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Facile Electrophilic Iodination of Icosahedral Carboranes. Synthesis of Carborane Derivatives with Boron−Carbon Bonds via the Palladium-Catalyzed Reaction of Diiodocarboranes with Grignard Reagents

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Electrophilic diiodination reactions of icosahedral *closo*-1,2-$C_2B_{10}H_{12}$ and *closo*-1,7-$C_2B_{10}H_{12}$ using 2 molar equiv of iodine monochloride in the presence of catalytic amounts of aluminum chloride yielded the corresponding *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ and *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ complexes in excellent yields. Palladium-mediated cross-coupling reactions of these diiodocarboranes with a variety of alkyl, aralkyl, and aryl Grignard reagents were reinvestigated, and it was demonstrated that the addition of copper(I) iodide as a cocatalyst is crucial to the success of this reaction. A reaction mechanism involving the initial formation of binary organocopper species (RCu; R = alkyl, aralkyl, aryl) followed by the reaction of (σ-carboranyl)palladium iodides ($L_2Pd(CbI)I$ and $L_2Pd(CbR)I$; L = PPh_3, Cb = *closo*-1,2-$C_2B_{10}H_{10}$, *closo*-1,7-$C_2B_{10}H_{10}$) via a four-centered transition state is proposed. The molecular structures of *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, and *closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$, **10**, have been determined. Crystallographic data are as follows: for **1**, monoclinic, space group $P2_1/c$, $a = 13.2719(6)$ Å, $b = 14.9718(6)$ Å, $c = 13.4734(6)$ Å, $\beta = 114.211(1)°$, $V = 2441.7(3)$ Å^3, $Z = 8$, $\varrho_{calcd} = 2.15$ g cm^{-3}, $R = 0.043$, $R_w = 0.064$; for **10**, tetragonal, space group $I4_1/a$, $a = 9.446(2)$ Å, $c = 39.949(8)$ Å, $V = 3564.1(1)$ Å^3, $Z = 8$, $\varrho_{calcd} = 1.10$ g cm^{-3}, $R = 0.056$, $R_w = 0.063$.

Introduction

We recently reported the synthesis and representative complexation chemistry of "mercuracarborands".[1] Parent unsubstituted host molecules of this type are only soluble in electron-donor solvents, and solvent molecules are always found to be coordinated to the Lewis acidic mercury atoms upon attempted isolation of the free host.[2,3] Obviously, this ubiquitous coordination of solvent by the parent mercuracarborands mitigates their potential usefulness as homogeneous electrophilic catalysts in organic reactions. In our ongoing "carborod"[4] and "carboracycle"[5] research, rigid rod and macrocyclic arrays have been constructed using carborane cages as modular building blocks. The successful synthesis of these components of supramolecular species portends the creation of novel materials based upon carboranes. As might be expected, the limited solubilities of the more complex species of this type complicate their characterization and retard greater progress in these fields. A possible, and probably the simplest, approach to the elimination of this problem is the alkylation or arylation of selected boron vertices of the supporting carborane cages[6] since B-substituted carborane derivatives would be expected to have greater solubility in a variety of noncoordinating organic solvents. The chemistry of carboranes containing boron−carbon bonds has been limited for some time because of the difficulty in selectively functionalizing or otherwise carrying out substitution reactions at specific boron vertices. Several methods have been developed toward this goal; however, very few of these are of significant utility because of the harsh reaction conditions required, lengthy reaction times, complexity of product mixtures, and attendant difficulty in product separation. Zakharkin and co-workers[7] have reported a general method leading to a quantitative conversion of *closo*-9-I-1,2-$C_2B_{10}H_{11}$ and *closo*-9-I-1,7-$C_2B_{10}H_{11}$ into the corresponding *closo*-9-R-1,2-$C_2B_{10}H_{11}$ and *closo*-9-R-1,7-$C_2B_{10}H_{11}$ (R = alkyl and aryl) by catalytic cross-coupling monoiodocarboranes with appropriate Grignard reagents. Recently, applying the same procedure, Jones and Li[8] reported the quantitative synthesis of *closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$ and *closo*-9,12-(allyl)$_2$-1,2-$C_2B_{10}H_{10}$. During our reinvestigation of these cross-coupling reactions, we found, to our surprise, that the yield is much lower than that reported[7,8] under the reported reaction conditions. Only upon the addition of copper(I) iodide as a cocatalyst could we obtain the desired products in low to moderate yields. We have synthesized *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$[9] and *closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$ and constructed mercuracarborand species from these derivatized molecules.[1a,b,10] The host−guest complexes prepared from the resulting B-substituted mercuracarborands do indeed exhibit enhanced solubilities in noncoordinating solvents such as benzene, toluene, chloroform, and methylene chloride. The molecular structure of the octaethyl-substituted mercuracarbo-

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(1) (a) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142. (b) Hawthorne, M. F.; Yang, X.; Zheng, Z. *Pure Appl. Chem.* **1994**, *66*, 245. (c) Grimes, R. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1289.

(2) Yang, X.; Johnson, S. E.; Khan, S. I.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 893.

(3) Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 123.

(4) (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.

(5) Chizhevsky, I. T.; Johnson, S. J.; Knobler, C. B.; Gomez, F. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 6981.

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

(7) Zakharkin, L. I.; Kovredou, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *J. Organomet. Chem.* **1982**, *226*, 217.

(8) Li, J.; Logan, C. M.; Jones, N., Jr. *Inorg. Chem.* **1991**, *30*, 4866.

(9) Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. Unpublished results.

(10) Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. Unpublished results.

