Synthesis of Alkyl and Aryl Derivatives of *closo*-$B_{12}H_{12}^{2-}$ by the Palladium-Catalyzed Coupling of *closo*-$B_{12}H_{11}I^{2-}$ with Grignard Reagents

Toralf Peymann, 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 September 19, 1997

The reaction of $[N(n\text{-}C_4H_9)_4]_2$[*closo*-$B_{12}H_{11}I$], $[N(n\text{-}Bu)_4]_2$[**2**], with Grignard reagents, RMgX, in the presence of catalytic amounts of *trans*-$Pd(PPh_3)_2Cl_2$ and CuI in either tetrahydrofuran or 1,4-dioxane solution produced the corresponding alkylated or arylated polyhedral borane anions, *closo*-$B_{12}H_{11}R^{2-}$, in good yield. By this method, we have synthesized $[N(n\text{-}C_4H_9)_4]_2$[*closo*-$B_{12}H_{11}CH_3$], $[N(n\text{-}Bu)_4]_2$[**3**]; $[N(n\text{-}C_4H_9)_4]_2$[*closo*-$B_{12}H_{11}C_6H_5$], $[N(n\text{-}Bu)_4]_2$[**4**]; and Cs_2[*closo*-$B_{12}H_{11}(n\text{-}C_{18}H_{37})$], Cs_2[**5**]. The structures of Cs_2[**3**] and PPN_2[**4**] have been determined by X-ray diffraction studies. Crystallographic data are as follows: for Cs_2[**3**], orthorhombic, space group *Pmcn*, $a = 954.6(6)$ pm, $b = 1077.0(7)$ pm, $c = 1396.8(9)$ pm, $Z = 4$, $R = 0.055$; for PPN_2[**4**], which cocrystallized with two molecules of DMSO and one molecule of toluene, triclinic, space group $P\bar{1}$, $a = 1138.4(10)$ pm, $b = 1920.1(17)$ pm, $c = 2143.2(18)$ pm, $\alpha = 93.26(2)°$, $\beta = 104.44(2)°$, $\gamma = 105.86(2)°$, $Z = 2$, $R = 0.076$.

Introduction

A variety of derivatives of the icosahedral borane cluster *closo*-$B_{12}H_{12}^{2-}$ (**1**) including species substituted by halogens,[1] oxygen,[2] sulfur,[3] or nitrogen[4] have been described. However, very little is known regarding similar derivatives which contain boron−carbon bonds. The first of these derivatives to be described were the carbonyl species *closo*-$B_{12}H_{11}CO^-$ and *closo*-$B_{12}H_{11}(CO)_2$ and their corresponding carboxylic acids.[5] In the reactions of **1** with alkenes, mixtures of hydroboration products were obtained that were difficult to separate.[2a] Preetz and coworkers later described the reaction of **1** with halobenzenes at high temperatures, from which isomeric mixtures of monoarylated, bisarylated, and more highly arylated boron clusters could be separated by chromatography.[6] Irradiation of the polyhalogenated (X = Cl, Br) derivatives *closo*-$B_{12}X_{12}^{2-}$ in water containing CN^- resulted in the partial replacement of the halogen by the nucleophile.[7] The interaction of **1** with tropenium bromide establishes a B−C bond in a process in which the tropenium ion serves as an electrophilic reagent. The product is an apparent tropenium-substituted *closo*-$B_{12}H_{12}^{2-}$ ion stabilized by intramolecular charge-transfer interaction.[8]

Recently, a new method for the alkylation and arylation of a B−I vertex of iodinated carboranes was developed.[9] It was shown that the B−I unit can be transformed to a B−R vertex (R = alkyl, aryl) with Grignard reagents in the presence of a palladium catalyst. This reaction resembles the palladium-catalyzed Stille coupling of organostannanes and alkyl or aryl halides.[10] Although the reactivities of the icosahedral $C_2B_{10}H_{12}$ carboranes differ from that of the *closo*-$B_{12}H_{12}^{2-}$ anion, one could expect similarities because the two families of polyhedral frameworks are isolobal. We have now utilized this catalytic methodology to convert *closo*-$B_{12}H_{11}I^{2-}$ to *closo*-$B_{12}H_{11}R^{2-}$ derivatives (R = alkyl, aryl). Thus, for the first time, such species are now available and a new area of organoborane chemistry is accessible for study.

