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Acid-Induced Opening of [*closo*-$B_{10}H_{10}]^{2-}$ as a New Route to 6-Substituted *nido*-$B_{10}H_{13}$ Decaboranes and Related Carboranes

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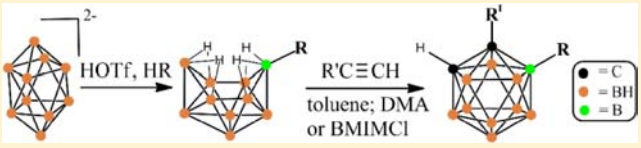
Supporting Information

ABSTRACT: Protonation of the polyhedral anion [*closo*-$B_{10}H_{10}]^{2-}$ under superacidic conditions apparently generates an electrophilic intermediate, $[B_{10}H_{13}]^+$, that forms 6-R-*nido*-$B_{10}H_{13}$ (R = aryl, alkyl, triflate) derivatives by electrophilic aromatic substitution, C−H bond activation, or ion-pair collapse, respectively. The proposed mechanism of formation of the 6-R-*nido*-$B_{10}H_{13}$ derivatives via the boranocation $[B_{10}H_{13}]^+$ is discussed. The synthesis of carboranes, starting from 6-R-*nido*-$B_{10}H_{13}$ decaboranes, and single-crystal X-ray diffraction analyses of several 6-R-*nido*-$B_{10}H_{13}$ decaboranes and carboranes are described.



INTRODUCTION

Since its first reported synthesis from $B_{10}H_{12}(ligand)_2$,[1] the [*closo*-$B_{10}H_{10}]^{2-}$ ion has been the subject of numerous studies pertaining to its chemical properties and reactivity.[2−7] It can be conveniently prepared by the reaction of $B_{10}H_{12}(ligand)_2$ with 2 equiv of base.[1,8] The geometric change of the open *arachno*-$B_{10}H_{12}(ligand)_2$ structure to the bicapped square-antiprismatic [*closo*-$B_{10}H_{10}]^{2-}$ ion structure involves the removal of the bridging hydrogen atoms as protons from *arachno*-$B_{10}H_{12}(ligand)_2$. The resulting filled two-center orbitals act as internal nucleophiles to displace the ligands from the 6 and 9 positions of the *arachno*-$B_{10}H_{12}(ligand)_2$ structure.[6] Additional research illustrates the cage-opening reaction of [*closo*-$B_{10}H_{10}]^{2-}$ with 2 equiv of strong acid and 2 equiv of ligand to produce *arachno*-$B_{10}H_{12}(ligand)_2$.[9] Monoprotonation of [*closo*-$B_{10}H_{10}]^{2-}$ with a strong acid, such as trifluoroacetic acid, produces a $[B_{10}H_{11}]^-$ anion.[10,11] The initial X-ray diffraction studies[12] of $[Ph_4P]^+$ and $[Ph_3P(Et)]^+$ salts of $[B_{10}H_{11}]^-$ did not locate the 11th hydrogen atom associated with the $[B_{10}H_{11}]^-$ cluster. However, a recent X-ray structural analysis of $[PPh_3(benzyl)][B_{10}H_{10}]$ shows that the B_{10} core of $[B_{10}H_{11}]^-$ is similar in shape to that of [*closo*-$B_{10}H_{10}]^{2-}$ and the 11th hydrogen atom symmetrically caps an apical face of the [*closo*-$B_{10}H_{11}]^-$ cluster.[13] It is possible that this is the first stage in the cage-opening process but that a superacid might be required to complete the process.

Earlier, we reported that [*closo*-$B_{10}H_{10}]^{2-}$ could be opened to selectively form 6-R-*nido*-$B_{10}H_{13}$ (R = triflate, phenyl, cyclohexyl) if treated with triflic acid in noncoordinating solvents such as benzene and cyclohexane, respectively.[7] We suggested that the formation of a boranocation intermediate, [*closo*-$B_{10}H_{13}]^+$, occurred through a facile protonation under noncoordinating conditions.

On the basis of this discovery, 6-(HO)-*nido*-$B_{10}H_{13}$ was synthesized from *closo*-$(NH_4)_2B_{10}H_{10}$ by treatment with sulfuric acid in hexane.[14] Sneddon et al. reported an efficient synthesis of 6-X-*nido*-$B_{10}H_{13}$ (X = Cl, Br, I) using the cage-opening reactions of *closo*-$(NH_4)_2B_{10}H_{10}$ with superacidic hydrogen halides in the presence of an ionic liquid.[15]

The 6-R-*nido*-$B_{10}H_{13}$ decaboranes are attractive compounds in both decaborane and substituted carborane syntheses. The syntheses of carboranes by reacting acetylenic compounds with decaborane−Lewis base mixtures are well-known.[16,17] As a part of our continued interest in the development of strategies for carborane syntheses, we report here an extension of our previous work[7] on the triflic acid induced opening of [*closo*-$B_{10}H_{10}]^{2-}$ to 6-R-*nido*-$B_{10}H_{13}$ (compounds **1**−**3**) and its subsequent conversion to carboranes (compounds **4**−**6**, respectively).

RESULTS AND DISCUSSION

6-Substituted *nido*-$B_{10}H_{13}$ Decaborane Derivatives. Our previously reported synthesis of 6-substituted decaborane by a triflic acid induced cage opening of [*closo*-$B_{10}H_{10}]^{2-}$ has been extended to other arene systems. These reactions proceed through a triflic acid induced opening of [*closo*-$B_{10}H_{10}]^{2-}$ to form a [*closo*-$B_{10}H_{13}]^+$ intermediate that functions as an electrophile in the presence of an aromatic substrate, such as toluene, mesitylene, chlorobenzene, and *α*,*α*,*α*-trifluorotoluene, to give the corresponding 6-substituted decaboranes in 12−92% yield (Scheme 1).

The reaction of *closo*-$Cs_2B_{10}H_{10}$ in chlorobenzene at room temperature with 5 equiv of triflic acid under anhydrous conditions rapidly produced 6-(ClC_6H_4)-*nido*-$B_{10}H_{13}$ in 77% yield (**1a**) as a mixture of predominantly ortho and para isomers. The ^{11}B, ^1H, and $^{13}C\{H\}$ NMR spectra are consistent with the 6-(ClC_6H_4)-*nido*-$B_{10}H_{13}$ structure. The phenyl proton

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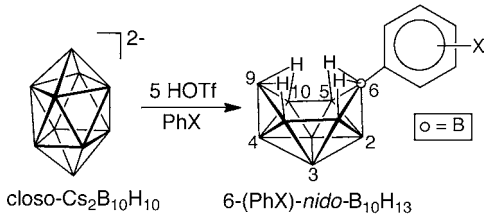
Scheme 1. Triflic Acid Induced Opening of $[closo\text{-}B_{10}H_{10}]^{2-}$ in the Presence of Aromatic Hydrocarbons



resonance in the ^1H NMR spectra, the two sets of signals in the $^{13}C\{H\}$ NMR, and a two-dimensional (2D) HMQC (heteronuclear multiple quantum correlation) experiment confirmed the characteristic phenyl-substitution pattern for the ortho and para isomers. Gas chromatography/mass spectrometry (GC/MS) analysis showed the ratio of ortho and para isomers as 35.7/63.5. However, GC/MS analysis showed the presence of the meta isomer (0.8%), which was not evident in the ^1H and ^{13}C NMR spectra.

