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Preparation of 1-*p*-Halophenyl and 1-*p*-Biphenylyl Substituted Monocarbadodecaborate Anions [*closo*-1-Ar–$CB_{11}H_{11}$]$^-$ by Insertion of Arylhalocarbenes into [*nido*-$B_{11}H_{14}$]$^-$

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In the presence of a strong base, benzal chloride ($C_6H_5CHCl_2$) and its *p*-substituted derivatives react with [*nido*-$B_{11}H_{14}$]$^-$ to yield [*closo*-1-*p*-X–C_6H_4–$CB_{11}H_{11}$]$^-$ (X = H, F, Cl, Br, I, Ph), presumably by insertion of an arylhalocarbene and oxidation. On a 1-g scale, the yields are 30–40%, except in the case of *p*-iodobenzal chloride, which yields only 12% of the insertion product.

Introduction

Although 6-,[1] 10-,[2] 11-,[3] and 12-vertex[2,4] *closo*-monocarbaborate anions have been known for a long time and additional cage sizes have become known lately,[5−7] their use has been hampered by their high cost. The standard starting material for their preparation is the expensive decaborane, and the syntheses frequently involve multiple steps. We have recently reported that monocarborate anions are accessible in a single step by the insertion of halocarbenes into cage borate anions,[8] some of which are less expensive and readily available. Probably most important, [*closo*-$CB_{11}H_{12}$]$^-$ and its derivatives are accessible via the insertion of dichlorocarbene and similar carbenes into [*nido*-$B_{11}H_{14}$]$^-$. A mechanism has been proposed[9] for this reaction on the basis of density functional calculations. The starting [*nido*-$B_{11}H_{14}$]$^-$ anion is available in a single step from commodity chemicals in a 50% yield,[10] and the new two-step sequence thus provides an inexpensive route to gram amounts of $CB_{11}H_{12}^-$ and some of its 2-substituted derivatives. Unfortunately, we find that the reaction yields of $CB_{11}H_{12}^-$ drop from ∼40% to ∼10−20% upon scale-up from 1-g to 5-g or larger amounts of the starting anion, and the reaction becomes poorly reproducible.

Herein, we address specifically the synthesis of [*closo*-$CB_{11}H_{12}$]$^-$ anions carrying a phenyl or a *p*-substituted phenyl group in position 1 by the analogous insertion of appropriate arylhalocarbenes into [*nido*-$B_{11}H_{14}$]$^-$. Such C-arylated monocarbaborate anions of various cage sizes have recently attracted considerable interest,[8,11−15] and three types of reactions leading to the 12-vertex variety have been reported in rapid succession. One was Pd-catalyzed Negishi coupling of a metalated monocarbadodecaborate anion with an aryl iodide,[12] another used the Brellochs[16] reaction of decaborane with an aromatic aldehyde and subsequently inserted BH_3,[15,17]

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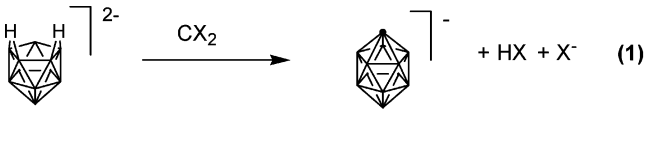
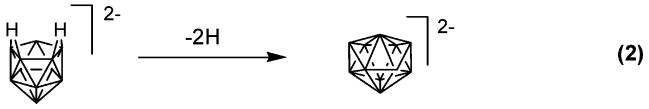
and a third was the above-mentioned insertion of an aryl-halocarbene into the nido-undecaborate anion [*nido*-$B_{11}H_{14}$]$^-$.[8] We now provide the full details for the third method, which was mentioned only briefly in the original disclosure. On a 1-g scale, this approach produces 1-aryl derivatives of the $CB_{11}H_{12}^-$ anion in 30−40% yields reproducibly, using inexpensive starting materials. Only the *p*-iodophenyl derivative is formed in a 12% yield.