Alkylated polyhedral borane anions are of particular interest since they resemble fatty acids insofar as they consist of a charged head group (the borane cluster) and a lipophilic tail (the alkyl group). These compounds may be useful candidates for incorporation in either the lipophilic bilayer or the aqueous core of unilamellar liposomes depending upon their structures and the relative lipophilicities of their sodium salts. Liposomes are known to be capable of selective in vivo localization in tumors. Therefore, boron-loaded liposomes have attracted considerable interest as a promising route to cancer treatment through boron neutron capture therapy.[11]

Experimental Section

General Considerations. Synthetic reactions were carried out in an atmosphere of dry nitrogen. THF was distilled over sodium benzophenone ketyl; dry 1,4-dioxane was purchased from Aldrich Chemical Co. Alumina (neutral Brockman activity I, 60−325 mesh)

---

(1) (a) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 159. (b) Srebny, H. G.; Preetz, W.; Marsmann, H. C. *Z. Naturforsch.* **1984**, *39B*, 189. (c) Haeckel, O.; Preetz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1454.

(2) (a) Knoth, W. H.; Sauer, J. C.; England, D. C.; Hertler, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 3973. (b) Peymann, T.; Lork, E.; Gabel, D. *Inorg. Chem.* **1996**, *35*, 1355. (c) Krause, U.; Preetz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 516.

(3) Gabel, D.; Moller, D.; Harfst, S.; Rösler, J.; Ketz, H. *Inorg. Chem.* **1993**, *32*, 2276.

(4) (a) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456. (b) Peymann, T.; Lork, E.; Schmidt, M.; Nöth, H.; Gabel, D. *Chem. Ber.* **1997**, *130*, 795.

(5) Knoth, W. H.; Sauer, J. C.; Balthis, J. H.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 4842.

(6) Preetz, W.; von Bismarck, R. *J. Organomet. Chem.* **1991**, *411*, 25.

(7) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1899.

(8) Harmon, K. M.; Harmon, A. B.; MacDonald, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 323.

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

(10) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(11) (a) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950. (b) Hawthorne, M. F.; Shelly, K. *J. Neuro-Oncol.* **1997**, *33*, 55. (c) Feakes, D. A.; Shelly, K.; Knobler, C. B.; Hawthorne, M. F. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 3029.

S0020-1669(97)01207-X CCC: $15.00

Table 1. $^{11}B\{^1H\}$ NMR Data (ppm) for Anions **3**−**5**

anion	B(1)	B(2−6)	B(7−11)	B(12)
3	−6.9	−13.2	−15.1	−18.6
4	−4.9	−13.3	−14.4	−16.2
5	−4.9	−14.0	−15.5	−18.3

was purchased from Fisher Scientific. Bis(tetrabutylammonium) iododoundecahydro-*closo*-dodecaborate(2−) was prepared as described in the literature.[1] The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 spectrometer. The ^{11}B NMR spectra (160 MHz) were obtained using a Bruker ARX-500 spectrometer and are reported in Table 1. Proton, carbon, and boron chemical shifts were referenced to residual solvent protons (DMSO-d_6) and external $BF_3{\cdot}Et_2O$, respectively. The NMR data obtained for the tetrabutylammonium cation and the B−H protons are not reported. Melting points were determined in a sealed tube and are uncorrected. High-resolution mass spectra (FAB) were obtained using a VG-ZAB spectrometer.