With the advent of the 2D $^{11}B-^{11}B$ NMR technique, structural elucidation of substituted polyhedral boranes using ^{11}B NMR has received additional attention. Several reports have demonstrated the potential of this powerful new NMR tool.[18] The $^{11}B\{H\}$ and $^{11}B-^{11}B$ correlated spectroscopy (COSY) NMR for **1a** provided ample information for making the structural assignments (see the Supporting Information). We could observe the cross peak for the B6 atom of para and ortho isomers connected to the B2 atom. However, the second cross peak connecting B6 to B5 and B7 was not observed because of the bridging hydrogen atoms across the B5 and B7 atoms. Thus, the following assignments can be made based on the contour plot: δ 22.1 (*p*-B6), 19.5 (*o*-B6), 10.4 (B1,3), 9.2 (B9), 0.9 (B8,10), −1.2 (*o*-B5,7), −4.1 (*p*-B5,7), −32.2 (*p*-B2), −33.8 (*o*-B2), −37.6 (B4).

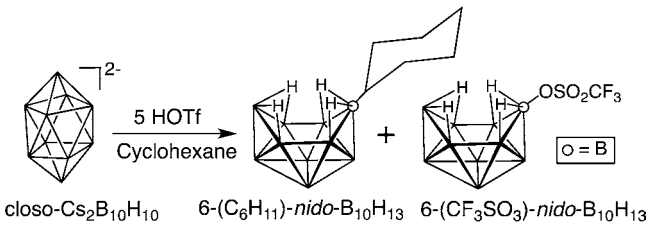
The reaction of *closo*-$Cs_2B_{10}H_{10}$ in toluene at room temperature with 5 equiv of triflic acid under anhydrous conditions rapidly produced 6-$(CH_3C_6H_4)$-*nido*-$B_{10}H_{13}$ (**1b**) as a mixture of ortho-, meta-, and para-substituted isomers with a 92% combined yield. The isomers were confirmed by ^1H and $^{13}C\{H\}$ NMR and a 2D HMQC experiment. GC/MS analysis showed the distribution of ortho/meta/para isomers to be 5.5/14.0/80.5. Brown and Nelson[19] have shown that the level of meta-substituted product formed in the electrophilic aromatic substitution of monosubstituted benzene such as toluene can be used as a measure of the reactivity of the electrophile used in the reaction. Using this analogy, the formation of 14% meta-substituted product will place the $[B_{10}H_{13}]^+$ electrophile next to the methanesulfonium cation (15% meta substitution) in reactivity. The low percentage of the ortho isomer may be due to steric hindrance. As in compound **1a**, a $^{11}B-^{11}B$ COSY NMR experiment was helpful to identify various ^{11}B resonances, which were assigned as follows: 23.6 (*m*/*p*-B6), 22.1 (*o*-B6), 10.2 (B1,3), 9.0 (B9), 1.1 (B8,10), −2.2 (*o*-B5,7), −4.7 (*m*/*p*-B5,7), −31.7 (*m*/*p*-B2), −33.0 (*o*-B2), −37.7 (B4). A molecular-ion peak at *m*/*z* 212.2054 in the APCI mass spectrum confirmed the molecular formula of $[B_{10}H_{13}C_6H_4CH_3]^-$ for **1b**. The strong absorption due to the terminal B−H bonds of the cage is seen at 2574 cm^{-1} in the IR spectrum.

The acid-induced opening of *closo*-$Cs_2B_{10}H_{10}$ in triflic acid in the presence of aromatic compounds with electron-withdrawing groups, such as α,α,α-trifluorotoluene, showed that the electrophilic substitution occurred slowly and with formation of the byproduct 6-(CF_3SO_3)-*nido*-$B_{10}H_{13}$ (**3**). Compound **3** was independently synthesized by the reaction of *closo*-$Cs_2B_{10}H_{10}$ with triflic acid and without additional solvent in 92% yield.[5] The desired 6-$(CF_3C_6H_4)$-*nido*-$B_{10}H_{13}$ (**1c**) was isolated mostly as the meta isomer with a 12% yield because the CF_3 group is strongly deactivating and meta-directing. Seven peaks with relative areas of 1/2/1/2/2/1/1 constitute the $^{11}B\{H\}$ NMR spectrum, in which one of the singlets is attributed to B6 substituted with an α,α,α-trifluorotolyl group. The ^1H NMR shows the characteristic meta-substituted aromatic system: δ 7.9 (s), 7.53 (d), 7.44 (d), 6.99 (t). The $^{13}C\{H\}$ and ^1H NMR spectra are in accordance with the **1c** structure. GC/MS analysis revealed the presence of a minor para isomer, with the ortho/meta/para products showing a 0/92/8 distribution.

Only one isomer was observed for 6-$[2,4,6\text{-}(CH_3)_3C_6H_2]$-*nido*-$B_{10}H_{13}$ (**1d**). Three peaks due to the ring carbon atoms and two peaks due to the methyl carbon atoms were seen in the $^{13}C\{H\}$ NMR spectrum. The carbon atom attached to the boron atom was not observed in the $^{13}C\{H\}$ NMR spectrum due to quadruple splitting of the boron atom. The aromatic protons were seen at δ 6.68, while the methyl group protons at δ 2.17 and 2.11 were observed with an integration of 2/6/3 in the ^1H NMR spectrum.

The use of cyclohexane rather than arenes in the cage-opening reaction gave 6-(C_6H_{11})-*nido*-$B_{10}H_{13}$ (**2**) in 8% yield, accompanied by 6-(CF_3SO_3)-*nido*-$B_{10}H_{13}$ derivative **3** (Scheme 2). Compound **2** was previously prepared by reacting

Scheme 2. Triflic Acid Induced Opening of $[closo\text{-}B_{10}H_{10}]^{2-}$ in the Presence of Cyclohexane



$B_{10}H_{13}MgBr$ with cyclohexyl fluoride.[20] The $^{11}B\{H\}$ NMR spectrum of **2** shows seven peaks consistent with the B6-substituted decaborane structure. Two sets of broad peaks arising from the cyclohexyl protons resonate at δ 1.67 and 1.18 in the ^1H NMR spectrum. The $^{13}C\{H\}$ NMR spectrum of the cyclohexyl carbon atoms shows four peaks at δ 32.5, 28.1, 27.4, and 26.2. A molecular-ion peak at *m*/*z* 204.2909 in the APCI spectrum confirms the molecular formula of **2**.

Proposed Mechanism of the Acid-Induced Cage Opening of $[closo\text{-}B_{10}H_{10}]^{2-}$. A remarkable array of reaction products is available from $[closo\text{-}B_{10}H_{10}]^{2-}$ and a strong protic acid, such as CF_3SO_3H.

