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New Weakly Coordinating Anions. 2.[†] Derivatization of the Carborane Anion $CB_{11}H_{12}^-$

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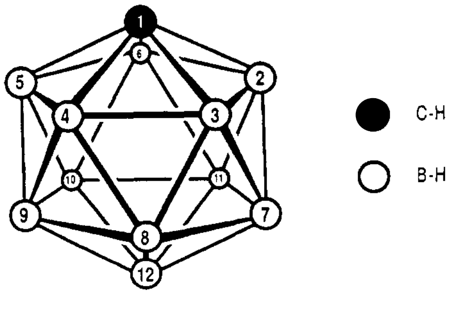
Of all the known classes of weakly coordinating anions (oxy anions, fluoro anions, tetraarylborates, carbanions, polyoxometalates, and carboranes), it is the carboranes that are perhaps most suited to further derivatization. With the ultimate goal of making the 12-vertex *closo*-carborane $CB_{11}H_{12}^-$ larger, more versatile, more chemically inert, less coordinating, less nucleophilic, and more soluble in low dielectric solvents, 13 new derivatives have been synthesized. C-Lithiation of $CB_{11}H_{12}^-$ followed by treatment with alkyl, silyl, or phosphine halides leads to the 1-ethyl, 1-(triphenylsilyl), 1-(trifluoromethyl), 1-(diphenylphosphino), and 1-benzyl derivatives and a mixture of the 7-(pentafluorophenyl) and 12-(pentafluorophenyl) derivatives. In general, conditions for high regiospecificity can be found. Conditions for the controlled halogenation of $CB_{11}H_{12}^-$ with halogens and/or *N*-halosuccinimides have been developed such that good syntheses of the 12-bromo, 7,12-dibromo, 12-chloro, and 7,12-dichloro derivatives can be achieved. The parent anion can also be derivatized in the 12-position with mercury(II) acetate or trifluoroacetate. Treatment of the 12-mercurated derivative with iodine gives the 7,12-diiodo derivative. All derivatives have been extensively characterized by ^{11}B NMR spectroscopy. The 12-bromo derivative has been characterized as its cesium and silver salts by single-crystal X-ray crystallography.

There has been considerable activity in the past 6 or 7 years in the synthesis of new weakly coordinating anions.[1] This is driven, in part, by the desire to synthesize coordinatively unsaturated cations such as $Fe(TPP)^+$ (TPP = tetraphenylporphyrinate)[2] or silicenium ions,[3] R_3Si^+. Enhancing the reactivity of cationic Zeigler–Natta-type polymerization catalysts by diminishing the nucleophicity of the counterion provides another motivation, and considerable success has been achieved recently.[4–6] The characterization of complexes of chlorocarbons has also been significantly advanced by the use of large fluoroanions.[7]

Of all the classes of weakly coordinating anions now recognized (oxy anions, fluoro anions, tetraarylborates, carbanions, polyoxometalates, and carboranes),[1] it is the carboranes that are perhaps the most suited to further elaboration. We have recently explored the icosahedral anion $CB_{11}H_{12}^-$ as a candidate for the least coordinating anion.[2]



It is quite stable, large in size and has no lone pairs. Its low nucleophilicity produces quite unexpected results in halide metathesis reactions of its silver salt.[8] With the ultimate goal of making it larger, more versatile, more chemically inert, less coordinating, less nucleophilic, and more soluble in low dielectric solvents, we have embarked on an exploration of its substitution chemistry.

The neutral dicarborane $C_2B_{10}H_{12}$ and the dianionic borane $B_{12}H_{12}^{2-}$ are isoelectronic with $CB_{11}H_{12}^-$ and all have the exceptional stability of the closo icosahedral structure. Conceptually, they are like three-dimensional analogues of benzene. The stability of the delocalized bonding in the boron (or carbon) framework allows ready electrophilic substitution of peripheral hydrogen atoms while keeping the core intact. The derivative chemistry of the dicarborane has been particularly well developed[9] as has the halogen substitution chemistry of $B_{12}H_{12}^{2-}$.[10] Much less attention has been given to the monoanionic analogue, $CB_{11}H_{12}^-$, even though it has been known now for 25 years.[11] An improved synthesis is now available.[12] There are also unique solubility applications[13] and possible neutron capture therapy applications[14] for this anion.

In the course of our work with the silver salt of $CB_{11}H_{12}^-$, we were puzzled by the difficulty of preparing a correspondingly useful hydride metathesis reagent, the trityl salt $[Ph_3C][CB_{11}H_{12}]$. Treatment of trityl bromide with $Ag(CB_{11}H_{12})$ in toluene appeared promising, because it proceeded with immediate and quantitative precipitation of AgBr, but intractable oils resulted from attempts

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[†] Part 1: see ref 3.

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to isolate a crystalline product. A possible redox incompatibility of trityl ion and $CB_{11}H_{12}^-$ (to give trityl radical) seemed very unlikely because the anion is reportedly stable to electrochemical oxidation up to >2.0 V (at Pt vs SCE in acetonitrile).[15] This is consistent with our observation of the inertness of $CB_{11}H_{12}^-$ to phenoxathiin radical cation (1.2 V vs SCE in dichloromethane)[16] and to Ce^{4+} ion (1.4 V vs SHE in water). Nevertheless, we have observed irreversible oxidation of $CB_{11}H_{12}^-$ at the surprisingly low threshold of ca. 0.7 V when cyclic voltammetry is carried out in dichloromethane rather than acetonitrile. A possible explanation is the formation of Pt–H bonds at the electrode via hydride abstraction from $CB_{11}H_{12}^-$. Similarly, hydride abstraction by trityl cation to give as yet uncharacterized boron products might explain the instability of the trityl salt.

Regardless of what the true explanation might be for the lack of inertness of $CB_{11}H_{12}^-$ under these two specific conditions, we were interested in preparing new anions that would be more inert. A particular focus is substitution at the 12-position (i.e., that antipodal to carbon in the icosahedron) since this is the most hydridic B–H bond. It is this B–H bond which is primarily coordinated to cationic centers[2,8] and is the first site of electrophilic substitution.[17] The 7-position is the next most reactive B–H bond. Although shutting down the reactivity of B–H bonds has been our primary goal, we have been led to a much more general exploration of the scope of the substitution chemistry of $CB_{11}H_{12}^-$. Both boron and carbon substitutions are reported.

The only major report of derivatives of $B_{11}CH_{12}^-$ appeared in 1986.[17] One of the most interesting findings was that the treatment with excess bromine or chlorine led to regiospecific *hexa*halogenation in 70% yield. The unique B–H and the five adjacent B–H bonds in the icosahedron (i.e., the six B–H bonds most remote from the C–H bond) were those substituted in forming 7,8,9,10,11,12-$Br_6CB_{11}H_6^-$ and 7,8,9,10,11,12-$Cl_6CB_{11}H_6^-$. Monohalogenation at the 12-position was achieved with reasonable selectivity by treatment with iodine. In addition, lithiation was demonstrated at carbon and led to C-substituted silyl,[10] amino,[17] sulfide,[17] oxy,[17] and carboxyl[17] derivatives.

In this paper we report several new derivatives of $CB_{11}H_{12}^-$. The reaction chemistry involves new ways of controlling halogenation, exploitation of a new B-mercurated intermediate, improved C-lithiation and new electrophilic additions. The positions of substitution sometimes vary in unpredictable ways. The mono-*B*-bromo derivative 12-$BrCB_{11}H_{11}^-$ has been characterized crystallographically as both the sodium and the silver salt. ^{11}B NMR spectroscopy has been particularly useful for characterizing the derivatives.

Experimental Section

All experimental manipulations were carried out using standard inert-atmosphere techniques. Spectrochemical grade THF, Et_2O, DMF, and DME[18] (Fischer) were distilled from NaH. CH_2Cl_2 was dried over P_2O_5 and distilled. $Cs(CB_{11}H_{12})$ was prepared as previously described.[12] Other commercially available chemicals were reagent grade and were used as received. All solvent evaporations were performed at reduced pressure on a standard rotary evaporator, unless otherwise stated. ^{11}B NMR spectra at 86.7 MHz, ^1H NMR spectra at 270 MHz, and ^{31}P NMR spectra at 109.4 MHz were obtained on a Bruker WP-270 spectrometer with the appropriate decoupling accessories. All ^{11}B chemical shifts (ppm) are referenced to $BF_3{\cdot}OEt_2$, positive shifts being downfield. The external reference was contained in a capillary within the sample tube. All proton chemical shifts were measured relative to internal residual protons from the lock solvent [99.5% $(CD_3)_2CO$] and then referenced to $(CH_3)_4Si$ (0.0 ppm). All ^{31}P chemical shifts were referenced to 85% aqueous H_3PO_4 in a capillary (0.0 ppm), positive shifts being downfield. Two-dimensional (2-D) ^{11}B–^{11}B NMR (64.18 MHz) spectra were recorded on a Varian XL-200 spectrometer via procedures described elsewhere.[19] The relative intensities of the off-diagonal interactions in the 2-D spectra (crosspeaks) are indicated with superscripts (s = strong, m = medium, w = weak, 0 = zero interaction). ^{19}F spectra (84.26 MHz) were recorded on a Jeol FX 90Q spectrometer and chemical shifts were referenced to $FCCl_3$ (0.0 ppm), positive shifts being downfield. All NMR spectra were recorded in acetone-d_6. NMR data are listed as follows: chemical shift (δ, ppm) [multiplicity, integrated intensity, ^{11}B–^1H or other coupling J in Hz, atom identity]. TLC was performed on Silufol (Kavalier, Votice, Czech Republic) starch-impregnated silica gel on aluminum foil, with detection by I_2 vapor, in 1:2 acetonitrile–chloroform.

