Inorg. Chem. **1996,** *35,* 4355−4359

Palladium-Catalyzed Coupling of Ethynylated *p*-Carborane Derivatives: Synthesis and Structural Characterization of Modular Ethynylated *p*-Carborane Molecules

Wei Jiang, David E. Harwell, Mark D. Mortimer, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, University of California at Los Angeles,
405 Hilgard Avenue, Los Angeles, California 90095-1569

Received December 21, 1995[⊗]

Methodology leading to a new class of rodlike *p*-carborane derivatives is described, involving the palladium-catalyzed coupling of B-iodinated *p*-carboranes with terminal alkynes. The products of these reactions contain an alkyne substituent at a boron vertex of the *p*-carborane cage. Reaction of *closo*-2-I-1,12-$C_2B_{10}H_{11}$ (**1**) with *closo*-2-($C\equiv CH$)-1,12-$C_2B_{10}H_{11}$ (**3**) in the presence of pyrrolidine and catalytic quantities of bis(triphenylphosphine)palladium dichloride and cupric iodide yields 1,2-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$ acetylene (**4**). Oxidative coupling of **3** in the presence of cupric chloride in piperidine affords 1,4-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$-1,3-butadiyne (**5**). Reaction of 2 molar equiv. of *closo*-2,9-I_2-1,12-$C_2B_{10}H_{10}$ (**6**) with *closo*-2,9-($C\equiv CH$)$_2$-1,12-$C_2B_{10}H_{10}$ (**7**) in the presence of pyrrolidine and catalytic quantities of bis(triphenylphosphine)palladium dichloride and cupric iodide yields *closo*-2,9-(*closo*-2′-I-9′-$C\equiv C$-1′,12′-$C_2B_{10}H_{10}$)$_2$-1,12-$C_2B_{10}H_{10}$ (**8**), a rigid, iodine-terminated carborod trimer in which the *p*-carborane cages are linked at the 2 and 9 B-vertices by alkyne ($C\equiv C$) bridges. The molecular structures of **5** and the previously described *closo*-2,9-($C\equiv CSiMe_3$)$_2$-1,12-$C_2B_{10}H_{10}$ (**9**) have been determined by X-ray crystallography. Crystallographic data are as follows: for **5**, monoclinic, space group $P2/a$, $a = 12.352(6)$ Å, $b = 14.169$ (6) Å, $c = 12.384(5)$ Å, $\beta = 109.69(2)°$, $V = 2041$ Å^3, $Z = 4$, $R = 0.098$, $R_w = 0.135$; for **9**, monoclinic, space group $C2/m$, $a = 22.111(4)$ Å, $b = 7.565(2)$ Å, $c = 6.943(2)$ Å, $\beta = 107.871(8)°$, $V = 1105$ Å^3, $Z = 2$, $R = 0.059$, $R_w = 0.090$.

Introduction

An interest in structurally well-defined molecular components suitable for further modular syntheses[1] has led us and other investigators to the synthesis of rods[2] and cycles[3] based upon stable icosahedral carborane cages as modular building units joined via a variety of linkers. These carborane-containing modular systems exhibit interesting and unusual properties such as anion complexation,[4] supramolecular assembly,[5] and the formation of rigid-rod molecules.[2] In an earlier report[2a] we presented a rational synthesis and the crystallographic characterization of a tetrameric *p*-carborane derivative in which icosahedral *p*-carborane molecules function as modular units linked together at the carbon vertices in a linear fashion. A copper-mediated carbon−carbon bond formation process was employed in these “carborod” syntheses. Due to their rigidity and linear shape, carborod molecules have potential uses in framework construction processes.[6] The solubility of carborods in common organic solvents was found to be greatly enhanced by silylation of the terminal carbon vertices, but the terminal sites were blocked to further extension reactions. Our continuing interest in this area has led us to search for new types of *p*-carborane-based modular units that are suitable for linear construction with enhanced solubility, rigidity, and reactivity, thus allowing the construction of longer carborod molecules.