The regiospecificity seen in these apparent electrophilic substitution reactions and the formation of the triflate derivative (vertex 6 in $B_{10}H_{14}$) suggest that the arylation,

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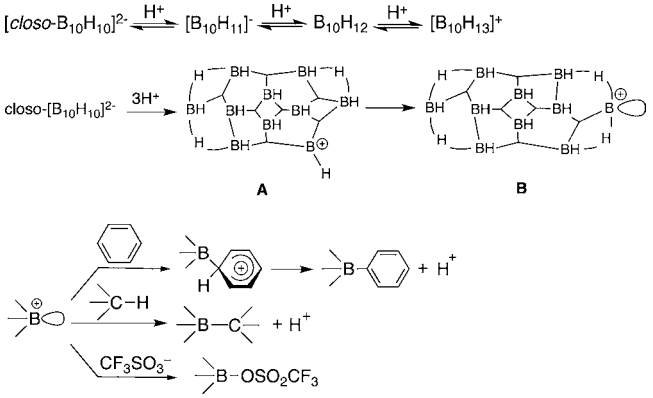
alkylation, and triflation reactions proceed from a common high-energy boranocation $[B_{10}H_{13}]^+$ intermediate (Scheme 3).

Scheme 3. Protonation of $[closo\text{-}B_{10}H_{10}]^{2-}$ Giving a Hypothetical $B_{10}H_{13}^+$ Electrophile



Not unexpectedly, this high-energy intermediate is produced only in noncoordinating solvents. It is presumed that the $[B_{10}H_{13}]^+$ cation is topologically similar to decaborane and may have numerous canonical structures. Scheme 3 shows one of many possible resonance structures that convey the picture of decaborane bonding.[21]

We previously postulated that the addition of three protons to $[closo\text{-}B_{10}H_{10}]^{2-}$ might produce an open $[B_{10}H_{13}]^+$ cage having 22 skeletal electrons (such as the **A** isomer shown in Scheme 3), which could possibly rearrange to an isomer **B** by converting an empty localized skeletal orbital to an empty terminal boron orbital by internal hydride migration.[7]

The B3LYP/6-311G(d)-optimized[22] geometry for $[B_{10}H_{13}]^+$, structure **B** illustrated in Figure 1, shows distinctions from the

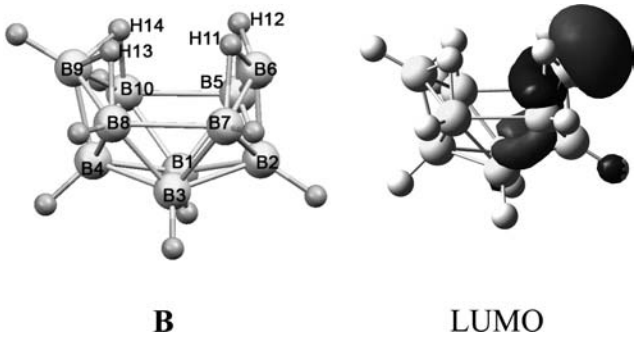
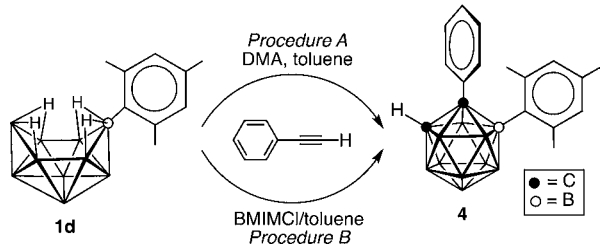


Figure 1. DFT B3LYP/6-311G(d)-optimized geometry of the $[B_{10}H_{13}]^+$ isomer **B** and its LUMO density surface.

$B_{10}H_{14}$ structure. The B–B distance between B6 and B9 is shorter (3.28 Å) than that in $B_{10}H_{14}$ (3.57 Å). Similarly, the B–B distance between B2 and B6 is also considerably shorter (1.63 Å) than that in $B_{10}H_{14}$ (1.71 Å). Also, the distances of the bridging hydrogen bonds between B6 and B7 and between B6 and B5 are shorter (1.25 Å) than those in $B_{10}H_{14}$. These shorter distances are most probably due to the cationic nature of the B6 atom. The lowest unoccupied molecular orbital (LUMO) density surface plot of **B** shows localization on B6, indicating the strong electrophilic nature of B6. The B6 cation in structure **B** is stabilized by two adjacent bridging hydrogen atoms, H11 and H12. The B6–H11 and B6–H12 distances have shortened to 1.26 Å (from the normal distance of 1.34 Å in decaborane).

Carboranes. Sneddon et al.[15] have recently reported a new high-yield route to carboranes through a decaborane dehydrogenative alkyne-insertion reaction in a biphasic ionic liquid/toluene mixture. Using this insertion procedure, we synthesized 1-phenyl-4-mesityl-1,2-dicarba-*closo*-dodecaborane (**4**) by treating **1d** with phenylacetylene in the presence of a catalytic amount of ionic liquid BMIMCl acting as a Lewis base in toluene (Scheme 4). The reaction was complete in 3 h. Product purification by flash chromatography and recrystallization from hexane gave the desired carborane (**4**) in 67% yield.

Scheme 4. Synthesis of 4



Alternatively, carborane **4** was also synthesized in 38% yield by heating a solution of **1d** and phenylacetylene in toluene at 120 °C for 72 h in the presence of *N*,*N*-dimethylaniline (DMA) acting as a Lewis base[16] (Scheme 4).

The $^{11}B\{H\}$ NMR spectrum of carborane **4** contained seven peaks in the δ −0.2 to −14.0 range that were distributed in a ratio of 1/1/1/1/2/2/2. The proton-coupled spectrum shows a singlet at δ −0.2 for the B4 atom, while all of the other signals appear as doublets (J_{BH} = 148–170 Hz). These results are consistent with a 4-substituted *closo*-1,2-carborane structure. In the ^1H NMR spectrum, the C_2H proton resonates at δ 3.98 and the mesityl methyl groups resonate at δ 2.67 and 2.17. A strong molecular-ion peak at *m*/*z* 338.2414 in the TIS-MS also confirms the structure of carborane **4**.

The conversion of decaborane to carborane derivatives strongly depends on the nature of the acetylene compounds used.[16] In the case of electron-withdrawing acetate groups attached to the acetylene moiety, the yields were significantly higher. Thus, treating 6-(C_6H_5)-*nido*-$B_{10}H_{13}$ with propargyl acetate in the presence of DMA for 7 days gave a mixture of two isomers, 1-(acetoxymethyl)-4-phenyl-1,2-dicarba-*closo*-dodecaborane (**5a**) and 1-(acetoxymethyl)-7-phenyl-1,2-dicarba-*closo*-dodecaborane (**5b**), with a 47% combined yield (Scheme 5, procedure A). Although the isomers were not distinguishable in the $^{11}B\{H\}$ NMR spectra, the $^{13}C\{H\}$ and ^1H NMR spectra showed isomers **5a** and **5b** with an isomer ratio of 3/1. Mass spectral analysis of the products agrees with structures **5a**/**5b**. Alternatively, this reaction in the presence of an ionic liquid BMIMCl/toluene mixture for 30 min at 120 °C gave 69% yield of predominantly isomer **5b**, with an isomer **5a**/**5b** ratio of 1/9 (Scheme 5, procedure B). Recrystallization from the benzene/hexane mixture gave a single regioisomer **5b** in 4% yield.

