6444 *Inorg. Chem.* **1998,** *37,* 6444−6451

Highly Chlorinated, Brominated, and Iodinated Icosahedral Carborane Anions: 1-H-$CB_{11}X_{11}^-$, 1-CH_3-$CB_{11}X_{11}^-$ (X = Cl, Br, I); 1-Br-$CB_{11}Br_{11}^-$

Zuowei Xie,* Chi-Wing Tsang, Eric Tung-Po Sze, Qingchuan Yang,
Dominic T. W. Chan, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin NT, Hong Kong, China

Received May 19, 1998

Direct chlorination of 1-CH_3-$CB_{11}H_{11}^-$ in glacial acetic acid gave the highly chlorinated carborane anion 1-CH_3-$CB_{11}Cl_{11}^-$, and treatment of 1-CH_3-$CB_{11}H_{11}^-$ with ICl in triflic acid afforded the highly iodinated carborane anion 1-CH_3-$CB_{11}I_{11}^-$. Under similar or more vigorous reaction conditions, however, the reaction of 1-CH_3-$CB_{11}H_{11}^-$ with Br_2 in triflic acid did not proceed to completion. The highly brominated carborane anion 1-CH_3-$CB_{11}Br_{11}^-$ was achieved via a sealed-tube reaction. This new method has led to the isolation of 1-H-$CB_{11}X_{11}^-$ (X = Cl, Br, I) and 1-Br-$CB_{11}Br_{11}^-$ in high yield. The lithiation of 1-H-$CB_{11}X_{11}^-$ resembles that of its parent anion $CB_{11}H_{12}^-$. Treatment of these lithio species with methyl iodide gave the methylated carborane anions 1-CH_3-$CB_{11}X_{11}^-$. These new weakly coordinating anions were fully characterized by ^1H, ^{13}C, and ^{11}B NMR, IR, and negative-ion MALDI MS spectroscopy. Some were further confirmed by single-crystal X-ray analysis.

Introduction

Icosahedral carboranes constitute a class of structurally unique molecules with exceptional thermal and chemical stabilities and with the ability to hold various substituents. These properties have made them as useful basic units for very weakly coordinating anions,[1] boron neutron capture therapy drugs,[2] and X-ray contrast agents.[3] Therefore, the derivatization of carboranes has received much attention.[1−4] We are particularly interested in the halogenation of icosahedral carborane anions since these derivatives constitute a new class of very weakly coordinating anions[1,5] and are finding many applications in metathesis, catalysis, and oxidation chemistry.[6−15] For example, the 7−12-hexahalogenated derivatives, $CB_{11}H_6X_6^-$ (X = Cl, Br, I), are larger, more thermodynamically stable, more chemically inert, less coordinating, and less nucleophilic than the parent $CB_{11}H_{12}^-$ ion.[6] They play a very important role in stabilizing coordinatively unsaturated cations such as the silylium ion (R_3Si^+),[7−10] the four-coordinate (tetraphenylporphyrinato)iron(III) ion (Fe(tpp)$^+$),[11] fullerene cation (C_{76}^+),[15] and hydronium ion ($H_9O_4^+$)[16] and in enhancing the reactivity of organolanthanide cations.[17] However, these anions along with the very recently reported polyfluorinated[18a] and permethylated[19] analogues are still not ideal weakly coordinating anions in terms of coordinating ability[7−10,18a] and stability toward oxidant[19] or extremely strong electrophiles.[17] Therefore, the search for the most stable and the least coordinating and soluble anion is of great interest and is a challenging target.

---

* Corresponding author. Fax: (852)26035057. Tel: (852)26096269. E-mail: zxie@cuhk.edu.hk.

(1) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.

(2) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950.

(3) (a) Peng, C. T. In *Burger's Medicinal Chemistry*, 4th ed.; Wolff, M. E., Ed.; John Wiley & Sons: New York, 1981; Part III, Chapter 61, p 1139. (b) Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. *J. Org. Chem.* **1996**, *61*, 9041.

(4) (a) Jelinek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982. (b) Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1332. (c) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2536. (d) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902. (e) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167. (f) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095. (g) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (h) Chizhevsky, I. T.; Johnson, S. E.; Knobler, C. B.; Gomez, F. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 6981. (i) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.

(5) (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955. (b) Shelly, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117.

(6) (a) Xie, Z.; Jelinek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907. (b) Reed, C. A.; Guiset, F. *J. Am. Chem. Soc.* **1996**, *118*, 3281.

(7) Xie, Z.; Liston, D. L.; Jelinek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384.

(8) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402.

(9) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933.

(10) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922.

(11) Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433.

(12) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

(13) (a) Turner, H. W. European Patent Application Nos. 88300698 and 88300699, 1988. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (c) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413.

(14) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897.

(15) Bolskar, R. D.; Mathur, R. S.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 13093.

(16) Xie, Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403.

(17) Xie, Z.; Liu, Z.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 3367.

(18) (a) Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 6419. (b) Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Paper presented at the 215th INOR 107; National Meeting of the American Chemical Society, Dallas, TX, March 29−April 2, 1998; see Abstract *J. Am. Chem. Soc.* **1998**, *120*, 4224.

(19) King, B. T.; Janousek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313.

10.1021/ic9805628 CCC: $15.00

It has been known that the halogenation of $CB_{11}H_{12}^-$ leads to not only increased stability but also decreased nucleophilicity.[6] The origin of this less coordinating ability may lie in a steric effect; that is, the five halogen atoms in the pentagonal belt (7−11-positions) can prevent the coordination of the most basic one (the 12-halo substituent) to the cation.[6−10] From this point of view, it seemed logical that the highly halogenated icosahedral carborane anions might be more stable and even less coordinating anions than other derivatives. On the other hand, highly iodinated carboranes are a new class of X-ray contrast agents.[3b] All of these features have driven us to initiate a program to carry out systematic studies on the halogenation of carborane anions and to search for the least coordinating anions. A preliminary result on the chlorination of 1-CH_3-$CB_{11}H_{11}^-$ has been communicated earlier.[20] We report here systematic studies on the chlorination, bromination, and iodination of the icosahedral carborane anions $CB_{11}H_{12}^-$ and 1-CH_3-$CB_{11}H_{11}^-$.

Experimental Section

General Procedures. All carborane anions prepared are air and moisture stable. However, some reagents used are moisture sensitive. Therefore, Schlenk and high-vacuum techniques were employed whenever necessary. The complexes $CB_{11}H_{12}^-$ [21] and 1-CH_3-$CB_{11}H_{11}^-$ [4a] were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on a Nicolet Magna 550 Fourier transform spectrometer. Negative-ion matrix-assisted laser desorption/ionization (MALDI) MS spectra were recorded on a Bruker APEX FTMS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to the residual protons of *d*-solvent or external TMS (0.00 ppm) for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts.

Preparation of [Me_3NH][1-CH_3-$CB_{11}Cl_{11}$] ([Me_3NH][1]). Chlorine gas was continuously bubbled into a glacial acetic acid solution (30 mL) of Cs[1-CH_3-$CB_{11}H_{11}$] (1.60 g, 5.52 mmol) at 85−90 °C under stirring for 1 week. The completion of this reaction can be monitored by ^{11}B NMR. After removal of most of the acetic acid, the viscous residue was dissolved in 5% sodium hydroxide (25 mL) and extracted with diethyl ether three times. The organic layer was concentrated and treated with an aqueous solution of Me_3NHCl. The precipitate was filtered off, washed with water, and dried under vacuum to give [Me_3NH][**1**] as a white solid (2.80 g, 85%). Recrystallization from a mixture of CH_3CN and toluene yielded colorless prisms of X-ray quality crystals. ^1H NMR (acetone-d_6): δ 1.55 (s, 3H), 3.18 (s, 9H). ^{13}C NMR (acetone-d_6): δ 49.67 (s, cage carbon), 44.98 [q, Me_3NH, $^1J(^{13}C-^1H) = 142.5$ Hz], 19.75 [q, CH_3, $^1J(^{13}C-^1H) = 128.6$ Hz]. ^{11}B NMR (acetone-d_6): δ −10.9 (s, 1B), −18.0 (s, 5B), −19.6 (s, 5B). IR (cm^{-1}, KBr): 3082 (m, br), 2803 (s), 1095 (s), 1035 (vs), 981 (s) 541(m). Negative-ion LSIMS, *m/z*: calcd for 1-CH_3-$CB_{11}Cl_{11}^-$ 535.9; found 535.8. The expected isotopic distribution of masses was also observed.

