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Synthesis and Structural Characterization of Bis- and Tris(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)-Substituted Biphenyl and Benzene

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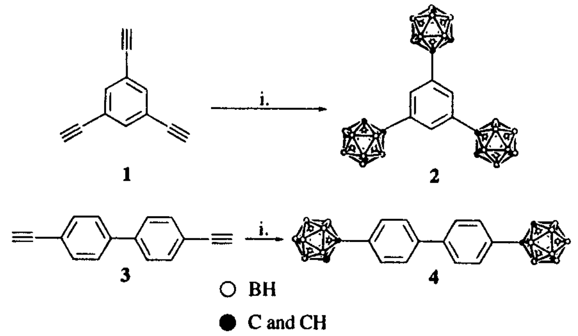
The icosahedral carboranes are remarkable molecular building blocks with excellent chemical stability and a high boron content.[1] The attachment of suitable organic moieties to a C-vertex of the carborane cage has resulted in the formation of a class of carborane-containing molecules which can further serve as rigid molecular building units,[2] molecular precursors for boron carbide B_4C thin film fabrication[3] and the development of carborane-based nonlinear optical materials.[4] The choice of the appropriate organic moiety to be attached to the C-vertex of the carborane molecule is critical to the success of any of these applications and the *C*-aryl derivatives of *o*-carborane are of particular importance in these applications. Here, we describe a facile synthetic route leading to the formation of aryl derivatives containing multiple carborane cages exemplified by 1,3,5-tris(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)benzene (**2**) and 4,4′-bis(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)biphenyl (**4**).

Results and Discussion

Compounds **2** and **4** have been efficiently prepared in high yield by reaction of their corresponding arylalkyne precursor with $B_{10}H_{12}(Et_2S)_2$[5] as shown in Scheme 1. This method is general for the preparation of a variety of C-substituted *o*-carborane derivatives.[6]

An earlier report[7] briefly described the application of this synthetic method to the preparation of several *bis*-aryl-substituted *o*-carborane derivatives. However, there has been no report of the application of this well estabished procedure to the one-step synthesis of aryl derivatives containing more than one carborane substituent. The reactions reported here proceeded smoothly with 1,3,5-triethynylbenzene, **1**,[8] and 4,4′-diethynylbiphenyl, **3**,[9] without the need for special conditions other than the use of a limited excess of $B_{10}H_{12}(Et_2S)_2$ in order to assure complete conversion of the alkyne functions to carborane cages. The procedure described here is generally useful for the synthesis of a variety of *C*-aryl-substituted *o*-carborane derivatives since a variety of arylalkyne derivatives are readily available.[10]

Scheme 1



i. $B_{10}H_{12}(Et_2S)_2$ in toluene, 80°C, 3 days

Previous studies have demonstrated the inability of anionic carborane species to replace the halogen atom of η^6-$Cr(CO)_3$ complexes of aryl halides in high yield.[11] Under those conditions, we were only able to obtain the *C*-aryl derivatives of *o*-carborane in very low yields. A general procedure for C-monoarylation of carboranes and C,C′-diarylation of *m*- and *p*-carborane based on copper(I) derivatives has recently been described.[12] A description of the simple preparation of a 1,3,5-tris(1-*closo*-1,12-$C_2B_{10}H_{11}$-1-yl) benzene derivative using a copper(I)-mediated coupling reaction has also appeared.[13] Both studies demonstrated that the copper(I)-mediated coupling reaction could afford a variety of C-substituted aryl derivatives of carborane in low to moderate yields.

Compound **2**, prepared directly from the reaction of 1,3,5-triethynylbenzene with $B_{10}H_{12}(Et_2S)_2$, is potentially trifunctional. One of the carbon vertices of each *o*-carborane cage is directly connected via a σ bond to a carbon atom in the aromatic benzene ring and an acidic hydrogen at the second C-vertex of each *o*-carborane cage is available for further derivatization. This rigid arene skeleton is a potentially important molecular building unit for the construction of carborane-based supramolecular species. As we expected, this molecule is thermally quite stable, having a melting point above 340 °C, and it is moderately soluble in benzene, which greatly facilitates its solution characterization. The remarkable thermal stability of **2** suggests a possible route for preparation of its *m*- and *p*-carborane counterparts by thermal isomerization at high temperatures.[14] The preparation of another similar molecule, 1,2,4-tris(*closo*-1,2-$C_2B_{10}H_{11}$-1-yl)benzene, an isomer of **2**, was reported earlier.[15] This compound was prepared from 1-ethynyl-1,2-carborane by the nickel(0)-catalyzed cyclotrimerization reaction. The production of the more sterically hindered 1,2,4 isomer in the trimerization of 1-ethynyl-1,2-carborane is attributed to catalytic specificity. Although *C*-aryl derivatives of *o*-carborane are well-known, examples of *C*-aryl derivatives of *o*-carborane containing more than one carborane cage on the aryl fragment are very limited.[16,17]

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Table 1. Details of Crystallographic Data Collection for **4**

empirical formula	$C_{16}H_{30}B_{20}$	γ (deg)	75.315(3)
fw	438.38	V (Å^3)	1805
space group	$P\bar{1}$,	Z	2
a (Å)	11.231(1)	d_{calc} (g/cm^3)	1.09
b (Å)	11.393(1)	μ (cm^{-1})	3.49
c (Å)	15.223(2)	R (%)[a]	0.093
α (deg)	81.932(4)	R_w (%)[b]	0.100
β (deg)	73.924(3)		

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2]^{1/2}$.

