Synthesis and Structural Characterization of Highly Chlorinated, Brominated, Iodinated, and Methylated Carborane Anions, 1-H-CB$_9$X$_9^-$, 1-NH$_2$-CB$_9$X$_9^-$ (X = Cl, Br, I), and 1-H-CB$_9$(CH$_3$)$_9^-$ †

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

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

The highly chlorinated, brominated, and iodinated carborane anions 1-R-CB$_9$X$_9^-$ (R = H, NH$_2$; X = Cl, Br, I) were prepared in high yields by treatment of [Me$_3$NH][1-R-CB$_9$H$_9$] with excess ICl, Br$_2$/triflic acid, and I$_2$/triflic acid, respectively, in sealed tubes at 180−240 °C. With the aid of a Pd catalyst, B−I bonds could be converted into the B−Me bonds by treatment with excess MeMgBr, which led to the preparation of the permethylated species 1-H-CB$_9$Me$_9^-$ in good yield. These new anions were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR, IR, and negative-ion MALDI MS spectroscopy. Some were further characterized by single-crystal X-ray analyses. The weakly coordinating nature of these new anions was probed by ^{29}Si chemical shifts.

Introduction

As a new class of the robust and weakly coordinating anions, carborane anions, in particular, the icosahedral CB$_{11}$H$_{12}^-$ anion and its derivatives, have attracted much attention.[1] The highly halogenated, methylated, and hydroxylated icosahedral anions 1-R-CB$_{11}$X$_{11}^-$ (R = H, alkyl; X = F,[2] Cl,[3] Br,[3] I[3,4]), 1-Me-CB$_{11}$Me$_{11}^-$,[5] and 1-H-CB$_{11}$(OH)$_{11}^{-~6}$ were recently reported. These anions are finding many applications in metathesis, catalysis, and oxidation chemistry,[7−11] as well as in stabilizing highly coordinatively unsaturated cations.[12−17] In contrast, the chemistry of the CB$_9$H$_{10}^-$ anion is less studied, and only a few halogenated derivatives are known.[12,18,19]

We have started a program to prepare highly halogenated carborane derivatives for use as new, chemically robust, weakly coordinating anions. A very effective methodology for the synthesis of 1-H-CB$_{11}$X$_{11}^-$ (X = Cl, Br, I) was recently developed in our laboratory.[3] We have now extended our research to the CB$_9$H$_{10}^-$ anion and report herein the synthesis and structural characterization of the highly halogenated carborane anions 1-R-CB$_9$X$_9^-$ (R = H, NH$_2$; X = Cl, Br, I) and the methylated derivative 1-H-CB$_9$Me$_9^-$. The similarities and differences between the reactivity patterns of the CB$_9$H$_{10}^-$ and CB$_{11}$H$_{12}^-$ anions are also discussed.

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 anions 1-H-CB$_9$H$_9^-$,[20a] 1-NH$_2$-CB$_9$H$_9^-$,[20b] and 1-H-CB$_{11}$H$_{11}^{-~7a}$ were prepared according to literature methods. All

† Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 65th birthday.

(1) (a) Reed, C. A. *Acc. Chem. Res*. **1998**, *31*, 133. (b) Reed, C. A. *Acc. Chem. Res*. **1998**, *31*, 325. (c) Strauss, S. H. *Chem. Rev*. **1993**, *93*, 927.

(2) (a) Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *J. Am. Chem. Soc*. **1998**, *120*, 4224. (b) Ivanova, S. M.; Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem*. **1999**, *38*, 3756.

(3) (a) Xie, Z.; Tsang, C.-W.; Xue, F.; Mak, T. C. W. *Inorg. Chem*. **1997**, *36*, 2246. (b) Xie, Z.; Tsang, C.-W.; Sze, E. T.-P.; Yang, Q.; Chan, D. T. W.; Mak, T. C. W. *Inorg. Chem*. **1998**, *37*, 6444.

(4) Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. *J. Org. Chem*. **1996**, *61*, 9041.

(5) (a) King, B. T.; Janoušek, Z.; Grüner, B.; Trammel, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc*. **1996**, *118*, 3313. (b) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc*. **1996**, *118*, 10902.

(6) Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed*. **1999**, *38*, 1062.

(7) (a) Xie, Z.; Jelínek, 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.

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

(9) (a) Turner, H. W. European Patent Applications 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.

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

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

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

(13) (a) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402. (b) Reed, C. A.; Fackler, N. L. P.; Kim, K.-C.; Stasko, D.; Evans, D. R. *J. Am. Chem. Soc*. **1999**, *121*, 6314.

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

(15) 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.

(16) (a) Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 2433. (b) Evans, D. R.; Fackler, N. L. P.; Xie, Z.; Rickard, C. E. F.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc*. **1999**, *121*, 8466.

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

(18) Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem*. **1973**, *12*, 785.

(19) (a) Ivanov, S. V.; Rockwell, J. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem*. **1996**, *35*, 7882. (b) Ivanov, S. V.; Lupinetti, A. J.; Solntsev, K. A.; Strauss, S. H. *J. Fluorine Chem*. **1998**, *89*, 65. (c) Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chim. Acta* **1999**, *289*, 76.

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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B and ^{29}Si NMR spectra were recorded on a Varian Inova 400 spectrometer at 128.32, and 79.46 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of deuterated solvent or external TMS (0.00 ppm) for proton and carbon chemical shifts, to external BF$_3$·OEt$_2$ (0.00 ppm) for boron chemical shifts, and to external TMS for ^{29}Si chemical shifts.

Preparation of [Me$_3$NH][1-H-CB$_9$Cl$_9$] ([Me$_3$NH][1]). A thick-walled Pyrex tube was charged with Cs[1-H-CB$_9$H$_9$] (0.12 g, 0.47 mmol), triflic acid (1.0 mL), and iodine monochloride (1.0 mL, 19.6 mmol). This tube was cooled with liquid N$_2$, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 230 °C, and this temperature was maintained for 2 days. After removal of excess iodine monochloride and triflic acid, the residue was treated with a 5% aqueous NaOH solution until the pH of the solution was about 7. The solution was then extracted with diethyl ether (10 mL × 2). The ether portions were combined, concentrated, and treated with an aqueous solution of Me$_3$NHCl until no more precipitate was formed. The white precipitate was filtered off, washed with deionized water, and dried under vacuum, giving [Me$_3$NH][1] as a white solid (0.20 g, 87%). ^{1}H NMR (acetone-d_6): δ 3.46 (s, 1H, cage CH), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 45.00 [q, Me$_3$NH, $^1J(^{13}$C$-^1$H) = 143 Hz], 39.77 [d, cage carbon, $^1J(^{13}$C$-^1$H) = 193 Hz]. ^{11}B NMR (acetone-d_6): δ 23.2 (s, 1B), −1.2 (s, 4B), −1.7 (s, 4B). IR (cm^{-1}; KBr): ν 3087 (w), 2960 (w), 2915 (w), 2728 (m), 1467 (m), 1386 (s), 1265 (m). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-H-CB$_9$Cl$_9$$^-$ 427 (92), 428 (98), 429 (100), 430 (85), 431 (76); found 427 (73), 428 (92), 429 (100), 430 (85), 431 (76).

