrum (Figure 3) of the compound shows four resonances of relative intensities 1:1:2:2. The presence of two -BH_2 groups is clearly indicated by the triplet resonance of intensity two at -17.6 ppm. This peak is also seen to have additional fine structure characteristic of coupling with a bridging hydrogen ($J \approx 28$ Hz). The doublet at -29.5 ppm has similar fine structure ($J = 39$ Hz) and is therefore assigned to the 8,10-borons in the structure. The two remaining borons give rise to the two sharp doublets at lower field and are assigned to B3 and B9. These assignments and the proposed structure are additionally supported by the results of a 2D NMR investigation of the compound.

Grimes has recently demonstrated^{8b,c} that 2D J -correlated ^{11}B NMR can be used to determine boron-atom connectivities in polyhedral boranes and carboranes. These techniques were applied to $5,6\text{-C}_2\text{B}_6\text{H}_{12}$, and its 2D ^{11}B NMR spectrum is shown in Figure 4. The peaks on the diagonal correspond to the 1D proton spin-decoupled ^{11}B NMR spectrum, while the off-diagonal cross-peaks indicate boron-boron connectivity. In agreement with the proposed structure for $5,6\text{-C}_2\text{B}_6\text{H}_{12}$, cross-peaks are observed between B8,10 and B9 and between B8,10 and B2,4. The expected

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

(19) Fehlner, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8355-8356; **1980**, *102*, 3424-3430.

(20) (a) Hollander, O.; Clayton, W. R.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1974**, 604-605. (b) Mangion, M.; Clayton, W. R.; Hollander, O.; Shore, S. G. *Inorg. Chem.* **1977**, *16*, 2110-2114.

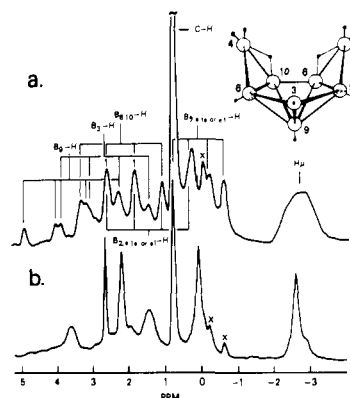


Figure 5. ^1H NMR spectrum (200 MHz) of $5,6\text{-C}_2\text{B}_6\text{H}_{12}$: (a) ^{11}B spin-coupled; (b) ^{11}B spin-decoupled. X indicates impurity.

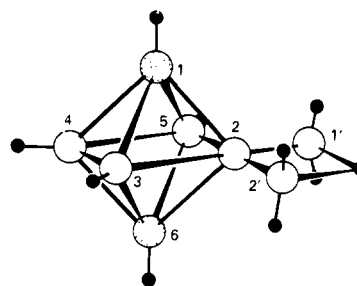


Figure 6. Proposed structure for $2:1',2'\text{-}[1,6\text{-C}_2\text{B}_4\text{H}_5][\text{B}_2\text{H}_5]$.

cross-peak was not observed between B3 and B9, however. This may arise because B3 is situated between the two carbon atoms on the open face, resulting in a localization of the bonding and decreased interactions with B9. We have previously noted²¹ similar behavior for the boron situated between two carbons on the open face of the carborane $\text{C}_4\text{B}_7\text{H}_{11}$.

The 200-MHz ^{11}B spin-decoupled ^1H NMR spectrum (Figure 5) is also consistent with the proposed structure for $5,6\text{-C}_2\text{B}_6\text{H}_{12}$, showing seven different resonances corresponding to the five types of terminal -BH , the -CH , and the B-H-B bridging protons. The chemical shift of the bridging protons (-2.61 ppm) is at somewhat higher field than is normally observed for most boron hydrides but is in the range observed for B_8H_{12} (-2.33 and -3.17 ppm)²² and B_8H_{14} (-3.20 ppm).¹⁵ As expected, the ^{13}C NMR spectrum shows only a single resonance, further indicating equivalent carborane carbons.

The $5,6\text{-C}_2\text{B}_6\text{H}_{12}$ was found to be somewhat unstable in the liquid phase at room temperature, and thermolysis of the compound in vacuo at 65°C resulted in H_2 evolution and transformation to the nido carborane $\text{C}_2\text{B}_6\text{H}_{10}$.

