Reactions of $CB_9H_{10}^-$ with Electrophiles, Including the Regioselective Mono- and Dihalogenation of the Lower Belt

Sergei V. Ivanov,[1a,b] Juston J. Rockwell,[1a] Susie M. Miller,[1a] Oren P. Anderson,[1a] Konstantin A. Solntsev,*,[1b] and Steven H. Strauss*,[1a]

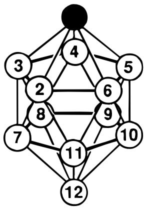
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907, Russia

Received July 25, 1996[⊗]

The ^{11}B NMR spectrum of $CpFe(CO)_2(CB_9H_{10})$ dissolved in dichloromethane shows the presence of two isomers in a 75:25 ratio. In the predominant isomer, the C_{4v}-symmetry $CB_9H_{10}^-$ anion is coordinated to the iron atom *via* the B10−H10 bond (the antipodal B−H bond). In the less abundant isomer, the $CB_9H_{10}^-$ anion is coordinated to the iron atom *via* the B6−H6 bond, one of four equivalent B−H bonds (the lower-belt B−H bonds) adjacent to B10−H10. In spite of the preference of the electrophilic cation $[CpFe(CO)_2]^+$ for the antipodal B−H bond, mono- and dihalogenation with the electrophilic reagents (i) anhydrous hydrogen fluoride, (ii) *N*-chlorosuccinimide, (iii) *N*-bromosuccinimide, and (iv) elemental iodine occurred almost exclusively at lower-belt boron atoms (>95% regioselectivity). The new anions 6-$CB_9H_9X^-$ (X = F, Cl, Br, I) were isolated as cesium salts. Little or no isomeric 10-$CB_9H_9X^-$ was observed. Dihalo derivatives were predominantly 6,8-$CB_9H_8X_2^-$, with varying amounts of 6,7-$CB_9H_8X_2^-$ present. Small amounts of 6,10-$CB_9H_8X_2^-$ were present in some reaction mixtures. In contrast to the nearly exclusive lower-belt halogenations, electrophilic H/D exchange of $CB_9H_{10}^-$ with 20% aqueous DCl occurred equally rapidly at the antipodal and lower-belt boron atoms, forming 6,7,8,9,10-$CB_9H_5D_5^-$. The order of deuteration rates for 6-$CB_9H_9F^-$ under the same conditions was B8 > B10 > {B7,B9}. No deuterium exchange was observed even after 1 month for 6-$CB_9H_9I^-$ under the same conditions. All of the carborane cluster anions were characterized by a combination of 1D and 2D NMR and mass spectroscopy. The anions 6-$CB_9H_9F^-$, 6,7-$CB_9H_8F_2^-$, and 6,8-$CB_9H_8F_2^-$ are the first examples of 10-vertex *closo*-borane or -heteroborane clusters containing B−F bonds. The structure of $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$ was determined by X-ray crystallography: orthorhombic, space group $P2_12_12_1$, $a = 7.945(2)$ Å, $b = 11.274(2)$ Å, $c = 20.756(4)$ Å, $V = 1859.2(7)$ Å^3, $Z = 4$, $T = -100$ °C, least-squares refinement on F^2, $R_1(I>2\sigma(I)) = 0.078$, wR_2(all data) $= 0.197$. The difluorinated carborane cluster has the same overall structure as the parent ion $CB_9H_{10}^-$, but B6 and B8 each bear a single, terminal fluorine atom. The silver(I) ion is coordinated to two benzene molecules in distorted η^2 fashion and to hydrogen atoms H9 and H10 from the same 6,8-$CB_9H_8F_2^-$ anion.

Introduction

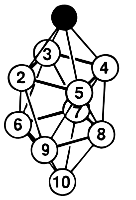
The halogenation of *closo*-borane and *closo*-heteroborane clusters has been studied for a wide variety of cluster types, heteroatoms, and halogenating agents.[2] In particular, halogen-substituted derivatives of $CB_{11}H_{12}^-$ ($\mathbf{1}^-$) and $CB_9H_{10}^-$ ($\mathbf{2}^-$) have received attention because of their potential use as weakly coordinating anions.[3−5] The former anion is the more extensively studied.[3a−d,f,g,4] When $\mathbf{1}^-$ undergoes electrophilic monohalogenation, the predominant or exclusive product is 12-$CB_{11}H_{11}X^-$, where X = F,[4] Cl,[3c] Br,[3c] or I[3a] (in the case of iodine substitution, a small amount of 7-$CB_{11}H_{11}I^-$ is also formed[3a]). These observations are usually explained in terms of the distribution of negative charge in $\mathbf{1}^-$: the B12−H12 bond, which is antipodal to the carborane carbon atom, is believed to be the B−H bond bearing the greatest amount of negative charge density (i.e., it is believed to be the most hydridic B−H bond



$CB_{11}H_{12}^-$, $\mathbf{1}^-$

○ = B–H

● = C–H (C1–H1)



$CB_9H_{10}^{2-}$, $\mathbf{2}^-$

○ = B–H

● = C–H (C1–H1)

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) (a) Colorado State University. (b) Russian Academy of Sciences.

(2) Selected references: (a) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 159. (b) Lagow R. J.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2084. (c) Wong, E. H. *Inorg. Chem.* **1981**, *20*, 1300. (d) Lebedev, V. N.; Balagurova, E. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Y. T.; Zakharkin, L. I. *J. Organomet. Chem.* **1990**, *385*, 307. (e) Morrison, J. A. *Chem. Rev.* **1991**, *91*, 35. (f) Plešek, J. *Chem. Rev.* **1992**, *92*, 269. (g) Solntsev, K. A.; Mebel', A. M.; Votinova, N. A.; Kuznetsov, N. T.; Charkin, O. P. *Koord. Khim.* **1992**, *18*, 340.

