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Iodination Reactions of Icosahedral *para*-Carborane and the Synthesis of Carborane Derivatives with Boron−Carbon Bonds

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Reaction of *closo*-1,12-$C_2B_{10}H_{12}$ (*para*-carborane) with 2 molar equiv of ICl in the presence of catalytic quantities of $AlCl_3$ affords *closo*-1,12-$C_2B_{10}H_{10}I_2$ as a mixture of isomers. The 2,9- (**2**), 2,3- (**3**), and 2,7-isomers (**4**) have been isolated and characterized. Reaction of *closo*-1,12-$C_2B_{10}H_{11}$-2-I (**1**) with PhMgBr or **2** with RMgBr (R = Me, Ph) in the presence of $PdCl_2(PPh_3)_2$ and CuI gives high yields of *closo*-1,12-$C_2B_{10}H_{11}$-2-Ph (**6**) and *closo*-1,12-$C_2B_{10}H_{10}$-2,9-R_2 (**7**, R = Me; **8**, R = Ph), respectively. Reaction of **1** with HC≡CPh in the presence of $PdCl_2(PPh_3)_2$ and pyrrolidine yields *closo*-1,12-$C_2B_{10}H_{11}$-2-C≡CPh (**9**). Reaction of **1** or **2** with $HC{\equiv}CSiMe_3$ under the same conditions affords *closo*-1,12-$C_2B_{10}H_{11}$-2-$C{\equiv}CSiMe_3$ (**10**) and *closo*-1,12-$C_2B_{10}H_{11}$-2,9-$(C{\equiv}CSiMe_3)_2$ (**12**) which react with fluoride ion to give *closo*-1,12-$C_2B_{10}H_{11}$-2-C≡CH (**11**) and *closo*-1,12-$C_2B_{10}H_{11}$-2,9-$(C{\equiv}CH)_2$ (**13**), respectively. The structures of **1**, **3**, **4**, *closo*-1,12-$C_2H_2B_{10}I_{10}$ (**5**), and **8** have been determined by crystallographic studies. Crystallographic data are as follows: For **1**, monoclinic, space group $C2/c$, a = 10.824(2) Å, b = 9.439(1) Å, c = 21.414(3) Å, β = 102.121(4)°, Z = 8, R = 0.035; for **3**, orthorhombic, space group $Pmnb$, a = 12.868(1) Å, b = 14.144(2) Å, c = 7.069(1) Å, Z = 4, R = 0.038; for **4**, monoclinic, space group $C2/c$, a = 25.039(1) Å, b = 8.1129(4) Å, c = 14.3300(7) Å, β = 122.567(1)°, Z = 8, R = 0.050; for **5**, triclinic, space group $P\bar{1}$, a = 7.796(1) Å, b = 9.882(2) Å, c = 16.681(3) Å, α = 91.550(6)°, β = 100.271(6)°, γ = 110.854(5)°, Z = 2, R = 0.060; for **8**, orthorhombic, space group $Pcab$ ($Pbca\ \bar{c}ba$), a = 8.7706(8) Å, b = 10.559(1) Å, c = 18.081(2) Å, Z = 4, R = 0.067.

Introduction

The icosahedral carboranes belong to an unusual class of molecules with properties common to both organic and polyhedral borane chemistry. The presence of two moderately acidic CH vertices in the cage enables a wide range of substitution at these positions by common organometallic procedures which leave the relatively hydridic BH groups unaffected.[1] Substitution at the boron vertices is less well-understood, although the predominance of electrophilic substitution reactions provides a clear analogy with organic aromatic systems.[2] However, under suitable reaction conditions carboranes also have the potential, in common with boron hydrides, to change their geometry and to incorporate heteroatoms into the cage structure in ways which have no parallel with organic chemistry.[3]

The highly symmetric nature of the icosahedral cage skeleton, coupled with its remarkable thermal and chemical stability, has led to its use as a modular building unit with many promising applications.[4] Recently, progress has been made in this laboratory and elsewhere in the synthesis of structurally well-defined macromolecules containing multiple *ortho*-, *meta*-, and *para*-carboranes.[5] Of particular relevance to this article is the "carborod" work[5e,f] which entails the direct coupling of the carbon vertices of *p*-carborane molecules to synthesize rigid linear molecules. The synthesis of this structural motif is a challenging task which has recently attracted interest as a desirable feature in nanomechanical construction.[6] Unfortunately, these types of carborane-based molecules suffer from limited solubility in common organic solvents, and the problem becomes more acute as the number of carborane icosahedra in the molecule increases. The insolubility of these compounds has tended to hinder further synthesis and characterization. Therefore an incentive exists to develop carborane derivatives which impart better solubility properties to macromolecules of which they are a part.

Our aim has been to improve the solubility of the *p*-carborane-based carborods by attaching organic groups to the boron vertices. The most powerful route so far reported to introduce organic substituents to the boron vertices of *o*- and *m*-carborane cages involves iodination at one or more positions, followed by a palladium-catalyzed coupling reaction of a Grignard reagent with the BI vertex.[7] We have modified the published procedures and significantly improved both reaction rates and yields for *o*- and *m*-carborane derivatives.[8] However, analogous reactions with *p*-carborane have not previously received much attention.

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Multiple reactions at the boron vertices of *p*-carborane present some complications regarding isomer formation, in which *p*-carborane differs from the *o*- and *m*-isomers due to its higher symmetry. However, the potential for further research arising from the ability to selectively functionalize boron vertices of *p*-carborane while leaving the carbon vertices free for intercage bonding makes such reactions worthy of investigation. Monoiodinated *p*-carborane has been synthesized by Stanko *et al.*,[9] and some derivative chemistry has been carried out by Zakharkin and co-workers, including palladium-catalyzed arylation with fluorinated phenyl groups[7b] and alkylation with a methyl group.[10] Further iodination reactions are restricted to a preliminary report detailing the formation of mixtures of isomers of diiodo-*p*-carborane[11] and, very recently, the synthesis of decaiodo-*p*-carborane.[12] Our purpose has been to re-examine these iodination reactions in order to develop synthetically useful routes to *p*-carboranes with solubilizing or functional groups attached to their boron vertices. The results of this research are described herein.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of argon using a glovebox or standard Schlenk techniques. All solvents used were reagent grade. Dichloromethane and carbon tetrachloride were distilled from calcium hydride. THF and diethyl ether were distilled over sodium benzophenone ketyl. Benzene was distilled over sodium metal. Iodine, iodine monochloride, iodine monobromide, aluminum trichloride, aluminum tribromide, dichlorobis(triphenylphosphine)palladium, cupric iodide, (trimethylsilyl)acetylene, phenylacetylene, pyrrolidine, and piperidine were all purchased from Aldrich Chemical Co. and used as received. The Grignard reagents used were also purchased from Aldrich Chemical Co. and used without further treatment other than occasional titration to check their concentration by established literature measures.[13] *p*-Carborane was purchased from Consumer Health Research of Los Angeles. 2-Iodo-*p*-carborane (**1**) was made by literature procedures.[9] Both ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer. ^{11}B NMR spectra were obtained on a Bruker ARX-500 spectrometer. Proton and boron chemical shifts were referenced to residual solvent protons ($CDCl_3$, 7.26 ppm) and external $BF_3{\cdot}OEt_2$, respectively. All chemical shifts downfield of the reference are designated as positive. Mass spectra were obtained from the VG AutoSpec instrument.