The reaction of $1,6\text{-C}_2\text{B}_4\text{H}_6$ with excess B_2H_6 in the presence of catalytic amounts of PtBr_2 was carried out at room temperature for 48 h with periodic removal of evolved H_2 and resulted in the isolation of a single product in a -95°C trap. Repeated fractionations into a -95°C trap were needed, however, to obtain the product in pure form.

Exact mass determinations on the compound established the formula $\text{C}_2\text{B}_6\text{H}_{10}$; however, the spectral data indicated that the compound was not a single-cage carborane but instead had the coupled diborane-carborane structure shown in Figure 6. The structure is composed of a $1,6\text{-C}_2\text{B}_4\text{H}_5$ -carborane cage which is linked at B2 to an exopolyhedral $\text{-B}_2\text{H}_5$ unit by means of a boron-boron-boron three-center bond. The compound can also be viewed as a μ -substituted carborane derivative of diborane. Such a structure is, of course, very unusual but is not without precedent. In particular, we have recently reported²³ the synthesis and

(21) Astheimer, R. J.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 1928-1934.

(22) Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1972**, *11*, 1242-1244.

(23) Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1985**, *4*, 721-726.

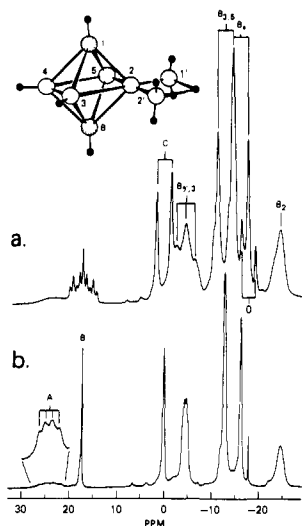


Figure 7. ^{11}B NMR spectrum (64.2 MHz) of 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5]: (a) proton spin-coupled; (b) proton spin-decoupled. Resonances from the following impurities: (A) 2:1'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5]; (B) B_2H_6 ; (C) 1,5- $\text{C}_2\text{B}_3\text{H}_5$; (D) 1,6- $\text{C}_2\text{B}_4\text{H}_6$.

structural characterization of the coupled diborane-cobaltacarborane complex, 5:1',2'-[1-($\eta\text{-C}_5\text{H}_5$)Co-2,3-(Me_3Si) $_2\text{C}_2\text{B}_4\text{H}_3$][B_2H_5], which was shown to have an exopolyhedral $-\text{B}_2\text{H}_5$ group bound to the cobaltacarborane cage in a manner similar to that proposed above for 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5].

The ^{11}B NMR spectrum of the compound, which is shown in Figure 7, strongly supports the proposed structure. The spectrum consists of four resonances in a 2:2:1:1 ratio. The triplet resonance of intensity two at -3.9 ppm clearly indicates the presence of the two diborane $-\text{BH}_2$ groups. Furthermore, in the proton spin-decoupled spectrum this resonance has a quartet structure indicating coupling of these borons with one other boron (B2). The magnitude of this coupling ($J = 23$ Hz) is similar to the boron-boron coupling which has been observed in triborane compounds, such as $\text{B}_3\text{H}_7\text{L}$.²⁴ The resonance for the carborane boron B2, which occupies the bridging site in the diborane fragment, is assigned to the singlet at -23.7 ppm. This peak is seen to be somewhat broadened, as would be expected owing to its boron-boron coupling with the B1',2' borons, but the predicted septet structure is not resolved. The fact that this peak is only slightly broadened eliminates the possibility that the compound could have the alternate structure, 2:1'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5], in which the diborane fragment would be terminally substituted. Such a structure would have a two-center, two-electron boron-boron linkage, and we have previously shown²⁵ that such bonds between chemically nonequivalent borons give rise to large boron-boron couplings ($\sim 90\text{--}150$ Hz) and result in quartet resonances with a much greater line width than that observed for the singlet B2 resonance in 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5]. It should be noted, however, that other peaks, in addition to those assigned to 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5], were sometimes seen in the ^{11}B NMR spectra of freshly prepared samples, indicating the possible presence of the terminally substituted isomer. In particular, a quartet resonance (which is barely visible in the spectrum shown in Figure 7) was observed at 24.8 ppm. The low field position of this resonance is typical²⁶ of that of substituted derivatives of diborane, and as mentioned above, the large coupling constant

(24) Jacobsen, G. B.; Morris, J. H.; Reed, D. *J. Chem. Res., Synop.* **1983**, 42-43.