To avoid the complexity of isomer formation in the carborane synthesis, we used the symmetrical 2-butyne-1,4-diol diacetate as the alkyne. Thus, 1,2-bis(acetoxymethyl)-4-phenyl-1,2-dicarba-*closo*-dodecaborane (**6**) was synthesized by reacting 6-(C_6H_5)-*nido*-$B_{10}H_{13}$ with 2-butyne-1,4-diol diacetate in the presence of an ionic liquid BMIMCl/toluene mixture for 1 h at 120 °C (Scheme 6). Purification by flash chromatography gave the carborane **6** in 70% yield. The $^{11}B\{H\}$, ^1H, and

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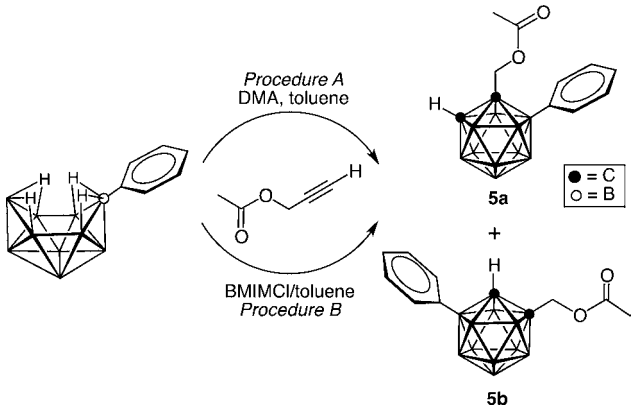
Scheme 5. Synthesis of 5a and 5b



^{13}C NMR spectra and MS analysis are consistent with compound **6**.

X-ray Crystallography. The crystallographic determinations of **1b** and **2** confirmed their previously proposed structures, in which the tolyl and cyclohexyl groups are bonded at the terminal positions on the B6 atom of the decaborane open face (Figures 2 and 3). The B6···B9 distance of 3.629(3) Å in both **1b** and **2** is longer than that in $B_{10}H_{14}$ (3.57 Å). The B2−B6−C1 angles of 131.01(17)° in **1b** and 134.31(9)° in **2** compare with the 132° angle in $B_{10}H_{14}$. The observed B6−C1 bond length of 1.555(3) Å in **1b** is comparable to that reported earlier for 6-(C_6H_5)-*nido*-$B_{10}H_{13}$ [1.563(14) Å]; however, it is significantly shorter than that in **2** [1.5772(15) Å]. This difference may be related to the improved π-type back-donation of the electron density from the π-delocalized aromatic system to the vacant LUMO p orbital centered on the B6 atom.[23] The B−B distances around B6 in **1b** and **2** are significantly elongated compared to those around B9 and to those that have been reported for unsubstituted $B_{10}H_{14}$ (Table 1). All of the other B−B distances are comparable to the B−B distances that have been reported for $B_{10}H_{14}$. These results indicate a slight distortion of the decaborane framework upon substitution at B6. Also, as shown in Figure 3, the six-membered cyclohexyl ring in **2** adopts a chair conformation.

One of the interesting features of the packing motif in **1b** is that the open face of decaborane is aligned with the aromatic ring of the tolyl group of the neighboring molecule, with an H_{bridge}···centroid separation in the 3.194−3.582 Å range (Figure 4). This structural motif is absent in the previously determined structure of 6-(C_6H_5)-*nido*-$B_{10}H_{13}$.[7]

The structures of carboranes **4** and **5b** were confirmed by single-crystal X-ray crystallography (Figures 5 and 6). Both compounds were crystallized as racemic mixtures. The carborane cage in **5b** (Figure 6) displays the B−B and B−C bond lengths of 1.765(3)−1.793(3) and 1.692(2)−1.723(2) Å,

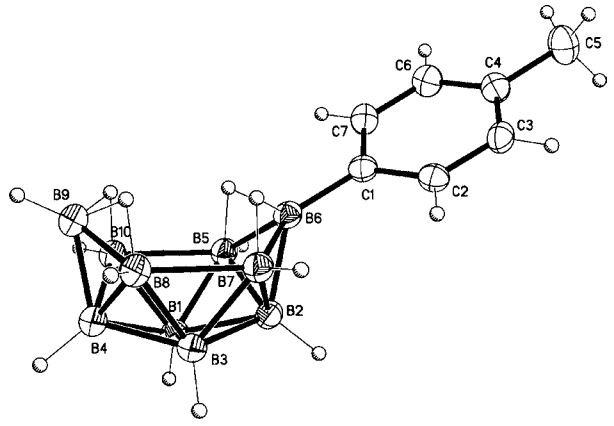


Figure 2. ORTEP representation of **1b**, drawn at the 40% probability level.

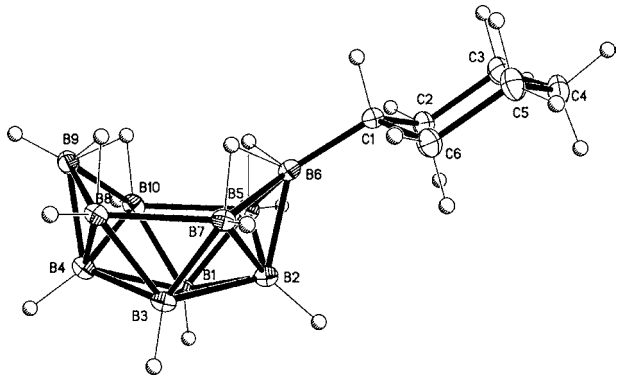


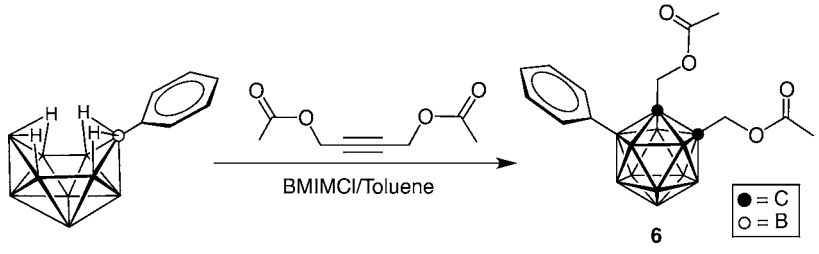
Figure 3. ORTEP representation of **2**, drawn at the 40% probability level.