Eaton and co-workers recently demonstrated the use of alkynylcubanes as precursors of rigid-rod molecules.[7] In addition, functionalized alkynes, which can be easily prepared in high yield,[8] have emerged as a class of versatile precursor molecules for the construction of nanostructures.[9] The highly selective modular incorporation of acetylenic moieties into novel oligomers has been demonstrated in the syntheses of large and structurally well-defined molecular nanostructures.[10]

Although a number of B-substituted *p*-carborane derivatives have been synthesized,[11] the previously described method

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) (a) Ulmer, K. M. *Molecular Electronic Devices*; Carter, F., Ed.; Marcel Dekker, Inc.: New York, 1982; pp 213−222. (b) Haddon, R. C.; Lamola, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 1874. (c) Hopfield, J. J.; Onuchic, J. N.; Beratan, D. N. *Science* **1988**, *241*, 817. (d) Drexler, K. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5275.

(2) (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9717. (b) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721. (c) Mortimer, M. D.; Hawthorne, M. F. *Chem. Br.* **1996**, *32*, 32.

(3) (a) Yang, X.; Johnson, S. E.; Khan, S. I.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 893. (b) Grimes, R. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1289. (c) Hawthorne, M. F.; Yang, X.; Zheng, Z. *Pure Appl. Chem.* **1994**, *66*, 245. (d) Chizhevsky, I. T; Johnson, S. J.; Knobler, C. B.; Gomez, F. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 6981. (e) Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 432. (f) Zheng, Z.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 12338.

(4) (a) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142. (b) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1507. (c) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 193. (d) Zheng, Z.; Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 5320.

(5) Yang, X.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 4904.

(6) (a) *Mesomolecules: from molecules to material*; Mendenhall, G. D., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: New York, 1995. (b) Drexler, K. E. *Nanosystems: molecular machinery, manufacturing, and computation*; John Wiley & Sons, Inc.; New York 1992.

(7) Eaton, P. E.; Galoppini, E.; Gilardi, R. *J. Am. Chem. Soc.* **1994**, *116*, 7588.

(8) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(9) (a) Moore, J. S.; Zhang, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 922. (b) Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (c) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354.

(10) (a) Diederich, F. *Nature* **1994**, *369*, 199. (b) Diederich, F.; Rubin, Y. *Angew. Chem., Int Ed Engl.* **1992**, *31*, 1101.

S0020-1669(95)01574-6 CCC: $12.00

for their fabrication was of only limited utility.[13] Our newly developed methodology,[12,13] providing B-vertex ethynylation of *p*-carborane, utilizes a palladium-catalyzed coupling reaction of terminal alkynes with *p*-carborane iodinated at either one boron vertex (*i.e.* at the 2-position) or at two opposite boron vertices (*i.e.* the 2- and 9-positions). The iodinated precursors are synthesized by electrophilic iodination of *p*-carborane under Friedel−Crafts conditions.[11] The 2-iodo- and 2,9-diiodo-*p*-carborane derivatives were found to couple with trimethylsilylacetylene in the presence of pyrrolidine and bis(triphenylphosphine)palladium dichloride to afford the corresponding ethynylated *p*-carborane products in good yield. Subsequent desilylation with fluoride ion afforded primary carboranyl acetylenes. We demonstrate that these compounds have the potential to serve as modular building blocks for the construction of *p*-carborane based, rod-shaped molecular structures with acetylenic linker groups.

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations except where otherwise stated. Pyrrolidine and piperidine were purchased from the Aldrich Chemical Co. and used as received. The compounds 2-iodo-*p*-carborane (**1**), 2-ethynyl-*p*-carborane (**3**), 2,9-diiodo-*p*-carborane (**6**), 2,9-bis(ethynyl)-*p*-carborane (**7**), and 2,9-bis(trimethylsilylethynyl)-*p*-carborane (**9**) were prepared according to methods described previously.[11,12] Melting points were measured in sealed capillaries on a Thomas-Hoover capillary melting point apparatus. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker AM 360 spectrometer at 360.13 and 90.55 MHz, respectively. Boron (^{11}B) NMR spectra were recorded on a Bruker AM 500 spectrometer at 160.46 MHz. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to residual ^{1}H and ^{13}C present in deuterated solvents. Chemical shift values for ^{11}B spectra were referenced relative to external $BF_3{\cdot}OEt_2$ (0.0 ppm with negative values upfield).

