Reaction of 1,2-Dehydro-*o*-carborane with Acetylenes. Synthesis and Structure of a Carborane Analogue of Benzocyclobutadiene[1]

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Although 1,2-dehydro-*o*-carborane reacts with 3-hexyne to give the product of an ene reaction, it adds in both ene and 2 + 2 fashions to 1-phenyl-1-propyne to give **9** and **10**, respectively. Single-crystal X-ray diffraction of **10** yields a structure for this three-dimensional analogue of benzocyclobutadiene. The stability of **10** shows that there is no strong orbital connection between the cage and the exo-cage π system. Compound **10** reacts photochemically with 1,3-butadiene to give the 2 + 2 adduct **12**.

Introduction

The icosahedral carboranes have long been described as "superaromatic," a term derived from the optimal occupancy of 13 bonding molecular orbitals by the 26 framework electrons. The chemistry of *o*-carborane, and of its *meta* and *para* isomers,

*o*-carborane   *m*-carborane   *p*-carborane

In this and other figures, the dots are carbon atoms and all other vertices are borons. There is a hydrogen at every otherwise unencumbered vertex atom.

reflects their characterization as aromatic. These molecules are thermodynamically very stable and undergo electrophilic substitution, the hallmark of aromatic systems.[2] The connection, both physical and intellectual, of the three-dimensional carboranes and the classical aromatic compounds, the two-dimensional benzenes, has been a fertile area for exploration. One particularly delicious question concerns fused compounds such as **1** and **2**, in which the two classes of aromatic molecules share
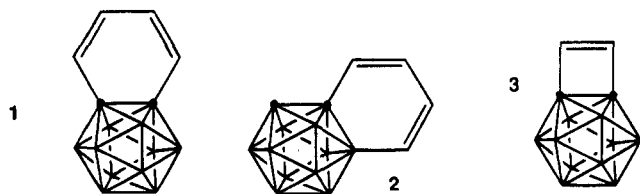
an edge. Are these compounds "naphthalenes"? Is there sufficient connection between the ring and the cage so that the

exo-cage ring can be considered as aromatic? There has been much discussion of this point,[3,4] but the question cannot yet be considered as settled. In this paper we take a different approach, construction of a molecule of the general structure **3** that would be strongly destabilized by effective conjugation between the cage and the exo-cage π system. The corresponding classical, two-dimensional, benzocyclobutadienes are known to be exceptionally unstable. The parent compound **4** is known, but it
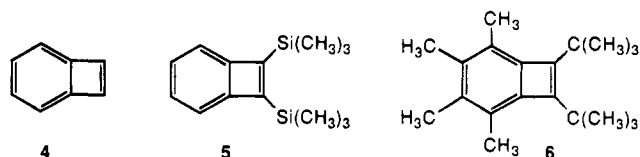
dimerizes at very low temperature and requires special techniques for observation.[5] A few substituted versions of **4** are known, but even though dimerization of compounds such as **5** and **6** is kinetically blocked, they do react rapidly with oxygen unless precautions are taken.[6,7] So, our strategy was to construct **3** and assess its stability. Strong orbital connection between the cage and the ring should be signaled by instability; by contrast, the more normal **3**, the less important the connection between the classical and nonclassical parts of the molecule.

In recent years, evidence has accumulated from a distant area that speaks to this question as well. EPR spectroscopy on several carboranylcarbenes and carboranylnitrenes has shown that the triplet carbenes and nitrenes have highly localized nonbonding electrons. In these reactive intermediates, there is no important connection between orbitals of the cage and those on an adjacent carbon or nitrogen atom. There is no classical benzyl position in carboranes.[8] Accordingly, there is good reason to suspect that "naphthalene" is an inappropriate term for **1** and **2** and that **3** will be a normal molecule.

(2) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. Muetterties, E. L. *Boron Hydride Chemistry*; Academic: New York, 1975. Grimes, R. N. *Carboranes*; Academic: New York, 1970. Onak, T. *Organoborane Chemistry*; Academic: New York, 1975. Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.
(3) Hota, N. K.; Matteson, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 3570. Matteson, D. S.; Hota, N. K. *J. Am. Chem. Soc.* **1971**, *93*, 2893.
(4) Wu, S.; Jones, M., Jr. *Inorg. Chem.* **1988**, *27*, 2005.
(5) Trahanovsky, W. S.; Fischer, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 4971 and references therein.
(6) Vollhardt, K. P. C.; Yee, L. S. *J. Am. Chem. Soc.* **1977**, *99*, 2010.
(7) Straub, H. *Tetrahedron Lett.* **1976**, 3513. Winter, W.; Straub, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 127. Winter, W.; Butters, T. *Acta Crystallogr.* **1981**, *B37*, 1524.
(8) Hutton, R. S.; Roth, H. D.; Chari, S. *J. Phys. Chem.* **1981**, *85*, 753. Blanch, R. J.; Li, J.; Bush, L. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 9236. Blanch, R. J.; Bush, L. C.; Jones, M., Jr. *Inorg. Chem.* **1994**, *33*, 198.