Preparation of $[N(n\text{-}C_4H_9)_4]_2$[*closo*-$B_{12}H_{11}CH_3$], $[N(n\text{-}Bu)_4]_2$[3]. A 3.0 M solution of methylmagnesium bromide (4.0 mL, 12.0 mmol) in THF was syringed into a stirred suspension of $[N(n\text{-}Bu)_4]_2$[**2**] (1.0 g, 1.33 mmol) in 20 mL of dry 1,4-dioxane followed by *trans*-dichlorobis(triphenylphosphine)palladium (0.05 g, 0.07 mmol) and copper iodide (0.01 g, 0.06 mmol). The mixture was refluxed for 1 day, resulting in a black solution. Water was added cautiously to destroy residual Grignard reagent, and all volatiles were evaporated in vacuo. The residue was extracted with acetonitrile. The extracts were passed through a bed of alumina, and the acetonitrile was evaporated to yield an orange oil. The oil was stirred overnight in 200 mL of diethyl ether, which caused it to solidify. The solid was filtered off and twice recrystallized from ethanol to afford crystals of $[N(n\text{-}Bu)_4]_2$[**3**] (0.43 g, 0.67 mmol, 51%), mp 245 °C. ^1H NMR, δ: 0.09 (s, br, 3H, CH_3). HRMS (FAB) for $CH_{13}{}^{10}B_2{}^{11}B_{10}$ (m/z): calcd, 155.2207; found, 155.2212 $[M - H]^-$.

Preparation of $[N(n\text{-}C_4H_9)_4]_2$[*closo*-$B_{12}H_{11}C_6H_5$], $[N(n\text{-}Bu)_4]_2$[4]. A 3.0 M solution of phenylmagnesium bromide (4.0 mL, 12.0 mmol) in Et_2O was syringed into a stirred suspension of $[N(n\text{-}Bu)_4]_2$[**2**] (1.0 g, 1.33 mmol) in 20 mL of dry 1,4-dioxane followed by *trans*-dichlorobis(triphenylphosphine)palladium (0.05 g, 0.07 mmol) and copper iodide (0.01 g, 0.06 mmol). The mixture was refluxed for 1 day, resulting in a black solution. Water was added cautiously to destroy residual Grignard reagent, and all volatiles were evaporated in vacuo. The residue was extracted with 300 mL of acetonitrile. The extracts were passed through a bed of alumina, and the acetonitrile was evaporated to yield an orange oil. The oil was stirred overnight in 200 mL of diethyl ether. The ether was decanted and the solid dissolved in acetonitrile. The solution was added slowly to 100 mL of diethyl ether, and the mixture was stirred overnight. The resulting solid was filtered off, affording a white solid of $[N(n\text{-}Bu)_4]_2$[**4**] (0.75 g, 1.07 mmol, 81%), mp 210 °C. ^1H NMR, δ: 7.55 (m, 2H, C_6H_5), 6.86−6.74 (m, 3H, C_6H_5). $^{13}C\{^1H\}$ NMR, δ: 133.6, 125.0, 122.4 (C_6H_5). HRMS (FAB) for $C_6H_{15}{}^{10}B_2{}^{11}B_{10}$ (m/z): calcd, 217.2363; found, 217.2356 $[M - H]^-$.