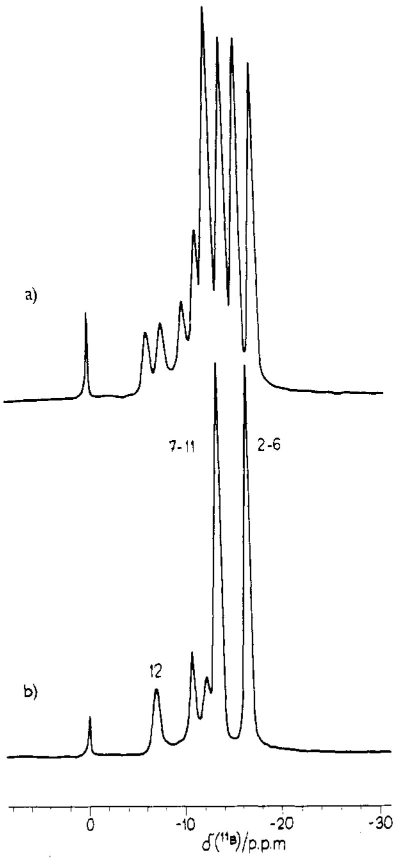

Figure 1. ^{11}B NMR spectrum of $Li[CB_{11}H_{12}]$ in d_8 THF/hexane prepared by addition of 1 equiv of BuLi to $[Me_3NH][CB_{11}H_{12}]$: (a) non-decoupled spectrum; (b) ^1H decoupled spectrum.

NMR of Li[*closo*-1-$LiCB_{11}H_{11}$] (1). An NMR tube was charged with $[Me_3NH][CB_{11}H_{12}]$ (150 mg, 0.932 mmol) and THF-d_8 (2 mL). Butyllithium (0.47 mL of 1.55 M solution in hexane) was added in one portion to give the spectra shown in Figure 1 and a second equivalent portion to give the spectra shown in Figure 2 (1). ^{11}B NMR: δ_B −7.77 [d, 1B, 120, B(12)], −10.67 [d, 5B, 128, B(7–11)], −12.19 [d, 5B, 137, B(2–6)].

Synthesis of $[Me_4N]$[*closo*-1-$C_2H_5CB_{11}H_{11}$] (2). $[Me_3NH][CB_{11}H_{12}]$ (2.03 g, 0.01 mol) was dissolved in THF (50 mL), and butyllithium (13 mL of a 1.55 M solution in hexane, 0.02 mol) was added dropwise with stirring over 30 min at room temperature. Bromoethane (1.1 g, 0.0109 mol) was dissolved in THF (10 mL) and added. The mixture was filtered and the solvent evaporated. The viscous residue was dissolved in 5% sodium hydroxide (40 mL) and extracted with two portions of diethyl ether (30 mL). The organic layer was treated with 1 M tetramethylammonium chloride (15 mL) and the diethyl ether was evaporated off. The aqueous suspension was filtered off, washed with water, and vacuum dried. The crude product was recrystallized from acetone–methanol, to give off-white crystals (1.55 g, 63%). R_f = 0.42. ^1H NMR: δ 3.44 [s, 12H, Me_4N^+], 1.83 [q, 2H, CH_2], 0.83 [t, 3H, CH_3]. ^{11}B NMR: δ_B −10.01 [d, 1B, 139, B(12)], −13.55 [d, 5B + 5B, B(7–11 and 2–6)]. Anal.

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(18) Abbreviations used in this paper: THF = tetrahydrofuran, Et_2O = diethylether, DME = 1,2-dimethoxyethane, DMF = N,N′-dimethylformamide, NBS = N-bromosuccinimide.

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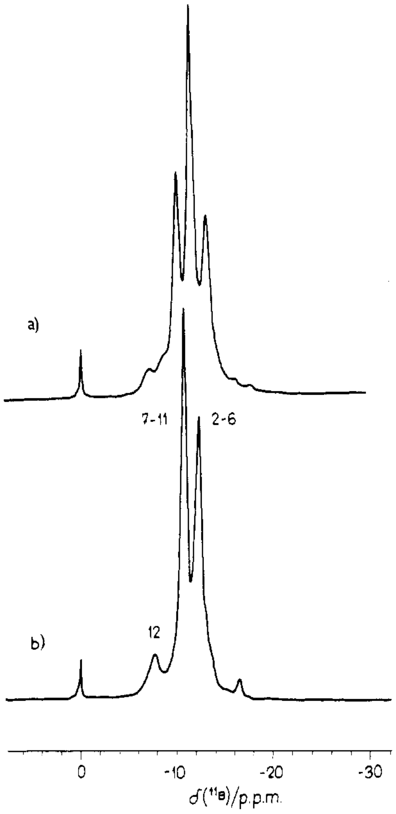

Figure 2. ^{11}B NMR spectrum of Li[1-LiCB$_{11}$H$_{11}$] in d$_8$ THF/hexane prepared by addition of 2 equiv of BuLi to [Me$_3$NH][CB$_{11}$H$_{12}$]: (a) nondecoupled spectrum; (b) ^{1}H decoupled spectrum.

Calcd for C$_7$H$_{28}$B$_{11}$N: C, 34.01; H, 11.33; B, 48.99; N, 5.69. Found: C, 34.19; H, 11.51; B, 48.70; N, 5.60.

Synthesis of [Me$_4$N][1-Ph$_3$Si-*closo*-CB$_{11}$H$_{11}$] (3). [Me$_3$NH][CB$_{11}$H$_{12}$] (2.03, 0.01 mol) was dissolved in THF (50 mL), and butyllithium (13 mL of a 1.55 M solution in hexane, 0.02 mol) was added dropwise with stirring over 30 min at room temperature. Ph$_3$SiCl (2.95 g, 0.01 mol) was dissolved in THF (20 mL) and added. The mixture was stirred at room temperature for 10 h. The mixture was filtered and the solvent was evaporated. The viscous residue was dissolved in 5% sodium hydroxide (60 mL) and filtered. The filtrate was treated with 1 M tetramethylammonium chloride (15 mL). The white precipitate was isolated by filtration, washed off with water, and vacuum-dried. The crude product was extracted with two portions of dichloromethane (40 mL), and the white precipitate was vacuum-dried to recover 0.85 (42%) of [Me$_4$N]-[CB$_{11}$H$_{12}$]. The filtrate was slowly reduced in volume to ca. 15 mL to precipitate white crystals which were filtered off, washed with benzene (ca. 15 mL), and vacuum-dried (1.92 g, 40%). $R_f = 0.40$. ^{1}H NMR: δ 7.76–7.31 [m, 15H, Ph$_3$Si], 3.42 [s, 12H, Me$_4$N$^+$]. ^{11}B NMR: δ_B −1.72 [d, 1B, 132, B(12)], −10.67 [d, 5B, 139, B(7–11)], −12.66 [d, 5B, 163, B(2–6)]. Anal. Calcd for C$_{23}$H$_{38}$B$_{11}$SiN: C, 57.86; H, 7.99; B, 25.37; Si, 5.87; N, 2.93. Found: C, 57.52; H, 8.09; B, 25.74; Si, 5.75, N, 2.90.

Synthesis of [Me$_4$N][1-CF$_3$-*closo*-CB$_{11}$H$_{11}$] (4). [Me$_3$NH][CB$_{11}$H$_{12}$] (1.5 g, 7.3 mmol) was dissolved in THF (40 mL), and butyllithium (10 mL of a 1.55 M solution in hexane) was added dropwise with stirring over 30 min at room temperature. The solution was cooled to −25 °C and CF$_3$I (3.95 g, 0.02 mol) was added. After the initial reaction had ceased, the mixture was allowed to warm with stirring and refluxed for 4 h. The solution was then filtered and the solvent was evaporated. The solid residue was dissolved in 5% sodium hydroxide (40 mL) and filtered. The filtrate was treated with 1 M tetramethylammonium chloride (10 mL). The precipitate was filtered off, washed with water, and vacuum-dried. The crude product was chromatographed in CH$_3$CN–CH$_2$Cl$_2$ (1:4) on a column (3.0 × 40 cm) of silica gel. Two main fractions developed (R_f 0.42 and 0.33 on TLC) which were evaporated, washed with diethyl ether, and vacuum-dried. The first fraction (0.30 g, 14%) was identified as the desired product. ^{1}H NMR: δ 3.45 [s, 12H, Me$_4$N$^+$]. ^{11}B NMR δ_B −7.62 [d, 1B, 129, B(12)], −10.46 [d, 5B, 149, B(7–11)], −11.39 [d, 5B, 148, B(2–6)]. ^{19}F NMR: δ_F 32.8 [s, 3F, CF$_3$]. Anal. Calcd for C$_6$H$_{23}$B$_{11}$F$_3$N; C, 25.20; H, 7.93; B, 42.22; F, 19.73; N, 4.92. Found: C, 25.09; H, 8.01; B, 42.16; F, 19.86; N, 4.89. As assessed by ^{11}B NMR, the second fraction, (0.7 g, 46.7%) was identifed as starting material (tetramethylammonium salt).