Results and Discussion

Our hope was to approach molecules like **3** in a very simple way, the cycloaddition of 1,2-dehydro-*o*-carborane, **7**, with acetylenes:
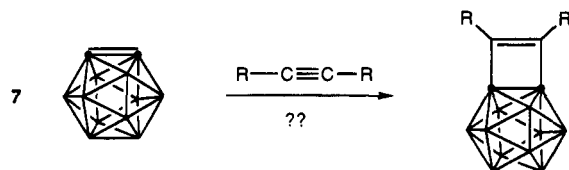

The chemistry of **7** has been described at some length in recent years,[9] and it generally quite closely resembles that of benzyne.[10] In particular, both 4 + 2 and 2 + 2 cycloadditions are common for **7**.[9a] Unfortunately, the ene reaction also appears to be especially easy for **7**,[9b,c] and seemed likely to interfere with the 2 + 2 cycloaddition to give compounds like **3**. For example, benzyne reacts with methylacetylene to give phenylallene as the overwhelming major product:[10,11]
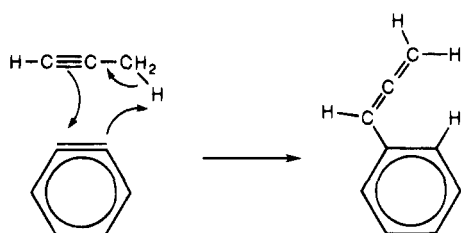
Compound **7** is, as we feared, similar. For example, reaction of **7** with 3-hexyne leads to a single product, **8**, of the mass
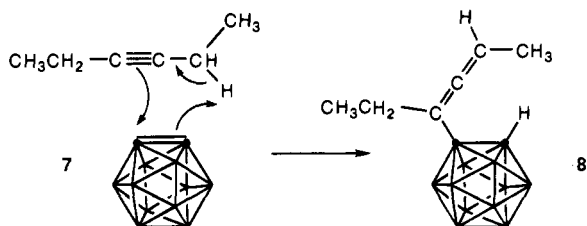
appropriate for a 1:1 adduct in about 30% yield. The ^{1}H NMR spectrum showed signals for single hydrogens at δ 3.72 (cage hydrogen) and 5.52 (hydrogen attached to a double bond). Signals appropriate for an ethyl group (δ 2.08, 0.94) and a methyl group attached to a double bond (δ 1.72) leave no doubt that the structure is **8**.

A similar reaction of **7** with 4-octyne leads to a related allene in >99% relative yield. However, there is a second product formed in the reaction with 3-hexyne. Although the yield of this compound is less than 1%, and its structure unknown, its very existence allowed us to hope that it might be the 2 + 2 adduct, and that an acetylene less prone to ene reaction might give significant amounts of 2 + 2 addition. Replacement of one ethyl group with hydrogen to give a 1-alkyne is not a productive procedure, as the presence of a relatively acidic acetylenic hydrogen shortcircuits our base-induced synthesis of **7**.[9a] Instead, we used a phenyl group to replace one ethyl. Phenyl obviously blocks ene reaction at one end, and favors

(9) (a) Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313. (b) Huang, Q.; Gingrich, H. L.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 3254. (c) Gingrich, H. L.; Huang, Q.; Morales, A. L.; Jones, M., Jr. *J. Org. Chem.* **1992**, *57*, 3803.
(10) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967.
(11) Jones, M., Jr.; DeCamp, M. R. *J. Org. Chem.* **1971**, *36*, 1536.

Table 1. Crystallographic Data for **10** and **12**

	10	12
formula; fw	$C_{11}H_{18}B_{10}$; 258.35	$C_{15}H_{24}B_{10}$; 312.44
color and habit	colorless needle	colorless plate
crystal size, mm	$0.05 \times 0.12 \times 0.50$	$0.20 \times 0.50 \times 0.50$
space group	$P2_1/c$	$P2_1/c$
a, Å	7.182(2)	10.183(2)
b, Å	9.756(2)	14.884(3)
c, Å	22.126(4)	24.725(3)
β, deg	93.06(2)	97.093(12)
V, Å^3	1548.1(5)	3718.9(10)
Z	4	8
d(calcd), Mg/m^3	1.108	1.116
abs coeff, mm^{-1}	0.053	0.055
radiation; λ, Å; T, K	Mo Kα; 0.710 73; 235	Mo Kα; 0.710 73; 296
scan width, deg: below/above Kα_{12}	0.6/0.6	0.6/0.6
scan mode; speed, deg/min	ω; 4−8	ω; 4−8
data collcd; uniq; obs $[I > 2\sigma(I)]$	2990; 2755; 1224	6996; 6598; 3547
2θ max, deg	50	50
data used; restraints; params	2755; 0; 236	6597; 0; 579
R1; wR2; GOF [for $I > 2\sigma(I)$]^a	0.050; 0.100; 1.05	0.047; 0.106; 1.06

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, and GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ where n is the number of reflections and p is the number of parameters refined.

the 2 + 2 reaction by stabilizing the intermediate diradical. In fact, methylphenylacetylene gives two isolable products. One, formed in about 6% yield, was the allene **9**, the product of the
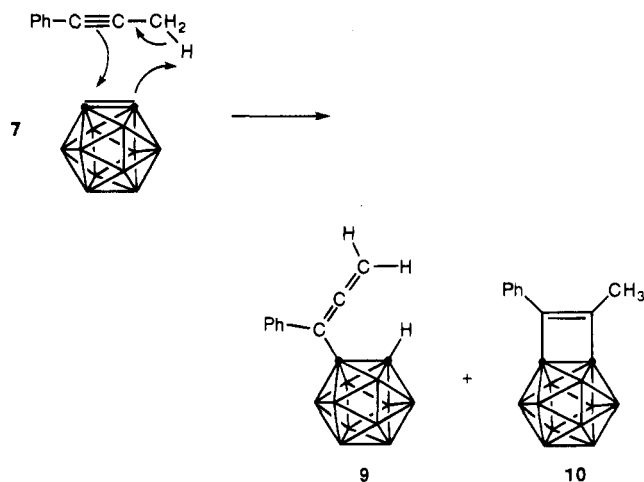
interfering ene reaction. The other, formed in 18% yield, was the hoped-for **10**. The spectral properties of **10** left little doubt as to its structure, but confirmation through single crystal X-ray diffraction removed any possible uncertainty.