Alternate Method. To a THF solution (40 mL) of [Me_3NH][1-H-$CB_{11}Cl_{11}$] ([Me_3NH][**4**]) (0.90 g, 1.55 mmol) was slowly added *n*-BuLi (5.0 mL of a 1.6 M hexane solution, 8.00 mmol) at 0 °C under stirring. The mixture was stirred at room temperature for 4 h and refluxed for 6 h. After removal of Me_3N along with the solvent (20 mL) under vacuum and addition of fresh THF (20 mL), a THF solution (5 mL) of CH_3I (0.60 mL, 9.59 mmol) was added dropwise at 0 °C under stirring. The reaction mixture was stirred at room temperature for 4 h and then refluxed overnight. After removal of the volatile solvents, the viscous residue was treated with 5% NaOH (30 mL) and extracted with diethyl ether three times (3 × 20 mL). The ether solution was concentrated and treated with an aqueous solution of Me_3NHCl to give [Me_3NH][**1**] as a white solid (0.83 g, 90%).

Preparation of Ag[1-CH_3-$CB_{11}Cl_{11}$] (Ag[1]). To a suspension of [Me_3NH][**1**] (0.20 g, 0.34 mmol) in 25 mL of water was added 2 equiv of NaOH solution, and the mixture was stirred at 90 °C for 1 h. After removal of all trimethylamine under vacuum and neutralization of the resulting aqueous solution with 1 N HNO_3, an aqueous solution of $AgNO_3$ (0.087 g, 0.51 mmol) was added to give a milky solution with a white precipitate. The precipitate was collected by filtration, and the resulting solution was extracted with benzene three times (3 × 20 mL). Concentration of the benzene solution afforded a gray solid. Two portions of the solid were combined and washed with cold water twice, giving Ag[**1**] as a gray solid (0.21 g, 95%). ^1H NMR (acetone-d_6): δ 1.52 (s, 3H). ^{13}C NMR (acetone-d_6): δ 49.67 (s, cage carbon), 20.63 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B NMR (acetone-d_6): δ −5.20 (s, 1B), −12.20 (s, 5B), −13.70 (s, 5B). IR (cm^{-1}, KBr): 2969 (m, br), 2925 (s), 2854 (s), 1692 (s), 1383 (s), 1039 (vs), 543 (s).

Preparation of [Me_3NH][1-CH_3-$CB_{11}Br_{11}$] ([Me_3NH][2]). A thick-walled Pyrex tube was charged with Cs[1-CH_3-$CB_{11}H_{11}$] (0.11 g, 0.40 mmol), triflic acid (99%, 1.0 mL, 11.3 mmol), and Br_2 (1.0 mL, 19.4 mmol). This tube was then sealed under vacuum and placed in an oven. The temperature of the oven was gradually increased to 250 °C, and this temperature was maintained for 2 days. After removal of excess bromine and triflic acid, the residue was treated with a 5% aqueous NaOH solution until the pH of the solution reached about 7. The solution was then extracted with diethyl ether (3 × 20 mL). The ether portion was concentrated and treated with an aqueous solution of Me_3NHCl until no more precipitate was formed. The white precipitate was filtered off, washed with deionized water, and dried under vacuum, giving [Me_3NH][**2**] as a white solid (0.35 g, 81%). ^1H NMR (acetone-d_6): δ 1.74 (s, 3H), 3.01 (s, 9H). ^{13}C NMR (acetone-d_6): δ 55.76 (s, cage carbon), 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 144.8$ Hz], 20.59 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B NMR (acetone-d_6): δ 0.58 (s, 1B), −5.63 (s, 5B), −7.17 (s, 5B). IR (cm^{-1}, KBr): 3063 (s), 2954 (m, br), 1633 (m), 1473 (s), 1384 (s), 987 (vs). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-CH_3-$CB_{11}Br_{11}^-$ 1023.2 (90), 1024.2 (99), 1025.2 (100), 1026.2 (95), 1027.2 (82); found 1023.2 (92), 1024.2 (100), 1025.2 (95), 1026.2 (95), 1027.2 (80).

Alternate Method. To a THF solution (60 mL) of Cs[1-H-$CB_{11}Br_{11}$] (Cs[**5**]) (1.50 g, 1.31 mmol) was slowly added *n*-BuLi (4.80 mL of a 1.6 M hexane solution, 7.70 mmol) at 0 °C under stirring. The mixture was stirred at room temperature for 4 h and refluxed for 6 h. After removal of Me_3N along with the solvent (25 mL) under vacuum and addition of fresh THF (30 mL), a THF solution (5 mL) of CH_3I (0.60 mL, 9.59 mmol) was added dropwise at 0 °C under stirring. The reaction mixture was stirred at room temperature for 2 h and then refluxed overnight, followed by the analogous procedures used for [Me_3NH][**1**], to produce [Me_3NH][**2**] as a white solid (1.32 g, 93%).

Preparation of Ag[1-CH_3-$CB_{11}Br_{11}$] (Ag[2]). This compound was prepared in 90% yield as a white solid in a manner analogous to that used for Ag[**1**]. X-ray-quality crystals were grown from a saturated chlorobenzene solution at room temperature. ^1H NMR (acetone-d_6): δ 1.75 (s, 3H). ^{13}C NMR (acetone-d_6): δ 55.83 (s, cage carbon), 20.63 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B NMR (acetone-d_6): δ 2.74 (s, 1B), −3.47 (s, 5B), −4.93 (s, 5B). IR (cm^{-1}, KBr): 2954 (s), 2854 (s), 1622 (m), 1384 (vs), 989 (s), 451 (s).

Preparation of (*p*-xylene)Ag[1-CH_3-$CB_{11}HBr_{10}$]. A mixture of Cs[1-CH_3-$CB_{11}H_{11}$] (0.11 g, 0.40 mmol), triflic acid (15 mL), and Br_2 (5.0 mL) was refluxed for 1 month, followed by the analogous procedures used for [Me_3NH][**2**], generating a mixture of octa-, nona-, and decabromocarborane anions [Me_3NH][1-CH_3-$CB_{11}Br_xH_{11-x}$] ($x = 8-10$) in an approximate 1:6:2 ratio based on analyses of the mass spectra. Negative-ion MALDI MS *m/z*: calcd for 1-CH_3-$CB_{11}Br_8H_3^-$, 1-CH_3-$CB_{11}Br_9H_2^-$, and 1-CH_3-$CB_{11}Br_{10}H^-$, respectively, 788.2, 867.1, and 946.0; found 788.2, 867.1, and 946.1. The expected isotopic distribution of masses was also observed. [Me_3NH][1-CH_3-$CB_{11}Br_xH_{11-x}$] was then converted into Ag[1-CH_3-$CB_{11}Br_xH_{11-x}$] ($x = 8-10$) in the same manner as for Ag[**2**]. Fractional crystallization of this mixture from a hot *p*-xylene solution containing a small amount of

---

(20) Xie, Z.; Tsang, C.-W.; Xue, F.; Mak, T. C. W. *Inorg. Chem.* **1997**, *36*, 2246.

(21) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274. (b) Plesek, J.; Jelinek, T.; Drdakova, E.; Hermanek, S.; Stibr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559.

MeCN gave a few colorless crystals which were suitable for X-ray analysis. The composition was confirmed to be (*p*-xylene)Ag[1-CH$_3$-CB$_{11}$HBr$_{10}$].