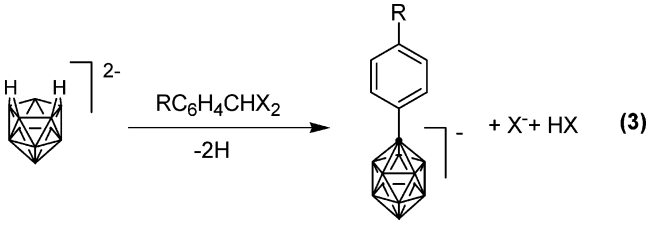
Results and Discussion

The stoichiometry of the transformation of [*nido*-$B_{11}H_{14}$]$^-$ into [*closo*-$CB_{11}H_{12}$]$^-$ requires the addition of one carbon atom and the removal of two hydrogen atoms. This is accomplished by reaction with a dihalocarbene CX_2 under elimination of 2 equiv of HX, which are taken up by excess base (eq 1). We noted[8] that the principal side product of this reaction is [*closo*-$B_{11}H_{11}$]$^{2-}$, which is formed by removal of two hydrogen atoms from [*nido*-$B_{11}H_{13}$]$^{2-}$ (eq 2). This suggests that CX_2, or its CHX_3 precursor, can also act as an oxidant. The ability to accept an electron increases from X = Cl to X = I, and indeed when CHI_3 was used as a carbene source the oxidation of [*nido*-$B_{11}H_{13}$]$^{2-}$ to [*closo*-$B_{11}H_{11}$]$^{2-}$ became the dominant process.[8]





These results suggested that similar results could be obtained by insertion of monohalocarbenes RCX into [*nido*-$B_{11}H_{14}$]$^-$, using excess carbene or carbene precursor as an oxidant. Such a process, represented formally by eq 3, would be a source of C-substituted [*closo*-$RCB_{11}H_{11}$]$^-$ anions.



We found that benzal chloride, $PhCHCl_2$, and substituted benzal chlorides, $RC_6H_4CHCl_2$, indeed react with [*nido*-$B_{11}H_{14}$]$^-$ in the presence of sodium ethoxide as the base to yield the desired salts of 1-substituted [*closo*-$RPhCB_{11}H_{11}$]$^-$ anions, but in yields lower than the 40% reported[8] for the reaction of $CHCl_3$ on a 1-g scale. A clue for improvement was found in the observation that the treatment of substituted benzal chlorides $RC_6H_4CHCl_2$ (R = Cl, Br, I) with the dianion [$B_{11}H_{13}$]$^{2-}$ in the presence of ethanol yields a side product in which the halogen has been reduced off, i.e., R = H.

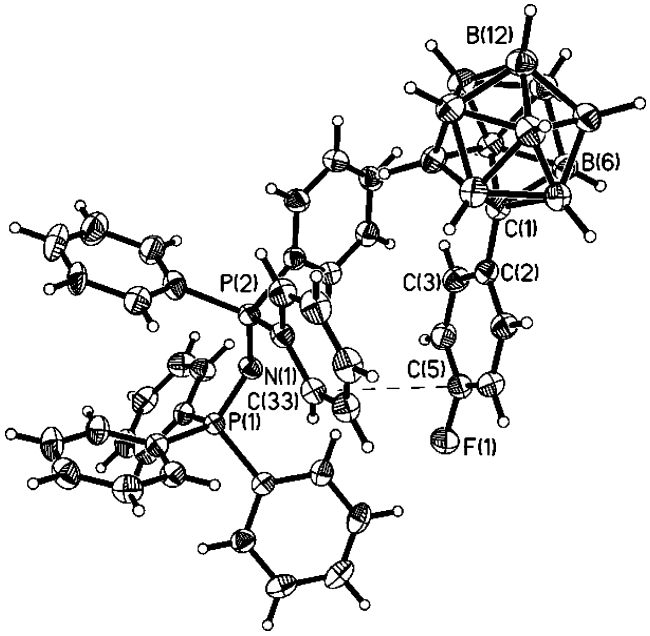


Figure 1. Single-crystal X-ray diffraction analysis structure of [PPN]$^+$[1-(*p*-fluorophenyl)-$CB_{11}H_{11}$]$^-$. The C(1)−C(2) distance is 1.507 Å, and the B(6)−C(1)−C(2)−C(3) dihedral angle is 88.6°.