Crystallization of material collected by preparative gas chromatography from ethyl ether led to colorless needles of **10**, mp 112−114 °C, suitable for X-ray analysis. Table 1 shows the crystallographic data, and Figure 1 gives the structure derived from the X-ray data, along with the numbering used in Tables 2 and 3, which give the bond lengths and selected bond angles.

The boron−boron distances in **10** are normal, ranging from a low of 1.718 Å to a high of 1.807 Å. The average boron−boron distance, 1.771 Å, is very similar to that for **11**.[12] The average carbon−boron bond is also normal, at 1.721 Å. In a pair of carbon-to-boron bridged *o*-carboranes, the average

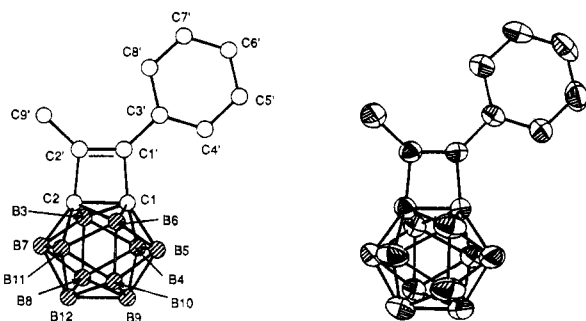(12) L'Esperance, R. P.; Li, Z.; Van Engen, D.; Jones, M., Jr. *Inorg. Chem.* **1989**, *28*, 1823.

Figure 1. X-ray-derived structure, numbering, and thermal ellipsoid plot for **10**.

Table 2. Bond Lengths (Å) for **10**

C(1)−C(1′)	1.550(3)	C(1)−C(2)	1.618(3)
C(1)−B(5)	1.695(4)	C(1)−B(4)	1.700(4)
C(1)−B(6)	1.742(4)	C(1)−B(3)	1.757(4)
C(2)−C(2′)	1.541(3)	C(2)−B(11)	1.681(4)
C(2)−B(7)	1.704(4)	C(2)−B(6)	1.737(4)
C(2)−B(3)	1.749(4)	B(3)−B(8)	1.728(4)
B(3)−B(7)	1.761(4)	B(3)−B(4)	1.764(4)
B(4)−B(9)	1.778(5)	B(4)−B(5)	1.778(5)
B(4)−B(8)	1.807(4)	B(5)−B(6)	1.756(5)
B(5)−B(9)	1.776(5)	B(5)−B(10)	1.800(5)
B(6)−B(10)	1.718(5)	B(6)−B(11)	1.766(5)
B(7)−B(11)	1.768(5)	B(7)−B(12)	1.779(4)
B(7)−B(8)	1.797(4)	B(8)−B(12)	1.769(5)
B(8)−B(9)	1.770(5)	B(9)−B(10)	1.766(5)
B(9)−B(12)	1.776(5)	B(10)−B(12)	1.771(5)
B(10)−B(11)	1.792(5)	B(11)−B(12)	1.773(5)
C(1′)−C(2′)	1.346(3)	C(1′)−C(3′)	1.454(3)
C(2′)−C(9′)	1.471(3)	C(3′)−C(4′)	1.394(3)
C(3′)−C(8′)	1.397(3)	C(4′)−C(5′)	1.389(3)
C(5′)−C(6′)	1.376(4)	C(6′)−C(7′)	1.381(4)
C(7′)−C(8′)	1.383(3)		

Table 3. Selected Bond Angles (deg) for **10**

C(1′)−C(1)−C(2)	84.6(2)	C(1′)−C(1)−B(5)	143.1(2)
C(2)−C(1)−B(5)	111.7(2)	C(1′)−C(1)−B(4)	143.0(2)
C(2)−C(1)−B(4)	111.8(2)	B(5)−C(1)−B(4)	63.2(2)
C(1′)−C(1)−B(6)	103.3(2)	C(2)−C(1)−B(6)	62.1(2)
B(5)−C(1)−B(6)	61.4(2)	B(4)−C(1)−B(6)	113.7(2)
C(1′)−C(1)−B(3)	103.3(2)	C(2)−C(1)−B(3)	62.3(2)
B(5)−C(1)−B(3)	113.6(2)	B(4)−C(1)−B(3)	61.3(2)
B(6)−C(1)−B(3)	114.4(2)	C(2′)−C(2)−C(1)	85.3(2)
C(2′)−C(2)−B(11)	142.8(2)	C(1)−C(2)−B(11)	112.9(2)
C(2′)−C(2)−B(7)	141.4(2)	C(1)−C(2)−B(7)	112.6(2)
B(11)−C(2)−B(7)	63.0(2)	C(2′)−C(2)−B(6)	104.1(2)
C(1)−C(2)−B(6)	62.5(2)	B(11)−C(2)−B(6)	62.2(2)
B(7)−C(2)−B(6)	114.5(2)	C(2′)−C(2)−B(3)	103.4(2)
C(1)−C(2)−B(3)	62.8(2)	B(11)−C(2)−B(3)	113.8(2)
B(7)−C(2)−B(3)	61.3(2)	B(6)−C(2)−B(3)	115.1(2)
C(2′)−C(1′)−C(3′)	136.7(2)	C(2′)−C(1′)−C(1)	95.1(2)
C(3′)−C(1′)−C(1)	128.2(2)	C(1′)−C(2′)−C(9′)	137.9(2)
C(1′)−C(2′)−C(2)	95.0(2)	C(9′)−C(2′)−C(2)	127.1(2)
C(4′)−C(3′)−C(8′)	118.8(2)	C(4′)−C(3′)−C(1′)	119.9(2)
C(8′)−C(3′)−C(1′)	121.2(2)	C(5′)−C(4′)−C(3′)	120.3(3)
C(6′)−C(5′)−C(4′)	120.4(3)	C(5′)−C(6′)−C(7′)	119.7(3)
C(6′)−C(7′)−C(8′)	120.7(3)	C(7′)−C(8′)−C(3′)	120.1(3)