Table 1. Selected Bond Distances (Å) in Selected Decaboranes

	6-R-$B_{10}H_{13}$, where R =			
	C_6H_5[c]	*p*-$CH_3(C_6H_5)$ (**1b**)	C_6H_{11} (**2**)	$B_{10}H_{14}$[24]
B1−B2[a]	1.786(16)	1.780(3)	1.7835(17)	1.778
B1−B3	1.794(18)	1.779(3)	1.7774(16)	1.772
B1−B5[a]	1.755(20)	1.755(3)	1.7541(16)	1.756
B2−B5[a]	1.789(19)	1.793(4)	1.7921(16)	1.786
B5−B10[b]	1.998(15)	1.984(3)	1.9831(17)	1.973
B6−B2	1.738(21)	1.735(3)	1.7456(16)	1.715
B9−B4	1.735(19)	1.713(3)	1.7276(17)	
B6−B5[b]	1.809(17)	1.803(3)	1.8071(16)	1.775
B9−B10[b]	1.779(19)	1.790(4)	1.7922(17)	
B6−C1	1.563(14)	1.555(3)	1.5772(15)	

[a]Averaged assuming C_{2v} symmetry. [b]Averaged assuming C_s symmetry. [c]Averaged for two crystallographically independent molecules.

Scheme 6. Synthesis of the Symmetrical Carborane 6



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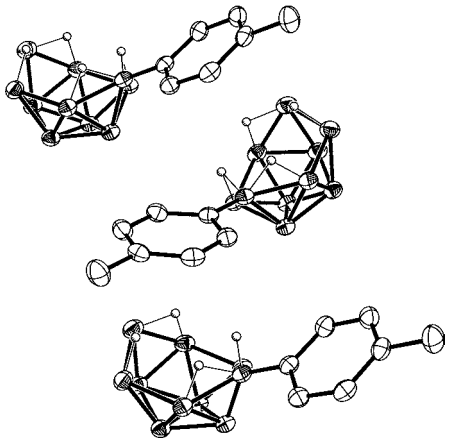

Figure 4. Fragment of the packing alignment in the *a* direction for compound **1b**. The selected intermolecular $H_{bridge}\cdots$centroid separations are in 3.194−3.582 Å range.

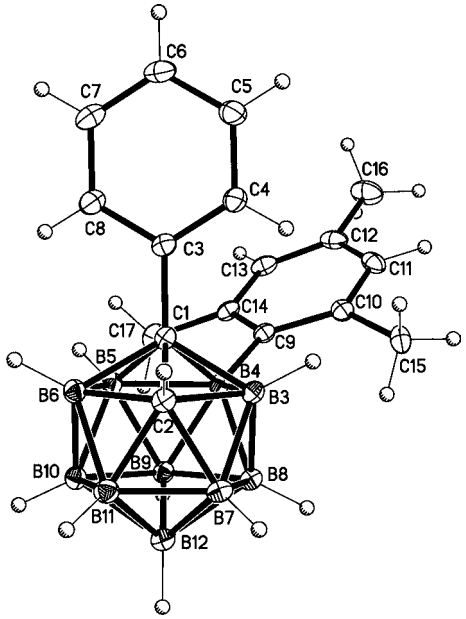

Figure 5. ORTEP representation of 1-(C_6H_5)-4-[2,4,6-$(CH_3)_3C_6H_2$]-$C_2B_{10}H_{10}$ (**4**), drawn at the 40% probability level. The enantiomers of **4** were cocrystallized as a racemic mixture. The selected interatomic distances are C1−C3 = 1.5089(19) Å and B4−C9 = 1.602(2) Å.

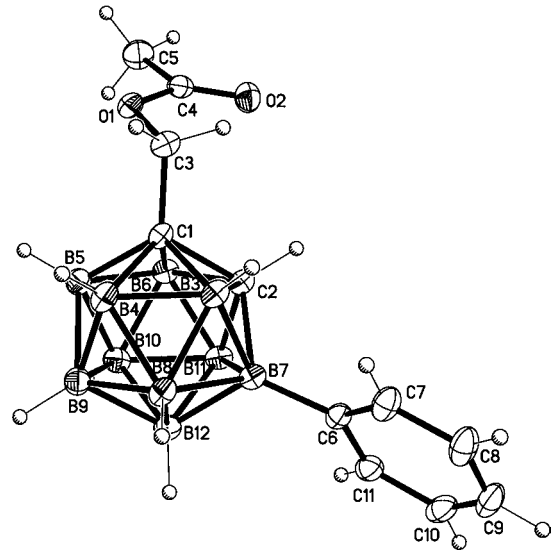

Figure 6. ORTEP representation of the major (95%) orientation of 1-(CH_2COOCH_3)-7-(C_6H_5)-$C_2B_{10}H_{10}$ (**5b**), drawn at the 40% probability level. The selected interatomic distance is C1−C3 = 1.523(2) Å.

respectively. These bond lengths are within the expected range for the carborane cage.[25] Although a wide variety of *o*-carboranes have been reported in the literature, compound **4** (Figure 5) is the second that has been structurally characterized as 1,4-substituted *o*-carborane. The first compound was 1,4-[1,2-dicarbadodecaborane(12)-1,4-diyl]-2-butanone, in which C1 and B4 are linked through the exocage cyclohexenone ring.[26] The icosahedron in **4** is not severely distorted by substitution, and the majority of the B−B and B−C distances are within the expected ranges for the carborane cage [1.764(2)−1.791(2) and 1.693(2)−1.747(2) Å, respectively]. However, the 1,4-substitution in **4** does influence the structure in the vicinity of the B4 atom, which can be seen from the bond lengths around B4 being slightly longer [B−B = 1.797(2)−1.822(2) Å and B−C = 1.7793(19) Å] than the respective bonds in a typical *o*-carborane cage (B−B = 1.79 Å and B−C = 1.68−1.72 Å). The observed $B_{carborane}-C_{aromatic}$ bond lengths are 1.602(2) Å in **4** and 1.575(2) Å in **5b**.

An analysis of the solid-state packing (Figure 7) of **4** shows that the intermolecular hydrogen bonding is dominated by the

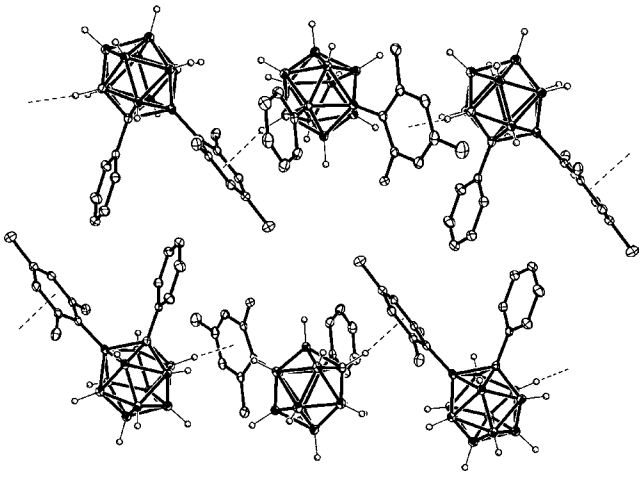

Figure 7. Fragment of the packing alignment in the *bc* plane for the structure of **4**.