Preparation of Cs_2[*closo*-$B_{12}H_{11}(n\text{-}C_{18}H_{37})$], Cs_2[5]. A 0.5 M solution of *n*-octadecylmagnesium chloride (20.0 mL, 10.0 mmol) in THF was syringed into a stirred suspension of $[N(n\text{-}Bu)_4]_2$[**2**] (1.0 g, 1.33 mmol) in 20 mL of dry THF followed by *trans*-dichlorobis-(triphenylphosphine)palladium (0.05 g, 0.07 mmol) and copper iodide (0.01 g, 0.06 mmol). The mixture was refluxed for 3 days, resulting in a dark solution. All volatiles were evaporated in vacuo. The residue was stirred in 300 mL of diethyl ether and the suspension passed through a frit containing alumina. Another 300 mL of diethyl ether was passed through the frit, and the combined ether solutions were discarded. The alumina was then extracted with acetonitrile. The acetonitrile extracts were evaporated to yield an orange oil. Dichloromethane (50 mL) was added to the oil, and the solution was filtered from the insoluble residue. The filtrate was evaporated, and the resulting solid was dissolved in warm ethanol (30 mL). The solution was allowed to stand at room temperature, precipitating a black solid that was removed by filtration. Cesium fluoride (0.61 g, 4.02 mmol) was dissolved in ethanol (20 mL), and the solution was added to the filtrate. The resulting white precipitate was isolated by filtration and heated in acetonitrile. Water was added to this suspension until the precipitate dissolved. Upon cooling, a white precipitate of Cs_2[**5**] (0.47 g, 0.71 mmol, 54%) formed, which was filtered off; mp >250 °C. ^1H NMR, δ: 1.20 (m, 32H, CH_2), 0.81 (t, 3 H, CH_3), 0.34 (m, br, BCH_2). $^{13}C\{^1H\}$ NMR, δ: 33.9, 31.9, 31.7, 30.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1 (CH_2), 22.5 (BCH_2), 14.4 (CH_3). HRMS (FAB) for $C_{18}H_{48}{}^{10}B_2{}^{11}B_{10}Cs$ (m/z): calcd, 527.4000; found, 527.4003 $[M + Cs]^-$.

Table 2. Selected Bond Lengths (pm) for Anion **3**

B(1)−B(4)	173(2)	B(2)−B(2)[a]	178.3(14)
B(1)−B(2)	184.4(15)	B(8)−B(8)[a]	177.0(13)
B(2)−B(7)	179.8(14)	B(2)−B(3)	180.9(14)
B(3)−B(8)	179.7(15)	B(3)−B(4)	176.6(12)
B(7)−B(12)	179.1(14)	B(7)−B(8)	175.5(14)
B(7)−B(11)	176.9(12)	B(8)−B(12)	175.9(16)
B(8)−B(9)	177.8(4)	B(11)−B(12)	177(2)
B(1)−B(3)	179.0(13)	B(4)−B(8)	183(2)
B(2)−B(11)	178.8(16)	B(3)−B(7)	175.2(14)
B(1)−C(1)	158(2)		

[a] Atoms denoted are related by a mirror at $x = {}^3/_4$.

Table 3. Selected Bond Lengths (pm) for Anion **4**

B(1)−B(4)	177.2(11)	B(4)−B(9)	179.5(12)
B(1)−B(2)	180.9(12)	B(5)−B(10)	178.1(12)
B(2)−B(7)	176.4(12)	B(2)−B(3)	178.9(12)
B(3)−B(8)	178.3(12)	B(3)−B(4)	178.0(12)
B(7)−B(12)	180.5(12)	B(7)−B(8)	179.6(12)
B(7)−B(11)	176.6(12)	B(8)−B(12)	178.6(12)
B(8)−B(9)	177.4(12)	B(11)−B(12)	181.1(12)
B(1)−B(3)	178.1(11)	B(4)−B(8)	178.4(12)
B(2)−B(11)	176.3(12)	B(3)−B(7)	178.8(12)
B(9)−B(12)	179.2(12)	B(1)−B(5)	177.0(12)
B(2)−B(6)	177.9(12)	B(4)−B(5)	177.6(11)
B(5)−B(6)	177.1(12)	B(6)−B(10)	178.8(12)
B(10)−B(11)	179.9(12)	B(1)−B(6)	178.9(11)
B(5)−B(9)	178.0(12)	B(6)−B(11)	178.5(12)
B(9)−B(10)	178.4(12)	B(10)−B(12)	180.6(12)
B(1)−C(1)	162.4(10)		