The reductive elimination of the halogen from the phenyl ring is avoided if only sodium hydride is used as the base. When the reaction is run at an elevated temperature, the yield then rises to 40%, and the procedure represents a good and inexpensive method for the production of small amounts of C-arylated derivatives of $CB_{11}H_{12}^-$. In the case of *p*-I−$C_6H_4CHCl_2$, the yields of the desired product still remain low, presumably because of the very easy reducibility of the C−I bond.

A note of caution is necessary, however: even trace amounts of benzaldehyde or substituted benzaldehydes RC_6H_4CHO (R = F, Cl, Br, I) found in the substituted benzal chloride reagents poison the insertion reaction. In this event, the yield of the desired products plummets below 5%. Column chromatography proved to be the only dependable way to remove this impurity entirely.

It is possible that the mechanism by which the insertion reaction proceeds involves the free carbenes and is similar to that proposed[9] for dichlorocarbene itself, but it is also possible that the free carbene is never formed and the benzal chloride *p*-X−$C_6H_4CHCl_2$ acts as a chlorobenzylating agent to yield *p*-X−C_6H_4−CHCl−$B_{11}H_{13}^-$, which is then deprotonated and loses a chloride anion to afford a carbenoid that inserts into a BH bond to give the observed product.

The [1-(*p*-fluorophenyl)-$CB_{11}H_{11}$]$^-$ anion was characterized by single-crystal X-ray diffraction analysis (Figure 1) as the bis(triphenylphosphine)iminium (PPN^+) salt.[18] A lone π stack is the only specific interaction between the weakly nucleophilic anion and the weakly electrophilic cation. The participating phenyl rings are separated by 3.764 Å (centroid−centroid), with the closest contact being 3.355 Å

(18) Crystal and structure refinement parameters: $C_{43}H_{45}B_{11}NFP_2$, T = 135 K, *P*1, Z = 2, a = 10.721(2) Å, b = 12.646 (3) Å, c = 15.917 (6) Å, α = 76.45(2)°, β = 86.77(2)°, γ = 88.17(2)°, V = 2094 Å^3, R1 = 0.0478, wR2 = 0.1321.

between C(33) and fluorine-substituted C(5). The dihedral angle between the least-squares planes of the C atoms of the two phenyl rings is 25°. The structure of the anion is unremarkable: the C(1)−C(2) bond length is 1.507 Å, and the C(1)−B(12) axis forms an angle of 4.6° with respect to the least-squares plane of the carbon atoms in the pendant phenyl ring. The B(6)−C(1)-C(2)−C(3) dihedral angle is 88.6°.

Experimental Section

Materials. Sodium hydride (95%), tetramethylammonium chloride, bis(triphenylphoshoranylidene)ammonium chloride, benzal chloride, and 4-fluorobenzal chloride were purchased from Aldrich. All solvents were dried prior to use. $[nido\text{-}B_{11}H_{14}]^-$ was prepared according to the procedure of Dunks and Ordonez.[10] The new anions were characterized as $[(C_6H_5)_3PNP(C_6H_5)_3]^+$ or PPh_4^+ salts, prepared by reaction of other salts with aqueous PNP^+Cl^- or $PPh_4^+Cl^-$.

General Methods. HPLC separations were done on a Waters 600 instrument with an ELS detector (SEDEX 65), employing a reverse-phase C_{18} column and a mobile phase based on methanol and water (MeOH/H_2O mixture, 10 L; NEt_3, 70 mL; HOAc, 100 mL). Column chromatography of the carboranes was done on reverse-phase C_{18} silica gel with a mobile phase based on methanol and water (MeOH/H_2O mixture, 10 L; NEt_3, 70 mL; HOAc, 100 mL). Other column chromatography was carried out on 60-Å silica gel. Electrospray negative ion mass spectra were obtained with acetonitrile or acetone solutions with a Hewlett-Packard 5989 API/ES/MS instrument. ^1H and ^{13}C NMR spectra were measured with a 400- and 500-MHz Varian Unity Inova instruments; positive shifts are downfield and are expressed against TMS standards. $^{11}B\{^1H\}$ spectra and some ^1H spectra were measured with a 300-MHz Varian VXR 300 instrument; the reference is $B(OMe)_3$ at 18.1 ppm. IR spectra were measured with an Avatar 360 FT-IR spectrophotometer. UV spectra were measured on a Hewlett-Packard 8452A diode-array spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