carbon−boron distance is 1.705 Å,[13] and in **11**, it is 1.692 Å.[12] It is the carbon−carbon bonds in the four-membered ring of **10** that are of most interest. The four-membered ring is a planar trapezoid, with a double-bond distance of 1.346 Å and carbon− carbon exo-cage single bonds of 1.550 and 1.541 Å. A comparison with a classical system, **6**, is shown in the following drawing.[7] The cage carbon−carbon bond is one of the shortest known for any *o*-carborane, 1.618(3) Å,[14] although it must be pointed out that there is no significant decrease over the 1.621-
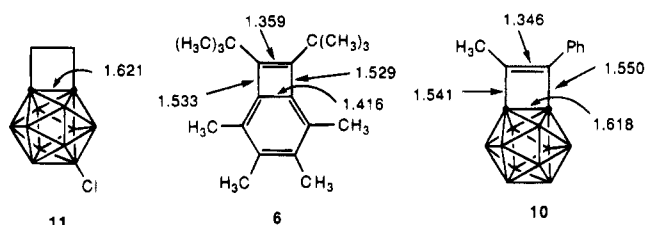

(4) Å distance in **11**. The calculated distance for the parent compound, *o*-carborane, is 1.634 Å.[17]

Compound **10** is not remarkably reactive. It survives in air indefinitely, melts cleanly, and shows no sign of dimerizing. It is clearly not significantly destabilized by interaction between the cage orbitals and those of the double bond. There is no antiaromaticity in **10**.

Although **10** does not dimerize, we have observed the photochemically-induced 2 + 2 cycloaddition of **10** to 1,3-butadiene to give **12**. The structure of **12** can be extracted from the spectral data, but we were sufficiently uncertain about the details of regiochemistry and stereochemistry that the assignment was confirmed by single crystal X-ray analysis. The three hydrogens attached to the four-membered ring appear as four-line multiplets in the ^{1}H NMR spectrum. Two of these, presumably those for the endo hydrogens, are shifted downfield (δ 2.90, 3.58) from the third (δ 2.10) by their proximity to the cage. The detailed structure of **12** can be rationalized through formation of the most stable possible diradical intermediate.
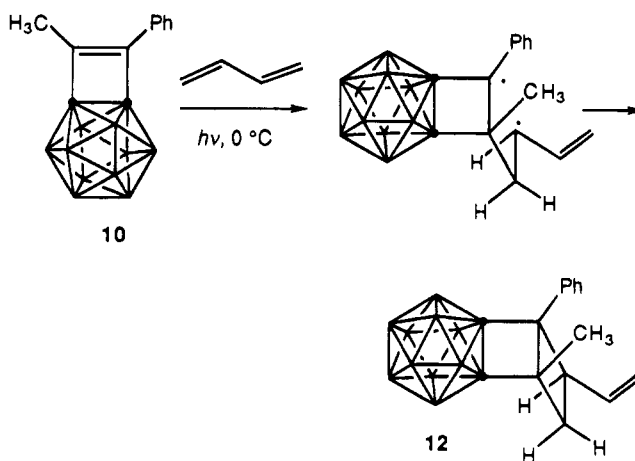
Closure takes place so as to minimize steric interaction between the cage and the vinyl group. Compound **12** is accompanied by 30−40% of a pair of compounds, **A** and **B**, that appear to be trienes. They are formed in the ratio 1/9. When **12** is heated in benzene-d_6 to 100 °C, these same two trienes are formed, but in the opposite ratio, about 9/1. The peaks for **12** vanish on heating and are replaced with signals in the vinyl region of the ^{1}H NMR spectrum (see Experimental Section for details). We cannot be certain of the details of stereochemistry of **A** and **B**, and further mechanistic discussion must be properly labeled as speculation. Nonetheless, there is a certain neatness to the

(13) Wu, S.; Van Engen, D.; Jones, M., Jr. *Acta Crystallogr.* **1990**, *C46*, 656.

(14) For reports of shorter bonds, see for example: Novak, C.; Subrtova, V.; Linek, A.; Hasek, J. *Acta Crystallogr.* **1983**, *C39*, 1393. This paper describes a boron-substituted thiocarborane. In light of the "normal" C−C distance (1.633 Å) in another, more reliable structural determination by this same research group,[16] we suggest that this short C−C distance be regarded with caution.

(15) Sayler et al. describe what is, essentially, a nickel complex of **7** in which the C−C bond distance is 1.57 ± 0.03 Å: Sayler, A. A.; Beall, H.; Sieckhaus, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 5790.

(16) Subrtova, V.; Linek, A.; Hasek, J. *Acta Crystallogr.* **1980**, *B36*, 858.