Preparation of [Me$_3$NH][1-CH$_3$-CB$_{11}$I$_{11}$] ([Me$_3$NH][3]). A mixture of Cs[1-CH$_3$-CB$_{11}$H$_{11}$] (0.20 g, 0.69 mmol), triflic acid (10 mL), and ICl (3.36 g, 20.69 mmol) was heated at 150 °C for 10 days under stirring. The completion of this reaction can be monitored by ^{11}B NMR. After removal of most of the triflic acid and excess ICl, the residue was treated with a 5% NaOH solution (25 mL) and then a 10% NaHSO$_3$ solution (10 mL), followed by extraction with diethyl ether (3 × 20 mL). The ether solution was concentrated and treated with an aqueous solution of Me$_3$NHCl until no more precipitate was formed. The precipitate was filtered off and washed twice with water and then with a mixture of CH$_2$Cl$_2$/hexane (1:5) to give [Me$_3$NH][**3**] as a pale-yellow solid (0.70 g, 64%). ^{1}H NMR (acetone-d_6): δ 2.08 (s, 3H), 3.12 (s, 9H). ^{13}C NMR (acetone-d_6): δ 62.5 (s, cage carbon), 45.0 [q, Me$_3$NH, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 143.0$ Hz], 35.4 [q, CH$_3$, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 134.8$ Hz]. ^{11}B NMR (acetone-d_6): δ −4.8 (s, 1B), −8.3 (s, 5B), −11.6 (s, 5B). IR (cm^{-1}, KBr): 3126 (m, br), 2960 (m), 2925 (m), 2741 (m), 1616 (m), 1466 (s), 1382 (s), 1097 (m), 1021 (m), 933 (vs), 803 (s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-CH$_3$-CB$_{11}$I$_{11}^-$ 1541.1 (74), 1542.1 (100), 1543.1 (81); found 1541.0 (72), 1542.0 (100), 1543.0 (85).

Alternate Method. A thick-walled Pyrex tube was charged with Cs[1-CH$_3$-CB$_{11}$H$_{11}$] (0.050 g, 0.17 mmol) and iodine monochloride (1.0 mL, 19.6 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 220 °C, and this temperature was maintained for 2 days. The reaction mixture was then treated in a manner analogous to that described previously, yielding [Me$_3$NH][**3**] as a pale-yellow solid (0.25 g, 90%).

Preparation of [Me$_3$NH][1-H-CB$_{11}$Cl$_{11}$] ([Me$_3$NH][4]). A thick-walled Pyrex tube was charged with Cs[CB$_{11}$H$_{12}$] (0.08 g, 0.29 mmol), triflic acid (1.0 mL), and iodine monochloride (1.0 mL, 19.6 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 200 °C, and this temperature was maintained for 2 days. The reaction mixture was treated in a manner analogous to that used for [Me$_3$NH][**3**], yielding [Me$_3$NH][**4**] as a white solid (0.15 g, 89%). ^{1}H NMR (acetone-d_6): δ 2.75 (s, 1H), 3.15 (s, 9H). ^{13}C NMR (acetone-d_6): δ 47.4 [d, cage carbon, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 199.4$ Hz], 45.00 [q, Me$_3$NH, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 143.3$ Hz]. ^{11}B NMR (acetone-d_6): δ 2.15 (s, 1B), −5.27 (s, 5B), −8.36 (s, 5B). IR (cm^{-1}, KBr): 3199 (s), 3067 (m), 3031 (s), 2924 (m), 2795 (m), 1614 (s), 1477 (s), 1120 (vs), 1009 (vs), 531 (s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-H-CB$_{11}$Cl$_{11}^-$ 519.8 (85), 520.8 (97), 521.8 (100), 522.8 (94), 523.8 (80); found 519.8 (84), 520.8 (100), 521.8 (88), 522.8 (87), 523.8 (81).

Alternate Method. A thick-walled Pyrex tube was charged with Na[1-H-CB$_{11}$I$_{11}$] (Na[**6**]) (0.16 g, 0.10 mmol), triflic acid (1.0 mL), and iodine monochloride (0.50 mL, 9.80 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 200 °C, and this temperature was maintained for 2 days. The reaction mixture was then treated in the same manner described above, affording [Me$_3$NH][**4**] as a white solid (0.047 g, 81%).

Preparation of Ag[1-H-CB$_{11}$Cl$_{11}$] (Ag[4]). This compound was prepared in 88% yield as a white solid in a manner analogous to that used for Ag[**1**]. ^{1}H NMR (acetone-d_6): δ 2.70 (s, 1H). ^{13}C NMR (acetone-d_6): δ 47.57 [d, cage carbon, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 199.9$ Hz]. ^{11}B NMR (acetone-d_6): δ 2.20 (s, 1B), −5.20 (s, 5B), −8.30 (s, 5B).

Preparation of [Me$_3$NH][1-H-CB$_{11}$Br$_{11}$] ([Me$_3$NH][5]). A thick-walled Pyrex tube was charged with Cs[CB$_{11}$H$_{12}$] (0.11 g, 0.40 mmol), triflic acid (1.0 mL, 11.3 mmol), and bromine (1.0 mL, 19.4 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 200 °C, and this temperature was maintained for 4 days. The reaction mixture was treated in a manner analogous to that used for [Me$_3$NH][**2**], yielding [Me$_3$NH][**5**] as a white solid (0.35 g, 81%). ^{1}H NMR (acetone-d_6): δ 2.88 (s, 1H), 3.01 (s, 9H). ^{13}C NMR (acetone-d_6): δ 54.14 [d, cage carbon, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 187.4$ Hz], 45.00 [q, Me$_3$NH, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 144.8$ Hz]. ^{11}B NMR (acetone-d_6): δ 1.42 (s, 1B), −5.32 (s, 5B), −9.16 (s, 5B). IR (cm^{-1}, KBr): 3071 (m, br), 3028 (m), 2920 (s), 2785 (m), 1610 (s), 1473 (m), 991 (vs), 969 (s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-H-CB$_{11}$Br$_{11}^-$ 1009.2 (90), 1010.2 (99), 1011.2 (100), 1012.2 (94), 1013.2 (82); found 1009.2 (85), 1010.2 (100), 1011.2 (94), 1012.2 (92), 1013.2 (84).

Preparation of Cs[1-H-CB$_{11}$Br$_{11}$] (Cs[5]). To a suspension of [Me$_3$NH][1-H-CB$_{11}$Br$_{11}$] ([Me$_3$NH][**5**]) (0.15 g, 0.14 mmol) in 30 mL of water was added 2 equiv of NaOH, and the mixture was stirred at 90 °C for 2 h. After removal of the remaining trimethylamine, acetone (2 mL) was added to give a clear solution, and then CsCl (0.035 g, 0.20 mmol) was added. Slow evaporation of the solvent gave colorless crystals. Concentration and cooling to 5 °C afforded second batch of crystals over a period of weeks. The total amount of colorless crystals was 0.13 g (82%). X-ray-quality crystals were obtained from the slow evaporation of an acetone/water solution. ^{1}H NMR (acetone-d_6): δ 2.88 (s, 1H). ^{11}B NMR (acetone-d_6): δ 1.42 (s, 1B), −5.32 (s, 5B), −9.16 (s, 5B). IR (cm^{-1}, KBr): 3010 (s), 1384 (vs), 1104 (s), 970 (vs), 441 (s).

Preparation of Ag[1-H-CB$_{11}$Br$_{11}$] (Ag[5]). This compound was prepared in 90% yield as a white solid in a manner analogous to that used for Ag[**2**]. ^{1}H NMR (acetone-d_6): δ 2.89 (s, 1H). ^{13}C NMR (acetone-d_6): δ 54.14 [d, cage carbon, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 187.4$ Hz]. ^{11}B NMR (acetone-d_6): δ 1.60 (s, 1B), −5.10 (s, 5B), −9.00 (s, 5B). IR (cm^{-1}, KBr): 3013 (m), 1650 (s), 1612 (s), 1384 (vs), 1105 (s), 987 (vs), 440 (s).

Alternate Method. To a suspension of [Me$_3$NH][1-Br-CB$_{11}$Br$_{11}$] ([Me$_3$NH][**7**]) (0.15 g, 0.13 mmol) in 50 mL of water was added 2 equiv of an aqueous solution of NaOH, and the mixture was stirred at 50 °C for 1 h. After removal of the remaining trimethylamine under vacuum and neutralization of the resulting aqueous solution with 1 N HNO$_3$, AgNO$_3$ (0.050 g, 0.29 mmol) in 5 mL of water was added to give a gray precipitate. The suspension was then extracted with toluene (3 × 20 mL). Concentration of the toluene solution under vacuum afforded a white solid, which was washed with cold water twice, giving Ag[**5**] (0.12 g, 82%).