Preparation of [Me$_3$NH][1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$] ([Me$_3$NH][2]). To a THF solution (20 mL) of [Me$_3$NH][1-CB$_9$Cl$_9$] ([Me$_3$NH][1]; 0.20 g, 0.40 mmol) was slowly added n-BuLi (1.5 mL of 1.6 M in hexane solution, 2.4 mmol) at 0 °C under stirring. The reaction mixture was stirred at room temperature for 4 h and then refluxed for 4 h. After removal of the generated Me$_3$N along with the solvent (10 mL) under vacuum and addition of freshly distilled THF (20 mL), a THF solution (2 mL) of C$_6$H$_5$CH$_2$Br (0.3 mL, 2.5 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 (10 mL) and then extracted with diethyl ether (10 mL × 2). The ether solutions were combined, concentrated, and treated with an aqueous solution of Me$_3$NHCl to give [Me$_3$NH][2] as a white solid (0.22 g, 95%). ^{1}H NMR (acetone-d_6): δ 7.30 (m, 5H, C$_6H_5$CH$_2$), 3.90 (s, 1H, C$_6$H$_5$CH_2), 3.36 (s, 1H, C$_6$H$_5$CH_2), 2.92 (s, 9H, (CH_3)$_3$NH). ^{13}C NMR (acetone-d_6): δ 132.09 (s, ipso C), 129.08 [d, $^1J(^{13}$C$-^1$H) = 165 Hz, ortho C], 128.72 [d, $^1J(^{13}$C$-^1$H) = 160 Hz, meta C], 127.74 [d, $^1J(^{13}$C$-^1$H) = 157 Hz, para C], 45.00 [q, Me$_3$NH, $^1J(^{13}$C$-^1$H) = 143 Hz], 42.52 (s, cage C), 34.40 [t, C$_6$H$_5$CH_2, $^1J(^{13}$C$-^1$H) = 150 Hz]. ^{11}B NMR (acetone-d_6): δ 22.3 (s, 1B), −0.4 (s, 4B), −1.8 (s, 4B). IR (cm^{-1}; KBr): ν 3059 (w), 2953 (m), 2928 (m), 1555 (s), 1472 (s), 1386 (s), 675 (s). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$$^-$ 517 (84), 518 (97), 519 (100), 520 (95), 521 (82); found 517 (72), 518 (91), 519 (100), 520 (98), 521 (87).

A cation exchange reaction in a mixed solvent of acetone/water afforded [(C$_6$H$_5$CH$_2$)NMe$_3$][2] in 90% yield. X-ray-quality crystals were grown from a saturated CH$_2$Cl$_2$ solution with n-hexane vapor diffusion at room temperature.

Preparation of Ag[1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$] (Ag[2]). To a suspension of [Me$_3$NH][2] (0.22 g, 0.38 mmol) in water (15 mL) was added 2

equiv of NaOH, and the mixture was heated at 90 °C for 2 h. After removal of all trimethylamine under vacuum and neutralization of the resulting solution with 1 N HNO$_3$, an aqueous solution of AgNO$_3$ (0.09 g, 0.53 mmol) was added. The resulting pale gray precipitate was filtered off, washed with cold water, and dried under vacuum, affording Ag[2] (0.23 g, 96%). ^{1}H NMR (acetone-d_6): δ 7.33 (m, 5H, C$_6H_5$-CH$_2$), 3.91 (s, 1H, C$_6$H$_5$CH_2), 3.35 (s, 1H, C$_6$H$_5$CH_2). ^{13}C NMR (acetone-d_6): δ 134.11 (s, ipso C), 131.12 [d, $^1J(^{13}$C$-^1$H) = 165 Hz, ortho C], 130.74 [d, $^1J(^{13}$C$-^1$H) = 160 Hz, meta C], 129.82 [d, $^1J(^{13}$C$-^1$H) = 157 Hz, para C], 42.52 (s, cage C), 34.40 [t, C$_6$H$_5$CH_2, $^1J(^{13}$C$-^1$H) = 150 Hz]. ^{11}B NMR (acetone-d_6): δ 21.69 (s, 1B), −0.92 (s, 4B), −2.51 (s, 4B). IR (cm^{-1}; KBr): ν 3068 (s), 2970 (m), 2933 (m), 1600 (m), 1472 (s), 1386 (s), 1046 (m), 677 (s).

Preparation of [Me$_3$NH][1-H-CB$_9$Br$_9$] ([Me$_3$NH][3]). A thick-walled Pyrex tube was charged with Cs[1-H-CB$_9$H$_9$] (0.15 g, 0.60 mmol), triflic acid (1.0 mL), and Br$_2$ (1.0 mL, 19.4 mmol). This tube was cooled with liquid N$_2$, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 230 °C, and this temperature was maintained for 3 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 was about 7. The solution was then extracted with diethyl ether (20 mL × 2). The ether portions were combined, concentrated, washed with Na$_2$SO$_3$, and treated with an aqueous solution of Me$_3$NHCl until no more precipitate was formed. The white precipitate was filtered off, washed with deionized water, and dried under vacuum, giving [Me$_3$NH][3] as a white solid (0.44 g, 82%). ^{1}H NMR (acetone-d_6): δ 3.51 (s, 1H, cage CH), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 50.11 [d, cage C, $^1J(^{13}$C$-^1$H) = 194 Hz], 45.00 [q, Me$_3$NH, $^1J(^{13}$C$-^1$H) = 143 Hz]. ^{11}B NMR (acetone-d_6): δ 23.9 (s, 1B), −3.9 (s, 4B), −4.5 (s, 4B). IR (cm^{-1}; KBr): ν 3062 (w), 2959 (w), 2930 (m), 1430 (s), 1386 (s), 488 (m). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-H-CB$_9$Br$_9$$^-$ 827 (75), 828 (97), 829 (100), 830 (90), 831 (70); found 827 (82), 828 (95), 829 (100), 830 (97), 831 (85).

Preparation of Cs[1-H-CB$_9$Br$_9$] (Cs[3]). To a suspension of [Me$_3$NH][3] (0.44 g, 0.50 mmol) in water (15 mL) was added 2 equiv of NaOH, and the mixture was heated at 90 °C for 2 h. After removal of all trimethylamine under vacuum and neutralization of the resulting solution with 1 N HNO$_3$, a small amount of acetone was added to give a clear solution. CsCl (0.13 g, 0.77 mmol) was then added to give a milky solution with some precipitate. After removal of acetone, the precipitate was collected by filtration. This solid was washed twice with cold water, giving Cs[3] as a white solid (0.43 g, 90%). Recrystallization from a CH$_2$Cl$_2$ solution at room temperature gave X-ray-quality colorless crystals. ^{1}H NMR (acetone-d_6): δ 3.55 (s, 1H, cage CH). ^{13}C NMR (acetone-d_6): δ 50.11 [d, cage C, $^1J(^{13}$C$-^1$H) = 194 Hz]. ^{11}B NMR (acetone-d_6): δ 23.9 (s, 1B), −3.9 (s, 4B), −4.5 (s, 4B). IR (cm^{-1}; KBr): ν 3062 (w), 1620 (m), 1384 (s), 1254 (w), 1038 (s).

Preparation of Ag[1-H-CB$_9$Br$_9$] (Ag[3]). Cs[3] (0.20 g, 0.21 mmol) was dissolved in hot water (20 mL), and AgNO$_3$ (0.05 g, 0.29 mmol) was dissolved in cold water (1 mL). The two solutions were then mixed at room temperature. The resulting pale gray precipitate was filtered off, washed with cold water, and dried under vacuum, affording Ag[3] (0.18 g, 91%). ^{1}H NMR (acetone-d_6): δ 3.60 (s, 1H, cage CH). ^{13}C NMR (acetone-d_6): δ 50.70 [d, cage C, $^1J(^{13}$C$-^1$H) = 194 Hz]. ^{11}B NMR (acetone-d_6): δ 23.60 (s, 1B), −3.87 (s, 8B). IR (cm^{-1}; KBr): ν 2959 (s), 2917 (s), 1383 (s), 1260 (w), 1081 (m). Recrystallization from a benzene/THF solution gave X-ray-quality colorless crystals, which were identified as (η^2-benzene)Ag(3). Among these colorless crystals were a few pale brown crystals that were identified as (η^2-benzene)(η^1-benzene)Ag$_3$[1-H-CB$_9$Br$_9$]$_2$[NO$_3$](THF) by X-ray analysis.