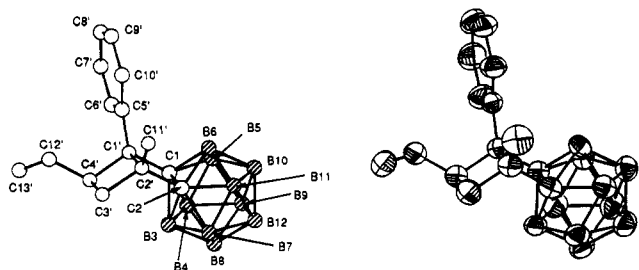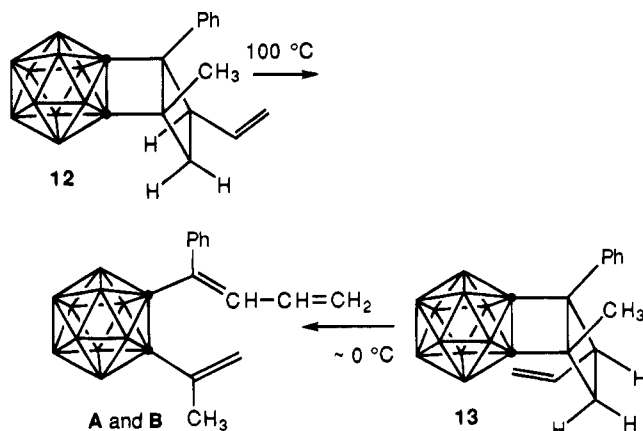(17) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673.

Figure 2. X-ray-derived structure, numbering, and thermal ellipsoid plot for **12**.

following scheme, in which we attribute the formation of the

trienes to simple opening of the four-membered rings in **12**. Were **13**, the endo version of **12**, to be formed in addition to **12** in the photochemical addition, it might well open to the trienes at far lower temperature than **12**.

Figure 2 gives the structure of **12** derived from the X-ray data. Tables 1, 4, and 5 give the crystallographic data, bond lengths, and selected bond angles for **12**.

Experimental Section

General Remarks. Reagents were used as obtained from commercial sources without special purification. ^{1}H NMR spectra were recorded on either a Bruker WM250 spectrometer at 250 MHz, a JEOL-270 NMR spectrometer at 270 MHz, or a General Electric QE-300 spectrometer at 300 MHz. Signals were referenced to the signal for residual CHCl$_3$ in CDCl$_3$, which was set at δ 7.24 ppm. Decoupled ^{11}B NMR spectra were obtained on a Bruker WM 250 spectrometer at 80 MHz, with signals referenced to external boric acid. Decoupled ^{13}C NMR spectra were obtained on a General Electric QE-300 spectrometer operated at 75 MHz. The chemical shift of the center peak of the CDCl$_3$ carbon was set at δ 77.0 ppm. Infrared spectra were recorded on a Nicolet 730 FT-IR spectrometer. Gas chromatographic/mass spectrometric analyses were performed on a Hewlett Packard 5890/5971 Series 2 gas chromatograph/mass spectrometer with a 25 m, 0.2 mm i.d., 0.33 mm film thickness HP-1 capillary column. Preparative gas chromatography was performed on a Gow-Mac 580 gas chromatograph. The columns used are described in the individual sections. Precise masses were determined on a KRATOS MS50 RFA high-resolution mass spectrometer. Melting points were determined on a Thomas Hoover Uni-Melt apparatus and are uncorrected. All trapping reactions of **7** were run under an atmosphere of argon.

General Procedure for Generation of 1,2-Dehydro-o-carborane (7). To a solution of 2.5 M BuLi (8 mL, 20 mmol) in 10 mL of cyclohexane, was added dropwise with stirring at 0 °C a solution of o-carborane (1.44 g, 10 mmol). The resulting curdy white precipitate was stirred at room temperature for 1 h. The mixture was cooled to 0 °C, and bromine (1.6 g, 10 mmol) was added dropwise with stirring. The reaction mixture was stirred for an additional 1 h at 0 °C and used to run the following reactions.

Table 4. Bond Lengths (Å) for **12**

Molecule A			
C(1A)–C(1')	1.567(2)	C(1A)–C(2A)	1.610(2)
C(1A)–B(4A)	1.714(3)	C(1)–B(5A)	1.728(3)
C(1A)–B(6A)	1.733(3)	C(1A)–B(3A)	1.743(3)
C(2A)–C(2')	1.562(3)	C(2A)–B(7A)	1.711(3)
C(2A)–B(11A)	1.725(3)	C(2A)–B(6A)	1.735(3)
C(2A)–B(3A)	1.735(3)	B(3A)–B(8A)	1.712(4)
B(3A)–B(7A)	1.761(4)	B(3A)–B(4A)	1.762(3)
B(4A)–B(5A)	1.772(4)	B(4A)–B(9A)	1.776(4)
B(4A)–B(8A)	1.793(4)	B(5A)–B(9A)	1.760(3)
B(5A)–B(6A)	1.761(3)	B(5A)–B(10A)	1.784(3)
B(6A)–B(10A)	1.722(3)	B(6A)–B(11A)	1.771(3)
B(7A)–B(12A)	1.764(4)	B(7A)–B(11A)	1.764(4)
B(7A)–B(8A)	1.793(4)	B(8A)–B(9A)	1.767(4)
B(8A)–B(12A)	1.768(4)	B(9A)–B(10A)	1.774(4)
B(9A)–B(12A)	1.798(4)	B(10A)–B(12A)	1.778(4)
B(10A)–B(11A)	1.787(4)	B(11A)–B(12A)	1.762(4)
C(1')–C(5')	1.501(3)	C(1')–C(4')	1.577(3)
C(1')–C(2')	1.620(3)	C(2')–C(11')	1.516(3)
C(2')–C(3')	1.546(3)	C(3')–C(4')	1.554(3)
C(4')–C(12')	1.495(3)	C(5')–C(10')	1.386(3)
C(5')–C(6')	1.389(3)	C(6')–C(7')	1.379(3)
C(7')–C(8')	1.378(3)	C(8')–C(9')	1.368(3)
C(9')–C(10')	1.384(3)	C(12')–C(13')	1.297(3)
Molecule B			
C(1B)–C(1'')	1.575(2)	C(1B)–C(2B)	1.613(2)
C(1B)–B(4B)	1.715(3)	C(1B)–B(5B)	1.720(3)
C(1B)–B(6B)	1.733(3)	C(1B)–B(3B)	1.741(3)
C(2B)–C(2'')	1.559(3)	C(2B)–B(7B)	1.711(3)
C(2B)–B(11B)	1.714(3)	C(2B)–B(3B)	1.733(3)
C(2B)–B(6B)	1.736(3)	B(3B)–B(8B)	1.712(4)
B(3B)–B(7B)	1.760(3)	B(3B)–B(4B)	1.761(3)
B(4B)–B(5B)	1.776(3)	B(4B)–B(9B)	1.778(4)
B(4B)–B(8B)	1.787(3)	B(5B)–B(6B)	1.759(3)
B(5B)–B(9B)	1.777(3)	B(5B)–B(10B)	1.799(3)
B(6B)–B(10B)	1.727(3)	B(6B)–B(11B)	1.764(3)
B(7B)–B(12B)	1.769(4)	B(7B)–B(11B)	1.771(3)
B(7B)–B(8B)	1.786(4)	B(8B)–B(12B)	1.763(3)
B(8B)–B(9B)	1.772(4)	B(9B)–B(10B)	1.772(3)
B(9B)–B(12B)	1.791(4)	B(10B)–B(12B)	1.782(4)
B(10B)–B(11B)	1.783(4)	B(11B)–B(12B)	1.768(4)
C(1'')–C(5'')	1.500(2)	C(1'')–C(4'')	1.574(3)
C(1'')–C(2'')	1.624(3)	C(2'')–C(11'')	1.511(3)
C(2'')–C(3'')	1.549(3)	C(3'')–C(4'')	1.566(3)
C(4'')–C(12'')	1.484(3)	C(5'')–C(10'')	1.375(3)
C(5'')–C(6'')	1.384(3)	C(6'')–C(7'')	1.375(3)
C(7'')–C(8'')	1.368(4)	C(8'')–C(9'')	1.366(4)
C(9'')–C(10'')	1.406(3)	C(12'')–C(13'')	1.296(3)