Preparation of Diiodo-*p*-carboranes from 1. To *ca.* 60 mL of dichloromethane was added 2-iodo-*p*-carborane (**1**) (3.00 g, 11.1 mmol), iodine monochloride (1.80 g, 11.1 mmol), and aluminum trichloride (0.30 g, 2.2 mmol). The reaction mixture was refluxed for 2 days with stirring. After the mixture was cooled to room temperature, a saturated aqueous solution of sodium thiosulfate (100 mL) was added to remove residual halogen and aluminum trichloride. The aqueous layer was separated and washed with diethyl ether (3 × 50 mL), the washings being added to the organic layer. The combined organics were washed with a concentrated aqueous solution of sodium chloride (3 × 50 mL) and then dried over anhydrous magnesium sulfate. Removal of solvent *in vacuo* afforded 3.82 g of a mixture of isomers of diiodo-*p*-carboranes as an oily solid (87%).

Preparation of Diiodo-*p*-carboranes from *p*-Carborane. Method a. In a similar manner to the preparation of **1**, *p*-carborane (4.00 g, 27.8 mmol) and aluminum trichloride (7.40 g, 55.6 mmol) were dissolved in *ca.*100 mL of dichloromethane. Iodine monochloride (9.03 g, 55.6 mmol) was then added to the solution. The mixture was refluxed for 2 days with stirring and then worked up as described above to yield a mixture of diiodinated *p*-carboranes (9.36 g, 85%). **Method b.** *p*-Carborane (5.10 g, 35.4 mmol) and aluminum tribromide (1.89 g, 7.1 mmol) were dissolved in *ca.*100 mL of dichloromethane, and a 1 M solution of iodine monobromide in dichloromethane (70.8 mL, 70.8 mmol) was added. The reaction mixture was refluxed for 2 days. After workup, 13.3 g of a mixture of diiodinated *p*-carboranes was isolated (95%).

Separation of Diiodo-*p*-carborane Isomers. The products of the reaction between **1** and iodine monochloride were washed with pentane (2 × 30 mL), leaving a white microcrystalline mass (1.03 g, 11%), mp 225−226 °C (sealed), characterized as 2,9-diiodo-*p*-carborane (**2**). ^{1}H NMR ($CDCl_3$): 3.33 (br s, 2H, CH), 1.80−3.80 (br, 8H, BH) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 70.0 (CH) ppm. $^{11}B\{^{1}H\}$ NMR (Et_2O): −11.0 (4B), −11.9 (4B), −28.6 (2B, BI) ppm. HRMS (EI) for $C_2B_{10}H_{10}I_2$ (*m/z*): calcd, 395.9875; found, 395.9872 (M$^+$). The remaining mixture was concentrated under reduced pressure and chromatographed on a silica column. Elution with pentane and removal of the solvent *in vacuo* yielded a light yellow oil. Further elution with a benzene/pentane mixture (3:1) and removal of solvent under reduced pressure afforded a white solid (0.66 g, 7%), mp 186−187 °C (sealed), characterized as 2,3-diiodo-*p*-carborane (**3**). ^{1}H NMR ($CDCl_3$): 3.16, 2.97 (br s, 1H, CH), 1.12−3.50 (br, 8H, BH) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 69.9, 66.8 (CH) ppm. $^{11}B\{^{1}H\}$ NMR (Et_2O): −10.0 (2B), −11.1 (1B), −12.8 (4B), −14.4 (1B), −25.1 (2B, BI) ppm. MS (EI) (*m/z*): 396.0 (100%), 522.9 (8%). The peak at *m/z* 522.9 arises from a small amount of a triiodo species. The light yellow oil obtained from the procedure described above was chromatographed again on an acidic alumina column and eluted with pentane. Removal of solvent *in vacuo* from the first fraction yielded 1.31 g (14%) of 2,7-diiodo-*p*-carborane (**4**) as a clear oil which crystallized on standing, mp 83−85 °C (sealed). ^{1}H NMR ($CDCl_3$): 3.33 (br s, 2H, CH), 1.80−3.80 (br, 8H, BH) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 70.0 (CH) ppm. $^{11}B\{^{1}H\}$ NMR (Et_2O): −3.7 (2B), −11.3 (4B), −18.2 (2B) −20.1 (2B, BI) ppm. HRMS (EI) for $C_2B_{10}H_{10}I_2$ (*m/z*): calcd, 395.9875; found, 395.9867 (M$^+$). The remainder of the sample resisted further separation.

Preparation of 2-Phenyl-*p*-carborane (6). A mixture of **1** (2.00 g, 7.4 mmol), dichlorobis(triphenylphosphine)palladium (0.21 g, 0.3 mmol), and cupric iodide (0.03 g, 0.2 mmol) was dissolved in 100 mL of THF, and a 3.0 M solution of phenylmagnesium bromide (9.8 mL, 29.6 mmol) in diethyl ether was syringed into the reaction flask, resulting in a color change from yellow to black. The reaction mixture was stirred for 3 days under reflux. After the mixture was cooled to room temperature, water was carefully added to deactivate remaining Grignard reagent, and the reaction mixture was diluted with diethyl ether (100 mL). The organic layer was separated and washed three times with a concentrated solution of sodium chloride and then dried over anhydrous magnesium sulfate. Solvent was carefully removed under reduced pressure at ambient temperature to give a crude product. This was redissolved in a minimum of benzene and chromatographed on silica gel. Elution with benzene and careful removal of solvent *in vacuo* yielded an oil. Sublimation under high vacuum at room temperature yielded **6** as an oil which became crystalline upon standing (1.31 g, 80%), mp 133−134 °C (sealed). ^{1}H NMR ($CDCl_3$): 7.30−7.62 (m, 5H, C_6H_5), 3.08, 2.91 (br s, 1H, CH), 1.45−3.30 (br, 9H, BH) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 141.2, 133.2, 128.7, 127.1 (C_6H_5), 65.4, 63.6 (CH) ppm. $^{11}B\{^{1}H\}$ NMR (Et_2O): −4.4 (1B, BC_6H_5), −13.5 (2B), −14.5 (6B), −17.5 (1B), −18.8 (1B) ppm. HRMS (EI) for $C_8B_{10}H_{16}$ (*m/z*): calcd, 220.2255; found, 220.2257 (M$^+$).