Synthesis of 1,2-bis(2′-*p*-carboranyl)acetylene (4). A mixture of **1** (0.10 g, 0.37 mmol), **3** (0.06 g, 0.37 mmol), bis(triphenylphosphine)palladium dichloride (15 mg), and cupric iodide (2 mg) was dissolved in *ca* 15 mL of pyrrolidine. The reaction mixture was stirred at reflux temperature for 2 days. Solvent was removed *in vacuo*, and the residue was then extracted with hexanes. The product was further purified by flash chromatography (silica/hexanes) followed by recrystallization from pentane to afford **4** as a white solid (0.11 g, 73%), mp 301−302 °C (sealed capillary). ^{1}H NMR ($CDCl_3$): 3.02, 2.77 (br s, 2H, CH), 1.31−3.30 (br, 18H, BH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): 87.2 (≡CB), 66.1, 62.3 (CH) ppm; ^{11}B{^{1}H} NMR (Et_2O): −12.8 (4B), −13.7 (6B), −14.3 (8B), −16.2 (2B, BC≡) ppm; HRMS (EI) for $C_6B_{20}H_{22}$ (*m/z*): calcd, 310.4607; found, 310.4611 (M^+).

Synthesis of 1,4-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$-1,3-butadiyne (5). A mixture of cupric chloride (10 mg) and **3** (17 mg) was dissolved in *ca* 2 mL of piperidine and 5 mL of toluene. The reaction solution was stirred open to air at reflux temperature for 18 h. Solvent was removed *in vacuo* and the residue extracted with hot hexanes. The extract was passed through a neutral alumina bed and concentrated under reduced pressure to yield a yellow solid. The crude product was further purified by flash chromatography (silica/benzene:hexanes (10:90)) to yield **5** as a white solid (9 mg, 53%), mp 289−290 °C (sealed capillary). ^{1}H NMR ($CDCl_3$): 2.86 (br s, CH, 2H), 3.05 (br s, CH, 2H), 1.35−3.36 (br, 18H, BH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 90.6 (≡CC≡), 86.4 (≡CB), 65.7, 62.8 (CH) ppm. ^{11}B{^{1}H} NMR (Et_2O): −12.6 (4B), −13.0 (8B), −14.1 (6B), −16.0 (2B, BC≡) ppm. HRMS (EI) for $C_8B_{20}H_{22}$ (*m/z*): calcd, 334.4827; found, 334.4823 (M^+).

Table 1. Details of Crystallographic Data Collection for **5** and **9**

	5	**9**
empirical formula	$C_8H_{22}B_{20}$	$C_{12}H_{28}B_{10}Si_2$
fw	334.48	336.27
cryst size (mm)	0.1 × 0.2 × 0.4	0.2 × 0.2 × 0.5
cryst syst	monoclinic	monoclinic
space group	*P*2/*a*	*C*2/*m*
a (Å)	12.352(6)	22.111(4)
b (Å)	14.169(6)	7.565(2)
c (Å)	12.384(5)	6.943(1)
α (deg)		
β (deg)	109.69(2)	107.871(8)
γ (deg)		
V (Å^3)	2041	1105
Z	4	2
d_{calc} (g/cm^3)	1.09	1.01
radiation (λ)	Cu Kα (1.5418 Å)	Cu Kα (1.5418 Å)
μ (cm^{-1})	2.86	13.9
scan rate (deg/min)	6	12
scan width: below $K_{\alpha 1}$ (deg)	1.3	1.3
above $K_{\alpha 2}$ (deg)	1.6	1.6
$2\theta_{max}$ (deg)	90	115
data collcd	$+h, +k, \pm l$	$+h, +k, \pm l$
no. of unique reflections	1747	813
no. of obsd reflns, $I > 3\sigma(I)$	1092	729
parameters refined	118 + 118[d]	70
R^a	0.098	0.059
$R_w{}^b$	0.135	0.090
GOF^c	4.40	3.14

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2]^{1/2}$. [c] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. [d] There are two crystallographically independent molecules.