Preparation of [Me$_3$NH][1-H-CB$_{11}$I$_{11}$] ([Me$_3$NH][6]). A thick-walled Pyrex tube was charged with Cs[CB$_{11}$H$_{12}$] (0.050 g, 0.18 mmol) and iodine monochloride (1.0 mL, 19.6 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 200 °C, and this temperature was maintained for 2 days. The reaction mixture was then treated in a manner analogous to that used for [Me$_3$NH][**3**], yielding [Me$_3$NH][**6**] as a pale-yellow solid (0.25 g, 87%). ^{1}H NMR (acetone-d_6): δ 2.93 (s, 1H), 3.12 (s, 9H). ^{13}C NMR (acetone-d_6): δ 62.13 [d, cage carbon, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 192.2$ Hz], 45.00 [q, Me$_3$NH, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 144.8$ Hz]. ^{11}B NMR (acetone-d_6): δ −4.7 (s, 1B), −9.2 (s, 5B), −16.0 (s, 5B). These data are very similar to those reported in the literature.[3b]

Preparation of [Me$_3$NH][1-Br-CB$_{11}$Br$_{11}$] ([Me$_3$NH][7]). A thick-walled Pyrex tube was charged with Cs[CB$_{11}$H$_{12}$] (0.070 g, 0.25 mmol), triflic acid (1.0 mL, 11.3 mmol), and bromine (1.0 mL, 19.4 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 250 °C, and this temperature was maintained for 6 days. The reaction mixture was then treated in a manner analogous to that used for [Me$_3$NH][**5**], giving [Me$_3$NH][**7**] as a white solid (0.25 g, 87%). X-ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. ^{1}H NMR (acetone-d_6): δ 3.15 (s, 9H). ^{13}C NMR (acetone-d_6): δ 53.06 (s, cage carbon), 45.00 [q, Me$_3$NH, $^1J(^{13}\mathrm{C}-^1\mathrm{H}) = 144.8$ Hz]. ^{11}B NMR (acetone-d_6): δ 1.30 (s, 1B), −6.5 (s, 10B). IR (cm^{-1}, KBr): 3167 (m, br), 2925 (s), 2789 (m), 1473 (s), 1383 (vs), 1005 (s), 970 (s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-Br-CB$_{11}$Br$_{11}^-$ 1088.1 (91), 1089.1 (97), 1090.1 (100), 1091.1 (94), 1092.1 (84); found 1088.1 (98), 1089.1 (99), 1090.1 (100), 1091.1 (91), 1092.1 (82).

Alternate Method. A thick-walled Pyrex tube was charged with Cs[1-H-CB$_{11}$Br$_{11}$] (Cs[**5**]) (0.10 g, 0.087 mmol), triflic acid (1 mL), and bromine (1.0 mL, 19.4 mmol). This tube was then sealed under vacuum and placed in the oven. The temperature of the oven was gradually increased to 250 °C, and this temperature was maintained for 6 days, followed by the procedures described above to give [Me$_3$NH][**7**] as a white solid (0.085 g, 85%).

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for Ag[**2**], Cs[**5**], [Me_3NH][**7**], and (*p*-xylene)Ag[1-CH_3-$CB_{11}HBr_{10}$]

	Ag[**2**]	(*p*-xylene)Ag[1-CH_3-$CB_{11}HBr_{10}$]	[Me_3NH][**7**]	Cs[**5**]
formula	$C_2H_3B_{11}Br_{11}Ag$	$C_{10}H_{14}B_{11}Br_{10}Ag$	$C_4H_{10}B_{11}NBr_{12}$	$CHB_{11}Br_{11}Cs$
crystal size (mm)	0.45 × 0.24 × 0.14	0.35 × 0.25 × 0.08	0.22 × 0.20 × 0.16	0.27 × 0.38 × 0.52
fw	1132.83	1160.09	1149.96	1143.85
crystal class	orthorhombic	orthorhombic	orthorhombic	rhombohedral
space group	$C222_1$	$Pna2_1$	*Fmmm*	*R*3
a, Å	13.986(3)	14.053(1)	17.743(1)	9.824(1)
b, Å	24.201(5)	10.895(1)	17.760(1)	9.824(1)
c, Å	9.369(1)	17.931(1)	17.767(1)	22.098(4)
V, $Å^3$	3171(1)	2745(1)	5598(1)	1847.1(5)
Z	4	4	8	3
D_{calcd}, Mg/m^3	2.373	2.807	2.729	3.085
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
2θ range, deg	3.0−51.0	4.5−50.0	4.5−50.0	4.0−50.0
μ, mm^{-1}	14.488	15.292	17.168	19.338
F(000)	2008	2104	4128	1506
T, K	293	293	293	293
no. of obsd reflns	1567	2347	1323	1136
no. of params refnd	116	229	86	82
goodness of fit	1.134	1.075	0.905	1.024
R_1	0.096	0.123	0.031	0.034
wR_2	0.234	0.296	0.069	0.073

X-ray Structure Determination of Ag[2], Cs[5], [Me_3NH][7], and (*p*-xylene)Ag[1-CH_3-$CB_{11}HBr_{10}$]. All single crystals were immersed in Paraton-N oil and then sealed in thin-wall glass capillaries. Data were collected at 293 K either on a MSC/Rigaku RAXIS-IIC imaging plate or on a Rigaku AFC7R diffractometer using Mo Kα radiation (0.710 73 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program[22] or by using an empirical ψ-scan method. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL V 5.03 program package (PC version).[23] The hydrogen atoms were geometrically fixed using the riding model. In the solid-state structure of Ag[1-CH_3-$CB_{11}Br_{11}$] (Ag[**2**]), the carbon and the boron atoms of the icosahedral cage are indistinguishable; they are represented by atoms B(1)−B(6). The exohedral CH_3 group is thus completely mixed with the 11 bromine atoms of the cage anion. Each of the six independent bromine atoms is assigned an SOF of 0.931, which is calculated from the equation (6 + 11 × 35)/(12 × 35). In the solid-state structure of Cs[1-H-$CB_{11}Br_{11}$] (Cs[**5**]), the carbon and the boron atoms of the icosahedral cage are indistinguishable; they are represented by atoms B(1)−B(4). The exohedral H atom is thus completely mixed with the 11 bromine atoms of the cage anion. Each of the four independent bromine atoms is assigned an SOF (site occupancy factor) of 0.919, which is calculated from the equation (1 + 11 × 35)/(12 × 35). The Cs atom in Cs[**5**] is disordered over two sets of positions with 0.50: 0.50 occupancies. Crystal data and details of data collection and structure refinement are given in Table 1. Further details are included in the Supporting Information.

Results and Discussion

Synthesis. Perchlorinated, perbrominated, and periodinated polyhedral boranes are known and were readily prepared from the reactions of the polyhedral analogues with excess amounts of *N*-chlorosuccinimide, *N*-bromosuccinimide, and iodine, respectively.[24] Under similar or more vigorous reaction conditions, however, the chlorination or bromination of $CB_{11}H_{12}^-$ did not proceed to completion, giving a mixture of polyhalocarborane anions. For example, treatment of $CB_{11}H_{12}^-$ with large excess amounts of chlorine gas in glacial acetic acid or CCl_2HCCl_2H at 90−120 °C for 1 month afforded a mixture of nona-, deca-, and undecachlorocarborane anions, $CB_{11}Cl_xH_{12-x}^-$ ($x = 9-11$), in an approximate 3:5:2 ratio based on analyses of the negative-ion MALDI MS spectra. Addition of a Lewis acid catalyst such as $AlCl_3$ to the reaction system or extension of the reaction time can only slightly change the molar ratio of each component but cannot result in the completion of this reaction. Similarly, reaction of $CB_{11}H_{12}^-$ with large excess amounts of bromine in reflux glacial acetic acid or CCl_2HCCl_2H or triflic acid for 4 weeks gave a mixture of hepta-, octa-, and nonabromocarborane anions $CB_{11}Br_xH_{12-x}^-$ ($x = 7-9$), in an approximate 4:6:1 ratio based on analyses of the negative-ion MALDI MS spectra. This reaction did not proceed to completion even with the aid of $AlCl_3$ or a UV lamp. However, treatment of $CB_{11}H_{12}^-$ with large excess amounts of ICl in CCl_2HCCl_2H at 150 °C produced 1-H-$CB_{11}I_{11}^-$ in 56% yield;[3b] reaction of $CB_{11}H_{12}^-$ with diluted F_2 gas at room temperature afforded 1-H-$CB_{11}F_{11}^-$.[18b] It seems that both the halogenation reagents and the halogen substituents on the cage could affect the results of these halogenation reactions. On one hand, the electron-withdrawing nature of the halogen atoms can reduce the electron density of the cage so as to slow or perhaps inhibit the electrophilic substitution reactions of the remaining B−H bonds of the carborane anion; on the other hand, the stronger halogenation reagent can promote such electrophilic substitution reactions. In case of the halogenation reagents being identical, the overall electronic effect of substituents on the carborane cage plays an important role in the halogenation of carborane anions. It is therefore logical to introduce an electron-donating group onto the cage to balance the electronic effects caused by the halogen substituents in order to promote the electrophilic substitution reactions of B−H bonds.