Preparation of 2,9-Dimethyl-*p*-carborane (7). A mixture of **2** (2.87 g, 7.3 mmol), dichlorobis(triphenylphosphine)palladium (0.51 g, 0.7 mmol), and cupric iodide (0.07 g, 0.4 mmol) was dissolved in 70 mL of THF. To the resulting yellow solution was added a 1.4 M solution of methylmagnesium bromide (42.0 mL, 58.8 mmol) in a mixture of toluene/THF (3:1), resulting in a gradual color change to black. The mixture was refluxed for 4 days and then worked up to give a crude product as described above. Further purification by sublimation on a high vacuum line at room temperature afforded **7** as a white solid (0.98 g, 78%), mp 104−105 °C (sealed). ^{1}H NMR

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($CDCl_3$): 7.30–7.62 (m, 5H, C_6H_5), 2.78 (br s, 2H, CH), 1.30–2.95 (br, 8H, BH), 0.43 (s, 6H, BCH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 67.2 (CH), 3.5 (br, BCH_3) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −8.4 (2B, BCH_3), −13.1 (8B) ppm. HRMS (EI) for $C_4B_{10}H_{16}$ (*m/z*): calcd, 172.2255; found, 172.2250 (M^+).

Preparation of 2,9-Diphenyl-*p*-carborane (8). A mixture of **2** (0.27 g, 0.68 mmol), dichlorobis(triphenylphosphine)palladium (0.05 g, 0.06 mmol), and copper iodide (0.01 g, 0.03 mmol) was dissolved in 20 mL of THF, and a 3.0 M solution of phenylmagnesium bromide in diethyl ether (4.0 mL, 12.0 mmol) was added. The reaction mixture was stirred at gentle reflux for 3 days. After workup, the crude product was further purified by chromatography on silica gel and elution with a mixture of benzene and pentane (2:1) and then recrystallized from pentane/diethyl ether to yield **8** as a white solid (0.13 g, 65%), mp 213–214 °C (sealed). ^1H NMR ($CDCl_3$): 7.59 (d, 2H, C_6H_5, J_{HH} = 11 Hz), 7.37 (m, 2H, C_6H_5), 7.33 (s, 1H, C_6H_5), 3.24 (br s, 2H, CH), 1.65–3.45 (br, 8H, BH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 141.2, 133.4, 128.7, 127.1 (C_6H_5), 66.0 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −7.0 (2B, BC_6H_5), −13.9 (8B) ppm. HRMS (EI) for $C_{14}B_{10}H_{20}$ (*m/z*): calcd, 296.2568; found, 296.2563 (M^+).

Preparation of 2-(Phenylethynyl)-*p*-carborane (9). A mixture of **1** (0.44 g, 1.63 mmol), phenylacetylene (0.17 g, 1.63 mmol), dichlorobis(triphenylphosphine)palladium (0.06 g, 0.08 mmol), and cupric iodide (0.01 g, 0.04 mmol) was dissolved in a mixture of 10 mL of benzene and 10 mL of pyrrolidine. The reaction mixture was stirred at gentle reflux for 1 day. After workup, the crude product was further purified by chromatography on silica gel and elution with a mixture of benzene and pentane (1:3) and then recrystallized from hot hexane to yield **9** as a white solid (0.25 g, 63%), mp 73–75 °C (sealed). ^1H NMR ($CDCl_3$): 7.58 (d, 2H, C_6H_5), 7.30–7.39 (m, 3H, C_6H_5), 3.13, 2.84 (br s, 1H, CH), 1.22–3.58 (br, 9H, BH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 132.4, 129.2, 128.4, 121.7 (C_6H_5), 81.5 ($\equiv CC_6H_5$), 73.9 ($\equiv CB$), 66.1, 62.9 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −12.7 (3B), −14.5 (6B), 16.4 (1B, $BC\equiv$) ppm. HRMS (EI) for $C_{10}B_{10}H_{16}$ (*m/z*): calcd, 244.2255; found, 244.2252 (M^+).

Preparation of 2-((Trimethylsilyl)ethynyl)-*p*-carborane (10). A mixture of **1** (0.20 g, 0.74 mmol), (trimethylsilyl)acetylene (0.31 mL, 2.15 mmol), dichlorobis(triphenylphosphine)palladium (0.03 g, 0.04 mmol), and cupric iodide (0.01 g, 0.04 mmol) was dissolved in a mixture of 2 mL of benzene and 4 mL of piperidine. The reaction mixture was stirred at gentle reflux for 2 days. Solvent was removed *in vacuo*, and the residue was then extracted with pentane (3 × 10 mL). The extracts were passed through a neutral alumina bed, and the solution was concentrated under reduced pressure to yield an oily residue. A small amount of **1** (40 mg) was recovered by sublimation under high vacuum at room temperature, leaving **10** as a colorless oil (76 mg, 53%). ^1H NMR ($CDCl_3$): 3.02, 2.76 (br s, 1H, CH), 1.20–3.10 (br, 9H, BH), 0.16 (s, 9H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 104.8 ($\equiv CSi$), 95.2 ($\equiv CB$), 66.0, 62.9 (CH), −0.1 ($SiCH_3$) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −11.1 (1B), −12.8 (2B), −13.7 (4B), −14.4 (2B), −16.1 (1B, $BC\equiv$) ppm. HRMS (EI) for $C_7B_{10}SiH_{20}$ (*m/z*): calcd, 240.2337; found, 240.2335 (M^+).

Preparation of 2-Ethynyl-*p*-carborane (11). Compound **10** (0.07 g, 0.29 mmol) was dissolved in *ca.* 15 mL of dry diethyl ether at 0° C. To this solution was added dropwise a 1.0 M solution of tetrabutylammonium fluoride in THF (0.30 mL, 0.3 mmol). The reaction mixture was stirred at this temperature for 1 h, and then 10 mL of water was added. Diethyl ether (3 × 15 mL) was used to extract the product from the aqueous phase. The organic layer was dried over anhydrous magnesium sulfate, and then solvent was carefully removed under reduced pressure at ambient temperature to yield **11** as a white solid (0.05 g, 96%), mp 68–69 °C (sealed). ^1H NMR ($CDCl_3$): 3.03, 2.80 (br s, 1H, CH), 1.40–3.30 (br, 9H, BH), 2.20 (s, 1 H, $\equiv CH$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 85.3 ($\equiv CH$), 85.0 ($\equiv CB$), 66.1, 63.1 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −12.6 (2B), −13.5 (4B), −14.3 (3B), −16.2 (1B, $BC\equiv$) ppm. HRMS (EI) for $C_4B_{10}H_{12}$ (*m/z*): calcd, 168.1942; found, 168.1945 (M^+).

Preparation of 2,9-Bis((trimethylsilyl)ethynyl)-*p*-carborane (12). A mixture of **2** (0.19 g, 0.48 mmol), (trimethylsilyl)acetylene (0.35 mL, 2.48 mmol), dichlorobis(triphenylphosphine)palladium (0.03 g, 0.03 mmol), and cupric iodide (0.01 g, 0.02 mmol) was dissolved in a mixture of 2 mL of benzene and 4 mL of piperidine. The reaction mixture was stirred at gentle reflux for 60 h. Solvent was removed *in vacuo*, and the residue was then extracted with pentane (3 × 10 mL). The extracts were passed through a neutral alumina bed, and then the solution was concentrated under reduced pressure to give **12** as a white solid (0.11 g, 69%), mp 172–174 °C (sealed). ^1H NMR ($CDCl_3$): 3.02 (br s, 2H, CH), 1.35–3.15 (br, 8H, BH), 0.15 (s, $SiCH_3$, 18H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 105.7 ($\equiv CSi$), 93.8 ($\equiv CB$), 65.7 (CH), −0.17 ($SiCH_3$) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −13.1 (4B), −13.6 (4B), −15.5 (2B, $BC\equiv$) ppm. HRMS (EI) for $C_{12}B_{10}Si_2H_{28}$ (*m/z*): calcd, 336.2732; found, 336.2731 (M^+). In another experiment, chromatography of **12** on silica gel rather than alumina using a 1:4 mixture of wet benzene and diethyl ether afforded compound **13** directly in an overall yield of 75%.

