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Weakly Coordinating Nature of a Carborane Cage Bearing Different Halogen Atoms. Synthesis and Structural Characterization of Icosahedral Mixed Halocarborane Anions, 1-H-$CB_{11}Y_5X_6^-$ (X, Y = Cl, Br, I)

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Mixed halocarborane anions, 1-H-$CB_{11}Y_5X_6^-$ (X, Y = Cl, Br, I), have been prepared by treatment of [Me_3NH][1-H-$CB_{11}H_5X_6$] (X = Cl, Br, I) with proper halogenating reagents at 180−220 °C in a sealed tube in high yield. These new anions are fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR, IR, and negative-ion MALDI MS spectroscopy. Some are further confirmed by single-crystal X-ray analyses. The weakly coordinating nature of these anions is probed by ^{29}Si chemical shifts of the resulting Pr^i_3Si(1-H-$CB_{11}Y_5X_6$) compounds. The results suggest that the coordinating ability of these anions is mainly dependent on the substituents at 7−12 positions (namely, X atoms), and the contribution from the upper belt substituents Y is relatively small. These suggestions are consistent with the results obtained from the structural study of silver salts of mixed halo- and perhalocarborane anions.

Introduction

As a new class of robust and weakly coordinating anions, carborane anions have recently received much attention.[1] Various derivatives of $CB_{11}H_{12}^-$ and $CB_9H_{10}^-$ anions have been made[2−8] in order to search for the most useful and the least coordinating anion. They play a very important role in olefin polymerization[9] and stabilize highly reactive cations.[2b,c,10−22] These anions are all prepared by electrophilic substitution of the B−H bonds of the carborane cage. Since the CB_{11} or CB_9 cage is polarized, substitution occurs preferentially at the boron end of the cluster. Therefore, partially substituted carborane anions have been known for many years while full substitution has only been accomplished very recently. Most of fully substituted carborane anions consist of only one kind of B−X vertexes.[2a,3a,b,d,4,5a,b,6a] Those anions with more than one type of B−X vertexes have remained largely unexplored.[23]

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(23) Anions 1-H-6,7,8,9-F_4-10-OH-$CB_9H_4^-$ and 1-H-6,7,8,9-F_4-10-NHCOMe-$CB_9H_4^-$ (see ref 2g) and 1-Me-12-F-$CB_{11}Me_{10}^-$ (see ref 5b) were reported.

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We have recently developed a very effective methodology for the preparation of perhalocarborane anions,[3b] which makes it possible for us to synthesize mixed halocarboranes. It has been suggested that in the perhalocarborane anions such as $1\text{-H-CB}_{11}X_{11}^-$, halogen atoms at the lower part (7−12 positions) are more coordinating than those at the upper belt (2−6 positions)[3b] and that their coordinating ability follows the order F < Cl < Br < I.[3b,d] What is the possible coordination site in a mixed halocarborane anion such as $1\text{-H-CB}_{11}Y_5X_6^-$? We herein report the synthesis, structural characterization, and weakly coordinating nature of several mixed halocarborane anions, $1\text{-H-2,3,4,5,6-Y}_5\text{-7,8,9,10,11,12-X}_6\text{-CB}_{11}^-$ (X, Y = halogen atoms).

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. Compounds $[\text{Me}_3\text{NH}][1\text{-H-CB}_{11}\text{H}_5X_6]$ (X = Cl,[24] Br,[24] I[15]), $\text{Ag}(1\text{-CH}_3\text{-CB}_{11}\text{Cl}_{11})$,[3b] $\text{Ag}(1\text{-H-CB}_{11}\text{Cl}_{11})$,[3b] and $\text{Ag}(1\text{-H-CB}_{11}\text{Br}_{11})$[3b] were prepared according to literature methods. Single crystals of $(\eta^1\text{-mesitylene})(\text{CH}_3\text{CN})\text{Ag}(1\text{-H-CB}_{11}\text{Br}_{11})$, $(\eta^2\text{-}p\text{-xylene})_2\text{Ag}(1\text{-H-CB}_{11}\text{Cl}_{11})\cdot{}^1/_2(p\text{-xylene})$, and $\text{Ag}(1\text{-CH}_3\text{-CB}_{11}\text{Cl}_{11})$ were grown from a saturated CH_3CN/mesitylene solution of $\text{Ag}(1\text{-H-CB}_{11}\text{Br}_{11})$, a saturated *p*-xylene solution of $\text{Ag}(1\text{-H-CB}_{11}\text{Cl}_{11})$, and a saturated benzene solution of $\text{Ag}(1\text{-CH}_3\text{-CB}_{11}\text{Cl}_{11})$ at room temperature, respectively. 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. ^{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 the deuterated solvent or external TMS (0.00 ppm) for proton and carbon chemical shifts, to external $\text{BF}_3\cdot\text{OEt}_2$ (0.00 ppm) for boron chemical shifts, and to external TMS for ^{29}Si chemical shifts.

Preparation of $[\text{Me}_3\text{NH}][1\text{-H-2,3,4,5,6-Br}_5\text{-7,8,9,10,11,12-Cl}_6\text{-CB}_{11}]$ ($[\text{Me}_3\text{NH}]$[1]). A thick-walled Pyrex tube was charged with $[\text{Me}_3\text{NH}][1\text{-H-CB}_{11}\text{H}_5\text{Cl}_6]$ (0.50 g, 1.22 mmol), triflic acid (4.0 mL), and bromine (4.0 mL, 77.6 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 2 days. After removal of excess bromine and most triflic acid, the residue was treated with a 5% NaOH solution until the pH of the solution reached about 7. The solution was then extracted with diethyl ether (3 × 20 mL). The ether portions were combined, 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 $[\text{Me}_3\text{NH}]$[**1**] as a white solid (0.90 g, 92%). ^{1}H NMR (acetone-d_6): δ 3.01 (s, 9H, *Me*$_3$NH), 2.85 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 47.24 [d, cage *C*, $^1J(^{13}\text{C}-^1\text{H}) = 192$ Hz], 45.00 [q, *Me*$_3$NH, $^1J(^{13}\text{C}-^1\text{H}) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 4.50 (s, 1B), −2.90 (s, 5B), −11.60 (s, 5B). IR (cm^{-1}, KBr): ν 3015 (w), 2959 (s), 2908 (s), 1383 (vs), 1108 (s), 1013 (br). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for $1\text{-H-CB}_{11}\text{Br}_5\text{Cl}_6^-$ 741(83), 742(96), 743(100), 744(96), 745(73); found 741(77), 742(91), 743(100), 744(98), 745(82).

Preparation of $\text{Ag}[1\text{-H-CB}_{11}\text{Br}_5\text{Cl}_6]$ (Ag[1]). To a suspension of $[\text{Me}_3\text{NH}]$[**1**] (0.50 g, 0.62 mmol) in water (30 mL) was added 2 equiv of NaOH, and the mixture was heated at 90 °C for 2 h. After removal of all trimethylamine generated under vacuum and neutralization of the resulting solution with 1 N HNO_3, an aqueous solution of AgNO_3 (0.13 g, 0.77 mmol) was added. The resulting pale-gray precipitate was filtered off, washed with cold water, and dried under vacuum, affording Ag[**1**] (0.48 g, 90%). ^{1}H NMR (acetone-d_6): δ 2.90 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 47.24 [d, cage *C*, $^1J(^{13}\text{C}-^1\text{H}) = 192$ Hz]. ^{11}B NMR (acetone-d_6): δ 4.60 (s, 1B), −2.80 (s, 5B), −11.50 (s, 5B). IR (cm^{-1}, KBr): ν 2980 (w), 2854 (m), 1259 (w), 1027 (m). X-ray-quality crystals were grown from a saturated mesitylene solution.