Table 4. Details of Crystallographic Data Collection

	Cs_2[**3**]	$(PPN)_2$[**4**]$\cdot 2(CH_3)_2SO\cdot C_7H_8$
empirical formula	$CH_{14}B_{12}Cs_2\cdot H_2O$	$C_{89}H_{96}B_{12}N_2O_2P_4S_2$
fw	439.67	1543.49
space group	*Pmcn* (*Pnma*, 62)	$P\bar{1}$
a (pm)	954.6(6)	1138.4(10)
b (pm)	1077.0(7)	1920.1(17)
c (pm)	1396.8(9)	2143.2(18)
α (deg)		93.26(2)
β (deg)		104.44(2)
γ (deg)		105.86(2)
V (nm^3)	1.436	4.324
Z	4	2
μ (cm^{-1})	50.1	16.0
R^a	0.055	0.076
$R_w{}^b$	0.068	0.089

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

X-ray Crystallography

Tables 2−4 summarize the crystallographic data pertaining to compounds **3** and **4**.

Cs_2[*closo*-$B_{12}H_{11}CH_3$]. A colorless crystal, obtained from an aqueous solution, was placed on a fiber and mounted on a Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 37 accurately centered reflections (7.5° < 2θ < 20.2°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 2171 unique reflections measured, 1405 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 absorption. Programs used in this work include locally modified versions of the following programs: CARESS (Broach,

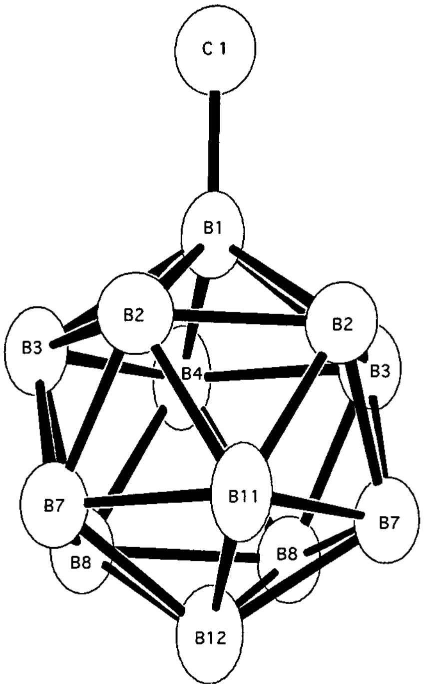


Figure 1. ORTEP representation of anion **3**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

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

Atoms were located by use of heavy-atom methods. All nonhydrogen atoms were refined with anisotropic parameters. Boron-bonded hydrogen atoms were located and were included in structure factor calculations, but parameters were not refined. Methyl hydrogen atoms were placed in calculated positions; C−H 100 pm, H−C−H 109.5°. Hydrogen atoms were assigned isotropic displacement values based approximately on the value of the attached atom. Scattering factors for hydrogen were obtained from ref 12. The largest peak on a final difference electron density map, near Cs, was 0.6 e Å^{-3}.

(PPN)$_2$[*closo*-$B_{12}H_{11}CH_3$]·2DMSO·toluene. A colorless crystal, obtained from DMSO and toluene, 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 35 accurately centered reflections ($20.0^\circ < 2\theta < 38.7^\circ$). Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Of the 11 882 unique reflections measured, 6098 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 absorption. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; SHELX76 (Sheldrick), a crystal structure package; SHELX86 (Sheldrick), a crystal structure solution package; and ORTEP (Johnson).

Atoms were located by use of direct methods (SHELX86). All nonhydrogen atoms were refined with anisotropic parameters. Boron-bonded hydrogen atoms were located and were included in structure factor calculations, but parameters were not refined. All phenyl groups were included as rigid C_6 hexagons; C−C 139.5 pm, angles 120°. Methylene, methyl, and phenyl hydrogen atoms were included in calculated positions. Hydrogen atoms were assigned isotropic displacement values based approximately on the value of the attached atom. Scattering factors for hydrogen atoms were obtained from ref 11. The largest maximum and minimum peaks on a final difference electron density map were 0.40 and −0.40 e Å^{-3}.