Preparation of [Me$_3$NH][1-H-CB$_9$I$_9$] ([Me$_3$NH][4]). A thick-walled Pyrex tube was charged with [Me$_3$NH][1-H-CB$_9$H$_9$] (0.20 g, 1.11 mmol), triflic acid (1.0 mL), and iodine (3.0 g, 11.82 mmol). This tube was cooled with liquid N$_2$, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 180 °C, and this temperature was maintained for 4 days. After removal of excess iodine and triflic acid, the residue was treated with a 5% aqueous NaOH solution until the pH of the solution was about 7. The solution was then extracted with diethyl ether (20 mL × 2). The ether

(20) (a) Nestor, K.; Štíbr, B.; Kennedy, J. D.; Thornton-Pett, M.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262. (b) Jelínek, T.; Štíbr, B.; Plešek, J.; Thornton-Pett, M.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 4231.

portions were combined, concentrated, washed with Na_2SO_3 solution, and treated with an aqueous solution of Me_3NHCl until no more precipitate was formed. The yellowish precipitate was filtered off, washed with deionized water, and dried under vacuum. Recrystallization from a CH_2Cl_2/hexane solution gave $[Me_3NH][\textbf{4}]$ as a pale yellow solid (1.20 g, 82%). ^1H NMR (acetone-d_6): δ 3.46 (s, 1H, cage CH), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 68.81 [d, cage C, $^1J(^{13}C-$ $^1H) = 198$ Hz], 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 22.2 (s, 1B), -12.3 (s, 8B). IR (cm^{-1}; KBr): ν 3050 (w), 2952 (m), 2700 (m), 1473 (m), 1383 (s), 1064 (s), 982 (s). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-H-CB$_9$I$_9^-$ 1251 (52), 1252 (100), 1253 (100); found 1251 (57), 1252 (99), 1253 (100).

Preparation of $[Me_3NH][1-NH_2-CB_9Cl_9]$ ($[Me_3NH][\textbf{5}]$). A thick-walled Pyrex tube was charged with $[Et_3NH][1-NH_2-CB_9H_9]$ (0.20 g, 0.85 mmol), triflic acid (1.0 mL), and iodine monochloride (1.0 mL, 19.6 mmol). This tube was cooled with liquid N_2, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 220 °C, and this temperature was maintained for 3 days. After removal of excess iodine monochloride and triflic acid, the residue was treated with a 5% aqueous NaOH solution until the pH of the solution was about 7. The solution was then extracted with diethyl ether (20 mL × 2). The ether portions were concentrated, washed with Na_2SO_3 solution, and treated with an aqueous solution of Me_3NHCl until no more precipitate was formed. The yellowish precipitate was filtered off, washed with deionized water, and dried under vacuum. Recrystallization from a CH_2Cl_2/hexane solution gave $[Me_3NH][\textbf{5}]$ as a pale yellow solid (0.40 g, 93%). ^1H NMR (acetone-d_6): δ 3.30 (br, NH_2), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 60.25 (s, cage C), 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 16.5 (s, 1B), -2.2 (s, 4B), -4.1 (s, 4B). IR (cm^{-1}; KBr): ν 3480 (m), 3270 (m), 2958 (w), 2910 (w), 2838 (w), 1629 (m), 1379 (s), 1022 (br s). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-NH$_2$-CB$_9$Cl$_9^-$ 442 (94), 443 (99), 444 (100), 445 (96), 446 (84); found 442 (74), 443 (92), 444 (100), 445 (97), 446 (85).

Preparation of $[Me_3NH][1-NH_2-CB_9Br_9]$ ($[Me_3NH][\textbf{6}]$). A thick-walled Pyrex tube was charged with $[Et_3NH][1-NH_2-CB_9H_9]$ (0.10 g, 0.42 mmol), triflic acid (1.0 mL), and Br_2 (1.0 mL, 19.4 mmol). This tube was cooled with liquid N_2, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 220 °C, and this temperature was maintained for 3 days. The same workup procedures as used in the synthesis of $[Me_3NH][\textbf{3}]$ gave $[Me_3NH][\textbf{6}]$ as a white solid (0.34 g, 89%). ^1H NMR (acetone-d_6): δ 3.30 (br, NH_2), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 61.40 (s, cage C), 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 17.3 (s, 1B), -3.9 (s, 4B), -6.9 (s, 4B). IR (cm^{-1}; KBr): ν 3556 (w), 3178 (m), 3080 (w), 1921 (w), 1604 (w), 1383 (s), 1101 (w), 1023 (m), 995 (m), 846 (w). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-NH$_2$-CB$_9$Br$_9^-$ 843 (82), 844 (93), 845 (100), 846 (97), 847 (83); found 843 (82), 844 (95), 845 (100), 846 (98), 847 (85).

Preparation of $Ag[1-NH_2-CB_9Br_9]$ ($Ag[\textbf{6}]$). To a suspension of $[Me_3NH][\textbf{6}]$ (0.34 g, 0.38 mmol) in water (20 mL) was added 2 equiv of NaOH, and the mixture was heated at 90 °C for 2 h. After removal of all trimethylamine under vacuum and neutralization of the resulting solution with 1 N HNO$_3$, a small amount of acetone was added to produce a clear solution. Addition of an aqueous AgNO$_3$ (0.08 g, 0.47 mmol) solution at room temperature gave a pale gray precipitate, which was filtered off, washed with cold water, and dried under vacuum, affording Ag[**6**] (0.30 g, 84%). ^1H NMR (acetone-d_6): δ 3.30 (br, NH_2). ^{13}C NMR (acetone-d_6): δ 61.70 (s, cage C). ^{11}B NMR (acetone-d_6): δ 19.7 (s, 1B), -3.6 (s, 4B), -6.6 (s, 4B). IR (cm^{-1}; KBr): ν 3556 (w), 3250 (m), 3110 (w), 1580 (m), 1101 (w), 1023 (m), 858 (w).

Preparation of $[Me_3NH][1-NH_2-CB_9I_9]$ ($[Me_3NH][\textbf{7}]$). A thick-walled Pyrex tube was charged with $[Et_3NH][1-NH_2-CB_9H_9]$ (0.05 g, 0.21 mmol), triflic acid (1.0 mL), and iodine (3.0 g, 11.8 mmol). This tube was cooled with liquid N_2, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 240 °C, and this temperature was maintained for 4 days. The same workup procedures as used in the synthesis of $[Me_3NH][\textbf{4}]$ gave $[Me_3$-NH][**7**] as a pale yellow solid (0.24 g, 86%). ^1H NMR (acetone-d_6): δ 3.30 (br, NH_2), 3.01 (s, 9H, Me_3NH). ^{13}C NMR (acetone-d_6): δ 58.00 (s, cage C), 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 24.6 (s, 1B), -10.8 (s, 8B). IR (cm^{-1}; KBr): ν 3420 (m), 3200 (w), 2956 (w), 2911 (w), 2696 (w), 1610 (m), 1476 (m), 1096 (m), 1036 (m), 800 (w). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-NH$_2$-CB$_9$I$_9^-$ 1266 (57), 1267 (87), 1268 (100), 1269 (81); found 1266 (57), 1267 (98), 1268 (100), 1269 ((2X)) (45).

Preparation of $[Me_3NH][1-H-CB_9H_9]$ from $[Me_3NH][1-NH_2-CB_9H_9]$. To a suspension of $[Et_3NH][1-NH_2-CB_9H_9]$ (0.50 g, 2.11 mmol) in water (20 mL) was added an aqueous solution of NaNO$_2$ (0.18 g, 2.60 mmol), and the mixture was stirred at 0 °C for 15 min. A 1 N HCl solution (5.2 mL, 5.2 mmol) was then slowly added to the above solution at 0 °C, and the mixture was stirred for another 15 min. To this solution was added H$_3$PO$_2$ (0.17 g, 2.60 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min. After the evolution of N$_2$ ceased, the solution was neutralized with NaOH, followed by extraction with diethyl ether (20 mL × 3). The ether portions were combined, concentrated, and treated with Me$_3$NHCl until no more precipitate was formed. The white precipitate was filtered off, washed with deionized water, and dried under vacuum to give [Me$_3$NH][1-H-CB$_9$H$_9$] as a white solid (0.42 g, 91%).