Preparation of 2,9-Diethynyl-*p*-carborane (13). Compound **12** (0.11 g, 0.33 mmol) was dissolved in *ca.* 15 mL of dry diethyl ether at 0 °C. To this solution was added dropwise a 1.0 M solution of tetrabutylammonium fluoride in THF (0.33 mL, 0.33 mmol). The reaction mixture was stirred at this temperature for 1 h, and then 10 mL of water was added. Diethyl ether (3 × 15 mL) was used to extract the product from the aqueous phase. The organic layer was dried over anhydrous magnesium sulfate, and then solvent was carefully removed under reduced pressure at ambient temperature to yield **13** as a white solid (0.06 g, 93%), mp 189–190 °C (sealed). ^1H NMR ($CDCl_3$): 3.12 ($\equiv CH$, 2H), 3.01 (CH, 2H), 1.45–3.50 (br, 8H, BH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 86.2 ($\equiv CH$), 85.3 ($\equiv CB$), 65.8 (CH) ppm. $^{11}B\{^1H\}$ NMR (Et_2O): −13.8 (4B), −14.3 (4B), −15.9 (2B, $BC\equiv$) ppm. HRMS (EI) for $C_6B_{10}H_{12}$ (*m/z*): calcd, 192.1910; found, 192.1914 (M^+).

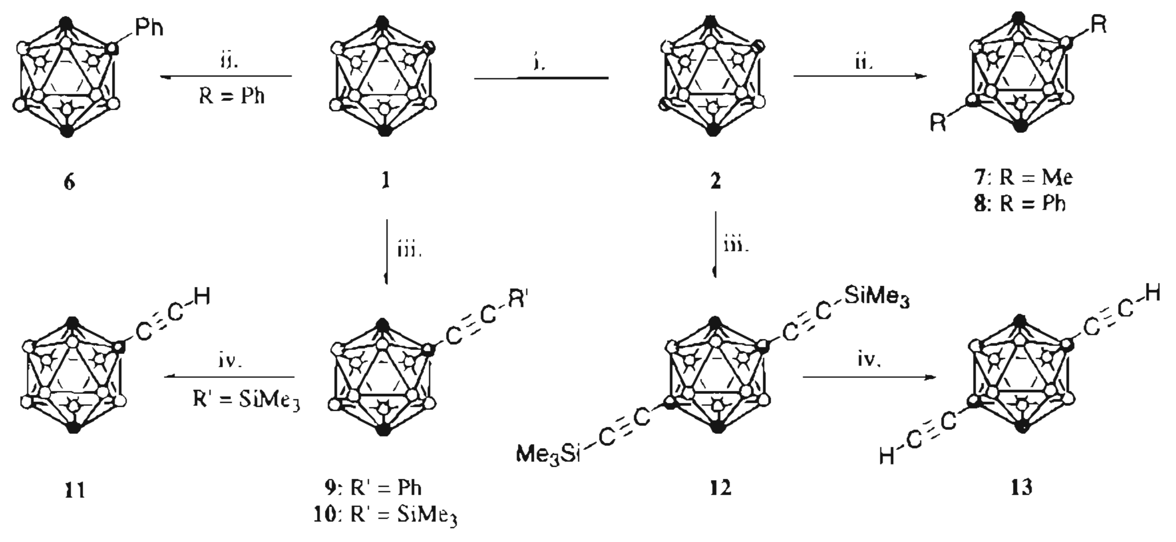
Results

Iodination Reactions of *para*-Carborane. Iodination of *p*-carborane was examined with several reagents. Our initial reactions were carried out with elemental iodine and catalytic amounts of aluminum trichloride, in a manner analogous to that reported by Jones[7a] *et al.* for *o*-carborane, and gave *ca.* 80% yields of 2-iodo-*p*-carborane (**1**). As mentioned above, this compound is well-known, but while it was used as a starting material for further reactions, high-quality single crystals were obtained. Consequently, a structural study was carried out (Figure 2), which revealed no unusual features other than a C–C cross-cage distance which is rather short compared to the few *p*-carborane derivatives which have been structurally characterized (*vide infra*).

We found the iodine reaction to be rather sluggish (3 days at the reflux temperature in methylene chloride), and contrary to an earlier report,[11] we were unable to attach a second iodine substituent to the cage even when using excess iodine, stoichiometric amounts of aluminum trichloride, and refluxing carbon tetrachloride. We therefore investigated the more reactive iodination reagents iodine monochloride and iodine monobromide, both of which proved capable of generating diiodinated *p*-carborane as a mixture of all five possible isomers (pictured in Figure 1). Overall yields were in the range of 85–95%, depending on the conditions used. These isomers were the subject of a previous investigation using gas chromatography,[11] but although separable by this technique, synthetically useful amounts of material were not available by this means and identification of the individual isomers was not achieved.

One isomer of diiodo-*p*-carborane separated from the rest of the mixture by virtue of its relative insolubility in pentane, and its high symmetry as evinced by ^1H, ^{13}C, and ^{11}B NMR allowed its assignment as 2,9-diiodo-*p*-carborane (**2**). The isolated yield of **2** was 11% of the diiodinated product mixture, precisely the amount that would be expected if the assumption is made that the first iodine on the carborane has no effect on the position of subsequent attack. However, the distribution of the other isomers, both in the previous study and in accord with our observations, suggests that this is not strictly the case (*vide infra*). Further separation of these remaining isomers was

Scheme 1



i. 1.0 eq. ICl/catalytic $AlCl_3$, CH_2Cl_2 reflux
ii. RMgBr, $Pd(PPh_3)_2Cl_2$/CuI, THF reflux, R=Me, Phenyl
iii. 1-Alkyne, $Pd(PPh_3)_2Cl_2$/CuI, Amine/C_6H_6 reflux, R'=$SiMe_3$ or C_6H_5
iv. $(n\text{-butyl})_4NF/Et_2O$, 0°C to RT

● CH
○ BH
⊘ BI
◕ B

Table 1. Positional and Displacement Parameters[a] for Significant Atoms of **1**

atom	*x*	*y*	*z*	U_{eq}
I1	0.67991(3)	0.61673(3)	0.09272(1)	0.0598(1)
C1	0.6785(3)	0.9695(4)	0.0644(2)	0.043(1)
B2	0.6961(4)	0.8370(4)	0.1200(2)	0.039(1)
B3	0.8283(4)	0.9386(5)	0.1076(2)	0.045(1)
B4	0.7743(6)	1.1131(5)	0.0850(2)	0.056(1)
B5	0.6080(5)	1.1193(5)	0.0834(2)	0.056(1)
B6	0.5597(4)	0.9489(5)	0.1049(2)	0.046(1)
B7	0.8054(4)	0.9059(5)	0.1864(2)	0.046(1)
B8	0.8536(5)	1.0769(6)	0.1644(2)	0.054(1)
B9	0.7176(5)	1.1888(5)	0.1491(2)	0.058(1)
B10	0.5852(5)	1.0869(5)	0.1617(2)	0.054(1)
B11	0.6398(4)	0.9121(5)	0.1844(2)	0.046(1)
C12	0.7349(4)	1.0563(4)	0.2055(2)	0.049(1)

[a] Displacement parameters are commonly called vibration or thermal parameters. Units of U_{eq} are angstroms squared. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. U_{eq} is defined as follows: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos\gamma) + 2U_{13}(aca^*c^* \cos\beta) + 2U_{23}(bcb^*c^* \cos\alpha)]$.