Reaction of [Me$_3$NH][*closo*-CB$_{11}$H$_{12}$] with Ph$_2$PCl. [Me$_3$NH]-[CB$_{11}$H$_{12}$] (2.03 g, 0.01 mol) was dissolved in THF (50 mL) and butyllithium (14 mL of a 1.55 M solution in hexane) was added dropwise with stirring over 30 min at room temperature. Ph$_2$PCl (2.75 mL, 0.015 mol) dissolved in THF (10 mL) was added and a red color developed. After the initial exothermic reaction had ceased, the mixture was stirred at room temperature for 5 h. The mixture was filtered and the solvent evaporated. The viscous residue was dissolved in 5% sodium hydroxide (60 mL) and extracted with two portions of diethyl ether (30 mL). The organic layer was added to 1 M tetramethylammonium chloride (15 mL), and the ether was evaporated off. The precipitate was filtered off, washed with water and vacuum dried. The pale yellow crude product was chromatographed with CH$_3$CN–CH$_2$Cl$_2$ (1:8) on a column (4 × 40 cm) of silica gel. Two main fractions developed with R_f 0.38 and 0.05 (TLC), which were evaporated and vacuum-dried. The first fraction (1.2 g, 29.8%) was identified as [Me$_4$N][1-Ph$_2$P-*closo*-CB$_{11}$H$_{11}$] (**5**). ^{1}H NMR: δ 7.83–7.32 [m, 10H, Ph], 3.43 [s, 12H, Me$_4$N$^+$]. ^{11}B NMR: δ_B −4.55 [d, 1B, 135, B(12)], −11.36 [d, 5B, 120, B(7–11)], −12.48 [d, 5B, 120, B(2–6)]. ^{31}P{^{1}H}: δ_P 21.96 [br s]. Anal. Calcd for C$_{16}$H$_{34}$B$_{11}$PN: C, 48.98; H, 8.67; B, 30.87; P, 7.91; N, 3.57. Found: C, 48.60; H, 8.50; B, 31.06; P, 8.10; N, 3.74. The product from the second fraction (0.25 g, 5.95%) was identified as 1-Ph$_2$P$^+$(OH)-*closo*-CB$_{11}$H$_{11}$$^-$ (**6**). Mp: 210 °C. *m/z*: 347 corresponding to the ion [^{11}B$_{10}$^{12}C$_{13}$^{1}H$_{22}$^{16}O^{32}P]$^+$. ^{1}H NMR: δ 8.07–7.27 [m, 10H, Ph], 3.02 [s, 1H, OH]. ^{11}B NMR: δ_B −2.03 [br d, 1B, 129, B(12)], −11.26 [d, 5B, 142, B(7–11)], −13.39 [br d, 5B, 178, B(2–6)], ^{31}P{^{1}H} δ_P 9.48 [s]. Anal. Calcd for C$_{13}$H$_{22}$B$_{11}$PO: C, 45.09; H, 6.36; B, 34.99; P, 8.96. Found: C, 45.20; H, 6.16; B, 35.12; P, 9.22.

Synthesis of [Me$_4$N][*closo*-1-PhCH$_2$-CB$_{11}$H$_{11}$] (7). [Me$_3$NH][CB$_{11}$H$_{11}$] (1.5 g, 7.3 mmol) was dissolved in THF (50 mL) and butyllithium (10 mL of a 1.55 M solution in hexane) was added dropwise with stirring over 30 min at room temperature. Benzylbromide (2.56 g, 0.015 mol) was dissolved in THF (10 mL) and was added. After the initial exothermic reaction had ceased, the mixture was stirred at room temperature for 3 h. The THF was filtered and evaporated. The viscous residue was dissolved in 5% sodium hydroxide (60 mL), and this solution was extracted in heptane (40 mL). The water layer was filtered through charcoal and treated with 1 M tetramethylammonium chloride (10 mL). The precipitate was filtered off, washed with water, and vacuum-dried. The crude product was extracted with two portions of dichloromethane (50 mL) and filtered. The white precipitate was identified as [Me$_4$N]-[CB$_{11}$H$_{12}$] (0.35 g, 23.3%). The filtrate was evaporated and the viscous residue was chromatographed in CH$_3$CN–CH$_2$Cl$_2$ (1:5) on a column (3.0 × 40 cm) of silica gel. One main fraction with R_f 0.46 and one minor fraction with R_f 0.65 developed (TLC). These were collected, evaporated, and vacuum-dried. The main fraction (0.65 g, 21.0%) was identified as [Me$_4$N][1-PhCH$_2$-*closo*-CB$_{11}$H$_{11}$] (7). ^{1}H NMR: δ 7.17–7.08 [m, 5H, Ph], 3.44 [s, 12H, Me$_4$N$^+$], 2.87 [m, 2H, CH$_2$]. ^{11}B NMR: δ_B −9.09 [d, 1B, 150, B(12)], −12.74 [d, 5B + 5B, 133, B(7–11 and 2–6)]. The product from the minor fraction (0.12 g) was identified as a mixture of an as yet uncharacterized B-substituted derivative (singlet at δ_B −9.80) and 7.

Reaction of [Me$_3$NH][*closo*-CB$_{11}$H$_{12}$] with C$_6$F$_5$Br. [Me$_3$NH]-[CB$_{11}$H$_{12}$] (1.5 g, 7.3 mmol) was dissolved in diethyl ether (40 mL) and butyllithium (10 mL of a 1.55 M solution in hexane) was added dropwise with stirring over 30 min at room temperature. C$_6$F$_5$Br (2.5 g, 0.01 mol) was dissolved in diethyl ether (20 mL) and added, with stirring at room temperature for 5 h. The ether was evaporated, the viscous residue dissolved in 5% sodium hydroxide (400 mL) and the solution was extracted in benzene (50 mL). The water layer was separated and filtered through charcoal. The filtrate was precipitated with 1 M tetramethylammonium chloride (40 mL). The precipitate was filtered off, washed with water, and vacuum-dried. The pale yellow crude product was chromatographed with CH$_3$CN–CH$_2$Cl$_2$ (1:4) on a column (2.0 × 30 cm) of silica gel. Concentration of the combined fractions (R_f ca. 0.38 on TLC) gave 0.70 g (60%). This product was identified as a mixture of [Me$_4$N][12-C$_6$F$_5$-CB$_{11}$H$_{11}$] (**8**) and [Me$_4$N][7-C$_6$F$_5$-CB$_{11}$H$_{11}$] (**9**) in an approximately 2:1 ratio. Anal. Calcd for C$_{11}$H$_{23}$B$_{11}$F$_5$N: C, 34.35; H, 5.56; B, 31.22; F, 25.07; N, 3.70. Found: C, 34.29; H, 5.97; B, 31.43; F, 24.66; N, 3.65. ^{1}H NMR (**8**): δ 3.46 [s, 12H, Me$_4$N$^+$], 2.43 [s, 1H, CH]. ^{11}B NMR (**8**): δ_B −1.55 [s, 1B, 150, B(12)], −12.49 [d, 5B, 138, B(7–11)], −16.21 [d, 5B, 154, B(2–6)]. ^{19}F NMR (**8**): δ_F 24.8 [s, 1F], 19.5 [m, 2F], −4.3 [m, 2F]. ^{1}H NMR (**9**): δ 3.46 [s, 12H, Me$_4$N$^+$], 2.38 [s, 1H, CH]. ^{11}B

NMR (**9**): δ_B –5.60 [d, 1B, 135, B(12)], –6.97 [s, 1B, B(7)], –12.08 [d, 2B, 142, B(8,11)], –5.60 [d, 2B, 142, B(9,10)], –16.21 [d, 5B, 154, B(2,3; 4,6,5)]. 2D ^{11}B–^{11}B NMR (**9**): B(12) [B(7)^{m}, B(8,11)^{m}, B(9,10)^{s}]; B(7) [B(12)^{m}, B(8,11)^{s}, B(2,3)^{s}]; B(8,11) [B(12)^{m}, B(7)^{s}, B(9,10)^{s} B(2,3 and 4,6)^{s}]; B(9,10) [B(12)^{s}, B(8,11)^{s}, B(4,6,5)^{s}]; B(2,3; 4,6,5) [B(7)s, B(8,11)s, B(9,10)s]. ^{19}F NMR (**9**): δ_F 23.53 [s, 1F], 10.3 [m, 2F], –6.0 [m, 2F].

Synthesis of Cs[12-Br-*closo*-$CB_{11}H_{11}$] (10). (a) Direct Bromination. [Me_3NH][$CB_{11}H_{11}$] (1.5 g, 7.3 mmol) was dissolved in water (30 mL) with NaOH (0.4 g, 0.01 mol). The trimethylamine evolved was removed in vacuo. K_2CO_3 (2 g, 0.1245 mol) was added, and the mixture was cooled at 0 °C. Then 1 M bromine in CCl_4 (7.4 mL, 7.4 mmol) was added dropwise with stirring over 4 h at ice temperature. The CCl_4 was separated and discarded, and the water layer was filtered. The filtrate was extracted with two portions of diethyl ether (30 mL). The organic layer was evaporated and solid residue was dissolved in water (20 mL). The solution was treated with CsCl (1.8 g, 0.01 mol in 10 mL water). The white precipitate was recrystallized from hot water. The crystals were filtered off, washed with a small quantity of cold water, and vacuum-dried to recover 1.85 g (71.0%) of white crystals. R_f = 0.35. ^{1}H NMR: δ 2.28 [br s, 1H, CH]. ^{11}B NMR: δ_B –2.36 [s, 1B, B(12)], –11.92 [d, 5B, 140, B(7–11)], –16.52 [d, 5B, 154, B(2–6)]. Anal. Calcd for $CH_{11}B_{11}BrCs$: C, 3.38; H, 3.10; B, 34.09; Br, 22.54. Found: C, 3.50; H, 3.05; B, 34.26; Br, 22.50.