General Procedure A for the Preparation of Substituted Benzal Chlorides. The aldehyde was added to a solution of $SOCl_2$ and dimethylformamide in several portions at 0 °C. After complete addition, the mixture was allowed to warm to room temperature, and stirring was continued for 18 h. The mixture was poured onto ice and extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude benzal chloride products were purified by column chromatography on silica gel using pentane as the eluent.

General Procedure B for the Preparation of Monocarborate Anions with NaOEt Formed in Situ. In a 250-mL two-necked flask, $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) was dissolved in anhydrous THF (10 mL) under an argon atmosphere. The solution was cooled to 0 °C, and NaH (95%) (1.5 g, 66 mmol) was added carefully. *Caution: In one instance, we observed a spontaneous ignition of NaH in the atmosphere.* After the mixture had been stirred for 15 min at room temperature, the THF and NMe_3 were removed under reduced pressure. THF (20 mL) was added to the residual $Na_2B_{11}H_{13}$, the suspension was cooled to 0 °C, and a mixture of the benzal chloride ($C_6H_5CHCl_2$, 2 mL) and ethanol (2 mL) was added slowly. The reaction mixture was stirred overnight at room temperature, and then the reaction was quenched carefully with EtOH (3 mL). After addition of water (50 mL), the THF and EtOH were removed under reduced pressure, and the solution was transferred to a separatory funnel where the residual benzal chloride was separated from the aqueous layer. Upon addition of $[Me_4N]^+[Cl]^-$ (1 g, 9.2 mmol) to the water layer, a white precipitate formed. It was separated and dried under reduced pressure. The residue was dissolved in methanol (10 mL) and filtered. The filtrate was injected onto an HPLC column, and MeOH/H_2O mixtures were used to elute the product. Methanol was removed under reduced pressure, the aqueous solution was extracted three times with diethyl ether (40 mL), the combined ether extracts were evaporated to dryness, and the colorless oil was dissolved in water (50 mL). After addition of a solution of $[PNP]^+[Cl]^-$ (1.1 g, 2 mmol) in H_2O (100 mL), the white precipitate was filtered and dried under reduced pressure to yield a pure carborate salt.

General Procedure C for the Preparation of Monocarborate Anions Using NaH as the Only Base. NaH (95%), (1.5 g, 59 mmol) was added at 0 °C to a solution of $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) in anhydrous THF (10 mL) under argon atmosphere. After the mixture had been stirred for for 15 min at room temperature, THF and NMe_3 were removed under reduced pressure, leaving behind $Na_2B_{11}H_{13}$. This residue was dissolved in THF (20 mL), and the benzal chloride (10.0 mmol) was added slowly. The reaction mixture was heated to 50 °C and stirred until no starting material was detected by ESI-MS and ^{11}B NMR spectra. The mixture was allowed to cool to room temperature, and the reaction was carefully quenched with pure water (20 mL). The organic solvents were removed under reduced pressure, and the solution was transferred to a separatory funnel where the residual benzal chloride was separated from the aqueous layer. Upon addition of $[Me_4N]^+[Cl]^-$ (1 g, 9.2 mmol) to the water layer, a white precipitate formed. It was separated and dried under reduced pressure. The crude product was purified by column chromatography on reverse-phase C_{18} silica gel using MeOH/H_2O mixtures as the eluent. Methanol was removed under reduced pressure, the aqueous solution was extracted three times with diethyl ether (3 × 10 mL), the combined ether extracts were evaporated to dryness, and the colorless oil was dissolved in water (20 mL). After addition of a 20% aqueous solution of $[PPh_4]^+[Cl]^-$, the white precipitate that was formed was filtered and dried under reduced pressure to yield a pure carborate salt.