Preparation of $[Me_3NH][1-H-CB_9Cl_9]$ from $[Me_3NH][1-NH_2-CB_9Cl_9]$. Under reaction conditions similar to those mentioned above, only a mixture of $[Me_3NH][\textbf{1}]$ and $[Me_3NH][\textbf{5}]$ was isolated in a molar ratio of about 2:3 on the basis of ^{11}B NMR and MS analyses.

Preparation of $[Me_3NH][1-H-CB_9(CH_3)_9]$ ($[Me_3NH][\textbf{8}]$). A thick-walled Pyrex tube was charged with $[Me_3NH][1-H-CB_9I_9]$ ($[Me_3NH]$-[**4**]; 0.30 g, 0.23 mmol), (Ph$_3$P)$_2$PdCl$_2$ (0.29 g, 0.41 mmol), copper(I) iodide (0.075 g, 0.39 mmol), and methylmagnesium bromide (2.0 mL of 3.0 M in diethyl ether, 6.0 mmol). This tube was cooled with liquid N$_2$, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased from 25 to 220 °C with an increment of 20$-$25 °C per day (10 days). The resulting dark brown reaction mixture was cooled to 0 °C, and excess Grignard reagent was destroyed by the addition of water (20 mL). Diethyl ether was removed under vacuum, and the remaining aqueous solution was washed with benzene (10 mL × 3) to remove the Pd compound. The washed solution was then acidified with 6 M HCl and extracted with diethyl ether (20 mL × 3). The combined ether portions were washed with dilute HCl, concentrated, and treated with an aqueous solution of Me$_3$NHCl until no more precipitate was formed. The yellowish precipitate was filtered off, washed with deionized water, and dried under vacuum. This product was then recrystallized from a mixed CH$_2$Cl$_2$/hexane (1:5) solution to give $[Me_3NH][\textbf{8}]$ as a white solid (0.04 g, 71%). ^1H NMR (acetone-d_6): δ 3.01 (s, 9H, Me_3NH), -0.29 [s, 12H, $CH_3(2-5)$], -0.55 [s, 15H, $CH_3(6-10)$]. ^{13}C NMR (acetone-d_6): δ 52.62 [d, cage C, $^1J(^{13}C-$ $^1H) = 193$ Hz], 45.00 [q, Me_3NH, $^1J(^{13}C-^1H) = 143$ Hz], -4.10 [br, $CH_3(2-10)$]. ^{11}B NMR (acetone-d_6): δ 37.04 (s, 1B), -4.19 (s, 4B), -8.24 (s, 4B). IR (cm^{-1}; KBr): ν 2919 (br s), 2863 (m), 1623 (m), 1456 (m), 1384 (m), 1093 (s), 1032 (s), 804 (w). Negative-ion MALDI MS, m/z (relative isotopic abundance): calcd for 1-H-CB$_9$(CH$_3$)$_9^-$ 243 (20), 244 (54), 245 (95), 246 (100), 247 (51); found 243 (17), 244 (51), 245 (92), 246 (100), 247 (49).

Alternate Method. To a stirred solution of $[Me_3NH][1-H-CB_9I_9]$ (0.50 g, 0.38 mmol) in THF (20 mL) was added methylmagnesium bromide (15.0 mL of 3.0 M in diethyl ether, 45.0 mmol), and the mixture was refluxed for 30 min. (PPh$_3$)$_2$PdCl$_2$ (0.48 g, 0.68 mmol) and copper(I) iodide (0.13 g, 0.68 mmol) were then added sequentially. The reaction mixture was refluxed, and the reaction was monitored by ^{11}B NMR spectroscopy. After 1 week, a major product, 1-H-CB$_9$-(CH$_3$)$_3$I$_6^-$, was detected by MADLI mass spectroscopy. The reaction was continued by adding more Grignard reagent (5.0 mL, 15.0 mmol) and more palladium(II) compound (0.12 g, 0.17 mmol) until a pure permethylated product was obtained (another 1 week). The workup procedures mentioned above gave $[Me_3NH][\textbf{8}]$ as a white solid (0.08 g, 68%).

Preparation of $[Me_3NH][1-H-CB_{11}I_{11}]$. A thick-walled Pyrex tube was charged with [Me$_3$NH][1-H-CB$_{11}$H$_{11}$] (0.10 g, 0.69 mmol), triflic acid (1 mL,), and I$_2$ (2.0 g, 7.9 mmol). This tube was cooled with liquid

Table 1. Crystal Data and Summary of Data Collection and Refinement Details for Cs[**3**](H$_2$O)$_{0.5}$, (η^2-benzene)Ag[**3**], (η^2-benzene)(η^1-benzene)Ag$_3$[**3**]$_2$[NO$_3$](THF), and [(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][**2**]

	Cs[**3**](H$_2$O)$_{0.5}$	(η^2-benzene)Ag[**3**]	(η^2-benzene)(η^1-benzene)-Ag$_3$[**3**]$_2$[NO$_3$](THF)	[(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][**2**]
empirical formula	CH$_2$B$_9$Br$_9$CsO$_{0.5}$	C$_7$H$_7$AgB$_9$Br$_9$	C$_{18}$H$_{22}$Ag$_3$B$_{18}$Br$_{18}$NO$_4$	C$_{18}$H$_{23}$B$_9$Cl$_9$N
crystal size, mm	0.28 × 0.26 × 0.17	0.85 × 0.28 × 0.16	0.52 × 0.50 × 0.48	0.35 × 0.32 × 0.12
fw	971.4	1015.5	2272.9	669.7
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$	$Pna2_1$	$P2_1/c$	$P\bar{1}$
a, Å	10.432(3)	12.716(3)	18.848(2)	9.226(2)
b, Å	12.291(4)	12.726(3)	16.323(2)	13.043(3)
c, Å	18.733(4)	14.638(3)	17.947(2)	13.816(3)
α, deg	90	90	90	79.17(3)
β, deg	93.40(1)	90	96.65(1)	72.62(3)
γ, deg	90	90	90	77.04(3)
V, Å^3	2397(1)	2368.8(8)	5484(1)	1533.1(5)
Z	4	4	4	2
D_{calcd}, Mg/m^3	2.691	2.847	2.753	1.451
radiation (λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
T, °C	23	23	20	20
2θ range, deg	4.0−50.0	4.0−51.0	3.2−50.0	4.0−50.0
μ, mm^{-1}	16.527	16.026	14.205	0.835
$F(000)$	1708	1824	4120	672
no. of obsd reflns	2724	3861	6238	5391
no. of params refnd	191	236	560	334
goodness of fit	1.099	1.110	1.175	1.001
R1^a	0.084	0.058	0.085	0.042
wR2^b	0.190	0.120	0.133	0.089

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum(wF_o^4)\}^{1/2}$.

N$_2$, sealed under vacuum, and then placed in a furnace. The temperature of the furnace was gradually increased to 240 °C, and this temperature was maintained for 5 days. The same workup procedures as used in the synthesis of [Me$_3$NH][**4**] gave [Me$_3$NH][1-H-CB$_{11}$I$_{11}$] as a pale yellow solid (0.98 g, 90%), which was characterized by spectroscopic data.[3]

^{29}Si NMR Measurements. A Pr$^i_3$Si(carborane) compound was generated according to a literature procedure.[13] An NMR tube was charged with [Ph$_3$C][1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$] (70 mg, 0.065 mmol; prepared by treatment of Ag[1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$] with 1 equiv of Ph$_3$CBr in toluene/CH$_3$CN according to literature procedures[7a]), Pr$^i_3$SiH (0.08 mL, 0.37 mmol), and dry toluene-d_8 (0.4 mL). This tube was sealed under vacuum and then placed in an ultrasonic bath at room temperature overnight. The reaction was monitored by ^{29}Si NMR. Within a period of 24 h, the ^{29}Si resonance for Pr$^i_3$SiH at δ 12.1 decreased in intensity and a new peak appeared at δ 106.0.

Pr$^i_3$Si(1-H-CB$_9$Br$_9$) was generated in the same manner. The reaction was monitored by ^{29}Si NMR, which showed a new ^{29}Si resonance at δ 100.9.