(b) Bromination with *N*-Bromosuccinimide. Cs[$CB_{11}H_{12}$] (3.2 g, 0.0115 mol) was dissolved in dimethylformamide (40 mL). *N*-Bromosuccinimide (2.1 g, 0.093 mol) was then added, and a yellow color developed. After the initial exothermic reaction had ceased, the mixture was stirred at room temperature for 48 h. The dimethylformamide was removed in vacuo, and the solid residue was extracted with two portions of CH_2Cl_2 (50 mL). The suspension was filtered off, and the crude product was dissolved in hot water (150 mL). The solution was filtered and cooled. The crystalline product was filtered off and recrystallized from hot water to give 2.54 g (61.9%) of off-white product.

Synthesis of Cs[7,12-Br_2-*closo*-$CB_{11}H_{10}$] (11). Cs[$CB_{11}H_{12}$] (3.2 g, 0.0115 mol) was dissolved in dimethylformamide (60 mL). *N*-Bromosuccinimide (5.5 g, 0.0243 mol) was added, and a yellow color developed. After the initial exothermic reaction had ceased, the mixture was stirred at room temperature for 14 days. The dimethylformamide was removed in vacuo and the viscous residue was extracted with CH_2Cl_2 (100 mL). The solid was filtered off and chromatographed with CH_3CN–CH_2Cl_2 (1:4) on a column (4 × 40 cm) of silica gel. The main fraction, R_f 0.35 (TLC), was evaporated and the solid residue was dissolved in hot water (80 mL). The hot solution was filtered and cooled to give crystalline product (4.5 g, 89.7%). ^{1}H NMR: δ 2.46 [br s, 1H, CH]. ^{11}B NMR: δ_B –2.25 [s, 1B, B(12)], –7.90 [s, 1B, B(7)], –10.68 [d, 2B, 142, B(8,11)], –12.27 [d, 2B, 142, B(9,10)], –15.86 [d, 2B, 149, B(2,3)], –17.52 [d, 2B, 157, B(4,6)], –19.72 [d, 1B, 187, B(5)]. Connectivities from 2-D ^{11}B–^{11}B NMR: B(12) [B(7)^{s}, B(8,11)^{s}, B(9,10)^{s}]; B(7) [B(12)^{s}, B(8,11)^{s}, B(2,3)^{s}]; B(8,11) [B(12)^{s}, B(7)^{s}, B(9,10)^{s}, B(2,3)^{s}, B(4,6)^{s}]; B(9,10) [B(12)^{s}, B(8,11)^{s}, B(4,6)^{s}, B(5)^{s}]; B(2,3) [B(7)^{s}, B(8,11)^{s}, B(4,6)^{m}]; B(4,6) [B(8,11)^{s}, B(9,10)^{s}, B(2,3)^{m}, B(5)^{m}]; [B(9,10)^{s}, B(4,6)^{m}]. Anal. Calcd for $CH_{10}B_{11}Br_2Cs$: C, 2.76; H, 2.30; B, 27.88; Br, 36.87. Found: C, 2.92; H, 2.10; B, 28.12; Br, 36.96.

Synthesis of Cs[12-Cl-*closo*-$CB_{11}H_{11}$] (12). Cs[$CB_{11}H_{12}$] (2.8 g, 0.01 mol) was dissolved in dimethylformamide (40 mL). *N*-Chlorosuccinimide (1.8, 0.01 mol) was then added, and a pale yellow color developed. Further work up of the reaction mixture as for **10** (method b) resulted in the isolation of 1.85 g crystalline product (59.1%). R_f = 0.33. ^{1}H NMR: δ 2.44 (br s, 1H, CH). ^{11}B NMR: δ_B 3.63 [s, 1B, B(12)], –12.79 [d, 5B, 140, B(7–11)], –17.57 [d, 5B, 151, B(2–6)]. Anal. Calcd for $CH_{11}B_{11}ClCs$: C, 3.86; H, 3.54; B, 38.97; Cl, 11.43. Found: C, 4.02; H, 3.33; B, 39.12; Cl, 11.40.

Synthesis of Cs[7,12-Cl_2-*closo*-$CB_{11}H_{10}$] (13). Cs[$CB_{11}H_{12}$] (2.8 g, 0.01 mol) was dissolved in dimethylformamide (60 mL). *N*-Chlorosuccinimide (3.6, 0.02 mol) was added, and the reaction was worked up in the same manner as that for **11** resulting in the isolation of 2.3 g of recrystallized product (66.3%). R_f = 0.30; ^{1}H NMR: δ [br s, 1H, CH_k]. ^{11}B NMR: δ_B 3.17 [s, 1B, B(12)], –2.42 [s, 1B, B(7)], –12.14 [d, 2B, 135, B(8,11)], –13.72 [d, 2B, 133, B(9,10)], –17.22 [d, 2B, 144, B(2,3)], –19.39 [d, 2B, 149, B(4,6)], –21.83 [d, 1B, 157, B(5)]. Connectivities from 2-D ^{11}B–^{11}B NMR: B(12) [B(7)^{s}, B(8,11)^{s}, B(9,10)^{m}]; B(7) [B(12)^{s}, B(8,11)^{s}, B(2,3)^{m}]; B(8,11) [B(12)^{s}, B(7)^{s}, B(9,10)^{s}, B(2,3)^{s}, B(4,6)^{s}]; B(9,10) [B(12)^{m}, B(8,11)^{s}, B(4,6)^{s}, B(5)^{s}]; B(2,3) [B(7)^{m}, B(8,11)^{s}, B(4,6)^{m}]; B(4,6) [B(8,11)^{m}, B(9,10)^{s}, B(2,3)^{m}, B(5)^{m}]; B(5) [B(9,10)^{s}, B(4,6)^{m}]. Anal. Calcd for $CH_{10}B_{11}Cl_2Cs$: C, 3.48; H, 2.90; B, 35.07; Cl, 20.58. Found: C, 3.60; H, 2.72; B, 35.19; Cl, 20.62.

Synthesis of [Me_3NH][12-CF_3COOHg-*closo*-$CB_{11}H_{11}$] (14a) and [Me_3NH][12-CH_3COOHg-*closo*-$CB_{11}H_{11}$] (14b). [Me_3NH][$CB_{11}H_{12}$] (6.1 g, 0.03 mol) was dissolved in anhydrous acetone (120 mL) and $(CF_3COO)_2Hg$ (12.85 g, 0.03 mol) or $(CH_3COO)_2Hg$ was added. The solution was stirred under reflux for 48 h. The acetone was evaporated and the viscous residue was dissolved in CH_2Cl_2 (200 mL). The solution was filtered and the white precipitate recovered (1.1 g, 18.03% of [Me_3NH][$CB_{11}H_{12}$]). The filtrate was evaporated and the residue was once more dissolved in CH_2Cl_2 (100 mL). The solution was filtered and the CH_2Cl_2 evaporated to give product **14a** (12.5 g, 71.8%). R_f = 0.42. ^{1}H NMR: δ 8.80 [br t, 1H, NH^+], 3.23 [s, 9H, Me_3N], 2.49 [br s, 1H, CH_2], 2.10 [s, 3H, CH_3COO] (for **14b** only). ^{11}B NMR: δ_B –5.38 [s, 1B, B(12)], –12.25 [d, 5B, 143, B(7–11)], –15.05 [d, 5B, 157, B(2–6)]. ^{19}F NMR (**14a**): δ_F –8.2 [s, 3F, CF_3COO]. Anal. Calcd for $C_6H_{27}B_{11}HgNO_2$ (**14b**): C, 15.43; H, 5.79; B, 25.93; Hg, 42.99; N, 3.00. Found: C, 15.60; H, 5.55; B, 26.20; Hg, 43.10; N, 3.12.

Reduction of [Me_3NH][12-$CF_3COOHgCB_{11}H_{11}$] by Zn. [Me_3NH][12-$CF_3COOHgCB_{11}H_{11}$] (0.6 g, 1.16 mol) was dissolved in THF (20 mL) and stirred 25 h with granulated zinc (1.0 g, 0.015 mol). The mixture was filtered out and the THF was evaporated. The solid residue was dissolved in acetone (20 mL) and after filtration was evaporated to dryness. The residue was recrystallized from aqueous acetone to give 0.23 g (97.0%) of white crystals, which were identified as [Me_3NH][$CB_{11}H_{12}$]. R_f = 0.35. ^{1}H NMR: δ 8.80 [br t, 1H, NH^+], 3.22 [s, 9H, Me_3N]; 2.24 [s, 1H, CH_k]. ^{11}B NMR: δ_B –6.21 [d, 1B, 127, B(12)], –12.64 [d, 5B, 138, B(7–11)], –15.71 [d, 5B, 149, B(2–6)] (see refs 4 and 13).