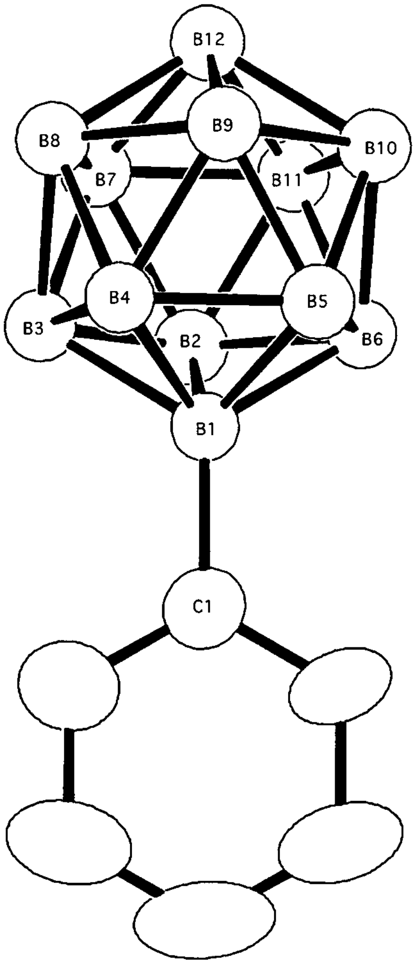


Figure 2. ORTEP representation of anion **4**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Results and Discussion

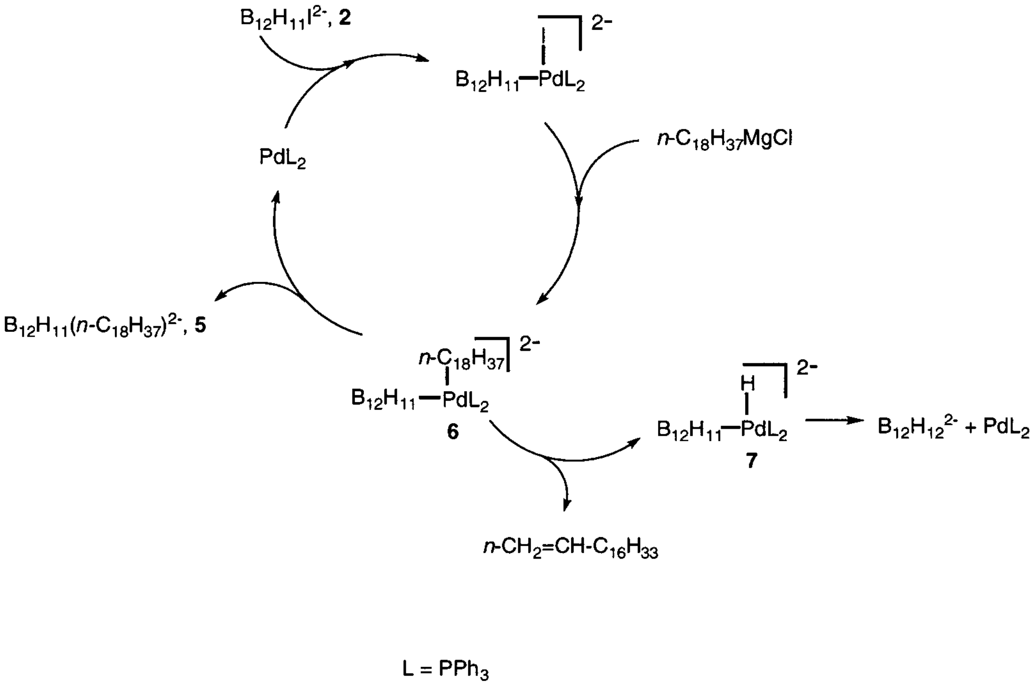
The most common *closo*-$B_{12}H_{12}^{2-}$ derivatives are probably the halogenated anions. Mono-, poly-, and persubstituted dodecaborate anions containing fluorine, chlorine, bromine, and iodine substituents have been described in the literature.[1] In many areas of chemistry, halogen derivatives are very reactive and serve as valuable precursors to other derivatives. Characteristically, the boron−halogen bonds of the *closo*-$B_{12}H_{12-n}X_n^{2-}$ ($n = 2, 12$) clusters are inert to the majority of reaction conditions[1a] that have been thus far investigated. No nucleophilic attack was observed when *closo*-$B_{12}H_{12-n}I_n^{2-}$ ($n = 2, 12$) anions were heated with sodium hydroxide, potassium amide, and phenyl- or methylmagnesium bromide. The only reported reactions of *closo*-$B_{12}H_{12-n}X_n^{2-}$ (X = Cl, Br, I) anions are the reduction of diiodododecahydro-*closo*-dodecaborate by alkali metals leading to *closo*-$B_{12}H_{12}^{2-}$ [1a] and the partial displacement of bromine or chlorine in the reaction of *closo*-$B_{12}X_{12}^{2-}$ with pseudohalogens (CN^-, N_3^-) under photochemical conditions.[7] This lack of reactivity is assumed to result from both the icosahedral geometry and the negative charge of the B_{12} cluster, conditions not conducive to S_N2 substitution reactions at a B−X vertex located in the polyhedral surface.