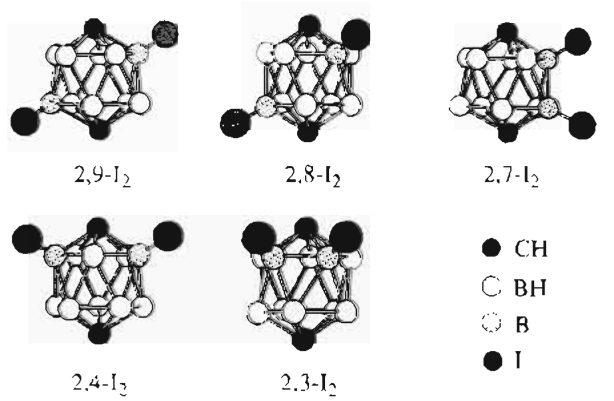


Figure 1. Isomers of diiodo-*p*-carborane.

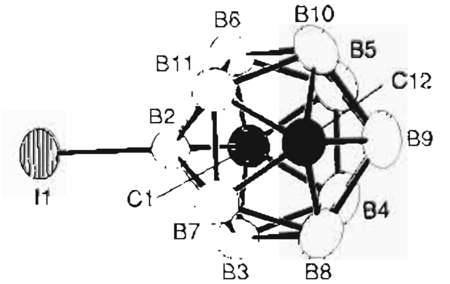


Figure 2. ORTEP representation of compound **1**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. Significant distances (Å) are as follows: B2–I1 2.156(4); C–B range 1.696(6)–1.720(6), average 1.709(6); B–B range 1.764(7)–1.793(8), average 1.778(7); C1–C12 3.065(5).

Table 2. Positional and Displacement Parameters[a] for Significant Atoms of **3**

atom	*x*	*y*	*z*	U_{eq}
I1	0.08815(3)	0.18864(3)	0.03566(8)	0.0675(2)
I7	0.2500	0.2820(8)	0.5299(16)	0.060(3)
C1	0.2500	0.0038(7)	0.1636(15)	0.067(2)
B3	0.1806(4)	0.1071(5)	0.2329(9)	0.045(2)
B4	0.1388(5)	−0.0065(5)	0.3099(11)	0.058(2)
B5	0.2500	−0.0632(6)	0.3608(13)	0.045(2)
B7	0.2500	0.1606(8)	0.4214(15)	0.053(2)
B8	0.1376(5)	0.0898(6)	0.4674(11)	0.059(2)
B10	0.3190(6)	-0.0208(6)	0.5446(11)	0.064(2)
C12	0.2500	0.0760(7)	0.5955(13)	0.060(2)

[a] Displacement parameters are commonly called vibration or thermal parameters. Units of U_{eq} are angstroms squared. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. U_{eq} is defined as follows: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos\gamma) + 2U_{13}(aca^*c^* \cos\beta) + 2U_{23}(bcb^*c^* \cos\alpha)]$.

somewhat laborious. After removal of **2**, chromatography of the remainder of the mixture on silica gel with benzene as the eluent led to the separation of a second isomer. This isomer was unambiguously characterized by *X*-ray diffraction as 2,3-diiodo-*p*-carborane (**3**) (Figure 3) and was isolated as 8% of the total product mixture. Mass spectral analysis of this fraction revealed the presence of a small amount (*ca.* 8%) of a triiodocarborane species. The structural study on **3** revealed that the crystal chosen had an impurity which was refined as

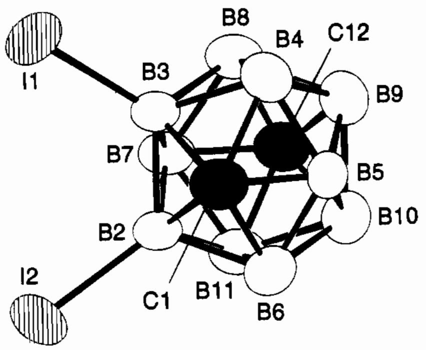


Figure 3. ORTEP representation of compound **3**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. The crystal contains a 6% impurity refined as 2,3,7-triiodo-*p*-carborane. Thus, atom B7 has iodine I7 (not shown) attached with 6% occupancy. Atoms I1, B3, B4, B8, and B9 are symmetry related to I2, B2, B6, B11, and B10, respectively, by a crystallographically imposed mirror plane passing through C1, B5, B7, and C12. Significant distances (Å) are as follows: B3−I1 2.166(6); C−B range 1.671(12)−1.780(11), average 1.724(12); B−B range 1.680(8)-1.788(10), average 1.754(11); C1−C12 3.220(14).

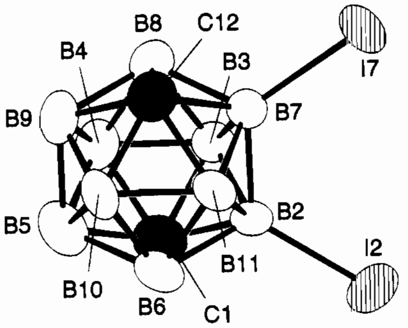


Figure 4. ORTEP representation of compound **4**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. Significant distances (Å) are as follows: B2−I2 2.169(11); B7−I7 2.162(10); C−B range 1.700(15)−1.78(2), average 1.732(16); B−B range 1.705(16)−1.80(2), average 1.747(17); C1−C12 3.22(1).