Thermal Decomposition of [Me_3NH][12-$CF_3COOHgCB_{11}H_{11}$]. [Me_3NH][12-CF_3COOHg-$CB_{11}H_{11}$] (1.3 g, 2.514 mmol) was heated in vacuo at 160° for 30 min in a reaction flask equipped with a glass sublimation tube. The product in the reaction flask was extracted with two portions of diethyl ether (30 mL). The ether solution was filtered to remove Hg metal, and the solvent was evaporated. The crude product was chromatographed with CH_3CH–CH_2Cl_2 (1:4) on a column (2.5 × 30 cm) of silica gel. Evaporation of the combined fractions of ca. R_f 0.35 (TLC) gave 0.32 g (62.2%) of [Me_3NH][$CB_{11}H_{12}$].

Reaction of [Me_3NH][12-$CF_3COOHgCB_{11}H_{11}$] with I_2. [Me_3NH][12-CF_3COOHg-1-$CB_{11}H_{11}$] (1.59 g, 3.075 mmol) was dissolved in 1,2-dimethoxyethane (30 mL). Iodine (1.2 g, 6.2 mmol) was added, and the solution was stirred under reflux for 3 h. The DME was evaporated off, and the viscous residue was dissolved in acetone (20 mL). The solution was filtered to remove precipitated HgI_2 (1.05 g, 75.2% theoretical) and treated with 1 M hydrochloric acid (10 mL) and $Na_2SO_3 \cdot 7H_2O$ (0.5 g). The solution was filtered, and the acetone was evaporated off. The suspension was extracted with two portions of diethyl ether (30 mL). The organic layer was separated and evaporated. The viscous residue was chromatographed in acetonitrile–CH_2Cl_2 (1:4) on a column (2.5 × 30 cm) of silica gel. The main fraction with R_f 0.33 (TLC) was collected, evaporated, and vacuum-dried (0.95 g, 67.7%). ^{1}H NMR: δ 8.70 [br t, 1H, NH^+], 3.21 [s, 9H, Me_3N] 2.74 [br s, 1H, CH_k]. ^{11}B NMR: δ_B –9.29 [d, 2B, 150, B(8,11)], –11.03 [9d, 2B, 154, B(9,10)], –14.65 [d, 2B, 171, B(2,3)], –15.47 [s + d, 1B + 2B, 150, B(–12 and 4,6)], –16.88 [d, –1B, 163, B(5)], –21.55 [s, 1B, B(7)]. Connectivities from 2-D ^{11}B–^{11}B NMR: B(8,11) [B(9,10)^{s}, B(2,3)^{s}, B(12)^{s} and B(2,3)^{s,} B(2,3)^{s}]; B(9,10) [B(8,11)^{s}, B(12)^{s} and B(4,6)^{s}, B(5)^{m}]; B(2,3) [B(8,11)^{s}, B(4,6)^{s}, B(7)^{s},]; B(12) and B(4,6) [B(8,11)^{s}, B(9,10)^{s}, B(2,3)^{s}, B(5)^{m}, B(7)^{s}]; B(5) [B(9,10)^{m}, B(4,6)^{m}]; B(7) [B(12)^{s}, B(8,11)^{s}, B(2,3)^{s}]. Anal. Calcd for $C_4H_{23}B_{11}I_2N$: C, 10.43; H, 5.00; B, 26.30; I, 55.22; N, 3.05. Found: C, 10.92; H, 4.74; B, 26.53; I, 55.12; N, 2.83.

Structure Determinations. Crystals of Cs[12-$BrCB_{11}H_{11}$] were grown from aqueous solution. Ag(12-$BrCB_{11}H_{11}$) was prepared in an identical manner to Ag($Br_6CB_{11}H_5$),[8] and crystals were grown from benzene. Both compounds were examined on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator. Crystalline Cs[12-$BrCB_{11}H_{11}$] was examined at room temperature while crystalline Ag(12-$BrCB_{11}H_{11}$) C_6H_6 had to be examined at 118 K in order to avoid loss of the benzene solvate and subsequent crystal decomposition. Intensity data reduction procedures made use of the Blessing profile analysis procedures;[20] empirical absorption correction procedures were also applied to the intensity data. Both structures were solved by a combination of a Patterson calculation to locate the heavy

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Table I. Summary of Crystal Data and Intensity Collection Parameters

compound	$CsBrCB_{11}H_{11}$	$AgBrCB_{11}H_{11}\cdot C_6H_6$
formula	$CsBrCB_{11}H_{11}$	$AgBrC_7B_{11}H_{17}$
fw, amu	354.818	407.90
crystal dimens, mm	0.6 × 0.2 × 0.2	0.4 × 0.3 × 0.2
space group	$P2_1/n$	$P2_1/c$
temp, K	293	118
a, Å	6.978(2)	7.356(4)
b, Å	16.582(3)	24.058(13)
c, Å	10.307(3)	8.896(4)
β, deg	97.68(1)	98.84(4)
V, Å^3	1181.4	1555.6
Z	4	4
d_{calc}, g/cm^3	1.994 (293 K)	1.742 (118 K)
radiation	graphite-monochromated Mo Kα (0.71073 Å)	
scan technique	θ–2θ	θ–2θ
maximum 2θ, deg	60	60
criterion for observed	$F_o > 3\sigma(F_o)$	
no. of data measured	4032	4450
no. of unique obsd data	2421	2689
bkgd	profile analysis	
merging R value (F)	1.4%	3.7
final no. of variables	171	249
μ(Mo Kα), mm^{-1}	6.403	3.802
rel transm coeff	1.00–0.648	1.00–0.594
R_1	0.027	0.058
R_2	0.027	0.067
goodness of fit	1.121	1.093

Table II. Final Atomic Coordinates for Cs(12-$BrCB_{11}H_{11}$)

atom	x	y	z
Cs	0.71779(4)	−0.092304(14)	0.793502(24)
Br	0.24485(5)	−0.033599(20)	0.90070(4)
C(1)	0.2117(5)	0.22224(23)	0.6086(4)
B(1)	0.2365(5)	0.06490(20)	0.7889(3)
B(2)	0.4463(5)	0.10633(22)	0.7343(4)
B(3)	0.0358(5)	0.08248(23)	0.6692(4)
B(4)	0.3279(6)	0.15878(22)	0.8523(4)
B(5)	0.4105(6)	0.21055(24)	0.7210(4)
B(6)	0.0742(6)	0.14402(23)	0.8122(4)
B(7)	0.1206(6)	0.13501(27)	0.5401(4)
B(8)	0.0028(6)	0.18777(24)	0.6573(4)
B(9)	0.3732(6)	0.14943(25)	0.5807(4)
B(10)	0.2649(6)	0.05818(24)	0.6221(4)
B(11)	0.1834(6)	0.23462(23)	0.7696(4)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

Table III. Final Atomic Coordinates for Ag(12-$BrCB_{11}H_{11}$)C_6H_6

atom	x	z	z
Ag	0.19835(10)	0.060172(27)	0.40180(7)
Br	0.24019(12)	−0.01971(3)	0.60803(9)
C(1)	0.2795(11)	−0.2084(3)	0.3384(10)
B(1)	0.2488(13)	−0.0920(4)	0.4989(10)
B(2)	0.1274(13)	−0.1046(4)	0.3126(10)
B(3)	0.4596(13)	−0.1296(4)	0.5233(11)
B(4)	0.0647(12)	−0.1390(4)	0.4747(10)
B(5)	0.0731(12)	−0.1761(4)	0.3054(10)
B(6)	0.2691(11)	−0.1538(3)	0.6063(10)
B(7)	0.4696(13)	−0.1665(4)	0.3540(10)
B(8)	0.4039(12)	−0.2002(4)	0.5152(10)
B(9)	0.2635(13)	−0.1514(4)	0.2234(10)
B(10)	0.3747(12)	−0.0989(4)	0.3419(10)
B(11)	0.1581(12)	−0.2060(3)	0.4854(10)
C(2)	0.0604(13)	0.0942(5)	0.1288(11)
C(3)	0.1453(14)	0.0451(4)	0.1222(11)
C(4)	0.3173(15)	0.0427(4)	0.0842(10)
C(5)	0.4087(15)	0.0897(5)	0.0517(11)
C(6)	0.3206(18)	0.1404(5)	0.0585(12)
C(7)	0.1469(17)	0.1439(4)	0.0970(11)
H(1)	0.290(9)	−0.240(3)	0.290(8)
H(2)	0.063(12)	−0.070(4)	0.242(10)
H(3)	0.569(11)	−0.118(3)	0.586(9)
H(4)	−0.063(13)	−0.132(4)	0.493(10)
H(5)	−0.026(12)	−0.187(4)	0.240(9)
H(6)	0.278(11)	−0.154(3)	0.731(9)
H(7)	0.608(14)	−0.184(4)	0.315(11)
H(8)	0.480(12)	−0.240(4)	0.569(9)
H(9)	0.244(13)	−0.155(4)	0.094(11)
H(10)	0.432(13)	−0.067(4)	0.298(10)
H(11)	0.099(12)	−0.237(4)	0.513(10)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

atoms followed by application of the program DIRDIF.[21] Other programs used in these structure determinations included local modifications of Jacobson's ALLS, Zalkin's FORDAP, Busing and Levy's ORFFE, and Johnson's ORTEP2. Atomic form factors were from Cromer and Mann.[22] Real and imaginary corrections for anomalous dispersion in the form factor of silver, cesium and bromine atoms were from Liberman[23] and scattering factors for hydrogen were from Stewart et al.[24] All calculations were performed on a VAX 11/730 computer to yield coordinates of the remaining atoms. Hydrogen atom positions were convincingly found in difference Fourier calculations; coordinates and an isotropic temperature factor for each hydrogen atom were refined in subsequent least-squares refinement cycles. Final full-matrix least-squares refinement cycles utilized anisotropic thermal parameters for all heavy atoms and were carried to convergence yielding the discrepancy indices listed in Table I. Final atomic coordinates are listed in Tables II and III for the cesium and silver salts respectively.