Preparation of $[\text{Me}_3\text{NH}][1\text{-H-2,3,4,5,6-Cl}_5\text{-7,8,9,10,11,12-Br}_6\text{-CB}_{11}]$ ($[\text{Me}_3\text{NH}]$[2]). A thick-walled Pyrex tube was charged with $[\text{Me}_3\text{NH}][1\text{-H-CB}_{11}\text{H}_5\text{Br}_6]$ (0.30 g, 0.44 mmol), triflic acid (3.0 mL), and iodine monochloride (3.0 mL, 58.8 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 220 °C, and this temperature was maintained for 2 days, followed by the workup procedures analogous to those used for $[\text{Me}_3\text{NH}]$[**1**], giving $[\text{Me}_3\text{NH}]$[**2**] as a white solid (0.34 g, 91%). ^{1}H NMR (acetone-d_6): δ 3.30 (s, 1H, cage C*H*), 3.00 (s, 9H, *Me*$_3$NH). ^{13}C NMR (acetone-d_6): δ 53.60 [d, cage *C*, $^1J(^{13}\text{C}-^1\text{H}) = 194$ Hz], 45.22 [q, *Me*$_3$NH, $^1J(^{13}\text{C}-^1\text{H}) = 142$ Hz]. ^{11}B NMR (acetone-d_6): δ −0.96 (s, 1B), −5.85 (s, 5B), −7.64 (s, 5B). IR (cm^{-1}, KBr): ν 3019 (w), 2918 (m), 2838 (m), 1632 (m), 1384 (m), 1259 (s), 981 (w), 648 (w). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for $1\text{-H-CB}_{11}\text{Cl}_5\text{Br}_6^-$ 786(81), 787(89), 788(100), 789(96), 790(88); found 786(84), 787(96), 788(100), 789(96), 790(86). Recrystallization of $[\text{Me}_3\text{NH}]$[**2**] from an acetone/H_2O solution of Me_3NHCl gave X-ray-quality crystals of $[\text{Me}_3\text{NH}]_2$[**2**][Cl](H_2O).

Preparation of $\text{Ag}[1\text{-H-CB}_{11}\text{Cl}_5\text{Br}_6]$ (Ag[2]). To a suspension of $[\text{Me}_3\text{NH}]$[**2**] (0.25 g, 0.29 mmol) in water (30 mL) was added 2 equiv of NaOH, and the mixture was heated at 90 °C for 2 h. After removal of all trimethylamine generated 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. AgNO_3 (0.06 g, 0.35 mmol) in cold water (2 mL) was then added in one portion at room temperature. The resulting pale-gray precipitate was filtered off, washed with cold water, and dried under vacuum, affording Ag[**2**] (0.23 g, 88%). ^{1}H NMR (acetone-d_6): δ 3.20 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 52.73 [d, cage *C*, $^1J(^{13}\text{C}-^1\text{H}) = 198$ Hz]. ^{11}B NMR (acetone-d_6): δ −0.90 (s, 1B), −5.70 (s, 5B), −7.55 (s, 5B). IR (cm^{-1}, KBr): ν 3015 (w), 2963 (m), 2911 (m), 1615 (m), 1381 (s). Recrystallization from a mesitylene/acetone solution gave X-ray-quality colorless crystals.

Preparation of $[\text{Me}_3\text{NH}][1\text{-H-2,3,4,5,6-Br}_5\text{-7,8,9,10,11,12-I}_6\text{-CB}_{11}]$ ($[\text{Me}_3\text{NH}]$[3]). A thick-walled Pyrex tube was charged with [Cs][$1\text{-H-CB}_{11}\text{H}_5\text{I}_6$] (0.40 g, 0.39 mmol), 1,1,2,2-tetrachloroethane (4.0 mL), and Br_2 (4.0 mL, 77.6 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 180 °C, and this temperature was maintained for 2 days. After removal of excess bromine and the solvent, the residue was treated with a 5% NaOH solution until the pH of the solution reached about 7. The solution was then extracted with diethyl ether (4 × 20 mL). The ether portions were combined, washed with Na_2SO_3, and 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 a mixed solvent of CH_2Cl_2/*n*-hexane (1:5), and then dried under vacuum, giving $[\text{Me}_3\text{NH}]$[**3**] as a white solid (0.42 g, 79%). ^{1}H NMR (acetone-d_6): δ 3.20 (s, 1H, cage C*H*), 3.00 (s, 9H, *Me*$_3$NH). ^{13}C NMR (acetone-d_6): δ 60.03 [d, cage *C*, $^1J(^{13}\text{C}-^1\text{H}) = 194$ Hz], 45.00 [q, *Me*$_3$NH, $^1J(^{13}\text{C}-^1\text{H}) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ −5.50 (s, 6B), −11.70 (s, 5B). IR (cm^{-1}, KBr): ν 2960 (w), 2918 (m), 1660 (w), 1383 (s), 1080 (s), 1026(s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for $1\text{-H-CB}_{11}\text{Br}_5\text{I}_6^-$ 1291(88), 1292(98), 1293(100), 1294(96); found 1291(81), 1292(96), 1293(100), 1294(91).

Preparation of $\text{Cs}[1\text{-H-CB}_{11}\text{Br}_5\text{I}_6]$ (Cs[3]). To a suspension of $[\text{Me}_3\text{NH}]$[**3**] (0.10 g, 0.074 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 generated 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 (0.019 g, 0.11 mmol) was then added to give a milky solution with some precipitates. After removal of acetone, the precipitate was collected by filtration. This solid was washed with cold water twice, giving Cs[**3**] as a white solid (0.09 g,

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90%). ^{1}H NMR (acetone-d_6): δ 3.20 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 60.50 [d, cage *C*, $^1J(^{13}C-^1H) = 194$ Hz]. ^{11}B NMR (acetone-d_6): δ $-$5.50 (s, 6B), $-$11.70 (s, 5B). IR (cm^{-1}, KBr): ν 2955 (w), 2922 (w), 1382 (s), 1096 (s), 1024 (s), 802 (m). Recrystallization from a THF/H_2O solution at room temperature gave X-ray-quality colorless crystals.

Preparation of Ag[1-H-$CB_{11}Br_5I_6$] (Ag[3]). Compound Cs[**3**] (0.09 g, 0.063 mmol) was dissolved in water (15 mL) containing a small amount of acetone. $AgNO_3$ (0.013 g, 0.077 mmol) was dissolved in cold water (1 mL). The two solutions were mixed at room temperature. After removal of acetone, the resulting pale-gray precipitate was filtered off, washed with cold water, and dried under vacuum, affording Ag[**3**] (0.081 g, 92%). ^{1}H NMR (acetone-d_6): δ 3.20 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 62.50 [d, cage *C*, $^1J(^{13}C-^1H) = 196$ Hz]. ^{11}B NMR (acetone-d_6): δ $-$3.00 (s, 1B), $-$5.40 (s, 5B), $-$11.20 (s, 5B). IR (cm^{-1}, KBr): ν 2921 (w), 2954 (m), 1383 (s), 1026 (m), 729 (w), 581 (w).