Direct chlorination of 1-CH_3-$CB_{11}H_{11}^-$ in glacial acetic acid at 85−90 °C for 1 week led to the isolation of the single product 1-CH_3-$CB_{11}Cl_{11}^-$ (**1**) in 85% yield. Methylation of the C−H bonds of polychlorocarborane anions $CB_{11}Cl_xH_{12-x}^-$ ($x = 9-11$) using the general procedure for *C*-alkylation[4a] and followed by direct chlorination can also generate the single product **1** in high yield. These results indicate that the presence of the methyl group on the carborane cage is critical for converting all BH to BCl vertexes. Similarly, treatment of 1-CH_3-$CB_{11}H_{11}^-$ with an

---

[22] Higashi, T. *ABSCOR*−*An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corp.: Tokyo, 1995.

[23] *SHELXTL V 5.03 program package*; Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1995.

[24] Wong, E. H.; Kabbani, R. M. *Inorg. Chem.* **1980**, *19*, 451.

excess of ICl in triflic acid at 150 °C for 10 days afforded $1\text{-}CH_3\text{-}CB_{11}I_{11}^-$ (**3**) in 64% yield. If CCl_2HCCl_2H was used as a solvent instead, the above iodination reaction proceeded slowly.

Unlike the chlorination and iodination reactions, under similar or more vigorous reaction conditions, bromination of $1\text{-}CH_3\text{-}CB_{11}H_{11}^-$ did not proceed to completion, giving a mixture of octa-, nona-, decabromocarborane anions $1\text{-}CH_3\text{-}CB_{11}Br_xH_{11-x}^-$ ($x = 8-10$), in an approximate 1:6:2 ratio based on analyses of the mass spectra. The results show that the electron-donating methyl group can only help to put one more bromine atom onto the carborane cage as compared to the bromination of its parent $CB_{11}H_{12}^-$ ion. A Lewis acid catalyst such as $AlCl_3$ does not promote the reaction to give a single product. To prepare $1\text{-}CH_3\text{-}CB_{11}Br_{11}^-$, a stronger bromination reagent and/or even more vigorous reaction conditions are needed.

Reaction of $1\text{-}CH_3\text{-}CB_{11}H_{11}^-$ with an excess of bromine in triflic acid in a sealed tube at 250 °C for 2 days surprisingly produced the exclusive complex $1\text{-}CH_3\text{-}CB_{11}Br_{11}^-$ (**2**) in almost quantitative yield according to ^{11}B NMR spectroscopy. This new synthetic method is so powerful that we extend it to the parent carborane anion $CB_{11}H_{12}^-$.

Under sealed-tube reaction conditions, treatment of $CB_{11}H_{12}^-$ with an excess of bromine in triflic acid at 200 °C for 4 days generated $1\text{-}H\text{-}CB_{11}Br_{11}^-$ (**5**) exclusively. If the reaction temperature was increased to 250 °C and maintained for 6 days, the C−H bond in **5** was also brominated to give the perbrominated carborane anion $1\text{-}Br\text{-}CB_{11}Br_{11}^-$ (**7**). Figure 1 shows the progress of this reaction followed by ^{11}B NMR. Interestingly, treatment of $CB_{11}Br_{12}^-$ with an aqueous solution of $AgNO_3$ at room temperature gave $1\text{-}H\text{-}CB_{11}Br_{11}^-$ quantitatively according to ^{11}B NMR. The mechanism of this debromination reaction is not clear. But it may involve a redox reaction.

Under similar reaction conditions, a mixture of $CB_{11}H_{12}^-$, excess of ICl, and triflic acid was sealed in a Pyrex tube and then heated at 200 °C for 2 days to give the unprecedented product $1\text{-}H\text{-}CB_{11}Cl_{11}^-$ (**4**) in high yield, which offers a new method to prepare the undecachlorocarborane anion. On the other hand, in the absence of triflic acid, the same reaction gave the sole product $1\text{-}H\text{-}CB_{11}I_{11}^-$ (**6**). Similarly, treatment of $1\text{-}CH_3\text{-}CB_{11}H_{11}^-$ with excess ICl in a sealed tube at 220 °C for 2 days produced the pure complex $1\text{-}CH_3\text{-}CB_{11}I_{11}^-$ (**3**). If this reaction was performed in triflic acid solution for 2 days, the major complex $1\text{-}CH_3\text{-}CB_{11}Cl_6I_5^-$ and a small amount of $1\text{-}CH_3\text{-}CB_{11}Cl_{11-x}I_x^-$ ($x = 4, 3$) were detected by negative-ion MALDI MS spectroscopy. To gain some insight into these reactions, treatment of $1\text{-}H\text{-}CB_{11}I_{11}^-$ with excess ICl in triflic acid under the reaction conditions mentioned above produced complex **4** exclusively. On the basis of the above results, a mechanism may be proposed. The electrophilic substitution of $CB_{11}H_{12}^-$ with ICl gives the intermediate $1\text{-}H\text{-}CB_{11}I_{11}^-$, followed by the nucleophilic substitution to generate $1\text{-}H\text{-}CB_{11}Cl_{11}^-$, which is promoted by the strong triflic acid. In the case of $1\text{-}CH_3\text{-}CB_{11}H_{11}^-$, the electron-donating methyl group could slow the nucleophilic substitution reaction so that the partially substituted products were detected.

The lithiation of $1\text{-}H\text{-}CB_{11}X_{11}^-$ is just similar to that of the parent $CB_{11}H_{12}^-$ ion.[4a] For example, $1\text{-}H\text{-}CB_{11}Cl_{11}^-$ can be easily lithiated with *n*-BuLi, and treatment of the lithio species with CH_3I leads to the *C*-methylated product $1\text{-}CH_3\text{-}CB_{11}Cl_{11}^-$ (**1**). In principle, *C*-alkylated products of the type $1\text{-}R\text{-}CB_{11}Cl_{11}^-$ could be prepared in the same manner. Since the solubility of these anions is dependent upon the substituent R, a variety of new weakly coordinating anions with different solubility would be available for various purposes. All of the above synthetic routes for highly halogenated carborane anions are summarized in Scheme 1.