4-Chlorobenzal Chloride. Procedure A was followed. 4-Chlorobenzaldehyde (5 g) was added to a solution of $SOCl_2$ (35 mL) and DMF (1 mL) to yield 4-chlorobenzal chloride (5.94 g, 86%), which was purified further by column chromatography on silica gel with pentane as the mobile phase. Spectral data agreed with those reported.[19]

4-Bromobenzal Chloride. Procedure A was followed. 4-Bromobenzaldehyde (5 g) was added to a solution of $SOCl_2$ (35 mL) and DMF (1 mL) to yield 4-bromobenzal chloride (5.77 g, 89%), which was identified by comparison of its spectra with those reported[19] and purified by column chromatography on silica gel with pentane as the mobile phase.

4-Iodobenzal Chloride. Procedure A was followed. 4-Iodobenzaldehyde (2 g) was added to a solution of $SOCl_2$ (20 mL) and DMF (1 mL) to yield crude 4-iodobenzal chloride. Column chromatography on silica gel with pentane (R_F = 0.75) yielded analytically pure material (2.20 g, 89%). ^1H NMR (300 MHz, $CDCl_3$) δ 6.64 (s, 1H, $CHCl_2$), 7.33−7.30 (m, 2H), 7.76−7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.0, 96.0, 127.8, 137.9, 140.0; IR (KBr pellet) 754, 799, 849, 1008, 1108, 1259, 1108, 1259, 1294, 1319, 1392, 1585, 1678, 2850, 2920; UV−vis (MeOH) λ_{max} (ϵ)

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296 (3140); LRMS (EI) *m*/*z* 288/286 (M^+, 13/22%), 253/251 ($M^+ - Cl$, 33/100), 126/124 ($M^+ - Cl - I$, 4/13), 89 ($M^+ - 2Cl - I$, 17). Anal. Calcd for $C_7H_5Cl_2I$: C, 29.30; H, 1.76; Cl, 24.71. Found: C, 29.25; H, 1.68; Cl, 25.08.

4-Phenylbenzal Chloride. Procedure A was followed. 4-Biphenylcarboxaldehyde (5 g) was added to a solution of $SOCl_2$ (35 mL) and DMF (1 mL) to give 4-phenylbenzal chloride. Purification by column chromatography on silica gel with pentane ($R_F = 0.51$) yielded analytically pure material (6.19 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (s, 1H, $CHCl_2$), 7.49−7.38 (m, 3H), 7.64−7.58 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.6, 126.6, 127.2, 127.5, 127.9, 128.9; IR (KBr pellet) 691, 731, 845, 1184, 1247, 1408, 1486, 3030; UV−vis (MeOH) λ_{max} (ϵ) 260 (54900); LRMS (EI) *m*/*z* 238/236 (M^+, 14/9%), 203/201 ($M^+ - Cl$, 100/33), 166/165/164/163 ($M^+ - 2Cl$, 3/24/11/7). Anal. Calcd for $C_{13}H_{10}Cl_2$: C, 65.85; H, 4.25; Cl, 29.90. Found: C, 66.13; H, 4.06; Cl, 30.18.

[PNP]$^+$[*closo*-1-C_6H_5-$CB_{11}H_{11}$]$^-$. $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) was treated with $C_6H_5CHCl_2$ (2 mL, 15.6 mmol) according to procedure B. The crude product was purified by HPLC, and a 58/42 MeOH/H_2O mixture was used to elute the [*closo*-1-C_6H_5−$CB_{11}H_{11}]^-$ product ($R_F = 28.0$). Addition of a solution of $[PNP]^+[Cl]^-$ (1.1 g, 2 mmol) in H_2O (100 mL) yielded pure $[PNP]^+$[*closo*-1-C_6H_5−$CB_{11}H_{11}]^-$ (1.06 g, 27%), identified by comparison of its spectra with those reported.[11]