Preparation of [Me_3NH][1-H-2,3,4,5,6-I_5-7,8,9,10,11,12-Br_6-CB_{11}] ([Me_3NH][4]). A thick-walled Pyrex tube was charged with [Me_3NH][1-H-$CB_{11}H_5Br_6$] (0.15 g, 0.22 mmol), triflic acid (2.0 mL), and iodine (2.0 g, 7.88 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, followed by the workup procedures analogous to those used for [Me_3NH][**3**], giving a pale-yellow solid that was recrystallized from a CH_2Cl_2/hexane solution to afford [Me_3NH][**4**] as a pale-yellow solid (0.23 g, 80%). ^{1}H NMR (acetone-d_6): δ 2.95 (s, 1H, cage C*H*), 2.80 (s, 9H, *Me*$_3$NH). ^{13}C NMR (acetone-d_6): δ 54.91 [d, cage C, $^1J(^{13}C-^1H) = 193$ Hz], 44.98 [q, *Me*$_3$NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 2.60 (s, 1B), $-$1.80 (s, 5B), $-$18.40 (s, 5B). IR (cm^{-1}, KBr): ν 2998 (w), 2952 (m), 2921 (m), 1694 (m), 1465 (m), 1382 (s), 988 (s). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-H-$CB_{11}I_5Br_6^-$ 1244(83), 1245(97), 1246(100), 1247(92), 1248(75); found 1244(70), 1245(84), 1246(100), 1247(98), 1248(79).

Preparation of Ag[1-H-$CB_{11}I_5Br_6$] (Ag[4]). This compound was prepared in 84% yield as a pale-brown solid in a manner analogous to that used for Ag[**3**]. ^{1}H NMR (acetone-d_6): δ 2.75 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 52.62 [d, cage *C*, $^1J(^{13}C-^1H) = 198$ Hz]. ^{11}B NMR (acetone-d_6): δ $-$2.01 (s, 1B), $-$6.53 (s, 5B), $-$23.40 (s, 5B). IR (cm^{-1}, KBr): ν 3067 (w), 3004 (w), 1610 (m), 1383 (m), 1098 (s), 955 (s).

Preparation of [Me_3NH][1-H-2,3,4,5,6-I_5-7,8,9,10,11,12-Cl_6-CB_{11}] ([Me_3NH][5]). A thick-walled Pyrex tube was charged with [Me_3NH][1-H-$CB_{11}H_5Cl_6$] (0.20 g, 0.49 mmol), triflic acid (2.0 mL), and iodine (2.0 g, 7.88 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. The reaction mixture was then treated in the same manner described for [Me_3NH][**4**], giving [Me_3NH][**5**] as a pale-yellow solid (0.43 g, 84%). ^{1}H NMR (acetone-d_6): δ 3.10 (s, 1H, cage C*H*), 2.94 (s, 9H, *Me*$_3$NH). ^{13}C NMR (acetone-d_6): δ 46.68 [d, cage *C*, $^1J(^{13}C-^1H) = 192$ Hz], 45.10 [q, *Me*$_3$NH, $^1J(^{13}C-^1H) = 143$ Hz]. ^{11}B NMR (acetone-d_6): δ 6.00 (s, 1B), 0.80 (s, 5B), $-$20.60 (s, 5B). IR (cm^{-1}, KBr): ν 3013 (w), 2954 (m), 2699 (s), 1474 (w), 984 (m). Negative-ion MALDI MS, *m/z* (isotopic abundance): calcd for 1-H-$CB_{11}I_5Cl_6^-$ 976(67), 977(89), 978(100), 979(93), 980(77); found 976(62), 977(87), 978(100), 979(95), 980(85).

Preparation of Ag[1-H-$CB_{11}I_5Cl_6$] (Ag[5]). This compound was prepared in 87% yield as a pale-gray solid in a manner analogous to that used for Ag[**3**]. ^{1}H NMR (acetone-d_6): δ 2.95 (s, 1H, cage C*H*). ^{13}C NMR (acetone-d_6): δ 47.30 [d, cage *C*, $^1J(^{13}C-^1H) = 192.0$ Hz]. ^{11}B NMR (acetone-d_6): δ 6.50 (s, 1B), 0.90 (s, 5B), $-$20.50 (s br, 5B). IR (cm^{-1}, KBr): ν 3015 (w), 2794 (m), 1380 (w), 987 (m).

Attempted Preparation of [Me_3NH][1-H-2,3,4,5,6-Cl_5-7,8,9,10,-11,12-I_6-CB_{11}]. Chlorine gas was continuously bubbled into a glacial acetic acid solution (15 mL) of Cs[1-H-$CB_{11}H_5I_6$] (0.10 g, 0.10 mmol) at 80 °C under stirring for 2 weeks. ^{11}B NMR, IR, and MS analyses revealed that the product was a mixture of carborane anions containing B$-$Cl, B$-$I, and B$-$H bonds.

A thick-walled Pyrex tube was charged with Cs[1-H-$CB_{11}H_5I_6$] (0.10 g, 0.10 mmol), 1,1,2,2-tetrachloroethane (2.0 mL), and *N*-chlorosuccinamide (0.50 g, 3.74 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 more than 4 days. This mixture was then treated in a manner analogous to that used for [Me_3NH][**2**], giving a pale-yellow solid. ^{11}B NMR, IR, and MS analyses showed that it was again a mixture of products containing B$-$Cl, B$-$I, and B$-$H bonds.

A thick-walled Pyrex tube was charged with Cs[1-H-$CB_{11}H_5I_6$] (0.10 g, 0.10 mmol) and iodine monochloride (2.0 mL, 39.2 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 2 days. This mixture was then treated in a manner analogous to that used for [Me_3NH][**2**], affording [Me_3NH][1-H-$CB_{11}Cl_{11}$] that was identified by spectroscopic data.[3b]

^{29}Si NMR Measurements. Pr^i_3Si(carborane) was generated according to the literature procedures.[13] An NMR tube was charged with [Ph_3C][1-H-$CB_{11}Br_5Cl_6$] (100 mg, 0.10 mmol; it was prepared by treatment of Ag[1-H-$CB_{11}Br_5Cl_6$] with 1 equiv of Ph_3CBr in toluene/CH_3CN following the literature procedures.[7]), Pr^i_3SiH (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. This reaction was monitored by ^{29}Si NMR. Within a period of 24 h, the ^{29}Si resonance for Pr^i_3SiH at δ 12.1 ppm decreased in intensity and a new peak appeared at δ 115.8 ppm.

Pr^i_3Si(1-H-$CB_{11}Cl_{11}$), Pr^i_3Si(1-H-$CB_{11}Cl_5Br_6$), Pr^i_3Si(1-H-$CB_{11}I_5Br_6$), and Pr^i_3Si(1-H-$CB_{11}Br_5I_6$) were generated in the same manner and subjected to ^{29}Si NMR measurements. New ^{29}Si resonances appeared at δ 114.4, 111.1, 108.8, and 104.5 ppm, respectively.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and then sealed in thin-walled 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[25] 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, version 5.03 program package (PC version).[26] The hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Tables 1 and 2, respectively. Further details are included in the Supporting Information.

Results and Discussion

Synthesis. We have recently reported the preparation of two series of perhalogenated *closo*-carborane anions 1-R-$CB_{11}X_{11}^-$ and 1-R-$CB_9X_9^-$ by using a newly developed sealed-tube method.[3b,d] This method can also be employed to make mixed halocarborane anions after some modifications.