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

formula	$C_2B_{10}H_{10}I_2$	$C_{14}B_{10}H_{20}$
crystal dimens, mm	0.19 × 0.38 × 0.59	0.40 × 0.35 × 0.50
crystal appearance	colorless cut parallelepiped	colorless cut parallelepiped
radiation; λ, Å	Mo Kα; 0.7107	Mo Kα; 0.7107
space group	$P2_1/c$	$I4_1/a$
a, Å	13.2719(6)	9.446(2)
b, Å	14.9718(6)	
c, Å	13.4734(6)	39.949(8)
β, deg	114.211(1)	
V, Å^3	2441.7(3)	3564.1(1)
Z	8^a	8^b
ϱ(calcd), g cm^{-3}	2.15	1.10
abs coeff, cm^{-1}	50.5	0.5
scan width, deg: below Kα_1; above Kα_1	1.3; 1.6	1.3; 1.6
scan mode; speed, deg/min	$\theta - 2\theta$; 12	$\theta - 2\theta$; 12
data collcd; unique data used	5595; 3299 ($I > 3\sigma(I)$)	1773; 882 ($I > 3\sigma(I)$)
2θ max, deg^{-1}	55	50
no. of params refined	314	109
R, R_w, GOF^c	0.043, 0.064, 2.06	0.056, 0.063, 1.84

[a] 2 molecules/asymmetric unit. [b] $^1/_2$ molecule/asymmetric unit. [c] $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}$. GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)^{1/2}$, where $w = 1/(\sigma^2|F_o|)$.

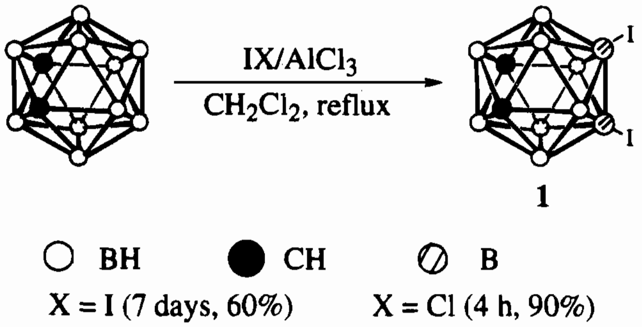
rand host reported recently contained no coordinated solvent molecules.[1a] Similarly, macrocyclic dimers (carboracycles) based upon *closo*-9,10-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$[11] and tetramers composed of *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$[12] show greatly enhanced solubilities in organic solvents when compared with the parent unsubstituted macrocycles.[5]

In order to avoid the formation of isomers during the construction of carborane-based structures, symmetrically disubstituted carborane derivatives would be required. Hence, an efficient synthesis of symmetrically substituted diiodocarboranes as the pivotal starting compounds provided the key to success. Although *closo*-9-I-1,2-$C_2B_{10}H_{11}$[13,14] and *closo*-9-I-1,7-$C_2B_{10}H_{11}$[13] have been synthesized successfully through the use of iodine in conventional iodination reactions, diiodination of carboranes is usually difficult, especially in the case of *closo*-1,7-$C_2B_{10}H_{12}$.[15] We have developed a general and expeditious procedure for the preparation of these diiodinated derivatives in which the more reactive iodine monochloride (ICl) is employed as the iodination reagent. In this article, we report a detailed investigation of the diiodination of *closo*-1,2-$C_2B_{10}H_{12}$, as well as its extension to the *closo*-1,7-$C_2B_{10}H_{12}$ system. The improved coupling reaction of diiodocarboranes with a variety of Grignard reagents will also be described, as well as the molecular structures of *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, and *closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$, **10**.

Experimental Section

General Considerations. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Diethyl ether and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl immediately prior to use. Methylene chloride was distilled from calcium hydride. Iodine monochloride and Grignard reagents were obtained from Aldrich Chemical Co. and used without further purification. Melting points were measured in sealed capillaries on a Thomas-Hoover capillary melting point apparatus and were uncorrected. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded with AM 360, AM 360, and AM 500 spectrometers, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to residual ^{1}H 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). Compounds previously reported exhibited satisfactory physical and spectroscopic properties in agreement with data taken from the literature.

Scheme 1



Procedure for the Diiodination of *closo*-1,2-$C_2B_{10}H_{12}$ and *closo*-1,7-$C_2B_{10}H_{12}$. A. Iodine as the Iodination Reagent.[8] A mixture of *closo*-1,2-$C_2B_{10}H_{12}$ (10.4 g, 71 mmol), iodine (18.2 g, 71 mmol), and $AlCl_3$ (1.00 g) in 250 mL of dry methylene dichloride was refluxed under nitrogen. A light brown homogeneous solution appeared after 20 min. A second portion of iodine (18.2 g, 71 mmol) was added and the reflux continued for 14 h, yielding a dark brown solution. The reaction mixture was poured into 100 mL of ice-cold water, and the organic phase was separated from the mixture. The aqueous layer was then extracted with diethyl ether. The combined organic phase was washed with dilute $Na_2S_2O_3$ solution followed by water and dried over $MgSO_4$. After removal of the solvent, the greenish residue was recrystallized from CH_2Cl_2 to yield a white crystalline solid (90%), identified by ^{1}H, ^{13}C, and ^{11}B NMR as *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$.[8]

For the *closo*-1,7-$C_2B_{10}H_{12}$ system, a mixture of *closo*-1,7-$C_2B_{10}H_{12}$ (10.4 g, 71 mmol), iodine (18.2 g, 71 mmol), and $AlCl_3$ (1.00 g) in 250 mL of dry methylene dichloride was refluxed under nitrogen. A light brown homogeneous solution appeared after 1 h. A second portion of iodine (18.2 g, 71 mmol) was added and the reflux continued for 7 days, yielding a purple mixture. After extraction as described above, the residue was recrystallized from CH_2Cl_2 to yield *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, as a white crystalline solid (60%): mp 189−190 °C (lit.[15a] mp 186−187 °C); ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 1.6−3.4 (carborane B*H*), 4.04 (s, carborane C*H*); ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C) δ 58.8 (s, carborane *C*H). ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −20.3 (s, 2B, *B*I), −17.6 (d, 4B), −11.0 (d, 2B), −3.67 (d, 2B); HREIMS for $C_2B_{10}H_{10}I_2$ calcd 395.9862, found 395.9875.