Synthesis of *closo*-2,9-(*closo*-2′-C_2-9′-I-1′,12′-$C_2B_{10}H_{10}$)$_2$-1,12-$C_2B_{10}H_{10}$ (8). A mixture of **6** (49 mg, 0.13 mmol), **7** (12 mg, 0.063 mmol), dichlorobis(triphenylphosphine)palladium (10 mg), and cupric iodide (2 mg) was dissolved in *ca*. 3 mL of toluene and 1 mL of pyrrolidine. The reaction mixture was stirred at reflux temperature for 45 h. The solvent was removed *in vacuo* and the residue extracted with a mixture of methylene chloride and pentane (1:1). The extract was passed through a neutral alumina bed and concentrated under reduced pressure to yield a yellowish solid. The crude product was further purified by flash chromatography (silica/dichloromethane: pentane (1:1)). Recrystallization from hot hexane produced **8** as a white solid (27 mg, 60%), mp 273−274 °C (sealed capillary). ^{1}H NMR ($CDCl_3$): 3.00 (br s, 2H, CH), 3.10 (br s, 2H, CH), 3.27 (br s, 2H, CH), 1.30−3.35 (br, 24H, BH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 87.6 (≡CB), 88.4 (≡CB), 68.4, 66.3, 67.7 (CH) ppm. ^{11}B{^{1}H} NMR (Et_2O): −13.2 (28B), −27.8 (2B, BI) ppm. HRMS (EI) for $C_{10}B_{30}H_{30}I_2$ (*m/z*): calcd, 728.3447; found, 728.3445 (M^+).

X-ray Crystallography. Table 1 summarizes crystallographic data for compounds **5** and **9**.

1,4-(*closo*-1,12-$C_2B_{10}H_{11}$-2-yl)$_2$-1,3-butadiyne (5). A colorless crystal, obtained from benzene solution, was placed on a fiber and mounted on a Syntex P$\bar{1}$ diffractometer. Unit cell parameters were determined from a least-squares fit of 38 accurately centered reflections (17.5° < 2θ < 40.1°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 1747 unique reflections measured, 1092 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and decay. Programs used in this work include locally modified versions of crystallographic programs listed in ref 14.

Atoms were located by direct methods (SHELX86). All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. All atoms of the carborane moieties were refined with anisotropic parameters. Carboranyl hydrogens were

---

(11) (a) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. (b) Grushin, V. V.; Bregadze, V. I.; Kalinin, V. N. *J. Organomet. Chem. Libr. 20*, **1988**, *20*, 1.

(12) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 3491.

(13) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A. *Akad. Nauk. SSSR. Ser. Khim.* **1985**, 809.

(14) CARESS (Broach, Coppens, Becker and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin and Levy), structure factor calculation and full-matrix least-squares refinement, ORTEP (Johnson) figure plotting, SHELX76 (Sheldrick) crystal structure package, and SHELX86 (Sheldrick) crystal structure solution package.

located and were included, but parameters were not refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Scattering factors for H were obtained from ref 15 and for other atoms were taken from ref 16. The largest peak on a final difference electron density map was 0.1 e Å^{-3}.

***closo*-2,9-(Me_3SiC_2)$_2$-1,12-$C_2B_{10}H_{10}$ (9)**. A colorless crystal, obtained from a deuterated chloroform solution, was placed on a fiber and mounted on a Syntex $P\bar{1}$ diffractometer. Unit cell parameters were determined from a least-squares fit of 10 accurately centered reflections (16.8° < 2θ < 35.7°). Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Of the 813 unique reflections measured, 729 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for secondary extinction and absorption. Programs used in this work include locally modified versions of crystallographic programs listed in ref 14.

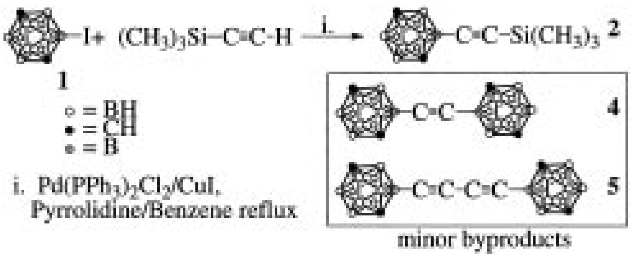
Atoms were located by use of direct methods (SHELX86). All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. All nonhydrogen atoms were refined with anisotropic parameters. All methyl H were included in calculated positions: C−H = 1.0 Å; H−C−H 109.5°. Carboranyl hydrogens were located and were included but parameters were not refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Scattering factors for H were obtained from ref 15 and for other atoms were taken from ref 16. The largest peak on a final difference electron density map was 0.23 e Å^{-3}.