A mixture of 1-H-$CB_{11}H_5Cl_6^-$, excess Br_2, and triflic acid was sealed in a Pyrex tube and then heated at 220 °C for 2 days to give the sole product 1-H-$CB_{11}Br_5Cl_6^-$ (**1**). Under similar reaction conditions, however, bromination of 1-H-$CB_{11}H_5I_6^-$ led to a 1:1 mixture of 1-H-$CB_{11}Br_{11}^-$ and 1-Br-$CB_{11}Br_{11}^-$ on the basis of spectroscopic analyses,[3b] and the final product of 1-Br-$CB_{11}Br_{11}^-$ would be isolated after a prolonged reaction. In the absence of triflic acid, this reaction resulted in the formation of a mixture of 1-H-$CB_{11}Br_xI_{11-x}^-$ ($x = 6-9$) based on the analyses of MS spectroscopic data. It suggests that triflic acid may enhance the reactivity of Br_2 and/or activate the B$-$I bonds, leading to a complete replacement of all B$-$H

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(25) Higashi, T. *ABSCOR, An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corp.: Tokyo, 1995.

(26) *SHELXTL*, version 5.03 (program package); Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

Table 1. Crystal Data and Summary of Data Collection and Refinement for (η^2-Mesitylene)$_2$Ag[**1**]·(mesitylene), (η^1-Mesitylene)Ag[**2**]·(mesitylene), (η^1-Mesitylene)(CH$_3$CN)Ag(1-H-CB$_{11}$Br$_{11}$), and (η^2-*p*-Xylene)$_2$Ag(1-H-CB$_{11}$Cl$_{11}$)·$^1/_2$(*p*-xylene)

	(η^2-mesitylene)$_2$Ag[**1**]· (mesitylene)	(η^1-mesitylene)Ag[**2**]· (mesitylene)	(η^1-mesitylene)(CH$_3$CN)-Ag(1-H-CB$_{11}$Br$_{11}$)	(η^2-*p*-xylene)$_2$Ag(1-H-CB$_{11}$Cl$_{11}$)· $^1/_2$(*p*-xylene)
formula	$C_{28}H_{37}AgB_{11}Br_5Cl_6$	$C_{19}H_{25}AgB_{11}Br_6Cl_5$	$C_{12}H_{16}AgB_{11}Br_{11}N$	$C_{21}H_{26}AgB_{11}Cl_{11}$
cryst size (mm)	0.30 × 0.20 × 0.14	0.30 × 0.60 × 0.70	0.45 × 0.40 × 0.27	0.90 × 0.82 × 0.46
fw	1212.61	1136.88	1280.05	895.15
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	10.207(2)	16.709(7)	12.860(2)	9.379(1)
b, Å	13.402(3)	12.168(6)	21.361(2)	11.682(1)
c, Å	16.351(3)	18.138(1)	12.233(2)	18.038(1)
α, deg	90.64(3)	90.00	90.00	100.15(1)
β, deg	96.46(3)	90.17(4)	89.96(1)	102.77(1)
γ, deg	97.43(3)	90.00	90.00	100.96
V, Å^3	2203.1(8)	3688(4)	3360.4(7)	1842.5(2)
Z	2	4	4	2
D_{calcd}, Mg/m^3	1.828	2.048	2.528	1.613
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	21	23	23	21
2θ range, deg	2.5−51.4	4.0−50.0	3.7−50.0	3.6−56.7
μ, mm^{-1}	5.378	7.426	13.689	1.362
F(000)	1168	2144	2328	882
no. obsd reflns	3916	6507	3606	9023
no. params refined	461	380	335	397
goodness of fit	1.111	0.907	1.209	1.048
R1[a]	0.078	0.054	0.078	0.038
wR2[b]	0.157	0.123	0.116	0.096

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

Table 2. Crystal Data and Summary of Data Collection and Refinement for Ag(1-CH$_3$-CB$_{11}$Cl$_{11}$), Cs[**3**](THF), and [Me$_3$NH]$_2$[**2**][Cl](H$_2$O)

	Ag(1-CH$_3$-CB$_{11}$Cl$_{11}$)	Cs[**3**](THF)	[Me$_3$NH]$_2$[**2**][Cl](H$_2$O)
formula	$C_2H_3AgB_{11}Cl_{11}$	$C_5H_9B_{11}Br_5CsI_6O$	$C_7H_{23}B_{11}Br_6Cl_6N_2O$
cryst size (mm)	0.30 × 0.30 × 0.20	0.50 × 0.30 × 0.28	0.70 × 0.30 × 0.20
fw	643.77	1497.89	962.34
cryst syst	cubic	orthorhombic	triclinic
space group	$Pa\bar{3}$	$Pna2_1$	$P\bar{1}$
a, Å	12.489(1)	19.736(2)	12.236(2)
b, Å	12.489(1)	11.319(4)	16.843(3)
c, Å	12.489(1)	13.804(5)	18.064(4)
α, deg	90.00	90.00	62.98(3)
β, deg	90.00	90.00	81.45(3)
γ, deg	90.00	90.00	80.92(3)
V, Å^3	1947.8(4)	3084(3)	3262(1)
Z	4	4	4
D_{calcd}, Mg/m^3	2.195	3.226	1.959
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	23	23	23
2θ range, deg	5.6−50.0	4.1−50.0	4.1−50.0
μ, mm^{-1}	2.529	13.689	7.885
F(000)	1216	2600	1816
no. obsd reflns	546	2821	11 466
no. params refined	41	264	608
goodness of fit	1.095	1.023	0.963
R1[a]	0.064	0.039	0.056
wR2[b]	0.170	0.086	0.148

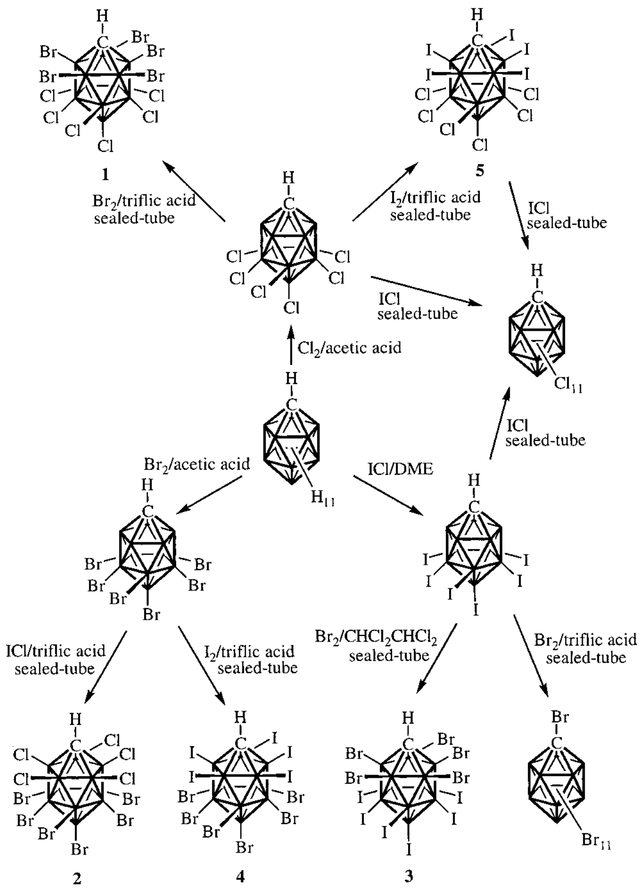
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

and B−I by B−Br bonds. This may also imply that the solvent could play an important role in this type of reaction. To prepare the mixed haloanion of 1-H-CB$_{11}$Br$_5$I$_6^-$ (**3**), a suitable solvent is desirable. After many experiments, we found that CHCl$_2$CHCl$_2$ is the best choice. Treatment of 1-H-CB$_{11}$H$_5$I$_6^-$ with excess Br$_2$ in CHCl$_2$CHCl$_2$ in a sealed tube at 180 °C for 3 days yielded the anion **3** in high yield.