X-ray Structure Determinations. All single crystals were immersed in Paratone-N oil and then sealed in thin-walled glass capillaries. Data were collected at 293 K either on an 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. Absorption corrections were applied by correlation of symmetry-equivalent reflections using the ABSCOR program[21] 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).[22] The hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of the data collections and structure refinements are given in Table 1, and selected bond distances are listed in Table 2. Further details are included in the Supporting Information.

Results and Discussion

Syntheses. We had previously developed a new methodology for the preparation of perhalogenated icosahedral carborane anions, 1-H-CB$_{11}$X$_{11}$,[3] and found that this methodology could also be applied to the preparations of 1-H-CB$_9$X$_9^-$ and 1-NH$_2$-

CB$_9$X$_9^-$ anions after some modifications. A mixture of 1-H-CB$_9$H$_9^-$, excess Br$_2$, and triflic acid, sealed in a Pyrex tube, was heated at 230 °C for 3 days to give a sole product, 1-H-CB$_9$Br$_9^-$ (**3**), in 82% isolated yield. 1-NH$_2$-CB$_9$Br$_9^-$ (**6**) could also be prepared under similar reaction conditions from 1-NH$_2$-CB$_9$H$_9^-$ in 89% isolated yield.

Reactions of 1-H-CB$_9$H$_9^-$ with excess ICl in triflic acid and in the absence of triflic acid in a sealed tube at 220 °C for 3 days gave the same product, 1-H-CB$_9$Cl$_9^-$ (**1**); no 1-H-CB$_9$I$_9^-$ was isolated, which differs significantly from the 1-H-CB$_{11}$H$_{11}^-$ case.[3,4,15,23] It is noted that reaction of 1-H-CB$_{11}$H$_{11}^-$ with neat ICl in a sealed tube afforded an iodinated product, 1-H-CB$_{11}$I$_{11}^-$.[3] These results may imply that 1-H-CB$_9$I$_9^-$ is more susceptible to nucleophilic attack than 1-H-CB$_{11}$I$_{11}^-$. This hypothesis is supported by the following experiments. Treatment of 1-H-CB$_9$H$_9^-$ with excess ICl in triflic acid or CHCl$_2$CHCl$_2$ at 150 °C for 1 week also generated a single product, 1-H-CB$_9$-Cl$_9^-$. This reaction was monitored by ^{11}B NMR, IR, and MS spectroscopy. The results showed that, at about 120 °C, a mixture of partially iodinated and chlorinated carborane species had been formed, while some of the B−H bonds had not yet been converted to B−X (X = Cl, I) bonds. As the temperature was increased and the reaction time was prolonged, the chlorination was close to completion.

To prepare periodinated species, a new method was definitely needed. It had been reported that I$_2$ is a relatively weak iodinating agent and exhaustive iodination of 1-H-CB$_{11}$H$_{11}^-$ with I$_2$ led only to the 7,12-diiodo species.[24] The electrophilicity of iodine could be greatly enhanced in triflic acid under sealed-tube conditions. Accordingly, we found that treatment of 1-H-CB$_9$H$_9^-$ with excess I$_2$ in triflic acid in a sealed tube at 180 °C

(21) Higashi, T. *ABSCOR−An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corp.: Tokyo, 1995.
(22) *SHELXTL V 5.03 Program Package*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.
(23) Xie, Z.; Tsang, C.-W.; Xue, F.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *577*, 197.
(24) Jelínek, T.; Plešek, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.

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

Cs[3](H$_2$O)$_{0.5}$			
Br(2)—B(2)	1.931(8)	Cs(1)—Br(4)#2	3.862(1)
Br(3)—B(3)	1.959(8)	Cs(1)—Br(6)	3.783(1)
Br(4)—B(4)	1.935(1)	Cs(1)—Br(6)#1	3.858(2)
Br(5)—B(5)	1.911(8)	Cs(1)—Br(7)#1	3.798(1)
Br(6)—B(6)	1.942(8)	Cs(1)—Br(9)	3.864(1)
Br(7)—B(7)	1.938(9)	Cs(1)—Br(9)#2	3.916(2)
Br(8)—B(8)	1.901(7)	Cs(1)—Br(10)#1	3.898(1)
Br(9)—B(9)	1.908(8)	Cs(1)—Br(5)#2	3.936(1)
Br(10)—B(10)	1.896(8)	Cs(1)—O(1)	3.019(1)
(η^2-benzene)Ag[3]			
Br(2)—B(2)	1.906(5)	Br(9)—B(9)	1.975(6)
Br(3)—B(3)	1.883(6)	Br(10)—B(10)	1.929(6)
Br(4)—B(4)	1.948(6)	Ag(1)—C(3)	2.629(8)
Br(5)—B(5)	1.922(6)	Ag(1)—C(4)	2.649(7)
Br(6)—B(6)	1.942(5)	Ag(1)—Br(9)	2.777(1)
Br(7)—B(7)	1.952(6)	Ag(1)—Br(7)#3	2.779(1)
Br(8)—B(8)	1.915(6)		
(η^2-benzene)(η^1-benzene)Ag$_3$[3]$_2$[NO$_3$](THF)			
Ag(1)—C(11)	2.592(6)	Br(13)—B(13)	1.912(5)
Ag(1)—C(12)	2.533(6)	Br(14)—B(14)	1.918(5)
Ag(1)—Br(14)	3.017(1)	Br(15)—B(15)	1.931(5)
Ag(1)—Br(17)	2.712(1)	Br(16)—B(16)	1.942(4)
Ag(1)—Br(26)	2.752(1)	Br(17)—B(17)	1.940(5)
Ag(1)—Br(30)	3.003(1)	Br(18)—B(18)	1.941(5)
Ag(3)—Br(19)#4	3.007(1)	Br(19)—B(19)	1.889(4)
Ag(3)—Br(20)#4	2.870(1)	Br(20)—B(20)	1.940(5)
Ag(3)—C(21)	2.510(6)	Br(22)—B(22)	1.926(4)
Ag(3) —O(2)	2.473(6)	Br(23)—B(23)	1.907(5)
Ag(3) —O(3)	2.549(6)	Br(24)—B(24)	1.905(5)
Ag(2)—Br(25)	2.912(2)	Br(25)—B(25)	1.961(5)
Ag(2)—Br(28)	2.738(1)	Br(26)—B(26)	1.929(5)
Ag(2) —O(1)	2.531(6)	Br(27)—B(27)	1.915(5)
Ag(2) —O(2)	2.455(6)	Br(28)—B(28)	1.952(5)
Ag(2) —O(4)	2.650(6)	Br(29)—B(29)	1.903(5)
Br(12)—B(12)	1.888(5)	Br(30)—B(30)	1.908(5)
[(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][2]			
Cl(2)—B(2)	1.773(4)	Cl(7)—B(7)	1.787(4)
Cl(3) —B(3)	1.763(4)	Cl(8)—B(8)	1.779(4)
Cl(4)—B(4)	1.770(4)	Cl(9)—B(9)	1.789(4)
Cl(5)—B(5)	1.765(4)	Cl(10)—B(10)	1.778(4)
Cl(6)—B(6)	1.791(4)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1$, $-y + z$, $-z$; (#2) $-x$, $-y + 2$, $-z$; (#3) $x + \frac{1}{2}$, $-y + \frac{3}{2}$, z; (#4) $x - 1$, y, z.

for 4 days led to almost quantitative yield of the 1-H-CB$_9$I$_9^-$ (**4**) anion. The 1-H-CB$_{11}$I$_{11}^-$ anion could also be prepared under the same reaction condition. This is probably the most convenient and effective method for preparing periodocarborane anions. The corresponding perchloro and periodo carborane anions, 1-NH$_2$-CB$_9$Cl$_9^-$ (**5**) and 1-NH$_2$-CB$_9$I$_9^-$ (**7**), could be prepared under reaction conditions similar to those mentioned above.