[PNP]$^+$[*closo*-1-(*p*-FC_6H_4)-$CB_{11}H_{11}$]$^-$. $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) was treated with *p*-$FC_6H_4CHCl_2$ (2 mL, 14.9 mmol) according to procedure B. Purification by HPLC (MeOH/H_2O, 58/42; $R_F = 28.3$) and cation exchange yielded the pure $[PNP]^+$[*closo*-1-(*p*-FC_6H_4)-$CB_{11}H_{11}]^-$ (1.17 g, 29%). ^{1}H{^{11}B} NMR (500 MHz, acetone) δ 1.71 (s, 10H, BH), 2.21 (s, 1H, BH), 6.85 (d, $J = 8$ Hz, 2H, PhH), 7.49(d, $J = 8$ Hz, 2H, PhH), 7.55−7.59 (m, 12H, PhH), 7.69−7.75(m, 18H, PhH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.3, 113.8, 113.9, 126.8, 127.6, 129.8, 129.9, 130.3, 132.3, 132.4, 134.1, 138.3; ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$) δ −8.2, −13.1; IR (Cs salt, KBr pellet) 547, 691, 724, 1116, 1269, 1295, 1438, 1510, 2550, 3057; LRMS (ESI) *m*/*z* 237. Anal. Calcd for $C_{43}H_{47}B_{11}FNOP_2$: C, 65.07; H, 5.97; N, 1.76. Found: C, 64.99; H, 5.87; N, 1.99.

[PPh_4]$^+$[*closo*-1-(*p*-Cl−C_6H_4)-$CB_{11}H_{11}$]$^-$. Procedure C was applied to $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) and *p*-Cl−$C_6H_4CHCl_2$ (2.37 g, 10.0 mmol) for 3 days. Precipitation with $[Me_4N]^+[Cl]^-$ (1 g, 9.2 mmol) yielded the crude product (1.33 g), which was purified by column chromatography (MeOH/H_2O, 60/40; $R_F = 0.39$) and cation exchanged to yield $[PPh_4]^+$[*closo*-1-(*p*-Cl−C_6H_4)-$CB_{11}H_{11}]^-$ (1.30 g, 43%). ^{1}H{^{11}B} NMR (500 MHz, acetone) δ 1.72 (s, 10H, BH), 2.22 (s, 1H, BH), 7.13 (d, $J = 8$ Hz, 2H, PhH), 7.47 (d, $J = 8$ Hz, 2H, PhH), 7.85−7.89 (m, 20H, PhH), 7.98−8.03 (m, 4H, PhH); ^{13}C NMR (100 MHz, acetone) δ 64.1, 119.3, 120.2, 128.5, 129.71, 129.75, 131.6, 131.6, 132.1, 132.2, 136.4, 136.5, 137.14, 137.17; ^{11}B{^{1}H} NMR (96 MHz, acetone) δ −7.7, −12.8; IR (Cs salt, KBr pellet) 526, 801, 1014, 1091, 1261, 1261, 1589, 1683, 2539, 2963; LRMS (ESI) *m*/*z* 254. Anal. Calcd for $C_{31}H_{35}B_{11}ClP$: C, 62.79; H, 5.95. Found: C, 63.55; H, 6.20.

[PPh_4]$^+$[*closo*-1-(*p*-Br−C_6H_4)-$CB_{11}H_{11}$]$^-$.[15] $[Me_3NH]^+[B_{11}H_{14}]^-$ (0.76 g, 3.9 mmol) was treated with *p*-Br−$C_6H_4CHCl_2$ (1.38 g, 5.8 mmol) according to procedure C, except that the reaction mixture was stirred for only 18 h at 40 °C instead of 3 days at 50 °C to minimize the formation of side products. Precipitation with $[Me_4N]^+[Cl]^-$ (1 g, 9.2 mmol) yielded the crude product (0.87 g), which was purified by column chromatography (MeOH/H_2O, 60/40; $R_F = 0.36$) and cation exchanged to give $[PPh_4]^+$[*closo*-1-(*p*-Br−C_6H_4)-$CB_{11}H_{11}]^-$ (0.74 g, 30%). ^{1}H{^{11}B} NMR (500 MHz, acetone) δ 1.72 (s, 10H, BH), 2.19 (s, 1H, BH), 7.28 (d, $J = 8$ Hz, 2H, PhH), 7.42 (d, $J = 8$ Hz, 2H, PhH), 7.84−7.87 (m, 20H, PhH), 7.99−8.01 (m, 4H, PhH); ^{13}C NMR (100 MHz, acetone) δ 56.8, 119.3, 120.1, 128.6, 129.9, 131.6, 131.9, 132.1, 132.2, 136.4, 136.5, 137.1, 137.2; ^{11}B{^{1}H} NMR (96 MHz, acetone) δ −7.4, −12.8; IR (Cs salt, KBr pellet) 525, 687, 721, 1008, 1107, 1436, 1483, 2520, 2921, 3058; LRMS (ESI) *m*/*z* 298. Anal. Calcd for $C_{31}H_{35}B_{11}BrP$: C, 58.41; H, 5.53. Found: C, 58.72; H, 5.63.