Treatment of 1-H-CB$_{11}$H$_5$Br$_6^-$ with excess ICl in triflic acid or in the absence of triflic acid in a sealed tube at 220 °C for 2 days gave the sole product 1-H-CB$_{11}$Cl$_5$Br$_6^-$ (**2**) in high yield. No 1-H-CB$_{11}$I$_5$Br$_6^-$ was isolated. Under the same reaction conditions, reaction of 1-H-CB$_{11}$H$_5$Cl$_6^-$ with excess ICl generated undecachlorocarborane anion 1-H-CB$_{11}$Cl$_{11}^-$, and no iodo species was isolated. It is noteworthy that treatment of 1-H-CB$_{11}$H$_{11}^-$ with excess ICl afforded 1-H-CB$_{11}$Cl$_{11}^-$ in triflic acid or 1-H-CB$_{11}$I$_{11}^-$ in the absence of triflic acid.[3b] In these reactions, 1-H-2,3,4,5,6-I$_5$-CB$_{11}$X$_6^-$ may serve as an intermediate followed by nucleophilic substitution to give 1-H-2,3,4,5,6-Cl$_5$-CB$_{11}$X$_6^-$ as the final product.[3b,d]

We have recently proposed that the electrophilicity of iodine can be greatly enhanced in triflic acid under sealed-tube reaction conditions.[3d] Accordingly, 1-H-CB$_{11}$I$_5$Br$_6^-$ (**4**) and 1-H-CB$_{11}$I$_5$Cl$_6^-$ (**5**) were prepared in high yield by treatment of 1-H-CB$_{11}$H$_5$Br$_6^-$ or 1-H-CB$_{11}$H$_5$Cl$_6^-$ with excess I$_2$ in triflic acid in a sealed tube at 180 °C for 4 days. Reaction of **4** or **5** with excess ICl in triflic acid in a sealed tube at 220 °C for 2 days

Scheme 1



afforded **2** or 1-H-CB$_{11}$Cl$_{11}^-$, respectively, which supports the reaction pathway proposed previously.

Although 1-H-CB$_{11}$Cl$_5$Br$_6^-$ (**2**) was prepared by reaction of 1-H-CB$_{11}$H$_5$Br$_6^-$ with excess ICl in a sealed tube at 220 °C, treatment of 1-H-CB$_{11}$H$_5$I$_6^-$ with excess ICl in triflic acid or in the absence of triflic acid always gave the perchlorinated species 1-H-CB$_{11}$Cl$_{11}^-$. Direct chlorination of 1-H-CB$_{11}$H$_5$I$_6^-$ with excess Cl$_2$ in glacial acetic acid or with excess NCS (*N*-chlorosuccinamide) in CHCl$_2$CHCl$_2$ resulted in a mixture of products containing B−Cl, B−I, and B−H bonds on the basis of NMR, IR, and MS analyses. All attempts to prepare 1-H-CB$_{11}$Cl$_5$I$_6^-$ anion failed. Scheme 1 summarizes all transformations described in this section.

These mixed halocarborane anions were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR, negative-ion MALDI MS, and IR spectroscopy. Some were further confirmed by single-crystal X-ray analyses. They are thermally very stable, with no decomposition up to 250 °C. They are also stable in very strong acids such as triflic acid and strong bases such as NaOH.

The silver salts of various carborane anions were readily prepared by treatment of their sodium salts with slightly excess AgNO$_3$ in aqueous solution or a mixture of water/acetone. The solubilities of these salts in various solvents are similar to those of perhalogenated analogues and follow the order Cl > Br > I.

NMR Spectra. Table 3 lists the ^{13}C and ^{11}B NMR spectra data for 1-H-CB$_{11}$Y$_5$X$_6^-$ anions. It is obvious that the ^{13}C chemical shifts of the 1-H-CB$_{11}$Y$_5$X$_6^-$ anions depend mainly on the halogen substituents at 7−12 positions (namely, X atoms) and follow the trend Cl < Br < I at about 47, 54, and 60 ppm, respectively, a trend previously observed in the ^{13}C chemical shifts of the 1-H-CB$_{11}$H$_5$X$_6^-$ anions.[15] The halogen substituents at 2−6 positions (namely, Y atoms) have a very little effect on the ^{13}C chemical shifts. The comparison of ^{11}B chemical shift data for three anions 1-H-CB$_{11}$Y$_5$Cl$_6^-$ clearly shows the following trends: (1) Cl < Br < I for the resonances of both B(12) and B(7)−B(11); (2) Cl > Br > I for that of B(2)−B(6); and (3) Cl < Br < I for the range of ^{11}B chemical shifts. These trends are also observed in the ^{11}B NMR spectra of the 1-H-CB$_{11}$Y$_5$Br$_6^-$ and 1-H-CB$_{11}$Y$_5$I$_6^-$ anions at least with respect to the present data available.

Table 3. NMR Spectral Data for 1-H-CB$_{11}$Y$_5$X$_6^-$ Anions[a]

anion	δ(^{13}C), ppm	δ(^{11}B), ppm B(12)	B(7)−B(11)	B(2)−B(6)	ref
1-H-CB$_{11}$Cl$_{11}^-$	47.40	2.15	−5.27	−8.36	3b
1-H-CB$_{11}$Br$_5$Cl$_6^-$	47.24	4.50	−2.90	−11.60	this work
1-H-CB$_{11}$I$_5$Cl$_6^-$	46.68	6.00	0.80	−20.60	this work
1-H-CB$_{11}$Cl$_5$Br$_6^-$	53.60	−0.96	−5.85	−7.64	this work
1-H-CB$_{11}$Br$_{11}^-$	54.14	1.42	−5.32	−9.16	3b
1-H-CB$_{11}$I$_5$Br$_6^-$	54.91	2.60	−1.80	−18.40	this work
1-H-CB$_{11}$Br$_5$I$_6^-$	60.03	−5.50	−11.70	−5.50	this work
1-H-CB$_{11}$I$_{11}^-$	62.13	−4.70	−9.20	−16.00	3b

[a] All spectra at 25°C. Me$_3$NH$^+$ salts in acetone-d_6. δ(^{13}C) for SiMe$_4$ = 0. δ(^{11}B) for BF$_3$·OEt$_2$ = 0.