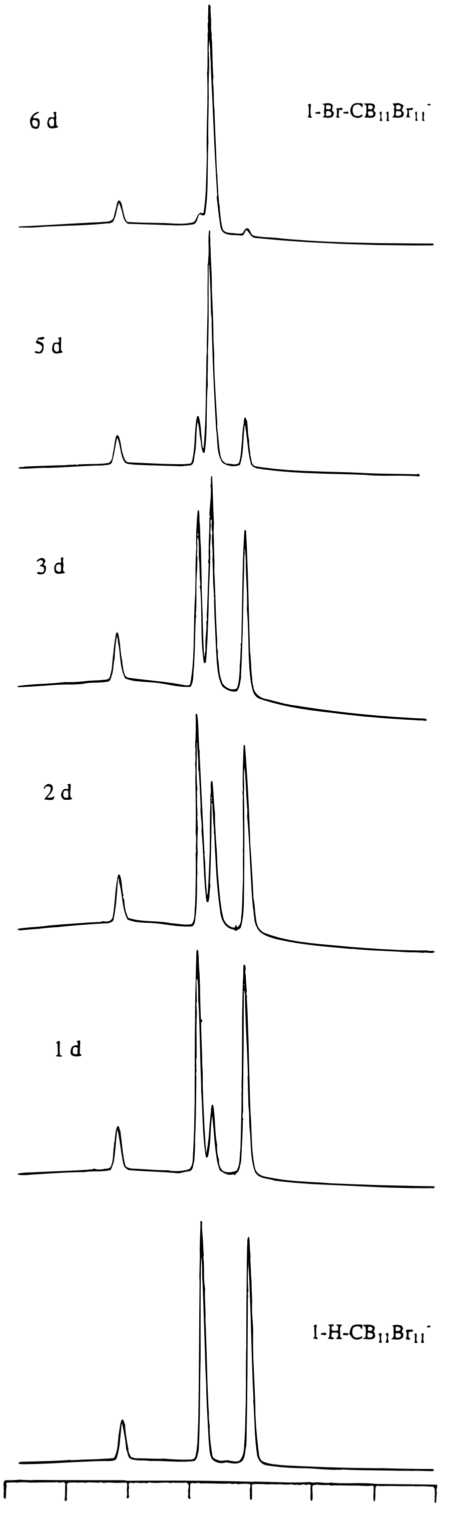
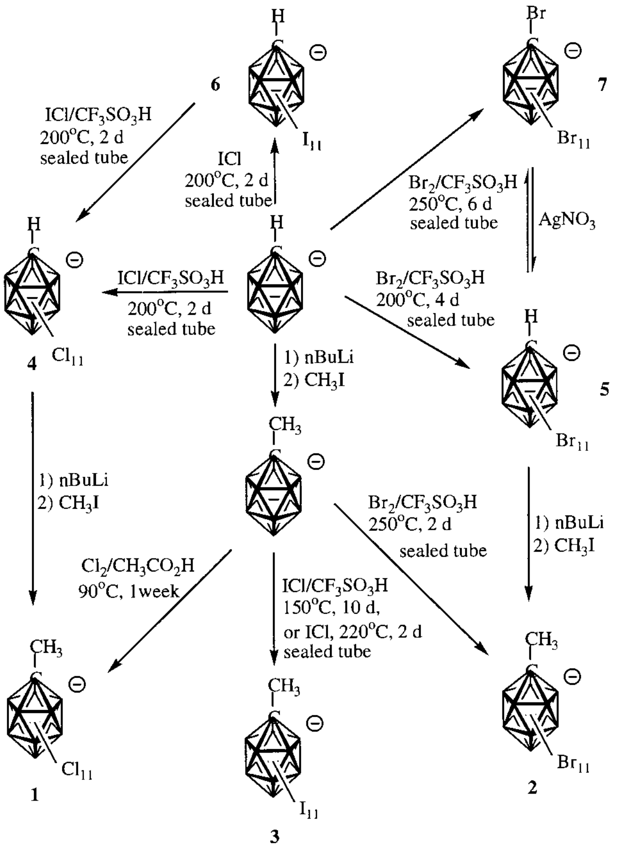


Figure 1. Progress of the reaction of $Cs[1\text{-}H\text{-}CB_{11}Br_{11}]$ with Br_2 followed by ^{11}B NMR.

These highly chlorinated, brominated, and iodinated icosahedral carborane anions were fully characterized by ^1H, ^{13}C, and ^{11}B NMR, negative-ion MALDI MS, and IR spectroscopy. Some of them were further confirmed by single-crystal X-ray analyses. They are quite thermally stable, with no decomposition up to 250 °C. They are also stable in very strong acids

Scheme 1. Synthetic Routes for Highly Halogenated Carborane Anions



such as triflic acid and strong bases such as NaOH. No new peak was detected by ^{11}B NMR if 1-CH$_3$-CB$_{11}$X$_{11}{}^-$ was treated with a saturated aqueous solution of NaOH at 90 °C for 24 h.

The silver salts of various carborane anions were readily prepared by treatment of their sodium salts with 1.2 equiv of AgNO$_3$ in water solution or a mixture of water/acetone. The solubilities of these silver(I) salts in various solvents are similar to those of the hexahalocarborane analogues.[6a]

Spectroscopic Characterization. ^{11}B NMR is an extremely useful technique for the characterization of boron compounds. Figure 2 shows the proton-coupled ^{11}B NMR spectra of [Me$_3$NH][1-CH$_3$-CB$_{11}$X$_{11}$] (X = Cl, Br, I) and [Me$_3$NH][1-CH$_3$-CB$_{11}$H$_{11}$] in acetone-d_6. Both proton-coupled and proton-decoupled ^{11}B NMR spectra of 1-CH$_3$-CB$_{11}$X$_{11}{}^-$ are identical, and they all exhibit typical 1:5:5 splitting patterns, which are consistent with undecahalocarborane anions and C_{5v} symmetry. The complete conversion of BH vertexes into BX vertexes is also indicated by the absence of the characteristic B−H absorption (ca. 2600 cm^{-1}) in their IR spectra. The presence of the CH$_3$ substituent on the cage is clearly shown by ^{1}H and proton-coupled ^{13}C NMR spectra as well as by the negative-ion MALDI MS spectra.

As expected for the undecahalocarborane anions 1-H-CB$_{11}$X$_{11}{}^-$ (X = Cl, Br, I), both proton-coupled and proton-decoupled ^{11}B NMR spectra are identical with the typical 1:5:5 splitting pattern (Figure 3). ^{1}H and proton-coupled ^{13}C NMR, IR, and negative-ion MALDI MS spectra all support the composition of 1-H-CB$_{11}$X$_{11}{}^-$. Upon comparison of Figures 2 and 3, it is interesting to note that, after conversion of the CH vertex into a CCH$_3$ vertex, the ^{11}B chemical shifts of 10 BH vertexes from 2- to 11-positions in 1-CH$_3$-CB$_{11}$H$_{11}{}^-$ become identical. Consequently, the differences in ^{11}B chemical shifts between two pentagonal belts in 1-CH$_3$-CB$_{11}$X$_{11}{}^-$ are smaller than those for 1-H-CB$_{11}$X$_{11}{}^-$, indicating the electron-donating effect of the CH$_3$ group. Similar results are also observed in their ^{13}C NMR spectra.

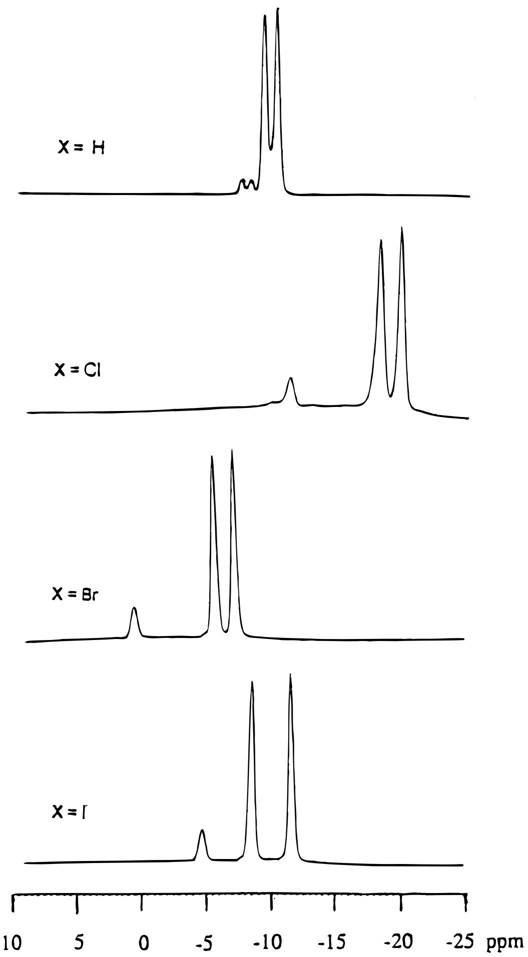


Figure 2. ^{11}B NMR spectra of [Me$_3$NH][1-CH$_3$-CB$_{11}$X$_{11}$] in acetone-d_6.