C−H···π interactions formed by the acidic C−H of the carborane and mesitylene ring of the neighboring molecule [the $C_{Cb}\cdots$centroid separation is 3.230(2) Å and the C_{Cb}−H···π angle 164(2)°]. The solid-state packing also displays very weak intermolecular $\pi\cdots\pi$ interactions formed between the two slipped-parallel benzene groups in adjacent carborane molecules [the intercentroid distance is 4.4923(9) Å, the dihedral angle between planes is 0°, and the slippage is 2.723 Å]. In addition, there are weak intramolecular $\pi\cdots\pi$ interactions of 4.7884(8) Å [the dihedral angle between the planes is 60.11(7)°] between the benzene and mesitylene groups at the B1 and B4 atoms. The intermolecular $C_{carborane}$−H···π contacts have been described elsewhere as weak nonclassical C−H···π hydrogen bonds[27] and are common in supramolecular

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assemblies of carboranes.[28] The solid-state packing motif of **5b** is mainly represented by C−H···O hydrogen bonds between the acidic C−H of carborane and the C=O of the acetoxymethyl group [the C···O bond is 3.135(2) Å, and the C−H···O angle is 140°].

CONCLUSION

The protonation reactions of the polyhedral anion [*closo*-$B_{10}H_{10}]^{2-}$ give valuable insight into the versatility of this anion's ability to form a series of substituted decaboranes. Depending on the Lewis basicity of the solvent, mono- or diprotonation of [*closo*-$B_{10}H_{10}]^{2-}$ can easily be achieved. Furthermore, in noncoordinating solvents, the addition of the third proton was shown to occur, generating a boranocation $[B_{10}H_{13}]^+$ that acts as an electrophile in the electrophilic aromatic substitution reaction to give the corresponding 6-substituted decaboranes. The density functional theory (DFT) calculations support the formation of 6-substituted *nido*-$B_{10}H_{13}$ products. Subsequent reactions with acetylenic substrates in the presence of a Lewis base gave corresponding substituted carboranes.

EXPERIMENTAL SECTION

General Procedures and Materials. Standard Schlenk-line techniques were employed for all manipulations of air- and moisture-sensitive compounds. The benzene, toluene, mesitylene, chlorobenzene, α,α,α-trifluorotoluene, cyclohexane, trifluoromethane sulfonic acid, phenylacetylene, propargyl acetate, 2-butyne-1,4-diol diacetate, and *N*,*N*-dimethylaniline (DMA) were distilled before use. *closo*-$Cs_2B_{10}H_{10}$ was precipitated from an aqueous solution of *closo*-$(Et_3NH)_2B_{10}H_{10}$ using CsOH, filtered, washed with EtOH and Et_2O, and dried under vacuum. 1-Butyl-3-methylimidazolium chloride [BMIMCl] (Fluka) and poly(methylhydrosiloxane) [PMHS] (Aldrich) were used as received.

The ^{11}B NMR spectra (160 MHz) were obtained on a Bruker AM-500 spectrometer and referenced to external $BF_3{\cdot}Et_2O$. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane (TMS) and were measured with respect to the residual protons and carbon, respectively, in deuterated solvents. The timed ion selector (TIS) and atmosphere-pressure chemical ionization (APCI) MS spectra were recorded by operating in negative-ion mode on an ABI Mariner mass spectrometer. The IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer using KBr pellets.

Preparation of 6-(ClC_6H_4)-*nido*-$B_{10}H_{13}$ (1a) from *closo*-$Cs_2B_{10}H_{10}$. *closo*-$Cs_2B_{10}H_{10}$ (0.50 g, 1.3 mmol) was suspended in 50 mL of chlorobenzene, and excess triflic acid (0.57 mL, 6.5 mmol) was added using an Eppendorf pipet with constant stirring. The reaction mixture was then stirred for an additional 1 h. The residue from the reaction mixture was filtered in air, and the solvent was evaporated under vacuum. The residue was chromatographed over silica gel using toluene to give **1a** as a white solid (232 mg, 77% yield). ^{11}B NMR (160.4 MHz, C_6D_6): δ 22.1 (*p*-B6, s), 19.5 (*o*-B6, s), 10.4 (B1,3), 9.2 (B9), 0.9 (B8,10), −1.2 (*o*-B5,7), −4.1 (*p*-B5,7), −32.2 (*p*-B2), −33.8 (*o*-B2), −37.6 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 7.64 (*o*-1H, dd, *J* = 7.4 and 1.7 Hz), 7.18 (*p*-2H, d, *J* = 8.4 Hz), 7.36 (*p*-2H, d, *J* = 8.4 Hz), 7.03 (*o*-1H, dd, *J* = 7.6 and 1.3 Hz), 6.84 (*o*-2H, m), 5.5−0.5 (9H, br), −1.21 (2H, s), −2.50 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 136.6 (ortho) 137.4 (para), 135.1 (para), 132.1 (ortho), 129.2 (para), 127.7 (ortho). MS (APCI). Calcd for $[B_{10}H_{13}C_6H_4Cl]^-$: *m*/*z* 232.2022. Found: *m*/*z* 232.1587. IR (KBr): ν 2577 (B−H), 2932, 1585, 1490, 1089, 823, 754, 684 (aromatic) cm^{-1}.

Preparation of 6-($CH_3C_6H_4$)-*nido*-$B_{10}H_{13}$ (1b) from *closo*-$Cs_2B_{10}H_{10}$. *closo*-$Cs_2B_{10}H_{10}$ (0.50 g, 1.3 mmol) was suspended in 50 mL of toluene, and an excess of triflic acid (0.57 mL, 6.5 mmol) was added using an Eppendorf pipet with constant stirring. The reaction mixture was then stirred for an additional 30 min. The reaction mixture residue was filtered in air, and the solvent was evaporated under vacuum. The residue was chromatographed over silica gel with toluene to afford **1d** as a colorless solid (253 mg, 92% yield). ^{11}B NMR (160.4 MHz, C_6D_6): δ 23.6 (*m*/*p*-B6, s), 22.1 (*o*-B6, s), 10.2 (B1,3), 9.0 (B9), 1.1 (B8,10), −2.2 (*o*-B5,7), −4.7 (*m*/*p*-B5,7), −31.7 (*m*/*p*-B2), −33.0 (*o*-B2), −37.7 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 7.60 (*o*-2H, d, *J* = 7.2 Hz), 7.48 (*p*-2H, d, *J* = 7.8 Hz), 7.43 (*m*-2H, s), 7.36 (*m*-2H, d, *J* = 7.8 Hz), 7.10 (*m*+*o*-4H, m), 6.99 (*p*-2H, d, *J* = 7.8 Hz), 6.96 (*o*-2H, d, *J* = 7.6 Hz), 5.5−0.5 (9H, br), 2.20 (*m*-3H, s), 2.11 (*p*-3H, s), 2.17 (*o*-3H, s), −1.19 (2H, s), −2.51 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 140.5, 133.2, 128.9, 21.1. MS (APCI). Calcd for $[B_{10}H_{13}C_6H_4CH_3]^-$: *m*/*z* 212.2566. Found: *m*/*z* 212.2054. IR (KBr): ν 2574 (B−H), 3046, 2918, 1614, 1496, 1456, 1001, 821, 808, 686 (aromatic) cm^{-1}.