Table 4. Downfield ^{29}Si Chemical Shifts for Pr$^i_3$SiZ

compound	solvent	δ(^{29}Si), ppm	ref
Pr$^i_3$SiH	toluene	12.1	12
[Pr$^i_3$Si(toluene)][B(C$_6$F$_5$)$_4$]	toluene	94.0	12
Pr$^i_3$Si[B(C$_6$F$_5$)$_4$]	none	107.6	27
Pr$^i_3$Si(1-H-CB$_{11}$H$_5$I$_6$)	none	97	15
Pr$^i_3$Si(1-H-CB$_9$H$_4$Br$_5$)	toluene	97.9	12
Pr$^i_3$Si(1-H-CB$_9$Br$_9$)	toluene	100.9	3d
Pr$^i_3$Si(1-H-CB$_{11}$Br$_5$I$_6$)	toluene	104.5	this work
Pr$^i_3$Si(1-H-CB$_{11}$H$_5$Br$_6$)	toluene	105	13
	none	110	15
Pr$^i_3$Si(1-benzyl-CB$_9$Cl$_9$)	toluene	106.0	3d
Pr$^i_3$Si(1-H-CB$_{11}$I$_5$Br$_6$)	toluene	108.8	this work
Pr$^i_3$Si(1-H-CB$_{11}$Cl$_5$Br$_6$)	toluene	111.1	this work
Pr$^i_3$Si(1-H-CB$_{11}$Cl$_{11}$)	toluene	114.4	this work
Pr$^i_3$Si(1-H-CB$_{11}$H$_5$Cl$_6$)	none	115	15
Pr$^i_3$Si(1-H-CB$_{11}$Br$_5$Cl$_6$)	toluene	115.8	this work
Pr$^i_3$Si(1-H-CB$_{11}$F$_{11}$)	toluene	120	2a

Coordinating Nature. It has been documented that the ^{29}Si shift of compound R$_3$SiZ is very sensitive to the coordinating nature of the counterion Z$^-$.[1a,b] We probed the weakly coordinating nature of 1-H-CB$_{11}$Cl$_{11}^-$, 1-H-CB$_{11}$Br$_5$Cl$_6^-$, 1-H-CB$_{11}$Cl$_5$Br$_6^-$, 1-H-CB$_{11}$I$_5$Br$_6^-$, and 1-H-CB$_{11}$Br$_5$I$_6^-$ by generating Pr$^i_3$Si(carborane) in toluene-d_8 following the literature procedures.[13] The ^{29}Si chemical shifts are listed in Table 4. No other ^{29}Si resonance was observed, indicating that no halide abstraction reaction occurred or that these carborane anions are stable in the presence of a strong electrophile such as a cationic silicon center.

Careful analyses of data in Table 4 suggest that (1) the highly halogenated carborane anions are less coordinating than the less halogenated ones, (2) the coordinating ability of halocarborane anions decreases in the order I > Br > Cl > F, and (3) the coordinating ability of various mixed halocarborane anions 1-H-CB$_{11}$Y$_5$X$_6^-$ is mainly dependent on the nature of the substituents at 7−12 positions, namely, X atoms, and the contribution from substituent Y is relatively small. The slightly more downfield ^{29}Si chemical shift of Pr$^i_3$Si(1-H-CB$_{11}$Br$_5$Cl$_6$) compared with that of Pr$^i_3$Si(1-H-CB$_{11}$Cl$_{11}$) may be rationalized in terms of anion displacement by toluene forming Pr$^i_3$Si(toluene)$^+$.

Structure. The molecular structures of silver(I) carborane complexes are very diverse and could not be predicted from a knowledge of the constituent parts. In the known structures, the carborane anion coordinates to Ag$^+$ via lone pairs on halo-

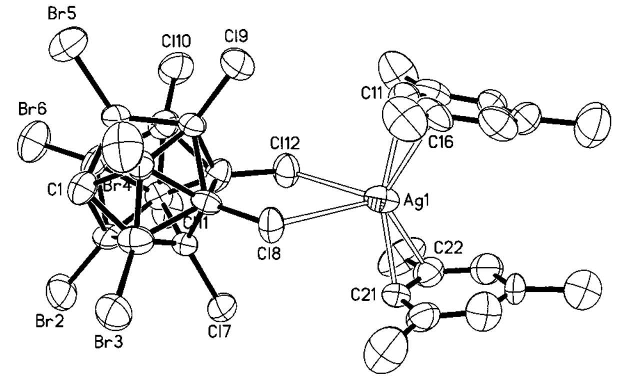


Figure 1. Perspective view of the coordinating sphere around the Ag atom in (η^2-mesitylene)$_2$Ag[**1**]·(mesitylene) (the solvated mesitylene molecule is not shown, and thermal ellipsoids are drawn at the 35% probability level).

gen atoms and/or via a complexation of B−H bonded pairs from the lower belt or the 12-position (antipodal to C cage atom) because of the higher electron density of these positions.[2d,e,3b−d,7,8,16,28] In the case of mixed halocarborane anions, there are two types of halogen atoms available on the cage. Is it possible to predict the coordination site? Which element (hard−soft acid−base rule, steric or electronic factor) plays a predominant role? It is hoped that we could gain some insight into the coordinating nature of these anions by the structural study of silver salts of mixed halocarborane anions.

Figure 1 shows the coordination around silver in the solid-state structure of (η^2-mesitylene)$_2$Ag(1-H-$CB_{11}Br_5Cl_6$)·(mesitylene). Unlike the silver(I) salts of other carborane anions,[2e,3b−d,7,8,16,28] it is a monomeric structure with no obvious intermolecular interactions. The closest intermolecular Ag···Cl(7) distance is greater than 5.6 Å. The closest Ag···Br(2) distance is 6.181 Å (to Br in another molecule). (η^2-Mesitylene)$_2$Ag[**1**] has a four-coordinate silver atom in a propeller arrangement of two η^2-mesitylene molecules and a single bidentate 1-H-$CB_{11}Br_5Cl_6^-$ anion through its Cl(8) and Cl(12) atoms. The Ag−Cl(8) and Ag−Cl(12) distances are 2.986(2) and 2.889(2) Å, respectively. These measured values are at the long end of the Ag−Cl distances (2.68−2.87 Å) normally observed in silver(I) salts of polychlorocarborane anions.[3c,d,28] The asymmetric η^2 fashion of mesitylene bonding, with Ag−C bond distances ranging from 2.328(6) to 2.662(6) Å, is typical of many silver−arene complexes.[29]

It is noteworthy that no interaction between Ag^+ and any one of the bromine atoms from the upper belt of the cage is observed, although Ag^+ prefers to bind to a bromine atom rather than a chlorine atom according to the hard−soft acid−base principle.

In contrast, a polymeric structure is observed in (η^1-mesitylene)Ag(1-H-$CB_{11}Cl_5Br_6$)·(mesitylene) as shown in Figure 2. The four-coordinate silver atom is in a distorted-tetrahedral arrangement of one η^1-mesitylene molecule, two bromine atoms from a bridging 1-H-$CB_{11}Cl_5Br_6^-$ anion, and one bromine atom from another bridging 1-H-$CB_{11}Cl_5Br_6^-$ anion (Figure 3), a coordination pattern that differs significantly from that discussed above although both silver salts were crystallized from saturated mesitylene solutions. The Ag−C(15) distance of 2.421(5) Å and the Ag−Br(7,8,10A) distances of 2.750(2)−2.873(1) Å are all comparable to the reported values.[3b−d,7,8,16,28,29]

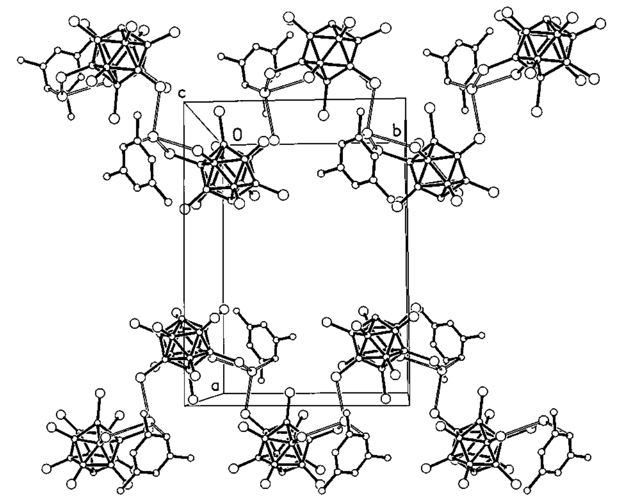


Figure 2. Packing diagram for (η^1-mesitylene)Ag[**2**]·(mesitylene) (the solvated mesitylene molecule is not shown).