Results and Discussion

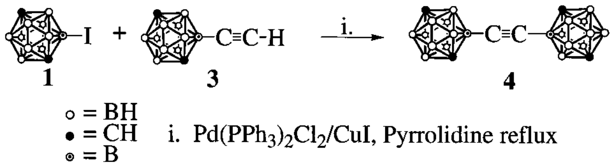
Ethynylated carborane derivatives are a class of compounds which have the potential to be used in the synthesis of polymeric precursors to boron carbide thin films. This application has recently been demonstrated using C-ethynylated derivatives of *o*- and *m*-carborane, where the acetylenic moiety attached to a carbon vertex of the carborane cage serves as a cross-linking group in UV-initiated polymerization reactions.[17] Control of the degree of cross-linking is crucial in determining the quality of the thin film produced.

C-ethynylated carborane derivatives have been prepared in low to moderate yields using a copper-mediated coupling reaction of *C*-lithiocarboranes with a terminally brominated acetylene.[18] An alternate route to *C*-ethynyl *o*-carborane is provided by the reaction of 1,3-butadiyne with 1 equiv of $B_{10}H_{12}(SMe_2)_2$.[19] The preparation of B-substituted acetylenic carborane derivatives has been limited to the coupling reaction of the B-iodinated carborane with an acetylenic Grignard reagent in the presence of a palladium catalyst.[13] Although moderate yields have been reported for these reactions, we have not found them to be synthetically useful. Recently, we reported an alternate method for the preparation of B-ethynylated *p*-carborane derivatives.[12] In this new method, reaction conditions similar to those used to prepare ethynylated aromatic derivatives[8] were utilized.

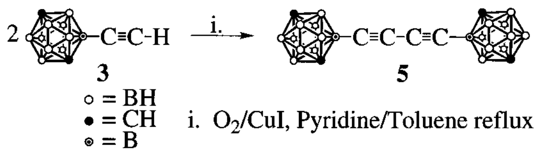
Scheme 1



Scheme 2



Scheme 3



Both 2-iodo- and 2,9-diiodo-*p*-carboranes are reacted with an excess of the appropriate 1-alkyne in the presence of pyrrolidine and catalytic amounts of $(PPh_3)_2PdCl_2$ under mild conditions to afford the corresponding B-alkynyl-*p*-carborane derivatives in good yield.[20,21] The reaction of *closo*-2-I-1,12-$C_2B_{10}H_{11}$ (**1**) with one molar equivalent of trimethylsilyl acetylene under these conditions produced the expected product, *closo*-2-($C{\equiv}CSiMe_3$)-1,12-$C_2B_{10}H_{11}$ (**2**), as well as small amounts of the actylene linked dimers **4** and **5** (Scheme 1).

In a similar manner, the reaction of 2-iodo-*p*-carborane (**1**) with an equimolar quantity of 2-ethynyl-*p*-carborane (**3**)resulted in the formation of **4** as the exclusive product (Scheme 2).

As might be expected, 2-ethynyl-*p*-carborane (**3**) displayed chemical reactivity analogous to that of ethynylated organic substrates.[22] In the presence of cupric chloride, a secondary amine and molecular oxygen, compound **3** was easily coupled oxidatively to produce **5** (Scheme 3). This dumbbell-shaped molecule is comprised of two *para*-carborane cages which are attached to either end of 1,3-butadiyne. The carborane moieties are bonded to the terminal carbons of 1,3-butadiyne through the boron atoms located in the 2-position of the cages. This result is in agreement with an earlier report[19] in which a similar molecule, 1,4-(*closo*-1′,2′-$C_2B_{10}H_{11}$-1′-yl)$_2$-1,3-butadiyne, was prepared directly from the oxidative coupling of 1-ethynyl-1,2-$C_2B_{10}H_{11}$.

Reaction of 2 equiv of 2,9-diiodinated *p*-carborane **6** with 1 equiv of 2,9-diethynyl-*p*-carborane (**7**) proceeded smoothly (Scheme 4). The desired product (**8**) was the exclusive product. This is the first example utilizing the boron vertices of *p*-carborane to assemble a trimer having two discrete types of modular units: an acetylenic linkage and a *p*-carborane cage. Compound **8** is a valuable synthetic intermediate, since it retains an iodine atom at each end of the molecule capable of further substitution. Use of such compounds in future modular assembly reactions should result in the formation of even longer B-substituted ethynyl-*p*-carborane derivatives. Compounds **4** and **8** exhibit greatly enhanced solubility in nonpolar solvents in contrast with the corresponding carborods constructed solely of carborane cages.[21] This enhanced solubility is a critical

---

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(16) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) Johnson, S. E.; Gomez, F. A.; Hawthorne, M. F.; Thorne, K. J.; Mackenzie, J. D. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 113.