One of the easily accessible derivatives of **1** is the monoiodinated anion *closo*-$B_{12}H_{11}I^{2-}$, **2**.[1a] Complex **2** possesses a single functionalized boron vertex and could conceivably be

---

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

Scheme 1



useful as a precursor to a wide variety of monosubstituted B_{12} derivatives. This would be of special interest, since it is often difficult to prevent multiple substitution in electrophilic reactions with the *closo*-$B_{12}H_{12}^{2-}$ system.

The reaction of $[N(n\text{-}Bu)_4]_2$[**2**] with methylmagnesium bromide in 1,4-dioxane at the reflux temperature in the presence of *trans*-dichlorobis(triphenylphosphine)palladium and copper iodide afforded methylundecahydro-*closo*-dodecaborate(2−), **3**, in 51% yield. Similarly, heating $[N(n\text{-}Bu)_4]_2$[**2**] with phenylmagnesium bromide gave phenylundecahydro-*closo*-dodecaborate(2−), **4**, in 81% yield. Surprisingly, it was found that the reaction of $[N(n\text{-}Bu)_4]_2$[**2**] with *n*-octadecylmagnesium chloride in boiling 1,4-dioxane was incomplete after 7 days, whereas it was completed after 3 days in THF at the reflux temperature.

All new compounds were characterized by multinuclear NMR spectroscopy and mass spectrometry. Monosubstituted B_{12} clusters possess C_{5v} symmetry and therefore give four signals in the $^{11}B\{^1H\}$ NMR spectra (see Table 1) with the intensity ratio 1:5:5:1. The signal of the substituted boron atom (the *ipso*-boron) appears as a singlet in the proton-coupled ^{11}B NMR spectrum, whereas the boron vertex opposite the *ipso*-boron (the antipodal boron) appears as a a doublet due to coupling with hydrogen. Only minor differences in the chemical shifts of the boron nuclei of $[N(n\text{-}Bu)_4]_2$[**3**], $[N(n\text{-}Bu)_4]_2$[**4**], and Cs_2[**5**] were observed. All spectra gave the same expected pattern. In contrast to the antipodal vertex, which appears upfield of the signals associated with the two B_5 belts, the *ipso*-boron atom is shifted approximately 10 ppm downfield in the $^{11}B\{^1H\}$ NMR spectra. The ^1H NMR and the $^{13}C\{^1H\}$ NMR spectra of $[N(n\text{-}Bu)_4]_2$[**3**], $[N(n\text{-}Bu)_4]_2$[**4**], and Cs_2[**5**] exhibited the expected signals of the *B*-alkyl and *B*-aryl groups, respectively. However, due to the quadrupole moment of the boron nucleus we did not observe a signal in the $^{13}C\{^1H\}$ NMR spectra due to the carbon atom directly bound to the cluster.