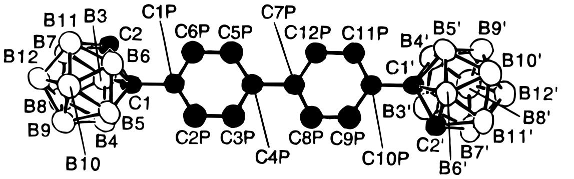

Figure 1. ORTEP diagram of the molecular structure of **4** with labeling scheme.

Both **2** and **4** have been characterized by multinuclear NMR and EI mass spectrometry. The ^{11}B NMR resonances of both **2** and **4** exhibit a similar mono-C-substituted *o*-carborane pattern. All attempts to establish the solid state structure of **2** by an X-ray diffraction study failed due to the disorder of crystals obtained from a variety of solvents. However, the molecular structure of compound **4** was successfully elucidated by X-ray diffraction studies. Table 1 summarizes crystallographic data obtained for **4**. Compound **4** contains two *o*-carboranyl units linked at the 4,4′-positions of a biphenyl fragment via two carborane carbon atoms, respectively. The molecular structure of **4**, shown in an ORTEP representation (Figure 1), reveals a linear arrangement of carborane icosahedra through the biphenyl fragment. The angles B(12′)−C(1′)−C(10P) and B(12)-C(1)-C(1P) are 174.3(3) and 174.7(3)°, respectively, and the angle C(1)−C(4P)−C(10P) is 175.4(1)°. The two carboranyl units orient themselves in a slightly "trans" arrangement about the axis defined by C(1P) and C(10P). The distance between "end" boron atoms of the cage, namely, B(12) and B(12′), is 16.62(1) Å. The interatomic distances between C(1) and C(1P) and between C(1′) and C(10P), are 1.514(6) and 1.516(6) Å, respectively, quite comparable to the values 1.510(4)−1.516(5) Å of the reported distances of the carborane carbon atom to the phenyl ring in earlier structural determinations of several aryl-substituted *o*-carborane derivatives.[11] An interesting feature of this structure is the biphenyl skeleton, which is nearly coplanar since the dihedral angle between the two phenyl rings is about 9.6°. The orientation of the *C-o*-carboranyl group with respect to the phenylene rings bound to them is different; the torsion angles of the C(6P)−C(1P)−C(1)−C(2) and C(9P)−C(10P)−C(1′)−C(2′) arrays are 10.2(6)° and 26.7(6)° respectively. The angles C(1P)−C(1)−C(2) and C(10P)−C(1′)−C(2′) are 117.6(4) and 117.0(4)°, respectively. Selected bond distances of **4** are given in Table 2. The average bond distances of the B−B and B−C bonds for **4** are 1.772(4) and 1.714(4) Å with a scatter of 1.751−1.811 and 1.694−1.752 Å, respectively. These interatomic distances within the carborane polyhedra are within the normal range for *closo*-$C_2B_{10}H_{12}$ carboranes.[18] The average C−C bond distance in the carborane cages of **4** is about 1.638 Å, which is the shortest interatomic distance in the icosahedron.

Table 2. Selected Bond Lengths for **4**

C(1)−C(2)	1.634(8)	C(1′)−C(2′)	1.643(7)
C(1)−B(3)	1.732(9)	C(1′)−B(3′)	1.724(9)
C(1)−B(4)	1.720(9)	C(1′)−B(4′)	1.720(9)
C(1)−B(5)	1.717(8)	C(1′)−B(5′)	1.728(9)
C(1)−B(6)	1.752(9)	C(1′)−B(6′)	1.745(9)
C(1)−C(1P)	1.514(6)	C(1′)−C(10P)	1.516(6)
C(2)−B(3)	1.730(10)	C(2′)−B(3′)	1.721(9)
C(2)−B(6)	1.715(9)	C(2′)−B(6′)	1.725(9)
C(2)−B(7)	1.718(10)	C(2′)−B(7′)	1.694(10)
C(2)−B(11)	1.697(10)	C(2′)−B(11′)	1.711(9)
C(4P)−C(7P)	1.519(4)		
B(12)−B(7)	1.768(11)	B(12′)−B(7′)	1.770(11)
B(12)−B(8)	1.800(12)	B(12′)−B(8′)	1.795(11)
B(12)−B(9)	1.780(11)	B(12′)−B(9′)	1.777(11)
B(12)−B(10)	1.781(11)	B(12′)−B(10′)	1.765(11)
B(12)−B(11)	1.768(12)	B(12′)−B(11′)	1.761(10)

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations. Toluene was dried over sodium benzophenone ketyl and distilled into the reaction vessel prior to use. Diethyl sulfide was purchased from Aldrich Chemical Co. and dried by the procedure previously described.[5] The aryl alkyne derivatives **1** and **3** were prepared by literature methods.[8,9] Melting points were measured in sealed capillaries on a Thomas-Hoover capillary melting point apparatus and were uncorrected. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded with AM 360, AM 360, and AM 500 spectrometers, respectively. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual ^1H and ^{13}C present in deuteriated 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). Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany.