Reaction of 1,2-Dehydro-o-carborane with 3-Hexyne To Give 8. To the solution of the bromo anion prepared as described above was added a solution of 3-hexyne (8.22 g, 100 mmol) in 10 mL of cyclohexane. The solution was then heated to reflux for 24 h. The mixture was cooled to 25 °C, and the reaction was quenched with 15 mL of water. The organic layer was separated, washed with saturated brine, and dried over MgSO$_4$. The solvent and excess 3-hexyne were removed by rotary evaporation to give a brown liquid. Purification by preparative gas chromatography on an aluminum 6 ft × 0.25 in. 10% OV-17 on Chromosorb WHP column at 200–215 °C led to a sample of **8**. IR (neat, cm^{-1}): 3085, 2950, 2590. ^{1}H NMR (300 MHz, CDCl$_3$) δ in ppm (multiplicity): 5.52 (m), 3.72 (br s), 2.08 (qd), 1.72 (d), 0.94 (t). HRMS, m/z: calcd for C$_8$H$_{20}{}^{11}$B$_9{}^{10}$B$_1$, 225.2532; found, 225.2521.

Reaction of 1,2-Dehydro-o-carborane with 4-Octyne. To the solution of the bromo anion prepared as described above was added a solution of 4-octyne (11.02 g, 100 mmol) in 10 mL of cyclohexane. The solution was then heated to reflux for 24 h. The mixture was cooled to 25 °C, and the reaction was quenched with 15 mL of water. The organic layer was separated from the mixture, washed with saturated brine, and dried over MgSO$_4$. The solvent and excess 4-octyne were removed by rotary evaporation to give a brown liquid. Purification by preparative gas chromatography on an aluminum 6 ft × 0.25 in. 10% OV-17 on Chromosorb WHP column at 200 °C led to a sample of the allene. IR (neat, cm^{-1}): 3060, 2970, 2585. ^{1}H NMR

Table 5. Selected Bond Angles (deg) for **12**

Molecule A

C(1′)−C(1A)−C(2A)	90.1(1)	C(1′)−C(1A)−B(4A)	143.9(2)
C(2A)−C(1A)−B(4A)	111.9(2)	C(1′)−C(1A)−B(5A)	137.1(2)
C(2A)−C(1A)−B(5A)	111.6(2)	B(4A)−C(1A)−B(5A)	62.0(1)
C(1′)−C(1A)−B(6A)	102.8(1)	C(2A)−C(1A)−B(6A)	62.4(1)
B(4A)−C(1A)−B(6A)	112.6(2)	B(5A)−C(1A)−B(6A)	61.2(1)
C(1′)−C(1A)−B(3A)	110.8(2)	C(2A)−C(1A)−B(3A)	62.2(1)
B(4A)−C(1A)−B(3A)	61.3(1)	B(5A)−C(1A)−B(3A)	112.1(2)
B(6A)−C(1A)−B(3A)	113.6(2)	C(2′)−C(2A)−C(1A)	90.3(1)
C(2′)−C(2A)−B(7A)	143.3(2)	C(1A)−C(2A)−B(7A)	112.5(2)
C(2′)−C(2A)−B(11A)	136.8(2)	C(1A)−C(2A)−B(11A)	112.3(2)
B(7A)−C(2A)−B(11A)	61.8(2)	C(2′)−C(2A)−B(6A)	103.3(2)
C(1A)−C(2A)−B(6A)	62.3(1)	B(7A)−C(2A)−B(6A)	112.7(2)
B(11A)−C(2A)−B(6A)	61.6(1)	C(2′)−C(2A)−B(3A)	110.6(2)
C(1A)−C(2A)−B(3A)	62.6(1)	B(7A)−C(2A)−B(3A)	61.5(2)
B(11A)−C(2A)−B(3A)	112.5(2)	B(6A)−C(2A)−B(3A)	113.9(2)
C(5′)−C(1′)−C(1A)	114.7(1)	C(5′)−C(1′)−C(4′)	116.3(2)
C(1A)−C(1′)−C(4′)	114.7(2)	C(5′)−C(1′)−C(2′)	128.5(2)
C(1A)−C(1′)−C(2′)	89.7(1)	C(4′)−C(1′)−C(2′)	88.7(1)
C(11′)−C(2′)−C(3′)	115.3(2)	C(11′)−C(2′)−C(2A)	114.6(2)
C(3′)−C(2′)−C(2A)	116.1(2)	C(11′)−C(2′)−C(1′)	128.4(2)
C(3′)−C(2′)−C(1′)	88.8(2)	C(2A)−C(2′)−C(1′)	89.9(1)
C(2′)−C(3′)−C(4′)	92.3(2)	C(12′)−C(4′)−C(3′)	115.0(2)
C(12′)−C(4′)−C(1′)	115.7(2)	C(3′)−C(4′)−C(1′)	90.2(2)
C(10′)−C(5′)−C(6′)	117.6(2)	C(10′)−C(5′)−C(1′)	123.5(2)
C(6′)−C(5′)−C(1′)	118.8(2)	C(7′)−C(6′)−C(5′)	121.3(2)
C(8′)−C(7′)−C(6′)	120.3(2)	C(9′)−C(8′)−C(7′)	119.2(2)
C(8′)−C(9′)−C(10′)	120.7(2)	C(9′)−C(10′)−C(5)	120.9(2)
C(13′)−C(12′)−C(4′)	124.3(3)		