(18) Zakharkin, L. I.; Kovderov, A. I.; Ol'shevskaya, V. A. *Akad. Nauk. SSSR. Ser. Khim.* **1986**, 1260.

(19) Callahan, K. P.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 4574.

(20) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *36*, 3491.

(21) Yang, X.; Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chim. Acta* **1995**, *240*, 371.

(22) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943.

Table 2. Selected Bond Lengths and Angles for **5**[a]

		Lengths (Å)			
C(1)−B(2)	1.713(10)	1.713(10)	B(2)−B(6)	1.713(10)	1.775(12)
C(1)−B(3)	1.707(11)	1.702(13)	B(2)−B(7)	1.815(12)	1.711(11)
C(1)−B(4)	1.683(11)	1.727(12)	B(2)−C(13)	1.528(10)	1.534(11)
C(1)−B(5)	1.683(11)	1.676(14)	C(13)−C(14)	1.209(9)	1.166(10)
C(1)−B(6)	1.746(11)	1.686(12)	C(14)−C(14)	1.418(8)	1.398(9)
		Angles (deg)			
C(1)−B(2)−B(3)	59.1(4)	56.9(5)	B(2)−C(13)−C(14)	179.1(6)	175.5(7)
C(1)−B(2)−B(6)	61.6(5)	57.1(5)	B(3)−B(2)−B(6)	109.6(6)	105.3(6)
C(1)−B(2)−B(7)	103.7(5)	102.1(6)	B(6)−B(2)−C(13)	125.0(6)	119.1(6)
C(1)−B(2)−B(11)	106.3(5)	103.6(5)	B(7)−B(2)−C(13)	121.0(6)	127.2(6)
C(1)−B(2)−C(13)	124.4(6)	121.2(6)	C(13)−C(14)−C(14)	177.5(6)	178.5(7)

[a] The second value given for each length or angle is the appropriate value for the "primed" atoms of a second unique molecule.

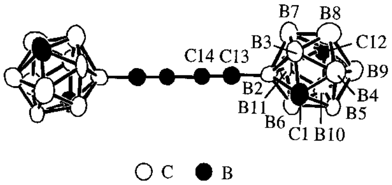
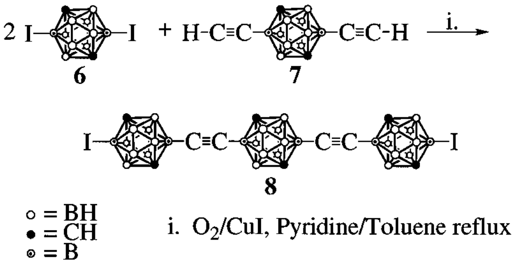


Figure 1. ORTEP representation of compound **5**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Scheme 4



feature for the construction of larger oligomers since nominal solubility in standard solvents is required for their synthesis and characterization.

All of the coupling products obtained in this study have been characterized by multinuclear nuclear magnetic resonance spectroscopy (NMR) and high resolution EI mass spectrometry. The ^{11}B NMR resonances of *closo*-2-R-1,12-$C_2B_{10}H_{11}$ and *closo*-2,9-R_2-1,12-$C_2B_{10}H_{10}$ species exhibit a distinctly different pattern from those of the corresponding iodo- and diiodo-*p*-carboranes. Although the chemical shifts of the signals due to the boron atoms bonded to hydrogens are essentially the same in all of these compounds, the carbon-substituted boron atoms are deshielded, thus giving low field resonances compared to their iodo counterparts. This chemical shift difference provides a simple way to confirm the presence of a B-alkynylated derivative. Also noteworthy is that the carbon nuclei directly bonded to boron vertices give rise to ^{13}C NMR signals which are broadened (sometimes beyond detection). This broadening must be attributed to their close proximity to boron atoms in the carborane cage.[23]

The molecular structures of both 1,4-(*closo*-1′,12′-$C_2B_{10}H_{11}$-2′-yl)$_2$-1,3-butadiyne (**5**) and *closo*-2,9-(C≡CSiMe_3)$_2$-1,12-$C_2B_{10}H_{10}$ (**9**) were established by X-ray diffraction studies (Figures 1 and 2, respectively). Although the synthesis of compound **9** was described in our earlier report,[11] an X-ray diffraction study was not performed at that time. To our knowledge, both structures presented here establish the first crystallographic characterization of B-alkynylated *p*-carborane derivatives. In the structures of compounds **5** and **9** the acetylenic fragments are present at either the 2- or 2,9-positions of the *p*-carborane cage. The 2- and 9-positions of *p*-carborane are symmetrically equivalent, and consequently they bear the same charge density.