Synthesis of 2. The $B_{10}H_{12}(Et_2S)_2$ derivative (15.0 mmol) was prepared using a previously described method.[5] To this species was added 0.60 g of **1** (4.0 mmol) in *ca* 100 mL of toluene. The reaction mixture was stirred at 80 °C for 3 days. The unreacted boron hydride was destroyed by a previously described method,[5] and diethyl sulfide was removed from the reaction mixture by codistillation with ethanol. After workup, the benzene solution of the product was filtered through a bed of basic alumina, and solvent was removed with a rotary evaporator to afford the crude product. Recrystallization from a mixture of benzene and hexane afforded 1.57 g of product (78%), mp > 340 °C (sealed capillary). ^1H NMR (C_6D_6): 2.65 (br s, 3H, CH), 7.52 (s, 3H, C_6H_3), 1.50−3.70 (br, 30H, BH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 135.1, 129.9 (C_6H_3), 74.3, 61.1 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −1.2 (3B), −2.8 (3B), −7.8 (6B), −10.2 (6B), −10.9 (6B), −11.9 (6B) ppm. EI-MS for $C_{12}B_{30}H_{36}$ (*m/z*): found 504.2 (M^+). Anal. Calcd for $C_{12}B_{30}H_{36}$: C, 28.56; B, 64.26; H, 7.18. Found: C, 28.50; B, 64.30; H, 7.20.

Synthesis of 4. The $B_{10}H_{12}(Et_2S)_2$ derivative (15.0 mmol) was prepared using a previously described method.[5] To this species was added 1.21 g of **3** (6.0 mmol) in ca 100 mL of toluene. The reaction mixture was stirred at 80 °C for 3 days. The unreacted decaborane derivative was destroyed by a previously described method,[5] and diethyl sulfide was removed from the reaction mixture by codistillation with ethanol. After workup, the benzene solution of the product was filtered through a bed of basic alumina and solvent was removed with a rotary evaporator to afford the crude product. Recrystallization from benzene afforded 2.18 g of product (83%), mp 297−298 °C (sealed capillary). ^1H NMR ($CDCl_3$): 4.01 (br s, 2H, CH), 7.52 (d, 4H, C_6H_4, $J = 8.4$ Hz), 7.59 (d, 4H, C_6H_4, $J = 8.6$ Hz), 1.20−3.90 (br, 20H, BH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 140.9, 133.0, 128.1, 127.3 (C_6H_4), 75.9, 60.0 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −1.9 (2B), −3.9 (2B), −8.4 (4B), −10.5 (8B), −12.4 (4B) ppm. EI-MS for $C_{16}B_{20}H_{30}$ (*m/z*): found 438.4 (M^+). Anal. Calcd for $C_{16}B_{20}H_{30}$: C, 43.81; B, 49.29; H, 6.90. Found: C, 43.67; B, 49.40; H, 6.93.

X-ray Diffraction Study of 4. A colorless crystal suitable for X-ray diffraction study, obtained from a benzene solution, was mounted in a capillary and placed on a Syntex $P\bar{1}$ diffractometer modified by Professor C. E. Strouse of this department. Unit cell parameters were

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determined from a least-squares fit of 16 accurately centered reflections (17.8° $< 2\theta < 39.3°$). Data were collected at 25 °C in the $\theta - 2\theta$ scan mode. Of the 4959 unique reflections measured, 2751 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 but not for absorption. Programs used in this work include locally modified versions of crystallographic programs listed in ref 19.

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. The crystal contains two molecules of benzene per molecule of biphenyl carborane. With the exception of biphenyl carbon atoms, all nonhydrogen atoms were refined anisotropically. Phenyl and benzene rings were refined as rigid groups, C−C = 1.395, C−H = 1.0 Å, angles = 120°, and isotropic displacement parameters for H (u) fixed at 0.07 and 0.10 Å^2 for phenyl and benzene, respectively. H atoms on the carborane were included in located positions and were not refined. These H atoms were assigned isotropic displacement values (u) of 0.08 Å^2. Scattering factors for H were obtained from ref 20 and for other atoms from ref 21. The largest peak on a final difference electron density map was 0.12 e·Å^{-3}.

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Supporting Information Available: Tables giving positional and thermal parameters, bond lengths, angles, torsion angles, and crystallographic data for **4** (17 pages). Ordering information is given on any current masthead page.

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