Under the proper reaction conditions, deaminations of 1-NH$_2$-CB$_9$X$_9^-$ could be achieved. The reaction of 1-NH$_2$-CB$_9$H$_9^-$ with NaNO$_2$/HCl at 0 °C, followed by treatment with H$_3$PO$_2$, led to a quantitative yield of 1-H-CB$_9$H$_9^-$. However, the deaminations of 1-NH$_2$-CB$_9$X$_9^-$ (X = Cl, Br) were more difficult than that of the parent anion, 1-NH$_2$-CB$_9$H$_9^-$, leading only to mixtures of 1-NH$_2$-CB$_9$X$_9^-$ and 1-H-CB$_9$X$_9^-$ in ratios of 3:2 for X = Cl and 7:3 for X = Br according to ^{11}B NMR and the negative-ion MALDI mass spectroscopy.

C-alkylated products of the type 1-R-CB$_9$X$_9^-$ could be prepared similarly to 1-R-CB$_{11}$H$_{11}^-$.[3,25] For example, the reaction of 1-H-CB$_9$Cl$_9^-$ with *n*-BuLi in THF, followed by

(25) Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982.

treatment with benzyl bromide, led to the C-benzylated product 1-benzyl-CB$_9$Cl$_9^-$ (**2**) in high yield. It is noted that the C-lithiated species Li[1-Li-CB$_9$Cl$_9$] is very soluble in THF, while Li[1-Li-CB$_{11}$Cl$_{11}$] is only sparingly soluble.

We previously proposed that the formation of 1-H-CB$_9$Cl$_9^-$ may occur through the electrophilic substitution of 1-H-CB$_9$H$_9^-$ with I$^+$, giving 1-H-CB$_9$I$_9^-$, followed by a nucleophilic substitution with Cl$^-$. Indeed, treatment of 1-H-CB$_9$I$_9^-$ with NaCl/triflic acid in a sealed tube at 220 °C gave a single product, 1-H-CB$_9$-Cl$_9^-$. We then examined other nucleophiles. Reaction of 1-H-CB$_9$I$_9^-$ with NaF/DMF or Me$_3$NHF/triflic acid in a sealed tube did not proceed at 100 °C or below. As the temperature was increased to 120 °C, the carborane cage began to degrade, and after workup, boric acid was formed as a final product on the basis of ^{11}B NMR.

It is noteworthy the B—I bonds in 1-H-CB$_9$I$_9^-$ remained intact if the mixture of 1-H-CB$_9$I$_9^-$ and neat CH$_3$MgBr or CH$_3$MgBr/CH$_3$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$ was heated at 180 °C in a sealed tube for 1 week. Such a reaction, however, could be promoted by a Pd catalyst.[26] Treatment of 1-H-CB$_9$I$_9^-$ with excess MeMgBr in THF in the presence of bis(triphenylphosphine)-palladium(II) dichloride and copper(I) iodide at reflux temperature for 1 week gave 1-H-CB$_9$(CH$_3$)$_3$I$_6^-$ as a major product on the basis of MS and ^{11}B NMR analyses. This reaction was then continued by adding more (Ph$_3$P)$_2$PdCl$_2$ and MeMgBr for another week, leading to a good yield of permethylated species, 1-H-CB$_9$(CH$_3$)$_9^-$. Preparation of the latter species could also be achieved via a sealed-tube reaction. Treatment of 1-H-CB$_9$I$_9^-$ with excess MeMgBr/THF in the presence of (Ph$_3$P)$_2$PdCl$_2$ and CuI in a sealed tube from 25 to 220 °C for 10 days, after workup, afforded 1-H-CB$_9$(CH$_3$)$_9^-$ in good yield. In this preparation, the reaction temperature should be slowly increased and carefully controlled; otherwise, the yield will be lower. All transformations described in this section are summarized in Scheme 1.

These highly chlorinated, brominated, iodinated, and methylated carborane anions were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR, negative-ion MALDI MS, and IR spectroscopy. Some were further characterized by single-crystal X-ray analyses. They are thermally quite stable, with no decomposition up to 240 °C. They are also stable in very strong acids such as triflic acid and in strong bases such as NaOH or MeMgBr.
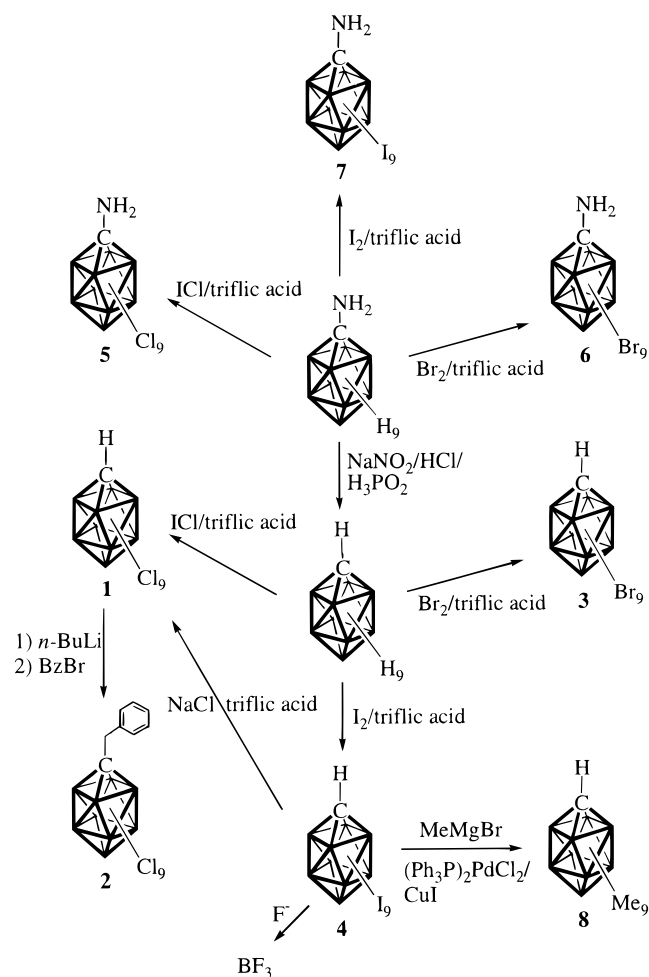
The silver salts of various carborane anions were readily prepared by treatment of their sodium salts with slightly excess amounts of AgNO$_3$ in aqueous solutions or mixtures of water/acetone. Excess AgNO$_3$ may result in the formation of 2:1 adducts of Ag(carborane) and AgNO$_3$, such as Ag$_2$(1-H-CB$_9$-Br$_9$)$_2$·AgNO$_3$. The solubilities of these silver(I) salts in various solvents are better than those of the 1-H-CB$_{11}$X$_{11}^-$ analogues.[3]

Spectroscopic Characterization. ^{11}B NMR spectroscopy is an extremely useful technique for the characterization of boron compounds. Figures 1 and 2 show the proton-coupled ^{11}B NMR spectra of [Me$_3$NH][1-H-CB$_9$X$_9$] (X = H, Cl, Br, I, Me) and [Me$_3$NH][1-NH$_2$-CB$_9$X$_9$] (X = H, Cl, Br, I) in acetone-d_6, respectively. Both proton-coupled and proton-decoupled ^{11}B NMR spectra of perhalocarborane anions are identical. Because of the different substituents on the carbon atoms of the carborane
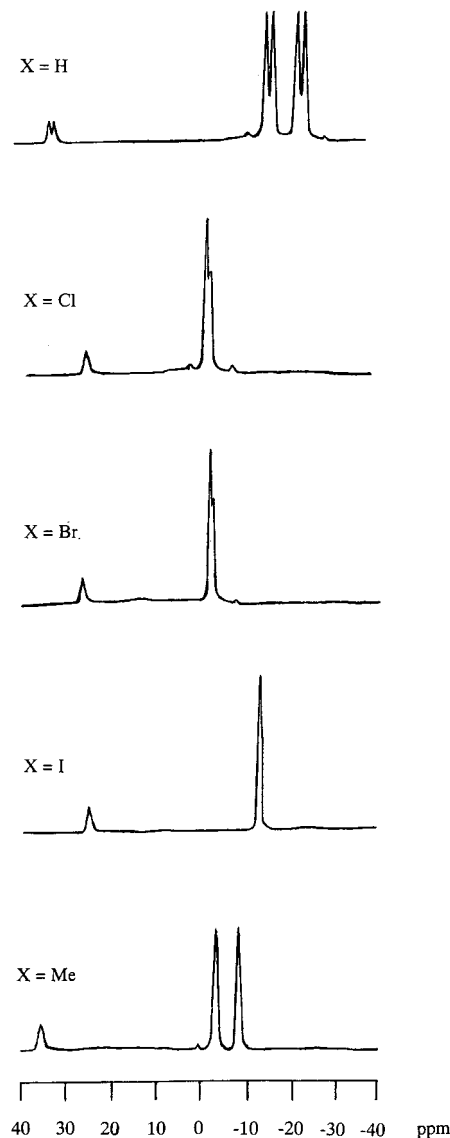
(26) (a) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095. (b) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 3491. (c) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1998**, *37*, 1544. (d) Mortimer, M. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 5750. (e) Grüner, B.; Janoušek, Z.; King, B. T.; Woodford, J. N.; Wang, C. H.; Všetecka, V.; Michl, J. *J. Am. Chem. Soc.* **1999**, *121*, 3122.