Table 3. Positional and Displacement Parameters[a] for Significant Atoms of **4**

atom	*x*	*y*	*z*	U_{eq}
I2	0.39470(4)	0.34604(10)	0.11390(6)	0.0696(2)
I7	0.42661(4)	0.34576(9)	0.42795(6)	0.0625(2)
C1	0.3099(5)	0.0136(14)	0.1023(8)	0.065(3)
B2	0.3737(5)	0.1380(13)	0.1840(8)	0.040(2)
B3	0.3092(5)	0.1388(14)	0.1980(9)	0.043(2)
B4	0.2785(5)	−0.0619(15)	0.1788(9)	0.051(3)
B5	0.3258(6)	−0.1915(16)	0.1493(10)	0.065(3)
B6	0.3848(6)	−-0.0674(15)	0.1562(9)	0.050(3)
B7	0.3859(5)	0.1381(13)	0.3165(8)	0.039(2)
B8	0.3257(6)	0.0163(15)	0.3107(9)	0.050(3)
B9	0.3369(7)	−0.1893(14)	0.2820(10)	0.059(3)
B10	0.4008(5)	−0.1860(13)	0.2666(9)	0.049(3)
B11	0.4313(5)	0.0133(14)	0.2870(8)	0.043(2)
C12	0.4014(5)	−0.0633(14)	0.3633(8)	0.058(3)

[a] Displacement parameters are commonly called vibration or thermal parameters. Units of U_{eq} are Angstroms squared. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. U_{eq} is defined as follows: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos \gamma) + 2U_{13}(aca^*c^* \cos \beta) + 2U_{23}(bcb^*c^* \cos \alpha)]$.

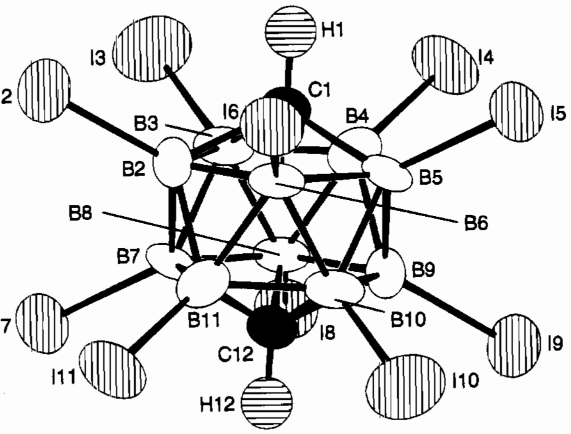


Figure 5. ORTEP representation of compound **5**, showing the crystallographic numbering scheme. There are two crystallographically independent molecules in the unit cell, and each molecule has a crystallographically imposed center of symmetry. Thus, atoms H12, C12, B7, B8, B9, B10, B11, I7, I8, I9, I10, and I11 are symmetry related to H1, C1, B5, B6, B2, B3, B4, I5, I6, I2, I3, and I4, respectively. Significant distances (Å) are as follows: B−I range 2.09(3)−2.17(2) average 2.12(3); C−B range 1.65(3)−1.74(3), average 1.70(4); B−B range 1.71(4)−1.86(4), average 1.78(4); C1−C12 3.014(5).

6% 2,3,7-triiodo-*p*-carborane, and a preliminary structure carried out on a second crystal gave similar results. The presence of a triiodocarborane impurity within the crystal lattice was independently verified by subsequent mass spectroscopic analysis of the crystal used for the structure determination. Further chromatography of the reaction product mixture on acidic alumina with pentane separated a further 16% of the total mixture as 2,7-diiodo-*p*-carborane (**4**), which was also identified by a structural study (Figure 4). The remainder of the mixture was primarily composed of the 2,4- and 2,8-isomers with residual amounts of the 2,3- and 2,7-isomers and resisted further separation by chromatographic techniques.

Very recently, the synthesis of decaiodo-*p*-carborane (**5**) was reported to result from the treatment of *p*-carborane with a neat 1:1 mixture of iodine monochloride and trifluoromethanesulfonic acid at reflux temperatures.[12] It was hoped that **5** might prove to be a useful precursor in the synthesis of other highly boron-substituted *p*-carboranes. Unfortunately, upon repetition of the synthesis, **5** was found to have poor solubility in common solvents, which limited its usefulness as a precursor. However, crystals were obtained which were suitable for *X*-ray diffraction and the structure of **5** was determined (Figure 5). Compound **5** shows an interesting deviation from the usual icosahedral geometry. The angles defined by each pair of adjacent borons, one belonging to the upper B_5 belt and the other to the lower B_5 belt, and the calculated midpoint of the icosahedron were determined and compared to the angles between the iodines attached to each pair of boron atoms. In each case, the iodine−midpoint−iodine angle was larger [average 65.89(4)°] than the corresponding boron−midpoint−boron angle [average 63(1)°]. In other words, the iodine atoms are displaced slightly toward the C1−C12 axis of the cage. This effect is accompanied by a C1−C12 and C1′−C12′ cross-cage distance of 3.03(3) and 3.01(3) Å, respectively, for the two crystallographically independent molecules in the unit cell. By contrast, the C−C distances for the other molecules determined during these investigations are as follows (Å): **1**, 3.065(5); **3**, 3.220(14); **4**, 3.22(1); **8**, 3.160(4). A tetrameric oligomer of *p*-carborane has been synthesized and structurally characterized as a silyl derivative;[5e] C−C cross-cage distances in this molecule are 3.157(7) and 3.142(7) Å. The C−C distance in *p*-carborane is unfortunately not available for comparison. The C−C cross-cage distance is thus markedly shorter in **5** than in other *p*-carborane derivatives with the exception of 2-iodo-*p*-carborane (**1**). We ascribe both the displacement of the iodine atoms and the short C−C distance in **5** to a "rollover" effect of the sp-hybridized orbitals of the boron atoms due to steric repulsion between the iodines. A short C−C distance of 3.014(5) Å (similar to that seen in **5** and significantly shorter than that seen

Table 4. Positional and Displacement Parameters[a] for Significant Atoms of **5**

atom	x	y	z	U_{eq}
I2	0.5680(3)	0.1852(2)	0.1130(1)	0.063(1)
I3	0.6668(3)	0.5636(3)	0.2299(1)	0.082(1)
I4	0.8549(2)	0.8784(2)	0.0875(1)	0.057(1)
I5	0.8814(2)	0.6815(2)	−0.1211(1)	0.053(1)
I6	0.7066(3)	0.2612(2)	−0.1045(1)	0.051(1)
I2'	0.2247(3)	−0.3461(2)	0.5859(1)	0.066(1)
I3'	0.2459(3)	0.0341(2)	0.6708(1)	0.066(1)
I4'	0.2697(3)	0.2848(2)	0.4882(1)	0.063(1)
I5'	0.2702(3)	0.0545(3)	0.2895(1)	0.085(1)
I6'	0.2314(3)	−0.3400(2)	0.3486(1)	0.064(1)
C1	0.600(3)	0.512(2)	0.034(1)	0.030(6)
B2	0.526(4)	0.354(3)	0.048(2)	0.032(7)
B3	0.568(3)	0.532(3)	0.103(2)	0.032(7)
B4	0.657(4)	0.670(3)	0.038(2)	0.042(8)
B5	0.667(3)	0.582(3)	−0.057(2)	0.031(8)
B6	0.585(3)	0.396(3)	−0.048(2)	0.027(7)
C1′	0.290(3)	−0.051(3)	0.479(1)	0.030(6)
B2′	0.388(4)	−0.154(3)	0.536(2)	0.046(8)
B3′	0.395(4)	0.020(3)	0.576(2)	0.032(7)
B4′	0.406(3)	0.129(2)	0.496(2)	0.026(8)
B5′	0.398(4)	0.022(3)	0.405(2)	0.039(8)
C6′	0.386(3)	−0.154(3)	0.429(2)	0.039(8)

[a] Displacement parameters are commonly called vibration or thermal parameters. Units of U_{eq} are Angstroms squared. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. U_{eq} is defined as follows: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos\gamma) + 2U_{13}(aca^*c^* \cos\beta) + 2U_{23}(bcb^*c^* \cos\alpha)]$.

in compound **1**) and displacement of methyl groups toward the C−C axis is also seen in the recently synthesized decamethyl-*p*-carborane[14] and is attributed to the same steric effect.