B. Iodine Monochloride as the Iodination Reagent. A mixture of *closo*-1,2-$C_2B_{10}H_{12}$ or *closo*-1,7-$C_2B_{10}H_{12}$ (10.4 g, 71 mmol), iodine monochloride (23.1 g, 142 mmol), and $AlCl_3$ (1.00 g) in 250 mL of

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(11) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. Unpublished results.

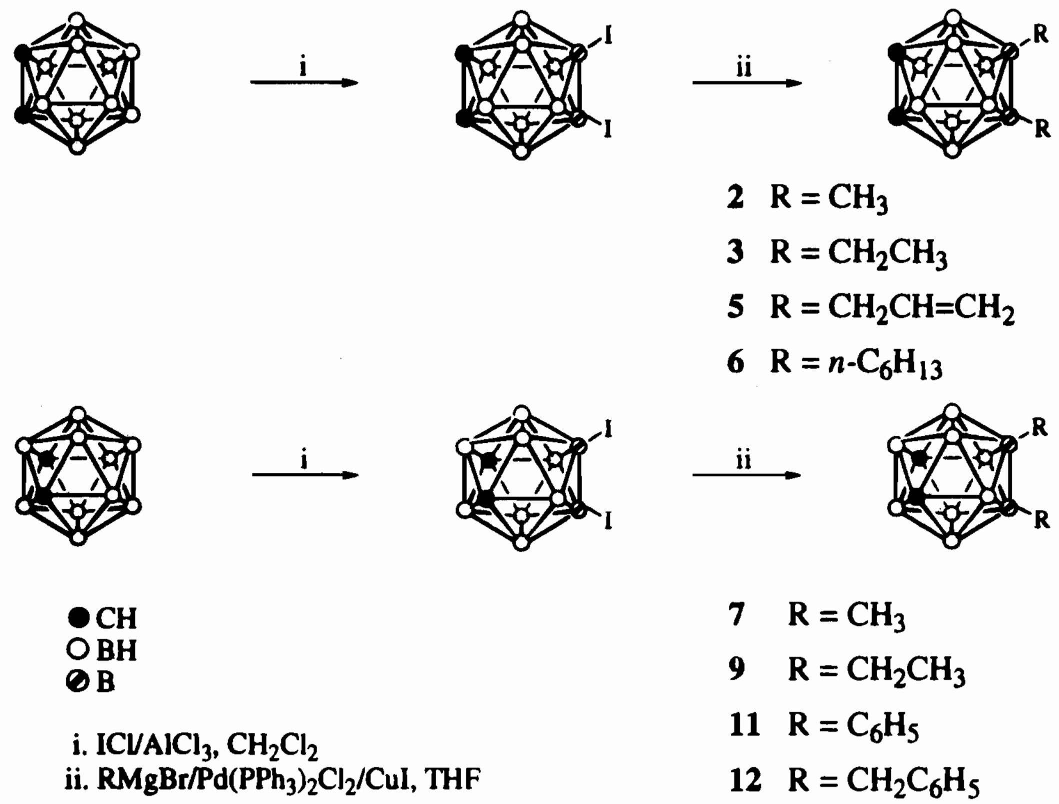
(12) Mortimer, M. D.; Hawthorne, M. F. Unpublished results.

(13) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 575.

(14) Andrews, J. S.; Zayas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715.

(15) (a) Stanko, V. I.; Klimova, A. Z. *Zh. Obshch. Khim.* **1966**, *36*, 432. (b) Stanko, V. I.; Klimova, A. Z.; Klimova, T. P. *Zh. Obshch. Khim.* **1967**, *37*, 2236.

Scheme 2



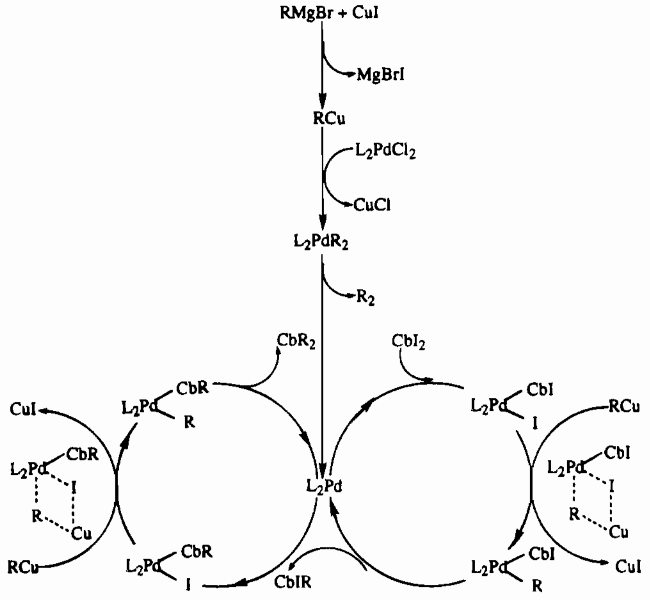
dry methylene dichloride was refluxed under nitrogen. A light brown homogeneous solution appeared after 20 min, and the reaction was stopped after 4 h. After extraction as described above, the residue was recrystallized from CH_2Cl_2 to yield a white crystalline solid (90%), which was identified by ^{1}H, ^{13}C, and ^{11}B NMR as *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ or *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$.