The structures of both Cs_2[**3**] (Figure 1) and $(PPN)_2$[**4**] (Figure 2) were confirmed by X-ray diffraction analysis. Compound **4** cocrystallized with two molecules of DMSO and one molecule of toluene.

In the structure of **3**, the boron−boron bond lengths vary in the range 173(2)−184.4(15) pm. These values are similar to those described for other monosubstituted B_{12} clusters, although the icosahedron of **3** appears to be distorted, probably due to packing interactions with the cesium cations.

The boron−boron distances of **4** are in the range 176.3(12)−181.1(12) pm, showing less deviation from icosahedral geometry than **3**. The boron−carbon bond of **4** [162.4(10) pm] is longer than the analogous distance in **3** [158(2) pm], which can be explained by the greater steric demands of the phenyl group. To our knowledge, these two solid-state structures are the first examples of *closo*-$B_{12}H_{12}^{2-}$ derivatives which contain either B-alkyl or B-aryl bonds. The boron−carbon distances found for the anionic boron clusters **3** and **4** are comparable to the boron−carbon bond lengths published for alkylated and arylated icosahedral carborane systems ranging from 153 to 158 pm.[9,13,14]

Attempts to alkylate $[N(n\text{-}Bu)_4]_2$[**2**] by reaction with unsaturated Grignard reagents were unsuccessful. No reaction of $[N(n\text{-}Bu)_4]_2$[**2**] with ethynyl-, vinyl-, or allylmagnesium bromide was detected by ^{11}B NMR spectroscopy after 3 days in THF at the reflux temperature. We assume that the formation of palladium π complexes with the unsaturated Grignard reagent competes with the generation of the σ B−palladium species **6** postulated as an intermediate in the catalytic cycle (Scheme 1).[9]

The Pd-catalyzed coupling of **2** with Grignard reagents described here is proposed to follow the mechanistic pathway shown in Scheme 1 and previously proposed for the similar Pd-catalyzed coupling of Grignard reagents with *B*-iodocarborane derivatives.[13,14] In the latter case, diminished yields are observed in these reactions in which the intermediate analogous to **6** in Scheme 1 is capable of β-hydrogen elimination. In the reaction of *n*-octadecylmagnesium chloride and **2** reported here, the formation of *closo*-$B_{12}H_{12}^{2-}$ is observed by ^{11}B NMR spectroscopy and attributed to β-hydrogen elimination through

---

(13) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095.

(14) Jiang, W.; Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 4355.

the hydride species **7** shown in Scheme 1. The desired coupling product **5** is formed from **6** as shown.

Conclusions

The palladium-catalyzed alkylation and arylation of *closo*-$B_{12}H_{11}I^{2-}$, **2**, with Grignard reagents was accomplished. This method allows the synthesis of monoalkylated and monoarylated derivatives of *closo*-$B_{12}H_{12}^{2-}$ without the formation of more highly substituted species and provides the first examples of synthetically useful substitution reactions which occurr at the boron−iodine vertex of an iodinated *closo*-polyhedral borane anion. We are now studying the incorporation of the compounds Na_2[**3**]−Na_2[**5**] in liposomes to determine their ability to deliver boron to tumor cells as required for boron neutron capture therapy.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by the Department of Energy (DOE), Contract No. DE-FG03-95ER61975.

Supporting Information Available: Listings of bond distances, bond angles, and positional and thermal parameters for Cs_2[**3**] and PPN_2-[**4**] (11 pages). Ordering information is given on any current masthead page.

IC9712075