Coupling Reactions of Iodinated Carboranes with Grignard Reagents. For the purposes of building macromolecular arrays from substituted *p*-carboranes, the 2,9-diiodo-*p*-carborane derivative **2** is the most desirable starting material since the high symmetry of its derivatives minimizes further isomer problems upon oligomerization. Exploration of the palladium-mediated coupling reactions between organic reagents and the iodinated carboranes was therefore restricted to the easily synthesized 2-iodo-*p*-carborane (**1**) and **2**. Reaction of **1** with phenylmagnesium bromide in the presence of dichlorobis(triphenylphosphine)palladium according to the methods of Zakharkin and Jones[7] gave 2-phenyl-*p*-carborane (**6**) in good yield. In a similar manner, reaction of **2** with either methylmagnesium bromide or phenylmagnesium bromide afforded 2,9-dimethyl-*p*-carborane (**7**) and 2,9-diphenyl-*p*-carborane (**8**), also in good yields. The structure of **8** was confirmed by an *X*-ray diffraction study which showed no unexpected features other than a slight elongation of the icosahedron along the axis defined by the two phenyl-substituted boron vertices [B2−B9 = 3.436(4) Å, other B−B cross cage distances 3.237(4)-3.381(4) Å] (Figure 6). We found, however, that to obtain these high yields in the coupling reactions it was necessary to use copper iodide as a cocatalyst. This has been found to be efficacious in the coupling of acetylenes with aryl iodides (*vide infra*).[15] Attempts to introduce an ethyl group to **1** by reaction of ethylmagnesium bromide resulted almost exclusively in formation of *p*-carborane, with insignificant amounts of the desired product, which was not isolated or fully characterized.

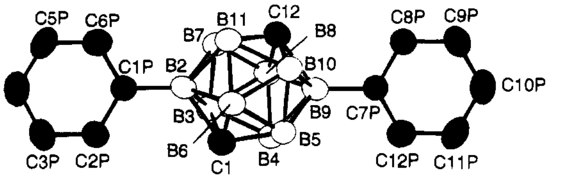


Figure 6. ORTEP representation of compound **8**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. There is a crystallographically imposed center of symmetry in the molecule. Thus, atoms B7, B8, B9, B10, B11, C12, C7P, C8P, C9P, C10P, C11P, and C12P are symmetry related to B5, B6, B2, B3, B4, C1, C1P, C2P, C3P, C4P, C5P, and C6P, respectively. Significant distances (Å) are as follows: B2−C1P 1.560(4); C−B range 1.694(4)−1.742(4), average 1.727(4); B−B range 1.730(4)−1.799(4), average 1.763(4); C1−C12 3.174(4); B2−B9 3.440(4); B3−B10 3.377(4); B4−B11 3.368(4); B5−B7 3.223(4); B6−B8 3.370(4).

Table 5. Positional and Displacement Parameters[a] for Significant Atoms of **8**

atom	x	y	z	U_{eq}
C1	0.6549(3)	0.9249(3)	0.5117(2)	0.051(1)
B2	0.3563(3)	0.9700(3)	0.5624(2)	0.042(1)
B3	0.4613(3)	1.1164(3)	0.5613(2)	0.044(1)
B4	0.4842(3)	0.8498(3)	0.5304(2)	0.043(1)
B5	0.5498(3)	0.9755(3)	0.5846(2)	0.041(1)
B6	0.6488(3)	1.0855(3)	0.5313(2)	0.044(1)
C1P	0.2254(3)	0.9486(2)	0.6194(1)	0.043(1)
C2P	0.0967(3)	1.0256(3)	0.6208(2)	0.059(1)
C3P	-0.0174(3)	1.0075(4)	0.6719(2)	0.067(1)
C4P	-0.0067(3)	0.9128(3)	0.7243(2)	0.062(1)
C5P	0.1192(4)	0.8346(3)	0.7238(2)	0.065(1)
C6P	0.2339(3)	0.8527(3)	0.6712(2)	0.058(1)

[a] Displacement parameters are commonly called vibration or thermal parameters. Units of U_{eq} are angstroms squared. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. U_{eq} is defined as follows: $(1/3)[U_{11}(aaa^*a^*) + U_{22}(bbb^*b^*) + U_{33}(ccc^*c^*) + 2U_{12}(aba^*b^* \cos\gamma) + 2U_{13}(aca^*c^* \cos\beta) + 2U_{23}(bcb^*c^* \cos\alpha)]$.

Coupling Reactions of Iodinated Carboranes with Acetylenes. When **1** was reacted with phenylacetylene in the presence of the palladium/copper catalyst system and excess pyrrolidine in a modification of the method of Hagihara *et al.*,[15] the alkyne-substituted compound 2-(phenylethynyl)-*p*-carborane (**9**) was formed in 63% yield. A similar reaction between **2** and a 3-fold excess of (trimethylsilyl)acetylene in the presence of the palladium/copper catalyst and excess piperidine gave 2-((trimethylsilyl)ethynyl)-*p*-carborane (**10**) in 53% conversion, with a 20% recovery of starting material. The silyl group could be removed almost quantitatively with fluoride ion to afford 2-ethynyl-*p*-carborane (**11**).

Reaction of **2** with (trimethylsilyl)acetylene and using piperidine as the base afforded 2,9-bis((trimethylsilyl)ethynyl)-*p*-carborane (**12**) in 69% yield in an analogous manner to the formation of **10**. Species **10** could similarly be desilylated with fluoride ion to give 2,9-diethynyl-*p*-carborane (**13**) in 93% yield. Compound **13** could be made more directly in similar yield by chromatographing the crude product **12** on silica gel, which accomplished the hydrolytic cleavage of the silyl group.

Discussion

All members of the icosahedral carborane family are susceptible to electrophilic halogenation of the boron vertices and form strong bonds between boron and halogen. The reaction rate decreases in the order chlorine > bromine > iodine and with greater substitution on the boron vertices due to the electron-withdrawing nature of the halogens. Reactivity also varies between the carboranes and within individual carboranes depending on the position of the boron relative to the carbon atoms. Calculations show that, as a general rule, borons furthest

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(14) Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Angew. Chem., Intl. Ed. Engl.*, in press.