Results

Lithiation. The reaction of 2 equiv of butyllithium with the trimethylammonium salt of $CB_{11}H_{12}^-$ is a convenient method of producing a soluble form of the *C*-lithio derivative, 1-$LiCB_{11}H_{12}^-$. The first equivalent reacts with the acidic cation producing butane and trimethylamine which are readily removed later by evaporation. The second equivalent reacts cleanly at room temperature with the anion to lithiate exclusively at carbon. Figures 1 and 2 show the stepwise progress of this reaction as followed by ^{11}B NMR spectroscopy. The chemical shifts of Li[$CB_{11}H_{12}$] (Figure 1) are very similar to those reported for the cesium salt of the parent carborane;[12] small solvents shifts of <1 ppm are evident. Upon conversion of the C–H bond to C–Li, the ^{11}B resonances respond with upfield shifts that chiefly seem to reflect proximity to the site of substitution. The five boron atoms closest to carbon, B(2–6), experience a ca. 4.2 ppm shift, the B(7–11) atoms experience ca. 2.8 ppm shift and the antipodal atom, B(12), is essentially uneffected. Judging from the absence of extraneous peaks in these spectra, the reaction appears to be clean and is limited only by one's ability to measure precise stoichiometries for the reagents. The reactivity of this species is summarized in Scheme I.

Treatment of this *C*-lithio derivative in situ with bromoethane, triphenylchlorosilane, trifluoroiodomethane and diphenylchlorophosphine lead to expected *C*-alkyl, *C*-silyl, and *C*-phosphino derivatives which were worked up via convenient extraction of their tetramethylammonium salts. The *C*-ethyl species from bromoethane, **2**, shows appropriate ^{1}H NMR resonances for the ethyl group (CH_2 quartet at 1.83, CH_3 triplet at 0.08 ppm) which are conveniently integrated against the Me_4N^+ counterion. The ^{11}B NMR shifts reflect substitution. There is an accidental degeneracy of the B(2–6) and B(7–11) resonances at −13.55 ppm and a moderate antipodal shift ca. 4 ppm upfield for B(12). The doublet for B(12) arises from splitting by its proton and, together with the simplicity of the spectrum, shows that ethylation has occurred exclusively at carbon rather than at any boron atom. The *C*-silyl species from triphenylchlorosilane, **3**, was characterized similarly. The *C*-trifluoromethyl species from trifluoroiodomethane, **4**, was characterized by ^{1}H, ^{11}B, and ^{19}F NMR. The ^{19}F signal at 32.8 ppm identifies the trifluoromethyl

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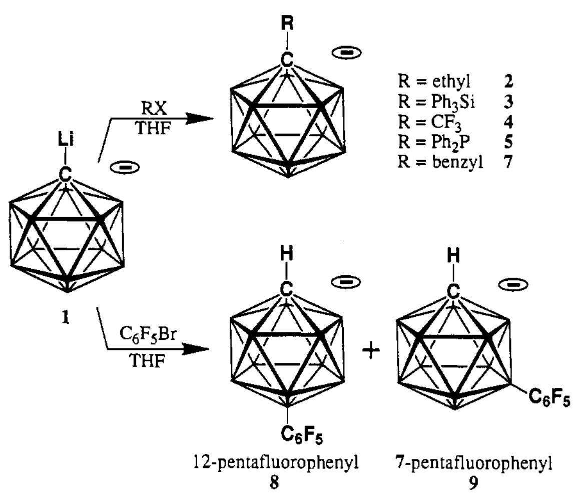
Scheme I. Reactivity of the 1-Lithio Derivative (**1**)



substituent, the ^{11}B shifts are large for the boron atoms close to this substituent, (4.4 ppm downfield for B(2–6), 2.2 ppm downfield for B(7–11)), and the proton-split doublet for B(12) proves that substitution has occurred at carbon. The *C*-phosphino species from diphenylchlorophosphine, **5**, was characterized in a similar manner via ^{1}H, ^{11}B, and ^{31}P NMR. The aerobic workup gives rise to some P(III) to P(V) oxidation giving 1-$Ph_2(OH)P$-$CB_{11}H_{11}$ (**6**) which although zwitterionic is overall neutral and is readily separated from anionic **5** by chromatography on silica gel.

Treatment of the *C*-lithio derivative with benzyl bromide leads to the expected *C*-benzyl derivative, **7**, as major product. It shows the expected ^{1}H and ^{11}B NMR features, and ^{11}B shifts are within <1 ppm of those of the analogous ethyl derivative, **2**. A minor product, partially purified from **7** by chromatography, is believed to be the 12-*B*-benzyl derivative since an unsplit singlet at –9.8 is observed in the nondecoupled ^{11}B spectrum.

Finally, treatment of the *C*-lithio derivative with pentafluorophenyl bromide leads to the unexpected B-substituted species **8** as the major product along with the 7-B-substituted species **9**. There is no evidence for a C-substituted derivative. HPLC was ineffective in achieving a good separation of these two B-substituted products. Nevertheless, the ^{11}B spectrum of the mixture could be readily analyzed in terms of the 12-(pentafluorophenyl) derivative showing the typical 1:5:5 splitting pattern which results from the high symmetry of 12-substitution along with the 1:1:1:2:2:2:2 splitting pattern of the C_{2v} 7-(pentafluorophenyl) derivative. Assignments were made unambiguous by 2-D ^{11}B–^{11}B NMR spectroscopy as indicated in the Experimental section.

Halogenation. Elemental bromine was used for monobromination at the 12-position by precise control of 1:1 stoichiometry in a two-phase solvent system. Alternatively, stoichiometric amounts of *N*-bromosuccinimide in dimethylformamide produce 12-$BrCB_{11}H_{11}^-$ (**10**). A slight deficit of reagent simplifies purification because starting material is readily removed by crystallization whereas the dibromo derivative, which arises from excess NBS, is difficult to separate. Similarly, *N*-chlorosuccinimide in a nearly 1:1 mole ratio produces the 12-chloro derivative **12**. Excess NBS effects 7,12-dibromination to give **11** and further halogenation does not appear to proceed at room temperature. To effect 7,12-di*chlor*ination with *N*-chlorosuccinimide to give **13**, however, the stoichiometry must be controlled close to 1:2 to prevent the apparent formation of a trichloro derivative. These halogenation reactions are summarized in Scheme II. All derivatives were characterized readily and unambiguously by their ^{11}B NMR spectra and by X-ray crystallography of the cesium and silver salts in the case of the mono-bromo derivative **10**. The ^{11}B NMR correlation diagram for the dihalogenation products is shown in Figure 3. The 1:5:5 splitting pattern of the C_{2v} parent carborane is seen to split into the 1:1:1:2:2:2:2 pattern of the C_{2v} products. As expected, the 12- and 7-positions show the greatest sensitivity to substitution.

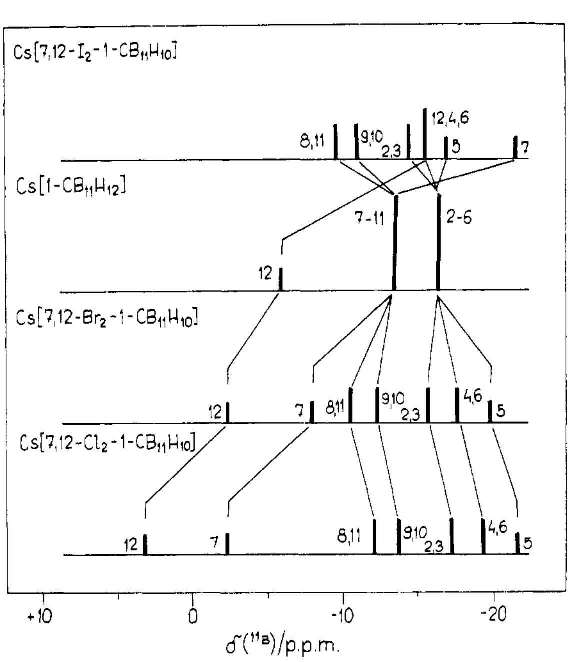
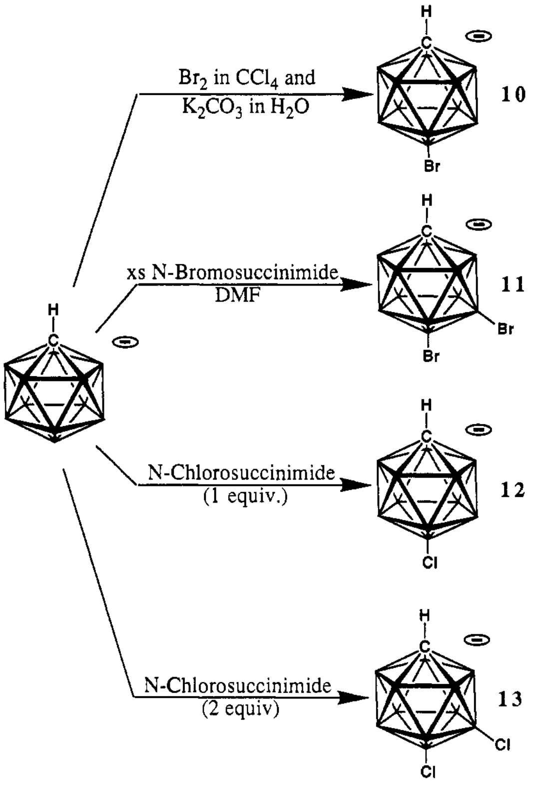


Figure 3. Correlation diagrams of chemical shifts and relative peak intensities in the ^{11}B NMR spectra of the Cs[7,12-$X_2CB_{11}H_{10}$] derivatives where X = I, Br, and Cl.