Scheme 1

Figure 1. Proton-coupled ^{11}B NMR spectra of [Me$_3$NH][1-H-CB$_9$X$_9$] in acetone-d_6.

cages, the differences in the chemical shifts of the lower and the upper belt boron atoms in the anions 1-H-CB$_9$X$_9^-$ and 1-NH$_2$-CB$_9$X$_9^-$ are not the same. It is noted that the ^{11}B NMR spectrum of 1-H-CB$_9$Me$_9^-$ exhibits a 1:4:4 splitting pattern, while that of 1-H-CB$_9$I$_9^-$ displays a 1:8 splitting pattern. Therefore, the transformation from 1-H-CB$_9$I$_9^-$ to 1-H-CB$_9$Me$_9^-$ can be closely monitored by ^{11}B NMR. The ^{13}C NMR spectrum of 1-H-CB$_9$Me$_9^-$ is very characteristic, showing broadening and upfield-shifted resonances due to the close proximity of carbon nuclei to both ^{11}B and ^{10}B, two nuclei with electric quadruple moments.[26a,27] The complete conversion of B–H vertexes into B–X vertexes is also indicated by the absence of the characteristic B–H absorption (ca. 2600 cm^{-1}) in their IR spectra. The ^{1}H, ^{13}C, ^{11}B NMR, IR, and MS spectra all support the compositions of the new carborane anions.

Coordinating Abilities. It has been documented that the ^{29}Si shifts of R$_3$SiY compounds are very sensitive to the coordinating nature of the counterion Y$^-$.[2a,12–15] We probed the weakly coordinating nature of 1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9^-$ and 1-H-CB$_9$Br$_9^-$ by generating Pr$^i_3$Si(carborane) compounds in toluene-d_8 according to the literature procedures.[12–15] Within a period of 24 h at room temperature, the ^{29}Si resonance for Pr$^i_3$SiH at δ 12.1 decreased in intensity and new ^{29}Si resonances appeared at δ 106.0 for 1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9^-$ and δ 100.9 for 1-H-CB$_9$Br$_9^-$. No other ^{29}Si resonance was observed, indicating that no halide abstraction reaction had occurred or that these carborane anions

are stable in the presence of strong electrophiles such as the cationic silicon center.

Comparison of the above measured values with $\delta(^{29}$Si) = 97.9 for Pr$^i_3$Si(1-H-CB$_9$H$_4$Br$_5$) in toulene,[12] $\delta(^{29}$Si) = 115 for Pr$^i_3$Si(1-H-CB$_{11}$H$_5$Cl$_6$) in the solid state,[15] and $\delta(^{29}$Si) = 120 for Pr$^i_3$Si(1-H-CB$_{11}$F$_{11}$) in toluene[2a] may suggest that (1) the icosahedral CB$_{11}$ anions are less coordinating than the corresponding CB$_9$ anions, (2) the highly halogenated carborane anions are less coordinating than the less halogenated ones, and (3) the coordinating ability of halocarborane anions decreases in the following order: I > Br > Cl > F. These results are consistent with recent reports in the literature.[2a,7a,15]

**Crystal Structure of (η^2-benzene)Ag(1-H-CB$_9$Br$_9$).** Figure 3 shows the coordination around silver in the solid-state structure of (η^2-benzene)Ag[**3**]. Like the other silver(I) salts of carborane anions,[2,3,7a,23,28] it is a one-dimensional coordination polymer with nonabromocarborane anions acting as bridging ligands. (η^2-benzene)Ag(1-H-CB$_9$Br$_9$) has a three-coordinate silver atom in a trigonal arrangement of one η^2-benzene and two monodentate bridging 1-H-CB$_9$Br$_9^-$ ions, a coordination pattern that is

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

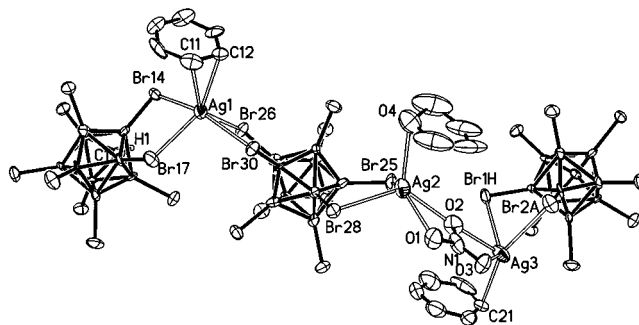(28) Xie, Z.; Wu, B.-M.; Mak, T. C. W.; Manning, J.; Reed, C. A. *J. Chem. Soc., Dalton Trans.* **1997**, 1213.
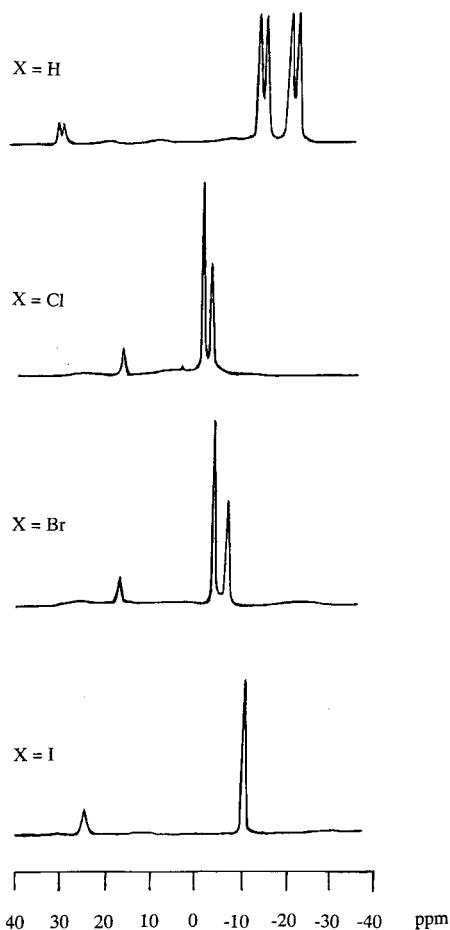
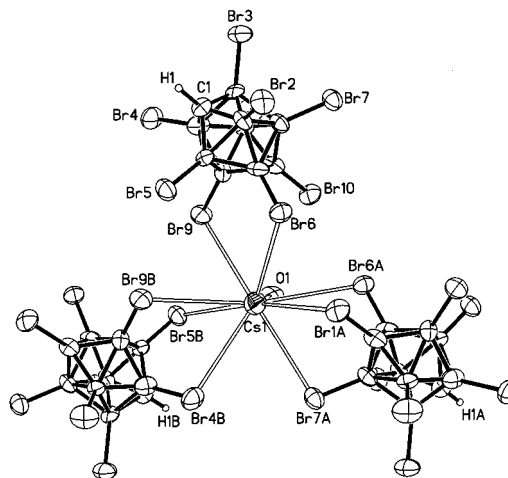**Figure 2.** Proton-coupled ^{11}B NMR spectra of [Me$_3$NH][1-NH$_2$-CB$_9$X$_9$] in acetone-d_6.
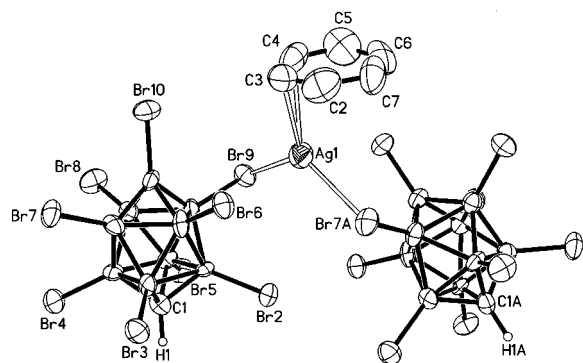
Figure 3. Perspective view of the coordinating sphere around the Ag atom in (η^2-benzene)Ag(1-H-CB$_9$Br$_9$). Thermal ellipsoids are drawn at the 35% probability level.