Preparation of 6-($C_6H_4CF_3$)-*nido*-$B_{10}H_{13}$ (1c) from *closo*-$Cs_2B_{10}H_{10}$. *closo*-$Cs_2B_{10}H_{10}$ (1.0 g, 2.6 mmol) was suspended in 50 mL of α,α,α-trifluorotoluene, and an excess of triflic acid (1.15 mL, 13 mmol) was added using an Eppendorf pipet with constant stirring. The reaction mixture was then stirred for an additional 2 h. The residue left in the reaction mixture was filtered in air, and the solvent was evaporated under vacuum. The residue was chromatographed over silica gel using hexanes to afford **1c** as a colorless solid (84 mg, 12% yield). ^{11}B NMR (160.4 MHz, C_6D_6): δ 22.4 (B6, s), 10.9 (B1,3), 9.9 (B9), 1.0 (B8,10), −3.2 (B5,7), −32.4 (B2), −37.1 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 7.90 (1H, s), 7.53 (1H, d, *J* = 5.9 Hz), 7.44 (1H, d, *J* = 5.9 Hz), 6.99 (1H, t, *J* = 5.9 Hz), 4.5−0.5 (9H, br), −1.40 (2H, s), −2.37 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 136.4, 130.2 (q, *J* = 32.6 Hz), 128.6, 129.2, 126.7, 124.7. $^{19}F\{H\}$ NMR (C_6D_6): δ −62.4. MS (APCI). Calcd for $[B_{10}H_{13}C_6H_4CF_3]^-$: *m*/*z* 266.2284. Found: *m*/*z* 266.2138. IR (KBr): ν 2582 (B−H), 2947, 1608, 1505, 1330, 1121, 1004, 956, 904, 804, 729, 661 (aromatic) cm^{-1}.

Preparation of 6-[2,4,6-$(CH_3)_3C_6H_2$)]-*nido*-$B_{10}H_{13}$ (1d) from *closo*-$Cs_2B_{10}H_{10}$. *closo*-$Cs_2B_{10}H_{10}$ (0.5 g, 1.3 mmol) was suspended in 50 mL of mesitylene, and an excess of triflic acid (0.57 mL, 6.5 mmol) was added using an Eppendorf pipet with constant stirring. The reaction mixture was then stirred for an additional 30 min. The residue from the reaction mixture was filtered in air, and the solvent was evaporated under vacuum. The resulting residue was chromatographed over silica gel using toluene to give 280 mg of **1d** as a colorless solid (90% yield). ^{11}B NMR (160.4 MHz, C_6D_6): δ 22.1 (B6, s), 9.9 (B1,3), 7.7 (B9), 2.4 (B8,10), −3.1 (B5,7), −32.4 (B2), −37.8 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 6.68 (2H, s), 2.17 (6H, s), 2.11 (3H, s), 4.5−0.5 (9H, br), −0.86 (2H, s), −2.08 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 142.3, 139.6, 129.3, 23.6, 20.8. MS (APCI). Calcd for $[B_{10}H_{13}C_9H_{10}]^-$: *m*/*z* 239.2802. Found: *m*/*z* 239.2714. IR (KBr): ν 2575 (B−H) cm^{-1}.

Preparation of 6-(C_6H_{11})-*nido*-$B_{10}H_{13}$ (2) from *closo*-$Cs_2B_{10}H_{10}$. *closo*-$Cs_2B_{10}H_{10}$ (1.0 g, 2.6 mmol) was suspended in 100 mL of cyclohexane. The suspension was warmed to 60 °C, and excess triflic acid (1.15 mL, 13 mmol) was added using an Eppendorf pipet with constant stirring. The reaction mixture was then stirred for an additional 2 h. The resulting light-yellow solution was filtered, and the solvent was evaporated under vacuum. The resulting residue was chromatographed over silica gel using hexane to give 42 mg (8% yield) of compound **2**. ^{11}B NMR (160.4 MHz, C_6D_6): δ 27.2 (B6, s), 10.8 (B1,3), 8.8 (B9), 0.9 (B8,10), −3.2 (B5,7), −34.3 (B2), −38.2 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 1.67 (5H, m), 1.18 (6H, m), 4.5−0.5 (9H, br), −2.04 (2H, s), −2.46 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 32.5, 28.1, 27.4, 26.2. MS (APCI). Calcd for $[B_{10}H_{24}C_6]^-$: *m*/*z* 204.2879. Found: *m*/*z* 204.2909. IR (KBr): ν 2594 (B−H) cm^{-1}.

Preparation of 6-(CF_3SO_3)-*nido*-$B_{10}H_{13}$ (3) from *closo*-$Cs_2B_{10}H_{10}$. Excess triflic acid (0.57 mL, 6.5 mmol) was added to a well-stirred powder of $Cs_2B_{10}H_{10}$ (0.50 g, 1.3 mmol). The reaction mixture was then stirred for an additional 15 min. Vacuum distillation into a −78 °C precooled flask yielded 325 mg (92%) of compound **3** as a white solid. ^{11}B NMR (160.4 MHz, C_6D_6): δ 14.8 (B6, s), 12.2 (B9), 7.8 (B1,3), 1.3 (B8,10), −5.1 (B5,7), −35.0 (B2), −40.1 (B4) (all doublets). ^1H NMR (500 MHz, C_6D_6): δ 4.5−0.5 (9H, br), −1.21 (2H, s), −2.44 (2H, s). $^{13}C\{H\}$ NMR (125.8 MHz, C_6D_6): δ 118.3 (q,

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J = 318.2 Hz). $^{19}F\{H\}$ NMR (C_6D_6): δ −76.6. MS (APCI). Calcd for $[B_{10}H_{13}CF_3SO_3]^-$: m/z 270.1537. Found: m/z 270.1276.

Preparation of 1-Phenyl-4-mesityl-1,2-dicarba-*closo*-dodecaborane (4) from 6-[2,4,6-$(CH_3)_3C_6H_2$)]-*nido*-$B_{10}H_{13}$ (1c). ***Procedure A:*** A solution of **1c** (0.24 g, 1.0 mmol), phenylacetylene (0.10 g, 1.0 mmol), and DMA (0.24 g, 2.0 mmol) in 10 mL of toluene was heated slowly until hydrogen evolution began. The temperature was then steadily raised to 120 °C, and the solution was heated for an additional 72 h. After cooling to room temperature, the volatiles were removed under vacuum to leave a yellow oil. The residue was chromatographed on silica gel with toluene as the eluent. The product was additionally washed with hexane to give a colorless crystalline product (**4**). The yield was 128 mg (38%).