(25) (a) Astheimer, R. J.; Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1108-1109. (b) Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275-2283.

(26) (a) Williams, R. E.; Fisher, H. D.; Wilson, C. O. *J. Phys. Chem.* **1960**, *64*, 1583-1584. (b) Gaines, D. F.; Schaeffer, R. *J. Phys. Chem.* **1964**, *68*, 955-957. (c) Lindner, H. H.; Onak, T. *J. Am. Chem. Soc.* **1966**, *88*, 1890-1894.

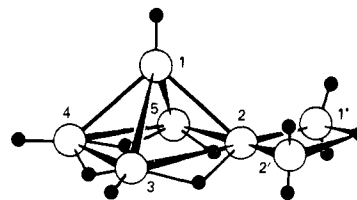


Figure 8. Proposed structure for 2:1',2'-[B_5H_8][B_2H_5].

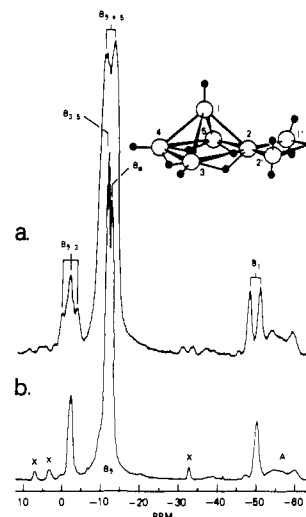


Figure 9. ^{11}B NMR spectrum (64.2 MHz) of 2:1',2'-[B_5H_8][B_2H_5]: (a) proton spin-coupled; (b) proton spin-decoupled. A indicates apical resonances from 1:2'-[B_5H_8] $_2$ impurity; X indicates impurity.

($J = 94$ Hz) is characteristic of a boron-boron terminal linkage.

The remaining two resonances in the ^{11}B NMR spectrum of 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5] are in an intensity ratio of 2:1 and at shifts characteristic²⁷ of 1,6- $\text{C}_2\text{B}_4\text{H}_6$. They are, therefore, assigned to the B3,5 and B4 borons, respectively. The 2D ^{11}B - ^{11}B NMR spectrum of this compound also supports the proposed structure and assignments, showing cross-peaks indicating boron-boron connectivities between B1',2' and B2 and between B3,5 and B2.

The proton NMR spectrum of 2:1',2'-[1,6- $\text{C}_2\text{B}_4\text{H}_5$][B_2H_5] shows a single $-\text{CH}$ resonance at 2.30 ppm, which is at a similar shift²⁷ as that found for the $-\text{CH}$ protons in 1,6- $\text{C}_2\text{B}_4\text{H}_6$, and a single bridge proton peak at -1.50 ppm. The terminal $-\text{BH}$ proton resonances are not resolved.

When the dehydrocoupling reaction of pentaborane(9) with diborane was carried out with a greater than 5:1 ratio of diborane to pentaborane(9), it was found to produce small amounts of 2:1',2'-[B_5H_8][B_2H_5] as the sole product, although NMR evidence, discussed below, also suggests the formation of the isomer 2:1'-[B_5H_8][B_2H_5] in trace amounts. If the diborane to pentaborane(9) ratio was less than 5:1, then the formation of small amounts of 1:2'-[B_5H_8] $_2$ was also observed.^{1,6}

The reaction was usually run for 36-48 h with periodic removal of evolved hydrogen, and the 2:1',2'-[B_5H_8][B_2H_5] product was purified by slow passage of the reaction mixture through a -45 , -78 , -196 $^\circ\text{C}$ trap series. The compound was isolated in the -78 $^\circ\text{C}$ trap as a white, noncrystalline solid which was observed to be thermally unstable in the liquid phase above 0 $^\circ\text{C}$. Heating the compound at 40 $^\circ\text{C}$ gave complete decomposition with pentaborane(9) and diborane as the only identifiable products.