Molecule B

C(1″)−C(1B)−C(2B)	90.2(1)	C(1″)−C(1B)−B(4B)	143.7(2)
C(2B)−C(1B)−B(4B)	111.7(1)	C(1″)−C(1B)−B(5B)	137.0(2)
C(2B)−C(1B)−B(5B)	111.9(1)	B(4B)−C(1B)−B(5B)	62.2(1)
C(1″)−C(1B)−B(6B)	103.0(1)	C(2B)−C(1B)−B(6B)	62.4(1)
B(4B)−C(1B)−B(6B)	112.6(2)	B(5B)−C(1B)−B(6B)	61.2(1)
C(1″)−C(1B)−B(3B)	110.3(2)	C(2B)−C(1B)−B(3B)	62.1(1)
B(4B)−C(1B)−B(3B)	61.2(1)	B(5B)−C(1B)−B(3B)	112.7(2)
B(6B)−C(1B)−B(3B)	113.8(1)	C(2″)−C(2B)−C(1B)	90.2(1)
C(2″)−C(2B)−B(7B)	142.6(2)	C(1B)−C(2B)−B(7B)	112.5(2)
C(2″)−C(2B)−B(11B)	137.2(2)	C(1B)−C(2B)−B(11B)	112.0(2)
B(7B)−C(2B)−B(11B)	62.3(1)	C(2″)−C(2B)−B(3B)	109.9(2)
C(1B)−C(2B)−B(3B)	62.6(1)	B(7B)−C(2B)−B(3B)	61.5(1)
B(11B)−C(2B)−B(3B)	112.7(2)	C(2″)−C(2B)−B(6B)	103.6(1)
C(1B)−C(2B)−B(6B)	62.1(1)	B(7B)−C(2B)−B(6B)	113.1(2)
B(11B)−C(2B)−B(6B)	61.5(1)	B(3B)−C(2B)−B(6B)	114.0(1)
C(5″)−C(1″)−C(4″)	115.9(2)	C(5″)−C(1″)−C(1B)	114.6(1)
C(4″)−C(1″)−C(1B)	114.7(2)	C(5″)−C(1″)−C(2″)	128.9(2)
C(4″)−C(1″)−C(2″)	89.4(1)	C(1B)−C(1″)−C(2″)	89.3(1)
C(11″)−C(2″)−C(3″)	115.2(2)	C(11″)−C(2″)−C(2B)	114.9(2)
C(3″)−C(2″)−C(2B)	115.9(2)	C(11″)−C(2″)−C(1″)	128.1(2)
C(3″)−C(2″)−C(1″)	88.5(1)	C(2B)−C(2″)−C(1″)	90.3(2)
C(2″)−C(3″)−C(4″)	92.4(2)	C(12″)−C(4″)−C(3″)	114.0(2)
C(12″)−C(4″)−C(1″)	116.4(2)	C(3″)−C(4″)−C(1″)	89.7(2)
C(10″)−C(5″)−C(6″)	118.7(2)	C(10″)−C(5″)−C(1″)	124.4(2)
C(6″)−C(5″)−C(1″)	116.7(2)	C(7″)−C(6″)−C(5″)	121.2(2)
C(8″)−C(7″)−C(6″)	120.3(3)	C(9″)−C(8″)−C(7″)	119.5(3)
C(8″)−C(9″)−C(10″)	120.6(3)	C(5″)−C(10″)−C(9″)	119.7(2)
C(13″)−C(12″)−C(4″)	124.1(2)		

(250 MHz, CDCl₃) δ in ppm (multiplicity): 5.56 (m), 3.70 (s), 2.0–2.2 (br m), 1.43 (m), 0.99 (t), 0.89 (t). HRMS, *m/z*: calcd for $C_{10}H_{24}{}^{11}B_{10}$, 254.2809; found, 254.2802.