Procedure B: Reacting **1c** (0.24 g, 1.0 mmol) with 0.12 g (1.2 mmol) of phenylacetylene in a biphasic toluene (10 mL)/BMIMCl (0.12 g, 0.69 mmol) mixture at 120 °C for 3 h gave, following toluene elution from a silica gel column and washing with hexane, 226 mg (67%) of **4** as a white solid. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ −0.2 (s), −0.7, −4.7, −7.7, −10.1, −11.7, −13.0 (all doublets). ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (3H, m), 7.06 (2H, m), 6.64 (2H, s), 3.98 (1H, s), 2.67 (6H, s), 2.17 (3H, s). $^{13}C\{H\}$ NMR (125.8 MHz, $CDCl_3$): δ 145.1, 137.7, 132.4, 130.7, 129.5, 128.5, 127.4, 77.8, 61.0, 26.7. MS (APCI). Calcd for $[B_{10}C_{17}H_{26}]^-$: m/z 338.3041. Found: m/z 338.2414. IR (KBr): ν 2577 (B−H), 3046, 3048, 2922, 1605, 1447, 1414, 1069, 860, 846, 759, 687 (aromatic) cm^{-1}.

Preparation of 1-(Acetoxymethyl)-4-phenyl-1,2-dicarba-*closo*-dodecaborane (5a) and 1-(Acetoxymethyl)-7-phenyl-1,2-dicarba-*closo*-dodecaborane (5b) from 6-(C_6H_5)-*nido*-$B_{10}H_{13}$. ***Procedure A:*** A solution of 6-(C_6H_5)-*nido*-$B_{10}H_{13}$ (0.40 g, 2.0 mmol), propargyl acetate (0.30 g, 3.0 mmol), and DMA (0.48 g, 4.0 mmol) in 10 mL of toluene was heated slowly until hydrogen evolution began. The temperature was then raised steadily up to 100 °C, and the solution was heated for an additional 7 days. After cooling to room temperature, the volatiles were removed under vacuum, leaving a yellow oil. The residue was chromatographed over silica gel with toluene as the eluent. The product was additionally washed with hexane to give a mixture of products **5a** and **5b** as a white solid. The yield was 274 mg (47%).

Procedure B: Reacting 6-(C_6H_5)-*nido*-$B_{10}H_{13}$ (0.40 g, 2.0 mmol) with propargyl acetate (0.24 g, 2.5 mmol) in a biphasic toluene (10 mL)/BMIMCl (0.17 g, 0.95 mmol) mixture at 120 °C for 30 min gave, following toluene elution from a silica gel column and washing with hexane, 402 mg (69%) of mixture **5a**/**5b** as a white solid. Recrystallization from a benzene/hexane mixture gave 25 mg (4%) of the single regioisomer **5b**. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ −1.9 (d), −2.6 (s), −3.6, −8.8, −9.7, −12.1, −13.1, −14.4 (all doublets). The assignments of the NMR signals for **5a** were made from the **5a**/**5b** mixture. ^1H NMR (500 MHz, $CDCl_3$) for **5a**: δ 7.67 (2H, d, J = 6.3 Hz), 7.39 (3H, m), 4.41 (2H, d, J = 7.6 Hz), 4.04 (1H, s), 2.07 (3H, s). $^{13}C\{H\}$ NMR (125.8 MHz, $CDCl_3$): δ 170.4, 135.6, 129.5, 128.3, 73.4, 65.4, 60.7, 21.1. ^1H NMR (500 MHz, $CDCl_3$) for **5b**: δ 7.64 (2H, d, J = 6.3 Hz), 7.43 (3H, m), 4.71 (2H, d, J = 4.3 Hz), 4.12 (1H, s), 2.24 (3H, s). $^{13}C\{H\}$ NMR (125.8 MHz, $CDCl_3$): δ 169.7, 134.8, 128.6, 127.9, 72.5, 64.6, 59.9, 20.4. MS (APCI). Calcd for $[B_{10}C_{11}H_{22}O_2]^-$: m/z 292.2467. Found: m/z 292.2531. IR (KBr): ν 2571 (B−H), 1749 (CO) cm^{-1}.

Preparation of 1,2-Bis(acetoxymethyl)-4-phenyl-1,2-dicarba-*closo*-dodecaborane (6) from 6-(C_6H_5)-*nido*-$B_{10}H_{13}$. The reaction of *nido*-Ph-$B_{10}H_{13}$ (0.20 g, 1.0 mmol) with 0.17 g (1.0 mmol) of 2-butyne-1,4-diol diacetate in a biphasic toluene (10 mL)/BMIMCl (0.12 g, 0.69 mmol) mixture at 120 °C for 1 h gave, following toluene elution from a silica gel column, 254 mg (70%) of **6** as a colorless oil. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ −0.4 (s), −1.9, −9.4, −11.3 (all doublets). ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (2H, d, J = 7.3 Hz), 7.38 (3H, m), 4.76 (2H, s), 4.62 (1H, d, J = 13.9 Hz), 4.43 (1H, d, J = 13.9 Hz), 2.15 (3H, s), 1.98 (3H, s). $^{13}C\{H\}$ NMR (125.8 MHz, $CDCl_3$): δ 169.8, 169.7, 136.5, 129.9, 128.9, 77.4, 76.5, 63.5, 61.8, 21.2, 20.9. MS (APCI). Calcd for $[B_{10}C_{14}H_{24}O_4]^-$: m/z 364.2680. Found: m/z 364.3026. IR (KBr): ν 2582 (B−H), 1757 (CO) cm^{-1}.

X-ray Diffraction Studies. X-ray-quality crystals were obtained for compounds **1b**, **2**, **4**, and **5b** as follows: **1b**, by the slow evaporation of a hexane mixture; **2**, upon cooling of a toluene/hexane mixture; **4**, upon the slow evaporation of a chloroform mixture; **5b**, upon the slow evaporation of a chloroform/hexane mixture. Each crystal was coated with paratone oil and mounted onto a MiTeGen MicroMount fiber. Complete and redundant data were collected on a single flash-cooled crystal (T = 100 K with an Oxford Cryostream LT device) using a Bruker X8 Prospector Ultra X-ray diffractometer system with a three-circle goniometer and an APEX II CCD area detector mounted on a D8 platform and equipped with a Cu-IμS (λ = 1.54178 Å) microfocus X-ray source operated at 30 W. The frames were collected with a scan width of 0.5° in ω and an exposure time of 10 s/frame. The intensity data sets consisted of ϕ and ω scans at a crystal-to-detector distance of 4.00 cm. The *APEX 2*[29] and *SAINT*[30] software packages were used for data collection and data integration. The data were corrected for absorption effects using the *SADABS* empirical method.[31] The structures were solved and were refined by full-matrix least-squares techniques based on F^2 (*SHELXL-97*).[32] All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The disorder of the acetoxymethyl group in the crystal structure of **5b** was modeled with two orientations in a 0.95/0.05 ratio. All of the hydrogen atoms in the crystal structures of **4** and **5b** were included at geometrically idealized positions. For **1b** and **2**, some of the hydrogen atoms were located in difference Fourier maps and were refined individually; thus, the refinement was mixed. The crystallographic data and details of the data collection and structure refinements of **1b**, **2**, **4**, and **5b** are provided in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, Cartesian coordinates of a DFT-optimized $B_{11}H_{13}^+$ structure, crystallographic details for compounds **1b**, **2**, **4**, and **5b**, the $^{11}B-^{11}B$ COSY NMR spectrum of **1a**, and the $^{11}B\{H\}$ NMR spectrum of compound **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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