The spectroscopic data for the compound again supports a μ -diborane-type structure such as shown in Figure 8, in which a $-\text{B}_5\text{H}_8$ cage is bound to one of the equatorial borons (B2) to a bridging position in an exopolyhedral $-\text{B}_2\text{H}_5$ group. The ^{11}B

(27) (a) Onak, T. P.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3378-3380. (b) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895-1899.

NMR spectrum, shown in Figure 9, exhibits a triplet resonance of intensity two, assigned to the B1',2' diborane borons, which has additional fine structure in the proton spin-decoupled spectrum, indicating boron-boron coupling. The coupling constants, $J_{B-H} = 128$ and $J_{B-B} = 26$ Hz, and shift, -1.5 ppm, of this resonance are similar to those observed for the analogous borons in 2:1',2'-[1,6-C₂B₄H₅][B₂H₅]. The doublet resonance at -50.5 ppm is characteristic²⁸ of the apical boron in pentaborane(9), while the two resonances at -10.9 and -12.0 ppm are assigned to the B3,5 and B4 borons, respectively. Each of the latter two resonances show additional coupling, $J_{B-B} = 18$ Hz and $J_{B-B} = 19$ Hz, in the proton spin-decoupled spectrum consistent with the apex to base coupling normally observed in pentaborane(9).²⁹ However, integration of these peaks gives an intensity of four, indicating that the resonance arising from B2, the boron which is linked to the exopolyhedral -B₂H₅ group, is underneath. Naturally, this resonance should be broadened, as was the analogous B2 resonance in 2:1',2'-[1,6-C₂B₄H₅][B₂H₅], owing to its coupling to the B1',2' borons. The 2D ¹¹B NMR spectrum of the compound shows two cross-peaks, indicating that both B1',2' and B1 are connected to one of the overlapping resonances (presumably B2) between -10.9 and -12.0 ppm.

The ¹H NMR spectrum of 2:1',2'-[B₅H₈][B₂H₅] shows overlapping terminal -BH quartets and a single bridging resonance at -2.75 ppm. The IR spectrum likewise shows absorptions at ~ 2600 and 1850 cm⁻¹, characteristic of terminal and bridging B-H stretches.

As was observed in the 1,5-C₂B₃H₅/B₂H₆ reaction, there was also present in the ¹¹B NMR spectra of some samples of 2:1',2'-[B₅H₈][B₂H₅] a quartet resonance (not shown in Figure 9) at low field (31.2 ppm) with a large coupling constant ($J = 93$ Hz), suggesting the presence of the terminally substituted isomer, 2:1'-[B₅H₈][B₂H₅], in trace amounts. This resonance gradually lessened with time, suggesting a possible 2:1'-[B₅H₈][B₂H₅] to 2:1',2'-[B₅H₈][B₂H₅] isomerization.

Discussion

The results presented above clearly demonstrate that platinum(II) bromide promotes the reaction of diborane with small boranes and carboranes to yield either dehydrocondensation or cage growth products. Furthermore, owing to the low temperature and mild conditions, these reactions were found to give new types of structurally unique compounds which have not been observed previously. Thus, in the case of 1,6-C₂B₄H₆ and B₅H₉, diborane-coupled compounds were obtained, whereas for 1,5-C₂B₃H₅ the cage expanded arachno carborane 5,6-C₂B₆H₁₂ was produced.

We have previously shown¹⁶ that platinum(II) bromide catalyzes the dehydrodimerization of 1,6-C₂B₄H₆, 1,5-C₂B₃H₅, or B₅H₉ to yield the corresponding boron-boron linked-cage compounds in quantitative yields. Therefore, a reasonable first step in the reactions reported herein may involve the formation of boron-boron-linked diborane-polyhedral borane species, and, in fact, NMR observations, as discussed in the Results section, of both the 1,6-C₂B₄H₆/B₂H₆ and B₅H₉/B₂H₆ reactions suggest the presence, in trace amounts, of 2:1'-[1,6-C₂B₄H₅][B₂H₅] and 2:1'-[B₅H₈][B₂H₅]. These compounds are apparently, however, unstable and easily rearrange to the isolated μ -substituted isomers, 2:1',2'-[1,6-C₂B₄H₅][B₂H₅] and 2:1',2'-[B₅H₈][B₂H₅].