General Procedure for the Cross-Coupling between Diiodocarboranes and Grignard Reagents. A modified literature procedure[7,8] was used for the cross-coupling reactions between *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ or *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ and Grignard reagents. A solution of the appropriate Grignard reagent (50 mmol) in either diethyl ether or THF was added dropwise to a stirred THF solution (100 mL) of *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ or *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ (3.96 g, 10.0 mmol) cooled in an ice–water bath, and the slurry was stirred at room temperature for 20 min. Both $(Ph_3P)_2PdCl_2$ (280 mg, 4% equiv) and CuI (76 mg, 4% equiv) were then added in a single portion, and the reaction mixture was refluxed for 2–5 days. After removal of the solvent, 200 mL of diethyl ether was added to the residue and the excess Grignard reagent was destroyed by the slow addition of dilute HCl. The organic phase was separated from the mixture, and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with H_2O (3 × 50 mL) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was subjected to flash silica gel chromatography using hexanes as the eluting solvent.

A. Di-B-Substituted *closo*-1,2-$C_2B_{10}H_{10}$. *closo*-9,12-$(CH_3)_2$-1,2-$C_2B_{10}H_{10}$ (2): white crystalline solid (70%); mp 185–186 °C; ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 0.15 (br, -BC*H*$_3$), 0.5–3.6 (carborane B*H*), 4.20 (s, carborane C*H*); ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C) δ 49.6 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −16.1 (d, 2B), −13.4 (d, 4B), −6.7 (d, 2B), 8.26 (s, 2B, -*B*CH_3); HREIMS for $C_4B_{10}H_{16}$ calcd 172.2255, found 172.2254.

***closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$ (3):** colorless liquid (30%); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ 0.69 (m, -BC*H*$_2CH_3$), 0.87 (m, -BCH_2C*H*$_3$), 1.3–2.7 (carborane B*H*), 3.38 (s, carborane C*H*); ^{11}B NMR (160 MHz, $CHCl_3$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −17.0 (d, 2B), −15.1 (d, 4B), −9.2 (d, 2B), 8.9 (s, 2B, -*B*CH_2CH_3). This known compound has been fully characterized previously.[8]

Scheme 3. Proposed Mechanism for the Cross-Coupling Reaction of Diiodocarboranes with Grignard Reagents Mediated by a Palladium Catalyst (L = Ph_3P; Cb = *closo*-1,2-$C_2B_{10}H_{10}$ or *closo*-1,7-$C_2B_{10}H_{10}$)



***closo*-9-I-12-(C_2H_5)-1,2-$C_2B_{10}H_{10}$ (4):** white crystalline solid (20%); mp 74–75 °C; ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 0.89 (br, -BC_2*H*$_5$), 0.5–4.0 (br, carborane B*H*), 4.59, 4.86 (s, carborane C*H*); ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C) δ 13.4 (-BCH_2*C*H_3), 51.4, 52.5 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −14.8 (d, 2B), −13.7 (3B), −13.0 (d, 2B), −7.3 (d, 2B), 8.45 (s, 1B, -*B*CH_2CH_3); HREIMS for $C_4B_{10}H_{15}I$ calcd 300.1149, found 300.1151.

***closo*-9,12-$(CH_2CH{=}CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (5):** colorless liquid (25%); ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 1.58 (br, -BC*H*$_2CH{=}CH_2$), 1.0–3.5 (br, carborane B*H*), 4.33 (s, carborane C*H*), 4.73 (m, -BCH_2-$CH{=}C$*H*$_2$), 5.69 (m, -BCH_2C*H*$={CH_2}$); ^{13}C NMR (90 MHz, $(CD_3)_2$-

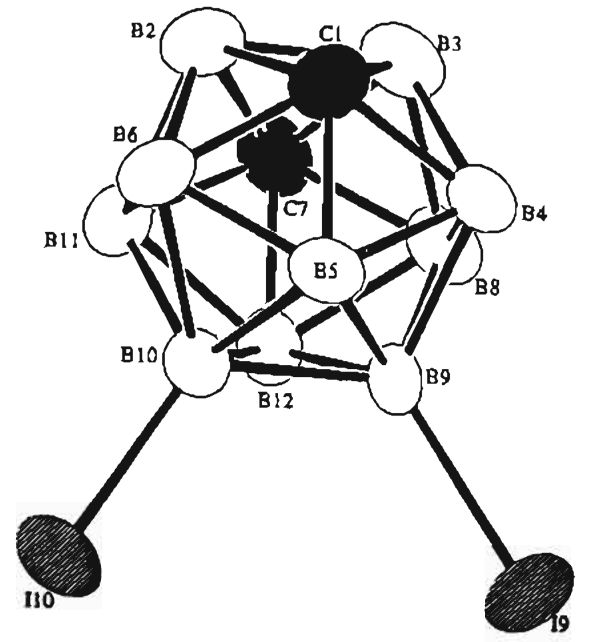


Figure 1. ORTEP representation of **1** with H atoms omitted for clarity.