Scheme II. Controlled Halogenation of $CB_{11}H_{12}^-$



Mercuration. $CB_{11}H_{12}^-$ reacts readily with either $Hg(OOCCF_3)_2$ or $Hg(OOCCH_3)_2$ to give exclusively the 12-(mercuriotrifluoroacetate) or acetate derivatives **14a** and **14b** in good isolated yields. The ^{11}B NMR spectra of the extracted products show the clean and simple diagnostic 1:5:5 splitting typical of 12-substitution. There is no evidence for 7-substitution or 7,12-disubstitution. $HgCl_2$ does react with $CB_{11}H_{12}^-$ but gives a very low isolated yield of the desired 12-$HgClCB_{11}H_{11}^-$ derivative and was not pursued. The reactivity of the 12-$Hg(OOCCF_3)$ derivative has been explored with respect to reduction, thermal

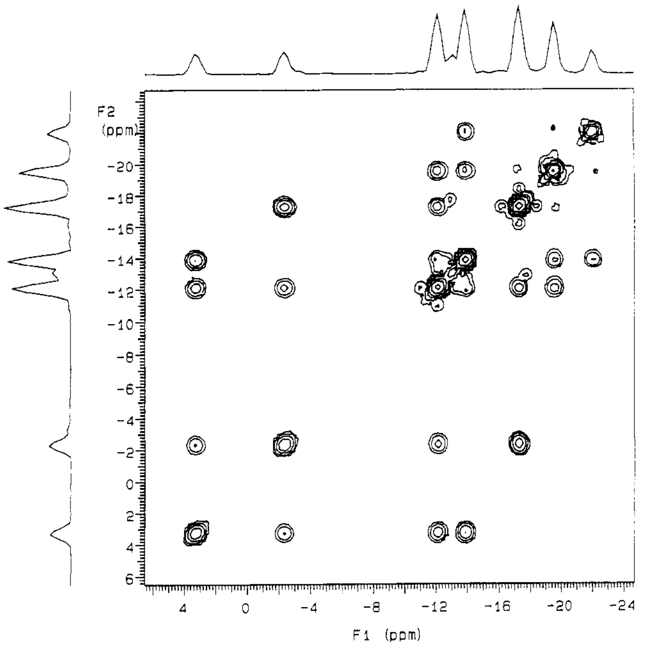
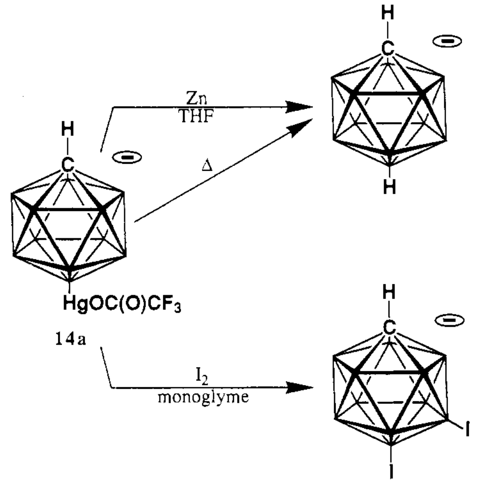


Figure 4. 2D ^{11}B–^{11}B NMR spectrum of $Cs[7,12\text{-}Cl_2CB_{11}H_{10}]$ (**13**) in $(CD_3)_2CO$.

Scheme III. Reactions of the 12-Mercury Trifluroacetate Derivative (**14a**)



decomposition and iodination. The reactions are summarized in Scheme III. Zinc in THF effects quantitative reduction to the parent carborane anion, $CB_{11}H_{12}^-$. Heating the Me_3NH^+ salt of the trifluoroacetate mercury derivative to ca. 160 °C in vacuo causes decomposition but ca. 60% recovery of the parent carborane is possible via appropriate extraction. Treatment of **14a** with 2 equiv of iodine gives a good yield of the 7,12-diiodo substituted product, which was characterized by comparison to the previously prepared cesium salt.[17]

X-ray Structures. Figure 5 displays the structure and numbering scheme for the carborane anion of $Cs[12\text{-}BrCB_{11}H_{11}]$; this figure also shows the position of the closest cesium ion. Despite involving the cesium ion to either a hydrogen or bromine atom of the closest six $12\text{-}BrCB_{11}H_{11}^-$ clusters are all long with Cs···H distances ranging from 3.04 Å upward and with Cs···Br distances ranging from 3.75 Å upward. Thus $Cs[12\text{-}BrCB_{11}H_{11}]$ is best described as a simple ionic salt; the environment around the cesium ion is shown in Figure 6. The cesium ions are well separated in the crystal lattice with the closest Cs···Cs distance equal to 6.20 Å. Individual values of bond distances and bond angles for $Cs[12\text{-}BrCB_{11}H_{11}]$ are tabulated in Tables SI and SII of the supplementary material. The average C–B distance is 1.701(6) Å,[25] and the average B–B distance is 1.768(10) Å. Neither set of distances are remarkable compared to the values found for derivatives of the $CB_{11}H_{12}^-$ ion.[2,26]

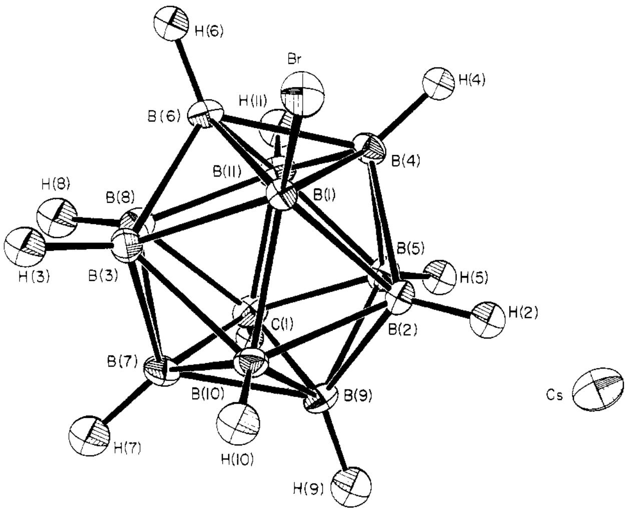


Figure 5. ORTEP diagram of the contents of an asymmetric unit of structure in $Cs[12\text{-}BrCB_{11}H_{11}]$. The labeling diagram for atoms of the carborane cage is illustrated. The same labeling scheme is also used for the cage in the silver salt. The position of the closest Cs^+ ion is shown.

The coordination geometry of the silver ion in $Ag[12\text{-}BrCB_{11}H_{11}]C_6H_6$ is shown in Figure 7. The silver ion has close contacts with three different cages and the benzene molecule; a more detailed view of the silver ion environment, along with its atomic separations, is given in Figure 8. The Ag···C distance of 2.485(9) Å and the Ag···H distances of 2.27 and 2.30 Å are all slightly longer than those seen in the silver salt of the $CB_{11}H_{12}^-$ ion,[26] in which the silver ion can be regarded as three-coordinate rather than four-coordinate as in the present case. This difference in coordination environment makes it difficult to draw conclusions about whether $BrCB_{11}H_{11}^-$ is more strongly coordinating than $CB_{11}H_{12}^-$. Individual values of bond distances and angles in the cluster and the silver ion are tabulated in Tables SIII and SIV. The average C–B distance is 1.701(9) Å, and the average B–B distance is 1.775(16) Å, and they are quite similar to those observed for $Cs[12\text{-}BrCB_{11}H_{11}]$. The B–Br distances are the same in both compounds with nominal values of 1.995(3) and 1.998(9) Å.