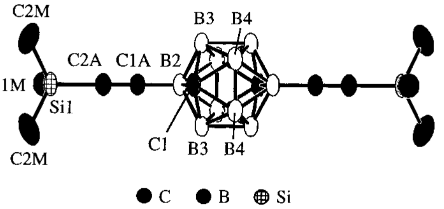


Figure 2. ORTEP representation of compound **9**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. The molecule has a crystallographically imposed center of symmetry.

Table 3. Selected Bond Lengths and Angles for **9**

	Lengths (Å)		
C(1)−B(2)	1.719(8)	B(4)−B(4)	1.785(7)
C(1)−B(3)	1.704(5)	B(2)−C(1A)	1.532(7)
C(1)−B(4)	1.725(6)	C(1A)−C(2A)	1.206(7)
B(2)−B(3)	1.767(6)	C(2A)−Si(1)	1.837(5)
B(2)−B(4)	1.786(6)	C(2M)−Si(1)	1.867(6)
	Angles (deg)		
B(2)−C(1)−B(4)	114.2(3)	B(3)−B(4)−B(4)	107.2(3)
B(2)−C(1A)−C(2A)	178.5(3)	B(4)−B(2)−C(1A)	125.4(3)
B(3)−C(1)−B(3)	112.6(3)	C(1)−B(2)−C(1A)	121.1(3)
B(3)−C(1)−B(4)	62.3(2)	C(2A)−B(2)−B(2)	175.0(2)
B(3)−B(2)−B(3)	106.7(3)	Si(1)−B(2)−B(2)	174.1(1)

In the structure of **5**, averaged bond distances are $C_{carborane}$−B = 1.696(13) Å, B−B = 1.761(13) Å, B−$C_{acetylene}$ = 1.534(11) Å, and C≡C = 1.166(10) Å. In the structure of **9**, the average bond distances are $C_{carborane}$−B = 1.716(6) Å, B−B = 1.775(6) Å, B−$C_{acetylene}$ = 1.532(7) Å, and C≡C = 1.206(7) Å. Selected bond distances and angles for **5** and **9** are listed in Table 2 and Table 3, respectively.

The primary axis of rotation in compound **5** is essentially linear, deviating less than 2° from the idealized case of 180°. The overall length of **5** as measured from the boron atom at one end of the molecule to the furthest boron atom at the opposite end of the molecule is calculated to be 13.579 Å. Compound **9** was also found to be nearly linear with the two silylated acetylenic fragments and the *p*-carborane cage situated along a line. [The Si−B(2)−B(2) angle is 174.1(1)° and C(2A)−B(2)−B(2) is 175.0(2)°.] The length of **9**, as measured by the interatomic distance from the methyl carbon of one trimethylsilyl group through the *p*-carborane moiety to the furthest methyl carbon of the other trimethylsilyl group is calculated to be 8.872(6) Å. This value is slightly longer than half the length (17.195 Å) reported for the corresponding tetrameric *p*-carborane.[2a] The calculated interatomic distance

---

(23) Harris, R. K.; Mann, B. E. Eds., *NMR and the Periodical Table*; Academic Press: London, 1978; p 195.

for B_2–B_9 [B(2) to the symmetrically equivalent B(2), 2] in the cage for **9** is about 3.405(5) Å, which is significantly longer than the averaged C_1–C_{12} distances (3.150 Å) for the reported C-vertex linked tetrameric *p*-carborane structure.[2a] On the basis of the above structural parameters, we estimate the molecular module size of **8** to be 18.707 Å.

Conclusions

Attachment of the acetylenic functionality to the boron vertices of *p*-carborane has been achieved via a palladium-catalyzed coupling process. This method provides ready access to a new series of ethynylated *p*-carborane molecules for use in the construction of modular carborods.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by the National Science Foundation under Grant CHE 9314037.

Supporting Information Available: Tables of position and thermal parameters, bond lengths and angles, and crystallographic data collection for compounds **5** and **9** (9 pages). See any current masthead page for ordering information and Internet access instructions.

IC951574L