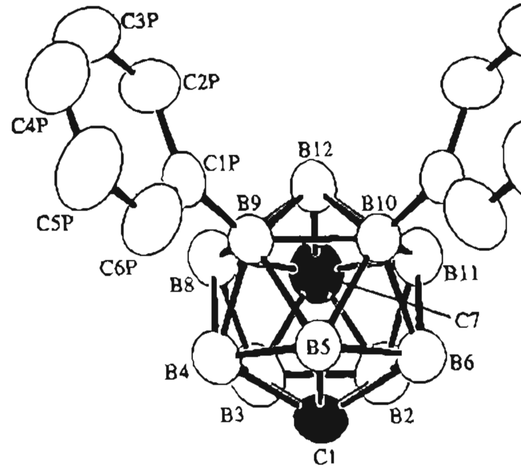


Figure 2. ORTEP representation of **10** with H atoms omitted for clarity. A 2-fold axis passes through the molecule through the midpoints of B(9) and B(10) and of B(2) and B(3). The following pairs of atoms are equivalent because of the 2-fold symmetry: C(1) and C(7), B(2) and B(3), B(4) and B(11), B(5) and B(12), B(6) and B(8), B(9) and B(10).

CO, 25 °C) δ 50.4 (s, carborane *C*H), 111.8 (s, $-BCH_2CH{=}CH_2$), 140.7 (s, $-BCH_2CH{=}CH_2$); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −15.7 (d, 2B), −13.9 (d, 4B), −8.5 (d, 2B), 7.12 (s, 2B, $-BCH_2CH{=}CH_2$). This known compound has been fully characterized previously.[8]

***closo*-9,12-(n-C_6H_{13})$_2$-1,2-$C_2B_{10}H_{10}$ (6):** colorless liquid (35%); ^1H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 0.69, 0.91, 1.31 (-B(n-C_6H_{13})), 4.11 (s, carborane C*H*); ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C) δ 14.5, 18.0 (br), 23.3, 30.2, 32.4, 33.1 (-B(n-C_6H_{13})), 49.5 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −15.2 (d, 2B), −13.5 (d, 4B), −7.8 (d, 2B), 9.0 (s, 2B, -*B*(n-C_6H_{13})); HREIMS for $C_{14}B_{10}H_{36}$ calcd 312.3815, found 312.3820.

B. Di-B-Substituted *closo*-1,7-$C_2B_{10}H_{10}$. *closo*-9,10-$(CH_3)_2$-1,7-$C_2B_{10}H_{10}$ (7): white crystalline solid (73%); mp 134−135 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 0.91(br, -BC*H*$_3$), 1.6−3.4 (carborane B*H*), 2.85 (s, carborane C*H*); ^{13}C NMR (90 MHz, $CDCl_3$, 25 °C) δ 52.1 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(C_2H_5)_2O$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −21.1 (d, 2B), −13.2 (d, 4B), −5.5 (d, 2B), −0.58 (s, 2B, -*B*CH_3); HREIMS for $C_4B_{10}H_{16}$ calcd 172.2255, found 172.2249.

***closo*-9,10-$(C_2H_5)_2$-1,7-$C_2B_{10}H_{10}$ (8):** colorless liquid (20%); mp 185−186 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 0.81 (br, -BC*H*$_2$CH$_3$), 0.97 (br, -BCH$_2$C*H*$_3$), 1.2−3.6 (carborane B*H*), 2.78 (s, carborane C*H*); ^{13}C NMR (90 MHz, $CDCl_3$, 25 °C) δ 14.1 (-BCH$_2$*C*H$_3$), 54.0 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(C_2H_5)_2O$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −20.4 (d, 2B), −13.5 (d, 4B), −6.1 (d, 2B), 1.8 (s, 2B, -*B*CH$_2$CH$_3$); HREIMS for $C_6B_{10}H_{20}$ calcd 200.2568, found 200.2562.

***closo*-9-I-10-(C_2H_5)-1,7-$C_2B_{10}H_{10}$ (9):** white crystalline solid (10%); mp 34−35 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 1.01 (br, -BC*H*$_2$CH$_3$), 1.7−3.7 (carborane B*H*), 2.98 (s, carborane C*H*); ^{13}C NMR (90 MHz, $CDCl_3$, 25 °C) δ 13.3 (-BCH$_2$*C*H$_3$), 54.4 (s, carborane *C*H); ^{11}B NMR (160 MHz, $(C_2H_5)_2O$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −21.2 (s, 1B, -*B*I), −20.2 (d, 1B), −19.3 (d, 2B), −13.3 (d, 2B), −12.4 (d, 1B), −5.3 (d, 2B), 1.5 (s, 1B, -*B*CH$_2$CH$_3$); HREIMS for $C_4B_{10}H_{15}I$ calcd 298.1221, found 298.1219.

***closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$ (10):** white crystalline solid (75%); mp 185−186 °C; ^1H NMR (200 MHz, $(CD_3)_2CO$, 25 °C) δ 1.6−3.5 (carborane B*H*), 3.73 (s, carborane C*H*), 7.07−7.43 (m, -BC$_6$*H*$_5$); ^{13}C NMR (90 MHz, $(CD_3)_2CO$, 25 °C) δ 52.5 (s, carborane *C*H), 127.9, 128.1, 133.9 (-B*C*$_6$H$_5$); ^{11}B NMR (160 MHz, $(CH_3)_2CO$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −19.8 (d, 2B), −12.9 (d, 4B), −6.7 (d, 2B), 1.37 (s, 2B, -*B*C$_6$H$_5$); HREIMS for $C_{14}B_{10}H_{20}$ calcd 298.2496, found 298.2501.