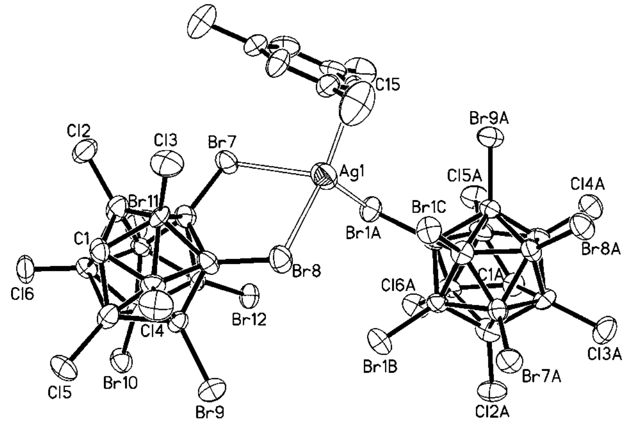


Figure 3. Perspective view of the coordinating sphere around the Ag atom in (η^1-mesitylene)Ag[**2**]·(mesitylene) (the solvated mesitylene molecule is not shown, and thermal ellipsoids are drawn at the 35% probability level).

There are no interactions between Ag^+ and any one of the five chlorine atoms from the upper belt of the cage, which is understandable because Br^- is a softer base than Cl^- and the lower belt atoms bear more negative charge than the upper belt ones. These results may suggest that the charge distribution on the icosahedral cage plays a predominant role in the coordination chemistry of carborane anions.

For comparison and discussion, the solid-state structures of silver(I) salts of perchloro- and perbromocarborane anions were also determined. Figure 4 shows the molecular structure of (η^1-mesitylene)Ag(CH_3CN)(1-H-$CB_{11}Br_{11}$). The silver atom is η^1-bound to one mesitylene and one CH_3CN and coordinated to two bromine atoms from the 1-H-$CB_{11}Br_{11}^-$ anion in a distorted-tetrahedral arrangement, a geometry that is very similar to that of Ag in (η^1-mesitylene)Ag(1-H-$CB_{11}Cl_5Br_6$). The coordination of CH_3CN breaks the polymeric chain, leading to the formation of the discrete molecule with no significant intermolecular interaction. The Ag−C(11) distance of 2.430(7) Å is very close to the 2.421(5) Å in (η^1-mesitylene)Ag(1-H-$CB_{11}Cl_5Br_6$). The Ag−Br distances of 2.772(1) and 2.776(1) Å are comparable to the corresponding values observed in (η^1-mesitylene)Ag(1-H-$CB_{11}Cl_5Br_6$) and other silver salts of polybromocarborane anions.[3b−d,7,8,16,28] The Ag−N distance of 2.235(5) Å is similar

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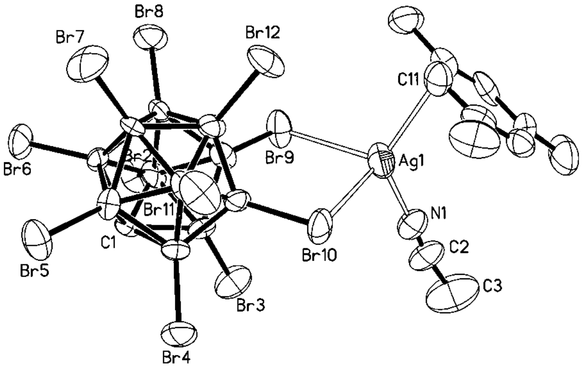

Figure 4. Perspective view of the coordinating sphere around the Ag atom in (η^1-mesitylene)(CH_3CN)Ag(1-H-$CB_{11}Br_{11}$) (thermal ellipsoids are drawn at the 35% probability level).

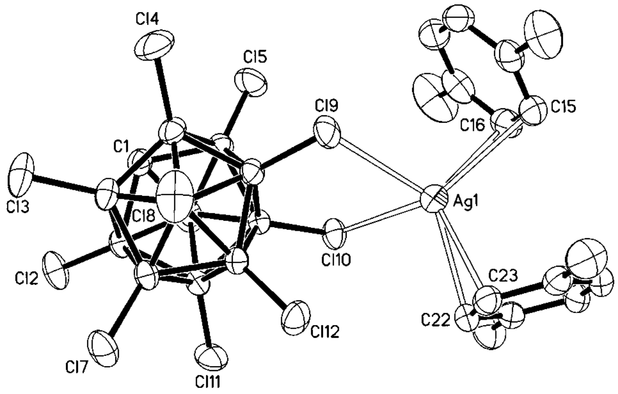

Figure 5. Perspective view of the coordinating sphere around the Ag atom in (η^2-*p*-xylene)$_2$Ag(H-1-$CB_{11}Cl_{11}$)·1/2(*p*-xylene) (the solvated *p*-xylene molecule is not shown, and thermal ellipsoids are drawn at the 35% probability level).

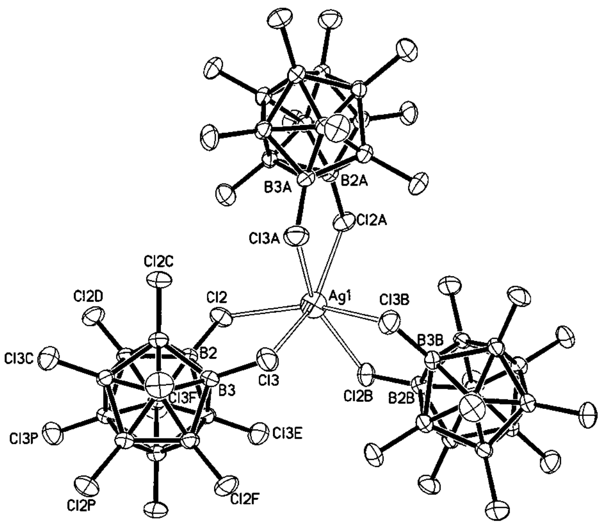

Figure 6. Perspective view of the coordinating sphere around the Ag atom in Ag(1-CH_3-$CB_{11}Cl_{11}$) (thermal ellipsoids are drawn at the 35% probability level).

to those normally observed in $Ag(CH_3CN)_n^+$ complexes.[30,31] It is noted that the Ag atom does not coordinate to the most electron-rich Br(12) atom in both silver salts. This should not be due to steric effects because all six bromine atoms (Br(7)−Br(12)) in the present compound have identical environments.