Figure 4. Perspective view of the coordinating sphere around the Ag atoms in (η^2-benzene)(η^1-benzene)Ag$_3$[1-H-CB$_9$Br$_9$]$_2$[NO$_3$](THF). Thermal ellipsoids are drawn at the 35% probability level.

Figure 5. Perspective view of the coordinating sphere around the Cs cation in Cs(1-H-CB$_9$Br$_9$)(H$_2$O)$_{0.5}$. Thermal ellipsoids are drawn at the 35% probability level.

Crystal Structure of (η^2-benzene)(η^1-benzene)Ag$_3$[1-H-CB$_9$Br$_9$]$_2$[NO$_3$](THF). The X-ray analysis reveals that this complex is a one-dimensional coordination polymer with both nonabromocarborane and nitrate anions acting as bridging ligands. Each asymmetric unit consists of two 1-H-CB$_9$Br$_9^-$ anions, one NO$_3^-$ anion, two benzenes, one THF, and three Ag$^+$ cations. Each Ag atom has a unique coordination environment although they are all five-coordinated (Figure 4). Ag(1) is in a propeller-like arrangement having one η^2-benzene and two bidentate bridging 1-H-CB$_9$Br$_9^-$ ions. Ag(2) is bound to one bidentate 1-H-CB$_9$Br$_9^-$ ion, one bidentate NO$_3^-$ ion, and the oxygen atom of the coordinated THF molecule in a distorted-square-pyramidal geometry. Ag(3) is in a highly distorted-square-pyramidal arrangement having one η^1-benzene, one bidentate 1-H-CB$_9$Br$_9^-$ ion, and one bidentate NO$_3^-$ ion. It is not common for a silver(I) complex to have both η^2- and η^1-benzene coordinations.[30] The average Ag(1)−C (η^2-benzene) distance of 2.563(6) Å is slightly longer than the Ag(3)−C (η^1-benzene) distance of 2.510(6) Å. The average Ag−Br distance of 3.140(2) Å and the average B−Br distance of 1.923(5) Å can be compared to the corresponding values found in (η^2-benzene)Ag(1-H-CB$_9$Br$_9$). It is very interesting to note that a bromine atom from the upper tetragonal belt such as Br(14) can also coordinate to an Ag$^+$ ion, which is a newly discovered

different from those observed in (η^2-*p*-xylene)Ag(1-CH$_3$-CB$_{11}$-HBr$_{10}$),[3] Ag(1-CH$_3$-CB$_{11}$Br$_{11}$),[3] and (η^2-toluene)Ag(1-H-CB$_9$H$_4$-Br$_5$).[7a] It is noteworthy that the bromine atom attached to B(10) antipodal to carbon (the so-called most basic bromine atom) does not coordinate to the silver atom, perhaps reflecting steric effects and/or the fact that the Br(10) may be no longer the most electron-rich bromine on the cage. The average Ag−Br distance of 2.778(1) Å and the average B−Br distance of 1.930(6) Å are comparable to those normally observed in polybromocarborane anions.[3,7a,23,28] The asymmetric η^2 fashion of benzene bonding, with Ag−C bond distances of 2.629(8) and 2.649(7) Å, is typical of many silver−arene complexes.[3,7a,23,28,29]

(29) (a) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743. (b) Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 6419.
(30) Andrei, S. B.; Simon, P. C.; Judith, A. K. H.; Christian, W. L.; Melvyn, K. J. *Organomet. Chem.* **1998**, *550*, 59.

coordination mode, never before observed in the silver(I) salts of any carborane anions.

Crystal Structure of Cs(1-H-CB$_9$Br$_9$)(H$_2$O)$_{0.5}$. X-ray-quality crystals were obtained from slow evaporation of a saturated CH$_2$-Cl$_2$ solution of Cs[**3**] at room temperature. Figure 5 shows the coordination around the Cs cation in the solid-state structure of Cs[**3**](H$_2$O)$_{0.5}$. The water molecule exhibits positional disorder and is assigned half site occupancy. Therefore, half of the Cs atoms in the solid-state structure coordinate to eight bromine atoms from three carborane cages, and other half each have one additional water coordination, with a formal coordination number of 9. The Cs−Br interatomic distances range from 3.783(1) to 3.936(1) Å, with an average value of 3.879(2) Å, which is longer than those found in Cs(1-H-CB$_{11}$Br$_{11}$)[3] and Cs-(1-H-12-Br-CB$_{11}$H$_{10}$),[25] probably due to the higher coordination number of the Cs atom in the present compound.

Crystal Structure of [(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][1-C$_6$H$_5$CH$_2$-CB$_9$Cl$_9$]. X-ray-quality crystals were grown from a saturated CH$_2$Cl$_2$ solution with *n*-hexane vapor diffusion at room temperature. The solid-state structure of [(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][**2**] is shown in Figure 6. This is an ordered structure with normal B−B, B−Cl, and C−B distances. For example, the average B−Cl distance of 1.777(4) Å is comparable to the 1.767(10) Å value for [Me$_3$NH][1-CH$_3$-CB$_{11}$Cl$_{11}$].[3]

Conclusions

The highly chlorinated, brominated, iodinated, and methylated carborane anions reported here can all be prepared via sealed-tube reactions. The results show that the electrophilicity of a halogen can be greatly enhanced by increasing the reaction temperature and pressure (sealed-tube conditions). With respect to the ^{29}Si chemical shifts, the weakly coordinating ability of various carborane anions follows the following order: (1)
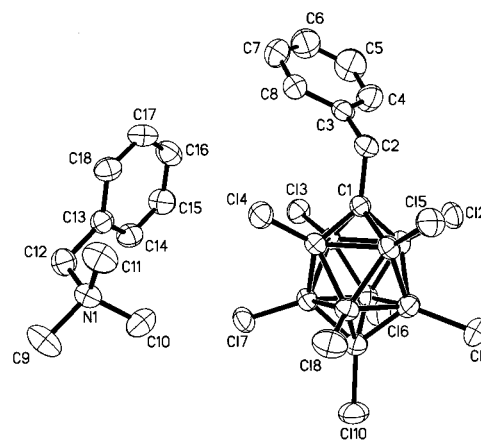
Figure 6. Perspective view of [(C$_6$H$_5$CH$_2$)N(CH$_3$)$_3$][**2**]. Thermal ellipsoids are drawn at the 35% probability level.

icosahedral CB$_{11}$ anions are less coordinating than the corresponding CB$_9$ anions, (2) coordinating ability is decreased as the number of halogen substituents on a cage is increased, and (3) fluorinated carborane anions are less coordinating than other halogenated anions, and iodinated carborane anions are the most coordinating.

Supporting Information Available: X-ray crystallographic files, in CIF format, for Cs[**3**](H$_2$O)$_{0.5}$, (η^2-benzene)Ag[**3**], (η^2-benzene)(η^1-benzene)Ag$_3$[**3**]$_2$[NO$_3$](THF), and [(C$_6$H$_5$CH$_2$)NMe$_3$][**2**]. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000137Q