Crystal Structure of Ag(1-CH$_3$-CB$_{11}$Br$_{11}$) (Ag[2]). Recrystallization of Ag[**2**] from chlorobenzene at room temperature gave X-ray-quality single crystals. Figure 4 shows the coordination around silver in the solid-state structure of Ag[**2**]. Like the other silver(I) salts of icosahedral carborane anions,[4a,5,6a,18a,25] it is a one-dimensional coordination polymer with undecabromocarborane anions acting as bridging ligands. The silver atom sits on a 2-fold axes, and its six-coordinate geometry is very similar to that found in Ag(CB$_{11}$H$_6$Br$_6$)[25] and in the complex ion Ag(CB$_{11}$H$_6$Br$_6$)$_2{}^-$,[11] with the metal atom bonding to three bromine atoms from each of two bridging 1-CH$_3$-CB$_{11}$Br$_{11}{}^-$ anions. The anion has crystallographically imposed C_2 symmetry, which prohibits differentiation of the carbon atom from the boron atoms within the cage. The exohedral CH$_3$ group is thus completely mixed with the 11 bromine atoms of the cage anion. Therefore it is not possible to distinguish the BBr vertex antipodal to carbon from other vertexes. Unlike in the solid-state structure of Ag(CB$_{11}$H$_6$Br$_6$),[25] where the most basic bromine atom attached to B(12) antipodal to carbon is shared by two silver ions, there is no bromine atom shared by the silver ion in Ag[**2**], perhaps reflecting the steric effect and/or the fact that there is no significantly electron-rich bromine atom on the

---

(25) Xie, Z.; Wu, B.-M.; Mak, T. C. W.; Manning, J.; Reed, C. A. *J. Chem. Soc., Dalton Trans.* **1997**, 1213.

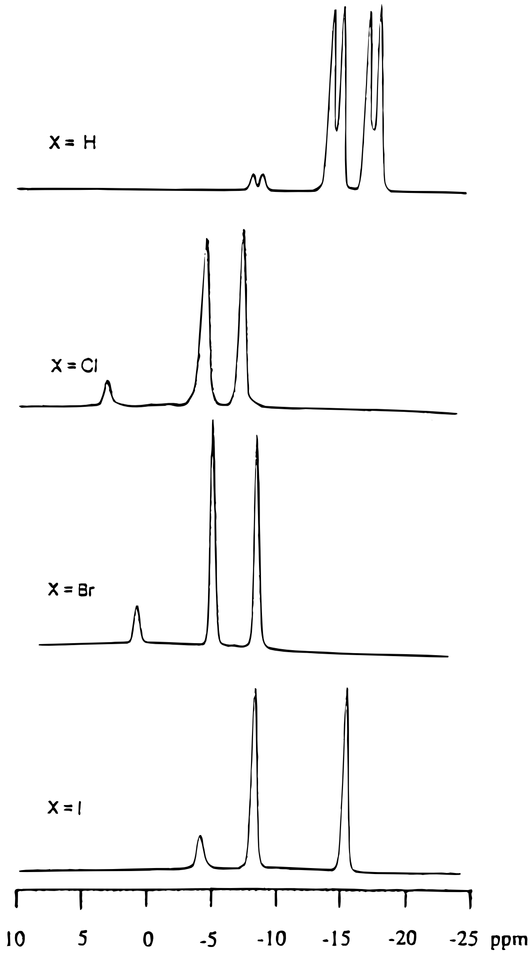


Figure 3. ^{11}B NMR spectra of $[Me_3NH][1\text{-}H\text{-}CB_{11}X_{11}]$ in acetone-d_6.

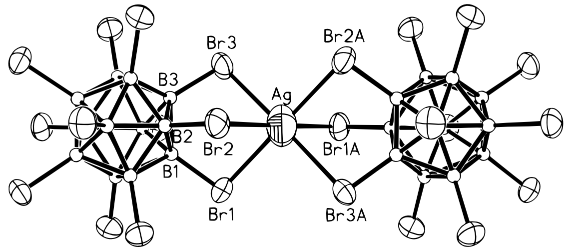


Figure 4. Perspective view of the coordinating sphere around the silver atom in Ag[**2**] showing a portion of the infinite Ag···[**2**]···Ag···[**2**] polymeric chain. Note that the C and B atoms of the icosahedral cage are indistinguishable and the exohedral methyl group is completely scrambled with the 11 Br atoms.

cage. The selected bond distances and angles for various carborane compounds are listed in Table 2. The average Ag−Br distance of 2.848(5) Å is slightly shorter than the 2.862(2) Å average in $Ag(CB_{11}H_6Br_6)$ and the 2.879(3) Å average in $Ag(CB_{11}H_6Br_6)_2^-$ [11] but lies in the range found in dibromoalkane complexes of silver(I): 2.816(2)−3.081(2) Å.[26] The average B−Br distance, 1.948(8) Å, falls in the range 1.92−2.05 Å normally observed in complexes of the $CB_{11}H_6Br_6^-$ anion.[8,9,11,25]

Due to the fact that the carbon atom is indistinguishable from the boron atoms within the cage in the crystal structure of Ag[**2**], it is not possible to know if the BBr vertex antipodal to C is still the most electron-rich side. To compare the charge distributions on the highly brominated carborane cage, it would be nice to have another crystal structure of similar molecule.

Table 2. Selected Bond Distances (Å)[a]

	Compound Ag[**2**]		
Br(1)−B(1)	1.950(8)	Br(1)−Ag	2.884(5)
Br(2)−B(2)	1.953(8)	Br(2)−Ag	2.811(5)
Br(3)−B(3)	1.950(8)	Br(3)−Ag	2.850(2)
Br(4)−B(4)	1.941(8)	Ag−Br(2)#1	2.811(5)
Br(5)−B(5)	1.950(8)	Ag−Br(3)#1	2.850(2)
Br(6)−B(6)	1.944(8)	Ag−Br(1)#1	2.884(5)
	Compound(η^2-*p*-xylene)Ag[1-CH_3-$CB_{11}HBr_{10}$]		
Ag(1)−C(4)	2.485(5)	Br(5)−B(5)	1.913(3)
Ag(1)−C(5)	2.514(5)	Br(6)−B(6)	1.912(4)
Ag(1)−Br(9)	2.972(2)	Br(7)−B(7)	1.921(3)
Ag(1)−Br(12)	2.818(2)	Br(8)−B(8)	1.912(5)
Ag(1)−Br(7)#2	2.824(2)	Br(9)−B(9)	1.907(4)
Ag(1)−Br(11)#2	2.944(2)	Br(10)−B(10)	1.916(4)
Br(3)−B(3)	1.902(4)	Br(11)−B(11)	1.919(4)
Br(4)−B(4)	1.901(5)	Br(12)−B(12)	1.912(4)
	Compound [Me_3NH][**7**]		
Br(1)−B(1)	1.933(5)	Br(3)−B(3)	1.925(5)
Br(2)−B(2)	1.922(5)	Br(5)−B(5)	1.924(5)
Br(4)−B(4)	1.923(5)	Br(6)−B(6)	1.924(5)
	Compound Cs[**5**]		
Br(1)−B(1)	1.917(3)	Cs(1)−Br(2)#3	3.708(1)
Br(2)−B(2)	1.922(4)	Cs(1)−Br(2)#4	3.708(1)
Br(3)−B(3)	1.930(3)	Cs(1)−Br(2)#5	3.708(1)
Br(4)−B(4)	1.925(3)	Cs(1)−Br(3)#6	3.757(1)
		Cs(1)−Br(3)#7	3.757(1)
		Cs(1)−Br(3)#8	3.757(1)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, y, -z - {}^{1}/_{2}$; (#2) $x - {}^{1}/_{2}, -y - {}^{1}/_{2}, z$; (#3) $x - {}^{1}/_{3}, y + {}^{1}/_{3}, z + {}^{1}/_{3}$; (#4) $-y + {}^{5}/_{3}, x - y + {}^{4}/_{3}, z + {}^{1}/_{3}$; (#5) $-x + y + {}^{2}/_{3}, -x + {}^{7}/_{3}, z + {}^{1}/_{3}$; (#6) $-x + y + {}^{5}/_{3}, -x + {}^{7}/_{3}, z + {}^{1}/_{3}$; (#7) $x - {}^{1}/_{3}, y + {}^{4}/_{3}, z + {}^{1}/_{3}$; (#8) $-y + {}^{2}/_{3}, x - y + {}^{1}/_{3}, z + {}^{1}/_{3}$.