***closo*-9,10-$(C_6H_5CH_2)_2$-1,7-$C_2B_{10}H_{10}$ (11):** white crystalline solid (64%); mp 107−109 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C) δ 2.42 (-BC*H*$_2$C$_6$H$_5$), 0.86−3.95 (carborane B*H*), 2.75 (s, carborane C*H*), 7.16, 7.34, 7.36 (-BCH$_2$C$_6$*H*$_5$); ^{13}C NMR (90 MHz, $CDCl_3$, 25 °C) δ 29.7 (s, -B*C*H$_2$C$_6$H$_5$), 52.5 (s, carborane *C*H), 124.2, 128.0, 128.5, 144.3 (-BCH$_2$*C*$_6$H$_5$); ^{11}B NMR (160 MHz, $(C_2H_5)_2O$, $BF_3{\cdot}OEt_2$ external, decoupled, 25 °C) δ −24.2 (d, 2B), −13.3 (d, 4B), −5.9 (d, 2B), 0.95 (s, 2B, -*B*CH$_2$C$_6$H$_5$); HREIMS for $C_{16}B_{10}H_{24}$ calcd 324.2881, found 324.2888.

X-ray Crystallography. Table 1 lists a summary of crystallographic data for *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, and *closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$, **10**.

***closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ (1).** A colorless crystal, obtained from a methylene chloride solution, was mounted on a fiber and placed on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 74 accurately centered reflections (7.7° < 2θ < 22.3°). Data were collected at 25° in the $\theta-2\theta$ scan mode. Of the 5595 unique reflections measured, 3299 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 crystallographic programs listed in ref 16.

Atoms were located by use of heavy-atom methods. All calculations were performed on a VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. All non-hydrogen atoms were refined with anisotropic parameters. Positional parameters were refined for all hydrogen atoms. H atoms were assigned isotropic displacement values of $u = 0.05$ Å^2. Scattering factors for H were obtained from ref 17 and for other atoms were taken from ref 18. Anomalous dispersion terms were included for the scattering of I. The largest peak on a final difference electron density map was 0.3 e·Å^{-3}.

***closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$ (10).** A colorless crystal, obtained from a $CDCl_3$ solution, was mounted on a fiber and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections (9.5° < 2θ < 17.9°). Data were collected at 25° in the $\theta-2\theta$ scan mode. Of the 1773 unique reflections measured, 882 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 or absorption.

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(16) 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; SHELX86 (Sheldrick), crystal structure solution package.

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

Table 2. Selected Bond Lengths and Angles for **1**[a]

			Lengths (Å)		
C(1)−B(2)	1.705(16)	1.689(16)	C(7)−B(2)	1.710(2)	1.652(16)
C(1)−B(3)	1.762(16)	1.723(16)	C(7)−B(3)	1.672(16)	1.655(16)
C(1)−B(4)	1.718(15)	1.737(16)	C(7)−B(8)	1.716(16)	1.707(15)
C(1)−B(5)	1.719(14)	1.722(15)	C(7)−B(11)	1.711(15)	1.706(14)
C(1)−B(6)	1.711(15)	1.715(15)	C(7)−B(12)	1.696(16)	1.737(14)
B(9)−I(9)	2.154(10)	2.187(10)	B(10)−I(10)	2.151(10)	2.146(9)
			Angles (deg)		
I(9)−B(9)−B(4)	119.8(6)	120.3(6)	I(10)−B(10)−B(5)	122.1(6)	122.1(6)
I(9)−B(9)−B(5)	121.6(6)	121.8(6)	I(10)−B(10)−B(6)	121.3(6)	120.7(6)
I(9)−B(9)−B(8)	120.8(6)	120.3(6)	I(10)−B(10)−B(9)	122.7(6)	123.8(6)
I(9)−B(9)−B(10)	123.4(6)	121.7(6)	I(10)−B(10)−B(11)	120.6(6)	120.5(6)
I(9)−B(9)−B(12)	123.0(6)	120.2(6)	I(10)−B(10)−B(12)	122.3(6)	121.9(6)

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

Table 3. Selected Bond lengths and Angles for **10**

	Lengths (Å)		
C(1)−B(2)	1.695(5)	C(1P)−B(9)	1.580(4)
C(1)−B(4)	1.702(4)	C(1P)−C(2P)	1.385(4)
C(1)−B(5)	1.700(4)	C(2P)−C(3P)	1.392(5)
C(1)−B(6)	1.710(4)	C(3P)−C(4P)	1.368(5)
B(1)−B(4)	1.783(4)	C(4P)−C(5P)	1.348(5)
B(9)−B(5)	1.780(4)	C(5P)−C(6P)	1.394(5)
B(9)−B(6)	1.785(4)	C(6P)−C(1P)	1.388(4)
B(9)−B(9)	1.814(4)		
	Angles (deg)		
C(1P)−C(2P)−C(3P)	122.0(3)	C(6P)−C(1P)−B(9)	121.3(2)
C(2P)−C(3P)−C(4P)	119.5(3)	C(2P)−C(1P)−B(9)	122.2(2)
C(3P)−C(4P)−C(5P)	120.2(3)	C(1P)−B(9)−B(4)	119.8(2)
C(4P)−C(5P)−C(6P)	120.5(3)	C(1P)−B(9)−B(5)	123.6(2)
C(5P)−C(6P)−C(1P)	121.3(3)	C(1P)−B(9)−B(6)	119.7(2)
C(6P)−C(1P)−C(2P)	116.5(3)	C(1P)−B(9)−B(9)	125.0(2)

Programs used in this work include locally modified versions of crystallographic programs listed in ref 16.