Reaction of 1,2-Dehydro-*o*-carborane with 1-Phenyl-1-propyne. Synthesis of 10. To the solution of the bromo anion prepared as described above was added a solution of 1-phenyl-1-propyne (11.62 g, 100 mmol) in 10 mL of cyclohexane. The solution was then heated to reflux for 24 h. The mixture was cooled to 25 °C, and the reaction was quenched with 15 mL of water. The organic layer was separated from the mixture, washed with saturated brine, and dried over MgSO₄. The solvent was removed by rotary evaporation to give a dark brown liquid. Purification by preparative gas chromatography on an aluminum 8 ft × 0.25 in. 10% OV-101 on Chromosorp WHP column at 180–220 °C led to samples of the allene **9** and compound **10**. Data for compound **10**, mp 112–114 °C, follow. IR (CHCl₃, cm⁻¹): 2925, 2575. ¹H NMR (250 MHz, CDCl₃), δ in ppm (multiplicity): 7.34 (dd,

2H), 7.17 (d, 2H), 1.98 (s, 3H). ¹¹B NMR (80 MHz, CDCl₃), δ in ppm (multiplicity): −51.18 (br s, 4B), −44.76 (br s, 2B), −32.42 (br s, 2B), ~−22 (br s, 2B). ¹³C NMR (CDCl₃, 75 MHz), δ in ppm: 141.1, 138.6, 129.4, 129.1, 129.0, 125.5, 73.9, 75.3, 14.3. HRMS, *m/z*: calcd for $C_{11}H_{18}{}^{11}B_8{}^{10}B_2$, 258.2412; found, 258.2402. Compound **9** was obtained as a ~60/40 mixture with **10**. ¹H NMR (300 MHz, CDCl₃), δ in ppm (multiplicity): 7.25–7.4 (br m), 7.16 (d), 5.15 (s), 3.60 (br s), 1.98 (s).

Photolysis of 10 in 1,3-Butadiene. A solution of 38 mg of **10** in 5 mL of benzene and 5 mL of 1,3-butadiene was photolyzed with a 450 W Hanovia mercury arc for 6 h at 25 °C in a Pyrex photolysis tube fitted with a Teflon valve. The solvents were removed by rotary evaporation to leave a brown liquid. Thin layer chromatography on silica gel with hexane as eluent led to samples of **12** and **A** + **B**. Compound **12** ¹H NMR (300 MHz, CDCl₃), δ in ppm (multiplicity): 7.1–7.4 (m), 6.81 (d), 5.14 (m), 4.83 (m), 3.58 (m), 2.90 (m), 2.10 (m), 1.80 (s). Compound **B** (see below for minor isomer, **A**) ¹H NMR (300 MHz, benzene-d₆), δ in ppm (multiplicity): 6.92–7.05 (m), 4.12 (d), 4.82–5.1 (m), 1.41 (s). Recrystallization from ethanol/ether led to a sample of **12** suitable for X-ray analysis.

Thermal Isomerization of 12. A ~5 mg sample of **12** was dissolved in 1 mL of benzene-d₆, and the solution was heated in a sealed NMR tube to 100 °C for 18 h. The products (**B** and **A** in ~1:9 ratio) were analyzed directly by ¹H NMR spectroscopy. Compound **A** (for **B** see above) ¹H NMR (300 MHz, benzene-d₆), δ in ppm (multiplicity): 6.76–7.03 (m), 5.81 (d), 4.71–5.16 (m), 1.47 (s).

X-ray Data and Structure Determinations for 10 and 12. Each sample was mounted on a glass fiber with epoxy cement and then transferred to a Siemens P4 diffractometer.[18] Lattice parameters were determined from 25 accurately centered reflections having $4° \le \theta \le 13°$ for **10** and $15° \le \theta \le 19°$ for **12**. One quadrant of data $(+h,+k,\pm l)$ was collected per sample and corrected for Lorentz and polarization effects but not for absorption or extinction. No decay was observed. Three standards were measured for every 97 reflections during each data collection and were within ±1.0% and ±1.3% of their mean intensity values for **10** and **12**, respectively. The R_{int} value for **10** was 2.68%, and that for **12** was 2.32%.

The structures were solved by direct methods (SHELXTL-PLUS)[19] and refined by full-matrix least squares on F^2 (SHELXL-93).[20] The C and B atoms were refined with anisotropic displacement coefficients, and the H atoms were assigned isotropic values $U(H) = 1.2U(C)$ or $1.2U(B)$. All of the positional parameters in both structures were varied. The methyl H atoms were located in difference-Fourier maps and idealized with tetrahedral angles, and their coordinates were then allowed to ride on the methyl C atoms. For **10**, the refinements converged to R1 = 5.00%, wR2 = 9.98%, and GOF = 1.05 for 1224 reflections with $I > 2\sigma(I)$ and to R1 = 12.13%, wR2 = 11.65%, and GOF = 0.77 for all 2755 unique reflections and 236 parameters.[21] For **12**, convergence yielded R1 = 4.70%, wR2 = 10.58%, and GOF = 1.06 for 3547 observed reflections and R1 = 9.18%, wR2 = 12.66%, and GOF = 0.84 for all 6597 unique reflections and 579 parameters. One reflection (011) had $\Delta F^2/\sigma = 31.64$ and was suppressed. The residual peaks on the final $\Delta \rho$ maps ranged from −0.179 to +0.159 e Å⁻³ for **10** and from −0.233 to +0.163 e Å⁻³ for **12**. Scattering factors were taken from ref 22.

(18) *Siemens P3/P4*, Release 4.21; Siemens Analytical X-ray Instruments, Inc: Madison, WI, 1989.
(19) Sheldrick, G. M. *SHELXTL-PLUS*, Release 4.21; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1989.
(20) Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.
(21) The equations defining R1, wR2, and GOF are given in Table 1.
(22) *International Tables for Crystallography: Mathematical, Physical, and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.