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

Table 6. Details of Crystallographic Data Collection

	1	**3**	**4**	**5**	**8**
empirical formula	$C_2H_{11}B_{10}I$	$C_2H_{10}B_{10}I_2$	$C_2H_{10}B_{10}I_2$	$C_2H_2B_{10}I_{10}$	$C_{14}H_{30}B_{10}$
fw	270.13	396.03	396.03	1403.19	306.54
space group	*C*2/*c*	*Pmnb*	*C*2/*c*	$P\bar{1}$	*Pcab* (*Pbca* $\bar{c}ba$)
a (Å)	10.824(2)	12.868(1)	25.039(1)	7.796(1)	8.7706(8)
b (Å)	9.439(1)	14.144(2)	8.1129(4)	9.882(2)	10.559(1)
c (Å)	21.414(3)	7.069(1)	14.3300(7)	16.681(3)	18.081(2)
α (deg)				91.550(6)	
β (deg)	102.121(4)		122.567(1)	100.271(6)	
γ (deg)				110.854(5)	
V (Å$^{3)}$	2136	1287	2453	1176	1674
Z	8	4	8	2	4
μ (cm$^{-1)}$	29.0	48.4	50.2	130.3	3.76
R (%)^a	0.035	0.038	0.050	0.060	0.067
$R_{w\,(\%)}{}^b$	0.047	0.052	0.068	0.077	0.093

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

from the carbon vertices have the highest ground state electron density which means that these boron vertices should be most susceptible to halogenation.[16] It follows, therefore, that *p*-carborane should be the least reactive member of the family since every boron vertex is adjacent to a deactivating carbon vertex. Our observations reflect this expectation, in that while it is easy enough to perform the first iodine substitution, elemental iodine is not sufficiently electrophilic to substitute a second boron vertex whereas the conditions used are sufficient to afford diiodinated *o*- and *m*-carboranes[7a] with the same reagent.

Unfortunately, despite the availability of high yields of 2-iodo-*p*-carborane (**1**), there is a complication in using it as a precursor to carborane oligomers (carborods). The iodine provides a valuable functionality for the introduction of organic groups, but upon oligomer formation it is possible for the carboranes to couple either head-to-head or head-to-tail. This rapidly results in the production of many isomers as the number of linked icosahedra increases. This problem can be avoided by synthesizing oligomers equipped with two identical substituents, one adjacent to each carbon in the cage. This endeavor requires either control in the formation of single isomers of diiodinated *p*-carborane or the ability to separate mixtures of diiodo-*p*-carborane isomers.

In common with the previous study of diiodinated *p*-carboranes,[11] we found that the first iodine placed on the cage does not strongly influence the course of subsequent electrophilic attack. Consequently, mixtures of isomers are unavoidable. Theoretical calculations based on the icosahedral borane anion $B_{12}H_{12}{}^{2-}$ suggest that electron-donating groups placed on the cage have an *ortho*-directing effect, while electron-withdrawing substituents should have a *meta*-, *para*-directing effect.[17] Gas chromatographic analysis of the product distribution of chlorinated *p*-carboranes implied that there was some deviation from a purely statistical distribution of isomers,[11] but the authors were unable to characterize a given isomer and confirm which effect was actually in operation. We were able to isolate and characterize three isomers from the diiodo-*p*-carborane product mixture. The *para* isomer **2** (2,9-I_2) was found in close to statistical amounts, but **3** (2,3-I_2) and **4** (2,7-I_2), both *ortho* isomers, were isolated in significantly less than the 22% yields expected from random substitution. Examination of the remainder of the reaction product mixture by ^{13}C NMR spectroscopy suggested that only traces of these isomers remained in the mixture and, thus, that the inseparable *meta* isomers 2,4-I_2- and 2,8-I_2-*p*-carborane are formed in disproportionately large amounts. This is in agreement with the theoretical prediction if iodine is assumed to be a net withdrawer of electrons, but of course it may only result from the steric effect of a bulky iodine atom which protects adjacent boron vertices from electrophilic attack.

Given that mixtures of isomers are unavoidable in this reaction, it is serendipitous that the most symmetric isomer **2** is the easiest to separate from the reaction mixture. The isolated yield of 11% from the product mixture is not particularly high but sufficient to carry on further reactions. Use of the 2,7-isomer **4**, which was isolated in 14% yield from the mixture, also avoids the head−head/head−tail isomeric oligomer problem, although coupling reactions with this isomer have not yet been explored.

In attempting to make organo-substituted *p*-carboranes, we have limited ourselves to the use of **1** and **2** as precursors. The formation of the 2-Ph- (**6**), 2,9-Me_2- (**7**), and 2,9-Ph_2-*p*-carborane (**8**) derivatives demonstrates that substitution can be effected with certain alkyl and aryl groups in good yields. Our failure to introduce an ethyl group to **1** is attributed to a β-hydride elimination step during the catalytic cycle. At some stage, the carboranyl and ethyl groups must both be attached to palladium, and rather than undergo reductive coupling, a competitive β-hydride elimination reaction occurs whereby the ethyl group is released as ethylene and the carborane is formed by reductive elimination of the resulting palladium carboranyl hydrides. This process is well-known in aromatic organic systems[18] and was noted to decrease yields in coupling reactions with *o*-carborane and Grignard reagents having available β-hydrogens,[7,8] though not to the extent observed with the present system. This β-hydrogen elimination process presents some limitations to the versatility of the coupling reaction, but the latter remains as a powerful synthetic procedure.

Experience with alkyl-substituted *o*-carboranes in supramolecular assemblies[5a] has demonstrated that alkyl groups considerably enhance solubility in nonpolar solvents, and we expect to find similar effects in the *para* system. However, in addition to solubility improvements, the ability to introduce one or more functional groups to the boron vertices of carboranes in a controlled fashion is highly desirable. In the formation of supramolecular arrays, the easily deprotonated carbon vertices provide the skeletal linkages which allow assembly of large structures, but other functionalities are needed to tailor the properties of such structures for particular applications. The formation of the alkyne-substituted compounds **9−13** represents an important step in this direction. Triple bonds are valuable

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synthons, and additional functional groups can be introduced by the use of differing 1-alkynes. Compounds **11** and **13** have terminal acetylenic hydrogens which are ready targets for deprotonation and substitution. One can envisage novel linear oligomers of *p*-carboranes joined at the boron vertices by C≡C groups from the reaction between acetylene and 2,9-diiodo-*p*-carborane, leaving the carbon vertices of the icosahedra available for either cross-linking or facile derivatization. The feasibility of such oligomers is being explored in our laboratory.

Conclusions

We have demonstrated that a variety of iodinated *p*-carboranes can be generated and isolated in synthetically useful amounts. Alkyl and aryl groups can be introduced by the use of Grignard reagents in metal-catalyzed reactions, and we describe a new synthesis under mild conditions for the formation of a variety of alkynyl derivatives with wide potential applications. We anticipate that these species will serve as valuable starting materials for the synthesis of functionalized oligomers of *p*-carborane either joined directly by C−C bonds or coupled *via* acetylene groups at the boron vertices.

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Supplementary Material Available: For compounds **1**, **3**−**5**, and **8**, crystallographic experimental details and tables listing full data collection and processing parameters, full bond lengths and angles, torsion angles, anisotropic displacement parameters and atom coordinates (19 pages). Ordering information is given on any current masthead page.

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