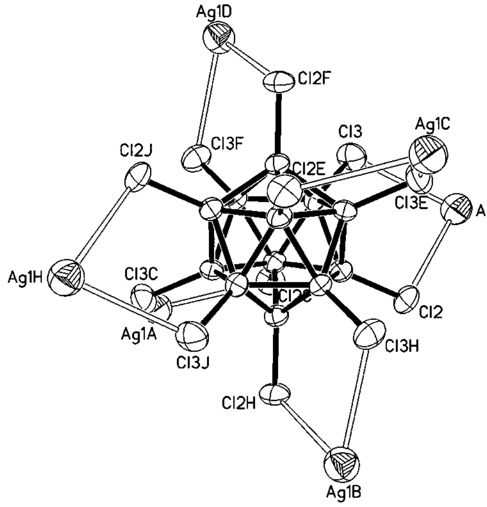

Figure 7. Perspective view of the coordinating sphere around the carborane anion in Ag(1-CH_3-$CB_{11}Cl_{11}$) (thermal ellipsoids are drawn at the 35% probability level).

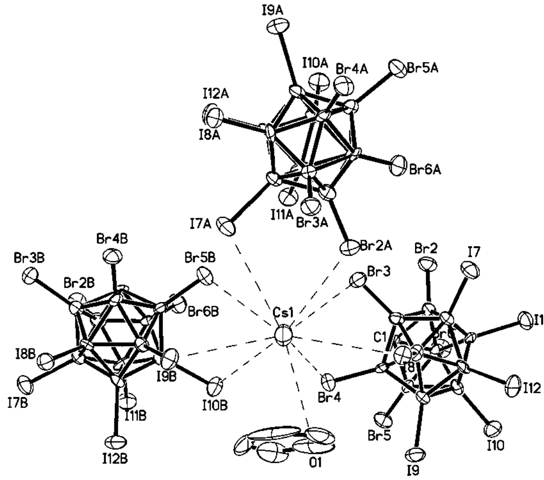

Figure 8. Perspective view of the coordinating sphere around the Cs cation in Cs[**3**](THF) (thermal ellipsoids are drawn at the 35% probability level).

The observed phenomenon may have been caused by crystal packing forces.

Similar in structure to (η^2-mesitylene)$_2$Ag(1-H-$CB_{11}Br_5Cl_6$), (η^2-*p*-xylene)$_2$Ag(1-H-$CB_{11}Cl_{11}$) has a monomeric structure and a four-coordinate silver atom in a propeller arrangement of two η^2-*p*-xylene molecules and a single bidentate 1-H-$CB_{11}Cl_{11}^-$ anion via its Cl(9) and Cl(10) atoms, as shown in Figure 5. Unlike the (η^2-mesitylene)$_2$Ag[**1**], no interaction between Ag^+ and Cl(12) is observed in the present compound, which perhaps indicates that the energy differences between Ag−Cl coordination bonds are small and can be made up by crystal packing forces. The Ag−C and Ag−Cl distances are all comparable to the corresponding values reported in the literature.[3c,d,16,28,29]

Figure 6 shows the coordination around silver in the solid-state structure of Ag(1-CH_3-$CB_{11}Cl_{11}$), which is significantly different from that of (η^2-*p*-xylene)$_2$Ag(1-H-$CB_{11}Cl_{11}$). Each silver atom coordinates to six chlorine atoms from the three 1-CH_3-$CB_{11}Cl_{11}^-$ anions in a distorted-octahedral arrangement at an average Ag−Cl distance of 2.882(1) Å, and each anion is surrounded by six silver atoms in a regular octahedral arrangement (as shown in Figure 7) to form a three-dimensional coordination polymer. As far as we are aware, this is the first

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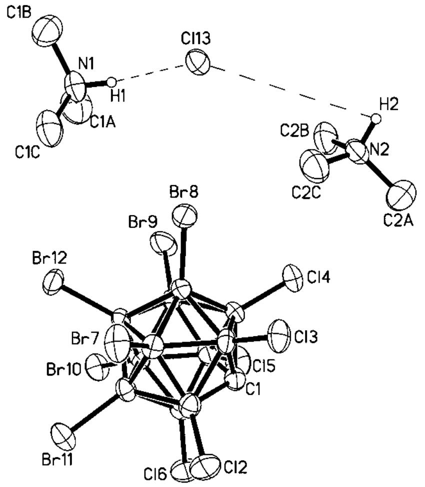

Figure 9. Perspective view of the molecular structure of $[Me_3NH]_2$-[**2**][Cl](H_2O) (the solvated H_2O molecule is not shown, and thermal ellipsoids are drawn at the 35% probability level).

example of a three-dimensional polymeric structure observed in the silver salts of any carborane anions. Since the anion has a crystallographically imposed 3-fold rotation−inversion axis, 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 chlorine atoms of the cage. Therefore, it is not possible to distinguish the BCl vertex antipodal to carbon from other vertexes.

Figure 8 shows the coordination around the Cs cation in the solid-state structure of Cs[1-H-$CB_{11}Br_5I_6$][THF]. The Cs atom coordinates to four bromine atoms and four iodine atoms from three 1-H-$CB_{11}Br_5I_6^-$ anions and one oxygen atom from the THF molecule. The Cs···Br and Cs···I interatomic distances range from 3.699(1) to 4.085(2) Å and from 3.872(2) to 4.260(1) Å, respectively. A comparison of these measured values to the 3.7−3.8 Å values observed in ionic structures of Cs[1-H-$CB_{11}Br_{11}$][3b] and Cs[12-Br-$CB_{11}H_{11}$][8] suggests that Cs[1-H-$CB_{11}Br_5I_6$] is also a simple ionic salt. Therefore, the Cs^+ cation can have some interactions with the bromine atoms from the upper belt of the cage because these are electrostatic interactions. Such a coordination environment of Cs^+ may also be due to crystal packing forces.

The solid-state structure of [Me_3NH][1-H-$CB_{11}Cl_5Br_6$]·Me_3-NHCl·H_2O has been subjected to X-ray analysis and is shown in Figure 9. It is a simple ionic salt. The bond distances and angles of the carborane anion is almost identical with those observed in (η^1-mesitylene)Ag(1-H-$CB_{11}Cl_5Br_6$).

In summary, several mixed halocarborane anions, 1-H-$CB_{11}Y_5X_6^-$, have been prepared in high yield by employing sealed-tube methods. Their coordinating nature is approached by comparing the ^{29}Si NMR data of compounds Pr^i_3Si(1-H-$CB_{11}Y_5X_6$) and structural data of complexes Ag(1-H-$CB_{11}Y_5X_6$). These results suggest that the coordinating ability of these anions depends mainly on the nature of the substituents at 7−12 positions (namely, X), and the contribution from substituent Y is relatively small. The structural studies of silver salts of perhalo- and mixed halocarborane anions indicate the structural diversity in these types of compound, varying from monomeric through one-dimensional polymeric to three-dimensional polymeric structures.

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Supporting Information Available: X-ray crystallographic data, in CIF format, and tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for compounds (η^2-mesitylene)$_2$Ag[**1**]·(mesitylene), (η^1-mesitylene)Ag[**2**]·(mesitylene), (η^1-mesitylene)(CH_3-CN)Ag(1-H-$CB_{11}Br_{11}$), (η^2-*p*-xylene)$_2$Ag(1-H-$CB_{11}Cl_{11}$)·1/2(*p*-xylene), Ag(1-CH_3-$CB_{11}Cl_{11}$), Cs[**3**](THF), and $[Me_3NH]_2$[**2**][Cl](H_2O). This material is available free of charge via the Internet at http://pubs.acs.org.

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