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 non-hydrogen atoms were refined with anisotropic parameters. All phenyl hydrogens were included in calculated positions, C−H = 1.0 Å. H atoms were assigned isotropic displacement values based approximately on the values for the attached atoms. Scattering factors for H were obtained from ref 17, and those for other atoms were taken from ref 18. The largest peak on a final difference electron density map was 0.1 e·Å^{-3}.

Results and Discussion

Comparison of Molecular Iodine and Iodine Monochloride as Iodination Reagents. Molecular iodine and a Lewis acid catalyst are the reagents most commonly used to achieve the iodination of icosahedral carboranes.[13] In principle, diiodocaboranes can be obtained by introducing a second equivalent of iodine to a monoiodocarborane and applying the same strategy. Although *closo*-9,12-I_2-1,2-$C_2B_{10}H_{10}$ can be isolated in this procedure in high yield,[8,14] an extension of this traditional iodination reaction to *closo*-1,7-$C_2B_{10}H_{12}$ proved to be sluggish and a mixture of *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$ and *closo*-9-I-1,7-$C_2B_{10}H_{11}$ was obtained. A comparative rate study showed that iodination of *closo*-1,7-$C_2B_{10}H_{12}$ proceeds 11 times slower than the corresponding *closo*-1,2-$C_2B_{10}H_{12}$ reaction.[19] This observation is in agreement with the reduced ground state charge separation of the *closo*-1,7-$C_2B_{10}H_{12}$ system, and as a result, *closo*-1,7-$C_2B_{10}H_{12}$ is much less susceptible to electrophilic iodination.[20]

Iodine monochloride (ICl) is a stronger iodinating agent than molecular iodine in aromatic electrophilic iodination reactions.[21] A comparison of ICl and I_2 in the reaction with *closo*-1,7-$C_2B_{10}H_{12}$ in CH_2Cl_2 at the reflux temperature and in the presence of $AlCl_3$ (10.5 mol %) proves that a higher yield of *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, can be obtained (90%) after dramatically reduced reaction time by the use of iodine monochloride as the iodination reagent. Iodine gives **1** in 60% yield in a sluggish reaction of 7 days' duration with *closo*-9-I-1,7-$C_2B_{10}H_{11}$ as the major byproduct (Scheme 1).

The usefulness of iodine monochloride for the iodination of carboranes can also be appreciated in a recent report[22] in which the elegant one-step syntheses of *closo*-I_8-1,2-$C_2B_{10}H_4$ and *closo*-I_8-1,7-$C_2B_{10}H_4$ were achieved by refluxing the corresponding carboranes in neat trifluoromethanesulfonic acid with iodine monochloride.

Cross-Coupling between Diiodocarboranes and Grignard Reagents. Zakharkin and co-workers[7] have proposed a general method for the synthesis of *closo*-9-R-1,2-$C_2B_{10}H_{11}$ and *closo*-9-R-1,7-$C_2B_{10}H_{11}$ in which the corresponding *closo*-9-I-1,2-$C_2B_{10}H_{11}$ and *closo*-9-I-1,7-$C_2B_{10}H_{11}$ are coupled with a variety of Grignard reagents in the presence of a palladium(0) catalyst. A quantitative synthesis of *closo*-9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$, **3**, and *closo*-9,12-$(C_3H_5)_2$-1,2-$C_2B_{10}H_{10}$, **5**, has also been reported applying the same methodology.[8] In our hands, the product yields of these reactions are not as high as has been reported, and in most of the cases we have studied the yields are extremely low. Incompletely coupled intermediates were obtained as the major products even when the Grignard reagents were present in excess. In the absence of the palladium catalyst, this reaction did not take place, indicating its indispensable role in facilitating the coupling reaction. We observed that a modification of the literature[7,8] procedure through the addition of copper(I) iodide as a cocatalyst was critical to the success of these coupling reactions, and only with this modification could we isolate the desired products in an acceptable yield. Several *closo*-9,12-R_2-1,2-$C_2B_{10}H_{10}$ and *closo*-9,10-R_2-1,7-$C_2B_{10}H_{10}$ complexes (R = alkyl, aralkyl, aryl) have been synthesized as shown in Scheme 2.

On the basis of these results, a possible mechanism for the overall coupling reaction is illustrated in Scheme 3.

Although the precise mechanism of this reaction is yet to be ascertained, copper(I) iodide is thought to catalyze both the generation of L_2Pd^0 species from L_2PdCl_2 (L = Ph_3P) and the transmetalation of (σ-carboranyl)palladium iodide complexes,

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

(19) Zakharkin, L. I.; Kalinin, V. N. *Zh. Obshch. Khim.* **1966**, *36*, 2218.

(20) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970; p 66.

(21) Hubig, S. M.; Jung, W.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 6233 and references therein.

(22) Srivastava, R. R.; Wilbur, D. S. *Abstracts of Papers*, 208th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1994; INOR 293.

$L_2Pd(CbI)I$ and $L_2Pd(CbR)I$.[23] Thus, the catalyst precursor L_2PdCl_2 is assumed to be reduced by the binary organocopper species RCu, which is prepared *in situ* from CuI and RMgBr and enters the catalytic cycle as PdL_2. The oxidative addition of a B−I vertex present in the diiodocarborane to this Pd(0) species results in the formation of a σ-*B*-monoiodocarboranyl−palladium iodide complex, $L_2Pd(CbI)I$. Transmetalation of this species by RCu generates the corresponding $L_2Pd(CbI)R$ complex (R = alkyl, allyl, aralkyl, aryl), which reductively eliminates the coupled product, CbIR, and regenerates catalytically active PdL_2. In a similar manner, subsequent cross-coupling between CbIR and RCu leads to the formation of the di-B-substituted carborane derivative, CbR_2, regenerating the copper(I) complex as well as PdL_2 to complete the catalytic cycle. The reaction of the presumably solvated RCu species with a palladium halide complex probably proceeds via a four-centered transition state as previously suggested[24,25] and as shown in Scheme 3.