Discussion

Schemes I–III summarize the reactions that have been achieved. There are certain aspects of the general synthetic methodology that facilitate the isolation of good yields of pure crystalline products. One aspect is the frequent use of the Me_3NH^+ salt of the parent carborane. Treatment with base (e.g. BuLi or NaOH(aq)) gives rise to trimethylamine which, by virtue of its volatility, effectively removes the cation from the reaction and allows replacement by the cation of choice. The cation of choice is frequently Me_4N^+ because of the particular solubilities of Me_4N^+ carborane anion salts. For example, the C-substituted derivatives are typically soluble in diethylether as alkali metal salts but can be precipitated by the addition of aqueous $[Me_4N]Cl$. This allows ready separation of the product from organic soluble byproducts. On the other hand, the Me_4N^+ salts of several of the B-substituted derivatives are efficiently extracted from aqueous solutions into dichloromethane to effect purification. Plešek has noted the peculiar solubility characteristics of carborane anions.[13] Ex-

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(25) The numbers in parentheses are the estimated standard deviations calculated on the assumption that all values are drawn from the same population.

(26) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

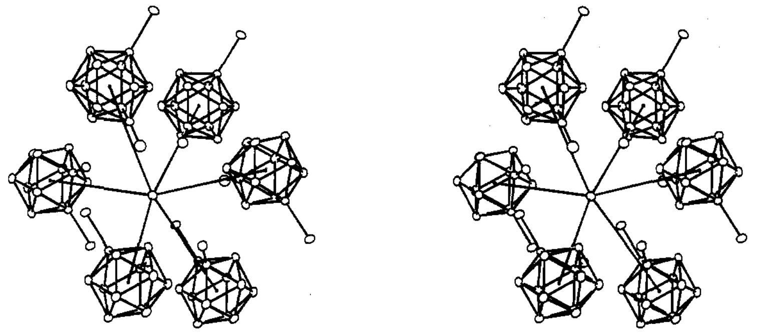

Figure 6. Stereoscopic diagram illustrating the environment of the cesium ion in Cs[12-BrCB$_{11}$H$_{11}$]. Lines are drawn between the Cs$^+$ ion and the center of each of the six cage ions that surround it. Only the bromine atoms and hydrogen atom substituents closest to the Cs$^+$ ion are shown.

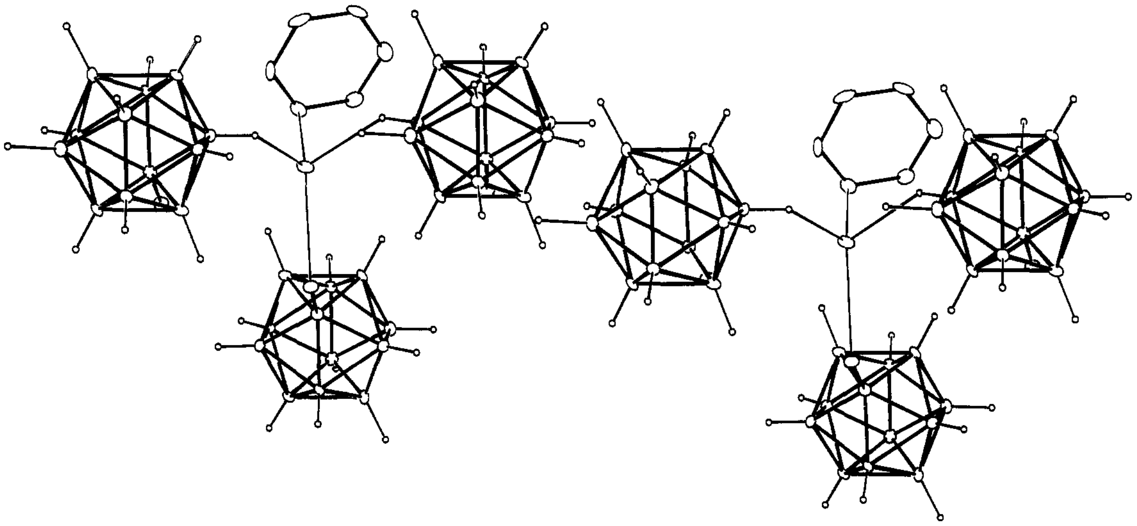

Figure 7. Stereoscopic diagram illustrating the pseudotetrahedral coordination around the silver ion in Ag(12-BrCB$_{11}$H$_{11}$)·C$_6$H$_6$.

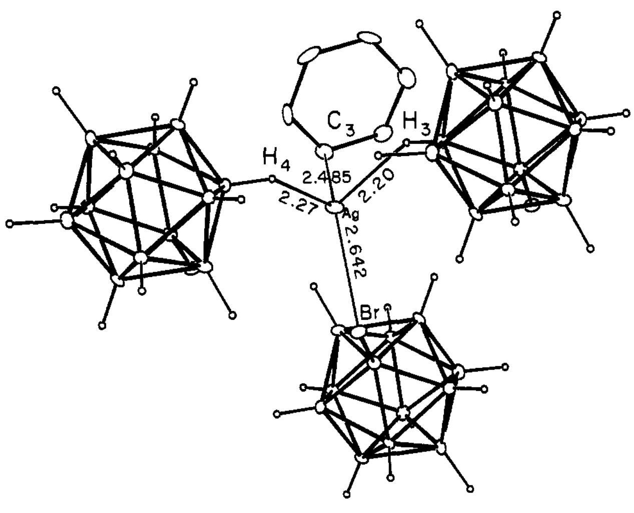

Figure 8. ORTEP diagram of the coordination sphere around the silver atom in Ag(12-BrCB$_{11}$H$_{11}$)·C$_6$H$_6$.

ploitation of these properties is essential to the successful isolation and purification of new carborane anions.

Solubility of the *C*-lithio compound has been achieved for the first time by capitalizing on some of the abovementioned phenomena and by virtue of the solubility of the lithium salt in ether solvents. Knoth et al.[10] had previously reported the lithiation of CB$_{11}$H$_{12}^-$ as the cesium salt but the marked insolubility of Cs[1-LiCB$_{11}$H$_{12}$] is problematic for controlled reactivity in subsequent substitution chemistry. Such solubility has allowed us to characterize the lithiated carborane by NMR spectroscopy.

The substitution that has been affected via the lithium derivative (Scheme I) further expands the scope of C-substitution. Various heteroatom-substituted derivatives have been reported with Si, S, O, and carboxy groups.[10,17] The present work extends this to *C*-alkyl, P, and fluorocarbon derivatives. The most unexpected result is the appearance of some B-substituted rather than C-substituted compounds. This is most notable in the C$_6$F$_5$ derivative where both B(12) and B(7) vertices are substituted and there is no evidence for any C-substitution. This unprecedented reaction raises interesting mechanistic questions. We are encountering further examples of substituent migration toward the most thermodynamically favored position in ongoing extensions of the present studies.

While butyllithium reacts with the most acidic proton in in CB$_{11}$H$_{12}^-$, and thus forms the C-metalated derivative, electrophilic mercury(II) salts attack at the most hydridic position to give B-metalated derivatives. The 12-position, antipodal to carbon, is the sole site of mercuration, and when the anion is acetate or trifluoroacetate, the reaction proceeds cleanly in good isolated yield. The use of this type of mercury derivative has considerable potential as an intermediate in the synthesis of a wide range of 12-substituted derivatives. In particular, we are finding that a variety of nucleophiles (sulfide, alkoxide, etc.) displace mercury to give 12- and sometimes 7-substituted derivatives. This work will be the subject of a future publication.

Finally, with regard to the synthetic accomplishments of the present work, the experimental conditions for control of mono-, di-, and hexahalogenation have been worked out to a high degree of selectivity. As expected for electrophilic attack, the mildest conditions give rise to monosubstitution at the 12-position. Disubstitution at the 12- and 7-positions has been facilitated by mercuration in the case of iodine, has been restricted to disubstitution by using *N*-bromosuccinimide in the case of bromine, and has been controlled by reagent stoichiometry in the case of chlorine. This degree of control is notable and contrasts sharply with disubstitution of the symmetrical parent borane $B_{12}H_{12}^{2-}$.[10]

Overall, the synthetic work opens up possibilities for the preparation of derivatives of $CB_{11}H_{12}^-$ with multiple and different substituents. Ultimately, many new anions should be available. Also, the present work suggests there is a comparably rich substitution chemistry to be explored in the analogous 10-vertex carborane $CB_9H_{10}^-$.[3] There are also opportunities to study the so-called *o*-, *m*-, and *p*-directing effects of substituents over the ring as well as opportunities to study the antipodal effect.[27] Future work will also include studies which systematically evaluate the relative nucleophilicity and chemical stability of these anions. Indications are that the brominated anions have surprisingly low nucleophilicity.[3]

Acknowledgment. This work was supported by the National Science Foundation (CHE 89-17666 to C.A.R.) and the National Institutes of Health (GM 38401 to W.R.S.). We thank Drs. J. Fusek for two-dimensional NMR spectra, J. D. Kennedy for ^{19}F spectra, B. Štíbr, J. Plešek, and S. Heřmánek for helpful discussions, and N. P. Rath for assistance with X-ray data collection and structure solution.

Supplementary Material Available: Tables SI–SIV, giving bond lengths and bond angles for $Cs(BrCB_{11}H_{11})$ and $Ag(12\text{-}BrCB_{11}H_{11}]\cdot C_6H_6$, respectively, and Tables SV–SVIII, giving anisotropic thermal parameters and hydrogen atom coordinates for the two structures, respectively (9 pages). Ordering information is given on any current masthead page. Structure factor tables are available from the authors.

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[27] Bühl, M.; Schleyer, P. v. R.; Halas, Z.; Hnyk, D.; Heřmánek, S. *Inorg. Chem.* **1991**, *30*, 3107.