[PPh_4]$^+$[*closo*-1-(*p*-I−C_6H_4)-$CB_{11}H_{11}$]$^-$. Procedure C was applied to a mixture of $[Me_3NH]^+[B_{11}H_{14}]^-$ (0.75 g, 3.9 mmol) and *p*-I−$C_6H_4CHCl_2$ (2.20 g, 7.8 mmol) (3 d). Precipitation with $[Me_3NH]^+[Cl]^-$ (1 g, 12.3 mmol) yielded the crude product (0.43 g), which was purified by column chromatography (MeOH/H_2O, 60/40; $R_F = 0.30$) and cation exchanged to yield $[PPh_4]^+$[*closo*-1-(*p*-I−C_6H_4)-$CB_{11}H_{11}]^-$ (0.32 g, 12%). ^{1}H{^{11}B} NMR (500 MHz, acetone) δ 1.71 (s, 10H, BH), 2.28 (s, 1H, BH), 7.29 (d, $J = 8$ Hz, 2H, PhH), 7.48 (d, $J = 8$ Hz, 2H, PhH), 7.85−7.87 (m, 20H, PhH), 7.99−8.03 (m, 4H, PhH); ^{13}C NMR (100 MHz, acetone) δ 45.9, 119.2, 120.1, 127.5, 128.5, 129.9, 132.1, 132.2, 136.3, 136.4, 137.1, 137.2, 137.7; ^{11}B{^{1}H} NMR (96 MHz, acetone) δ −7.5, −12.8; IR (Cs salt, KBr pellet) 526, 688, 722, 996, 1108, 1436, 2472, 3100; LRMS (ESI) *m*/*z* 345. Anal. Calcd for $C_{31}H_{35}B_{11}IP$: C, 54.40; H, 5.15. Found: C, 53.82; H, 5.37.

[PPh_4]$^+$[*closo*-1-(*p*-C_6H_5-C_6H_4)-$CB_{11}H_{11}$]$^-$. $[Me_3NH]^+[B_{11}H_{14}]^-$ (1 g, 5.2 mmol) was treated with *p*-C_6H_5−$C_6H_4CHCl_2$ (2.37 g, 10.0 mmol) according to procedure C (36 h). Precipitation of the carborane with $[Me_4N]^+[Cl]^-$ (1 g, 9.2 mmol) yielded the crude product (1.52 g), which was purified by column chromatography (MeOH/H_2O, 60/40; $R_F = 0.36$) and cation exchanged to give $[PPh_4]^+$[*closo*-1-(*p*-C_6H_5−C_6H_4)-$CB_{11}H_{11}]^-$ (1.25 g, 41%). ^{1}H{^{11}B} NMR (500 MHz, acetone) δ 1.74 (s, 10H, BH), 2.19 (s, 1H, BH), 7.21−7.67 (m, 9H, PhH), 7.82−7.90 (m, 20H, PhH), 7.98−8.04 (m, 4H, PhH); ^{13}C NMR (100 MHz, acetone) δ 66.8, 117.9, 127.1, 127.2, 128.1, 128.3, 128.6, 130.2, 130.3, 130.4, 132.1, 132.2, 136.4, 136.5, 137.15, 137.17; ^{11}B{^{1}H} NMR (96 MHz, acetone) δ −7.6, −12.9; IR (Cs salt, KBr pellet) 697, 761, 1049, 1231, 1367, 1404, 1707, 2227, 2541, 2926, 3029; LRMS (ESI) *m*/*z* 295. Anal. Calcd for $C_{37}H_{40}B_{11}P$: C, 70.03; H, 6.35. Found: C, 69.81; H, 6.35.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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