The low coupling yields observed with Grignard reagents such as ethyl- or *n*-hexylmagnesium bromide are attributed to a competitive β-hydrogen elimination[26] reaction of the alkylpalladium intermediate which results in the formation of a palladium hydride species and an alkene. Lending support to this hypothesis is the fact that the use of Grignard reagents such as methyl-, phenyl-, and benzylmagnesium bromides provides typical coupling yields of 70% or higher. In these cases, decomposition of the palladium complexes by the β-hydrogen elimination pathway is not possible due to the absence of a β-hydrogen in the ligand. In the case of allylic Grignard reagents, their reactions with the palladium catalyst undoubtedly result in the formation of an η^3-allylic palladium complex,[27] thus blocking the generation of the necessary σ-B−palladium intermediate in the catalytic cycle. As a result, the diallyl derivative, *closo*-9,12-$(C_3H_5)_2$-1,2-$C_2B_{10}H_{10}$, **5**, was isolated in yields as low as 25%.

In agreement with the results of others[7] and the discussion above, byproducts resulting from the reduction of diiodocarboranes were isolated. As an example, when *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1**, was coupled with an excess of ethylmagnesium bromide, *closo*-9,10-$(C_2H_5)_2$-1,7-$C_2B_{10}H_{10}$, **8**, *closo*-9-I-10-(C_2H_5)-1,7-$C_2B_{10}H_{10}$, **9**, and *closo*-9-I-1,7-$C_2B_{10}H_{11}$ (1:2.7:1) were obtained in an overall yield of 70%. Small amounts of biphenyl and bibenzyl were also isolated from the coupling reactions which involved phenyl- and benzylmagnesium bromides.

Characterization of Coupling Products. All of the coupling products obtained in this study have been characterized by multinuclear NMR and high-resolution EI mass spectroscopy. The ^{11}B NMR resonances of either a *closo*-9,12-R_2-1,2-$C_2B_{10}H_{10}$ or a *closo*-9,10-R_2-1,7-$C_2B_{10}H_{10}$ exhibit a distinctly different pattern from that of the corresponding diiodocarborane. Although the chemical shifts of the signals due to the boron atoms coupled with hydrogens are basically the same in both compounds, the carbon-substituted boron atoms are deshielded and always give the most downfield resonances, whereas ^{11}B NMR signals for the iodo-substituted borons appear as the most upfield ones. This provides a simple way to identify the presence of a B-substituted derivative. It is also noteworthy that the carbon nuclei directly bonded to boron vertices always give rise to ^{13}C NMR signals which are broadened and sometimes beyond detection. This must be attributed to their close proximity to both ^{11}B (80.4%, $I = {}^3/_2$) and ^{10}B (19.6%, $I = 3$), two nuclei with electric quadruple moments.[28]

The molecular structures of both *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, **1** (Figure 1), and *closo*-9,10-$(C_6H_5)_2$-1,7-$C_2B_{10}H_{10}$, **10** (Figure 2), have been established by X-ray diffraction studies.

In the structures, **1** and **10**, both the I and phenyl substituents are present at the 9,10-positions of the carborane cage. These vertices are the farthest removed from the carborane carbons, and they consequently bear the most negative charge in accord with theoretical calculations.[29] In the structure of **1**, averaged bond distances are C−B = 1.708(15) Å, B−B = 1.772(14) Å, and B−I = 2.160(10) Å, comparable to those found in an electron-diffraction study of **1**.[30] In the structure of **10**, the average C−B and B−B distances are 1.700(4) and 1.779(4) Å, respectively. The averaged bond distance of B−Cph is 1.580(4) Å. All these values as well as other angles and distances are similar to those found in related compounds.[31] Selected bond distances and angles for **1** and **10** are listed in Tables 2 and 3, respectively.

Conclusions. We have systematically explored electrophilic diiodination of *closo*-1,2-$C_2B_{10}H_{12}$ and *closo*-1,7-$C_2B_{10}H_{12}$ using iodine monochloride in the presence of catalytic aluminum chloride. The synthesis of *closo*-9,10-I_2-1,7-$C_2B_{10}H_{10}$, a derivative previously obtained with difficulty, was achieved in 90% yield. Palladium-mediated cross-coupling reactions between Grignard reagents and diiodocarboranes were reinvestigated, and it was demonstrated that the addition of copper(I) iodide as a cocatalyst is crucial to the success of this reaction.

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Supplementary Material Available: Tables giving positional and thermal parameters, bond lengths and angles, and crystallographic data and ORTEP views of **1** and **10** (11 pages). Ordering information is given on any current masthead page.

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(23) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahadron Lett.* **1975**, *50*, 4467.

(24) Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 4716.

(25) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 2163.

(26) (a) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (c) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

(27) (a) Powell, P. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley-Interscience: New York, 1982; p 325. (b) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmerman, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151.

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

(29) Dixon, D. A.; Kleier, D. A.; Helgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226 and the references therein.

(30) Vilkov, L. V.; Khaikin, L. S.; Zhigach, A. F.; Siryatskaya, V. N. *Zh. Strukt. Khim.* **1968**, *9*, 889.

(31) (a) Potenza, J. A.; Lipscomb, W. N. *Inorg. Chem.* **1967**, *6*, 874. (b) Potenza, J. A.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 1917.