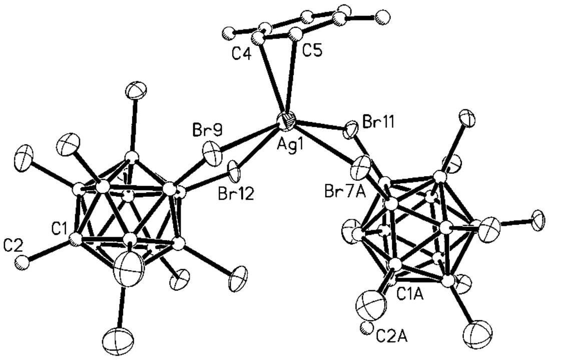


Figure 5. Perspective view of (*p*-xylene)Ag(1-CH_3-$CB_{11}HBr_{10}$).

Crystal Structure of (η^2-*p*-xylene)Ag(1-CH_3-$CB_{11}HBr_{10}$). Fractional crystallization of Ag(1-CH_3-$CB_{11}H_{11-n}Br_n$) (n = 8−10) from a hot *p*-xylene solution containing a very small amount of MeCN gave X-ray-quality crystals of (*p*-xylene)Ag(1-CH_3-$CB_{11}HBr_{10}$), which may be the least soluble salt among the others so as to crystallize out first. Unlike the unsolvated Ag[**2**], (*p*-xylene)Ag(1-CH_3-$CB_{11}HBr_{10}$) has a five-coordinate silver atom in a propeller arrangement of one η^2-*p*-xylene and two bidentate bridging 1-CH_3-$CB_{11}HBr_{10}^-$ ions (Figure 5), which is similar to the solid-state structure of (η^2-*p*-xylene)Ag($CB_{11}H_6Cl_6$).[25] The asymmetric η^2 fashion of *p*-xylene bonding, with Ag−C bond distances of 2.485(5) and 2.514(5) Å, is typical of many silver−arene complexes.[6a,18a,25,27] The Ag−Br distances range from 2.818(2) to 2.972(2) Å with an average value of 2.889(2) Å, which can be compared with those

---

(26) Seggen, D. M. V.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453.

(27) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743.

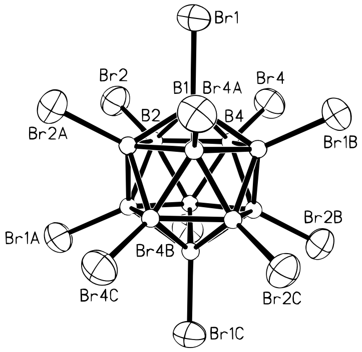


Figure 6. Perspective view of the carborane anion in [Me_3NH][**7**]. Note that the C and B atoms of the icosahedral cage are indistinguishable.

found in the silver(I) salts of brominated carborane anions.[11,25,26] Among four Ag−Br bond distances, that of Ag−Br(12) is the shortest, perhaps reflecting that Br(12) is still the most basic.[25]

Crystal Structure of [Me_3NH][1-Br-$CB_{11}Br_{11}$] ([Me_3NH][7]). X-ray-quality crystals were grown from a saturated diethyl ether solution at room temperature. There are two crystallographically independent molecules in the unit cell. One of them is shown in Figure 6. The carbon and boron atoms of the icosahedral cage in the 1-Br-$CB_{11}Br_{11}^-$ anion are indistinguishable due to the crystallographically imposed *m* symmetry, and they are represented by the three independent boron atoms B(1), B(2), and B(4). The average B−Br distances (2.926(5) and 2.924(5) Å) and B−B distances (1.781(7) and 1.784(7) Å) all fall in the range normally observed in the 12-vertex-brominated carborane anions.[4a,6a,8−11,25] This anion has an almost perfect spheroidal shape with an average Br−Br diameter of 7.24 Å, or 11.14 Å after adding the van der Waals radius of Br.[28]

Crystal Structure of Cs[1-H-$CB_{11}Br_{11}$] (Cs[5]). X-ray-quality crystals were obtained from the slow evaporation of a water/acetone solution of Cs[**5**] at room temperature. Figure 7 shows the coordination around the Cs cation in the solid-state structure of Cs[**5**]. Again, the carbon and boron atoms of the icosahedral cage in the 1-H-$CB_{11}Br_{11}^-$ anion are indistinguishable due to the crystallographically imposed C_3 symmetry, and they are represented by the four independent boron atoms B(1)−B(4). The C−H bond is thus completely mixed with the 11 B−Br bonds of the cage anion. The average B−Br distance of 1.924(4) Å can be compared to those normally observed in the 12-vertex-brominated carborane anions.[4a,6a,8−11,25] The Cs atom is disordered over two sets of positions with 0.5:0.5 occupancies. It coordinates to the six bromine atoms from three carborane cages with the Cs−Br interatomic distances ranging from 3.708(1) to 3.757(1) Å, which are similar to those found in Cs(12-Br-1-$CB_{11}H_{11}$).[4a] Thus Cs[**5**] is best described as a simple ionic salt.

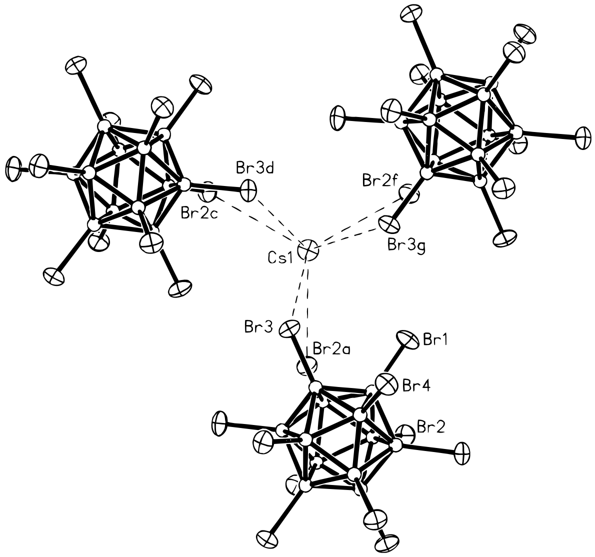


Figure 7. Perspective view of the coordinating sphere around the Cs cation in Cs[**5**]. Note that the C and B atoms of the icosahedral cage are indistinguishable and the H atom is completely scrambled with the 11 Br atoms.

Conclusions

The syntheses of highly chlorinated, brominated, and iodinated icosahedral carborane anions were achieved via sealed-tube reactions or by introducing an electron-donating group into the carborane cage (for complex **1**). The sealed-tube method can force the halogenation reactions of the parent carborane anion $CB_{11}H_{12}^-$ to proceed to completion, shorten the reaction time, and increase the reaction yield. This is a very convenient and useful new method and may be applicable to other carboranes or polyhedral boron clusters.

Like the parent carborane anion $CB_{11}H_{12}^-$, 1-H-$CB_{11}X_{11}^-$ (X = Cl, Br, I) can be lithiated with butyllithium, and treatment of the lithio species with alkyl halides leads to *C*-alkylation in 1-R-$CB_{11}X_{11}^-$ derivatives. By the combination of both *C*- and *B*-derivatizations, a variety of icosahedral carborane anions could be generated.

Acknowledgment. We thank the Hong Kong Research Grants Council (Earmarked Grant CUHK 306/96P) for financial support.

Supporting Information Available: Tables of crystallographic data collection information, atom coordinates and isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters and figures showing the atom-numbering scheme for Ag[**2**], (η^2-*p*-xylene)Ag(1-CH_3-$CB_{11}HBr_{10}$), Cs[**5**], and [Me_3NH][**7**] (27 pages). X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

IC9805628

---

(28) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.