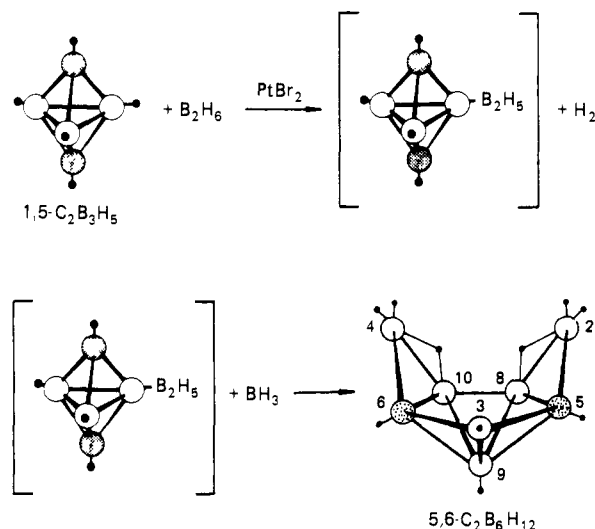
It is also of interest to note that a possible apex-substituted isomer of 2:1',2'-[B₅H₈][B₂H₅] has recently been reported³⁰ by

(28) Lipscomb, W. N.; Eaton, G. R. "NMR Studies of Boron Hydrides and Related Compounds"; Benjamin: New York, 1969; pp 92-99.

(29) Odom, J. D.; Ellis, P. D.; Walsh, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 3529-3530.

Morrison, who prepared the compound by the reduction of 1-(BCl₂)B₅H₈. These coupled diborane-pentaborane compounds are of special interest since, although there are now numerous boron hydride compounds known, one of the long-standing mysteries of boron hydride chemistry has been the absence of any neutral seven-boron boranes. Therefore, it is certainly of historical interest to note that 2:1',2'-[B₅H₈][B₂H₅] and Morrison's apex-substituted isomer are the first two such species.

The reaction with 1,5-C₂B₃H₅ may proceed in a similar fashion to that described above for 1,6-C₂B₄H₆ and B₅H₉, but a [1,5-C₂B₃H₄][B₂H₅] product is not observed. However, given that 1,5-C₂B₃H₅ has already been shown to undergo thermally induced polyhedral cage expansion with diborane,^{10,13} it would not be unexpected that the coupled-cage compound could further react with diborane, as shown diagrammatically below, to yield a single-cage carborane.



The fact that thermolysis of 5,6-C₂B₆H₁₂ was found to give C₂B₆H₁₀ in high yield suggests that the thermally induced reaction^{10,13} of 1,5-C₂B₃H₅ with diborane might also involve an initial dehydrocondensation to give a product which, because of the reaction temperatures (165-300 °C) employed, further dehydrogenates to give the final product. Indeed, one of the most significant points raised by this work is that intermolecular dehydrocondensation reactions may, in fact, play a more important role in traditional thermally induced cage growth reactions than previously assumed.³¹

This work also suggests that in the future, the use of linked-cage polyhedral boron clusters as precursors to larger fused-cage boranes and carboranes should be explored as a new route to such systems. Indeed, recent work³² in our laboratory has demonstrated that multicage to fused-cage condensations can be effected in high yields using a variety of reagents and conditions.

Acknowledgment. We thank the Army Research Office and the National Science Foundation for the support of this work. We also thank Dr. George Furst for his assistance in obtaining 2D NMR spectra.

(30) (a) Saulys, D. A.; Morrison, J. A. "Abstracts of Papers", 189th National Meeting of the American Chemical Society, Miami Beach, FL, 1985; American Chemical Society: Washington, DC, 1985; INOR 71. (b) Morrison, J. A., private communication.

(31) For a review of traditional thermally induced cage growth reactions see: Long, L. H. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1097-1115 and references therein.

(32) Corcoran, E. W., Jr.; Sneddon, L. G., in preparation.