(3) (a) Jelínek, T.; Plešak, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819. (b) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643. (c) Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982. (d) Mair, F. S.; Morris, J. H.; Gaines, D. F.; Powell, D. *J. Chem. Soc., Dalton Trans.* **1993**, 135. (e) Xie, Z.; Liston, D.; Jelínek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384. (f) Xie, Z.; Jelínek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907. (g) Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433. (h) Xie, Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403.

(4) Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 6419.

(5) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(6) (a) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 627. (b) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226. (c) Plešek, J.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1979**, *44*, 24. (d) Heřmánek, S.; Hnyk, D.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1859.

S0020-1669(96)00859-2 CCC: $12.00 © 1996 American Chemical Society

in the cluster). This explanation, in turn, is supported by cluster-bonding theories[6] as well as by other experimental observations: H12 is the hydrogen atom that forms the bridge between the carborane anion and the electrophilic metal center in both $Fe(TPP)(CB_{11}H_{12})$[7] and $CpFe(CO)_2(CB_{11}H_{12})$[3b] in the solid state. Furthermore, H12 exchanges with aqueous D^+ much more rapidly than do the other hydrogen atoms in $\mathbf{1}^-$.[8]

Only two halogenated derivatives of $\mathbf{2}^-$ are known. The anions $6,7,8,9,10\text{-}CB_9H_5Cl_5^-$ and $6,7,8,9,10\text{-}CB_9H_5Br_5^-$ ($\mathbf{3}^-$) were prepared in one-pot reactions from $\mathbf{1}^-$, so it was not determined whether the 10-position (antipodal to carbon) or the 6-position was halogenated first.[3e,9] Furthermore, the negative charge distributions in $\mathbf{2}^-$ and $\mathbf{3}^-$ have not been conclusively demonstrated. It is Br6, not Br10, that forms the bridge between $\mathbf{3}^-$ and the electrophilic silicon atom in solid $(i\text{-}Pr)_3Si(\mathbf{3})$, but this could be the result of less steric hindrance at Br6 than at Br10 instead of greater electron density at Br6 than at Br10.[3e]

We have started a program to prepare the unknown anion $6,7,8,9,10\text{-}CB_9H_5F_5^-$ and more highly fluorinated derivatives for use as new, chemically robust, weakly coordinating anions. As a component of this program, we have experimentally probed the apparent negative charge distribution in $\mathbf{2}^-$ and have attempted to correlate it with which cluster vertex is the first (and which is the second) to undergo halogenation. We herein report the results of this initial study.

Experimental Section

Inert Atmosphere. None of the carborane anions appeared to be oxygen or water sensitive. However, the silver(I) salts that were prepared and some of the halogenating reagents used were moisture sensitive. Therefore, preparations and physical measurements were carried out with rigorous exclusion of air and water whenever necessary. Schlenk, glovebox, and high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required.[10]

Reagents and Solvents. These were reagent grade or better. The following compounds were used as received: liquid anhydrous HF (LAHF, Matheson) (*caution*! HF is toxic and extremely corrosive to skin and eyes), I_2 (MCB), $AgNO_3$ (MCB), 20% DCl in D_2O (Aldrich). *N*-Bromosuccinimide (NBS, Aldrich) and *N*-chlorosuccinimide (NCS, Aldrich) were recrystallized from dichloromethane. Trifluoroacetic acid (Aldrich) was distilled. Decaborane(14) ($B_{10}H_{14}$, Callery) was sublimed at 70 °C under vacuum (*caution*! $B_{10}H_{14}$ is toxic and is an explosion hazard if heated in air). The following compounds were prepared following literature procedures: $CsCB_9H_{10}$,[11] $AgCB_9H_{10}$,[3f] $AgCB_{11}H_{12}$,[12] $CpFe(CO)_2I$ (FpI; Fp = $CpFe(CO)_2$),[13] $Fp(CB_9H_{10})$,[3b] and $Fp(CB_{11}H_{12})$.[3b] The following solvents were dried by distillation from sodium metal, P_2O_5, CaH_2, and/or activated 4 Å molecular sieves: acetone, acetone-d_6, dichloromethane, dichloromethane-d_2, benzene, and benzene-d_6.

Preparation of New Compounds. $Cs(6\text{-}CB_9H_9F)$. A mixture of $Cs(\mathbf{2})$ (0.45 g, 1.8 mmol) and LAHF (25 mL) was stirred at 20 °C for 2.5 h. All volatiles were removed under vacuum, leaving 0.480 g of a white residue. A ^{11}B NMR spectrum of the crude product mixture revealed that the following cesium salts were present (approximate relative abundances in parentheses): $Cs(\mathbf{2})$ (10%); $Cs(6\text{-}CB_9H_9F)$ (78%); $Cs(6,8\text{-}CB_9H_8F_2)$ (12%). The crude product mixture was treated with $AgNO_3$ (0.50 g, 2.9 mmol) and benzene (50 mL), stirred at 25°C for 24 h, and filtered. Benzene was removed from the filtrate, leaving a mixture of $Ag(\mathbf{2})$, $Ag(6\text{-}CB_9H_9F)$, and $Ag(6,8\text{-}CB_9H_8F_2)$. The solid mixture of silver(I) salts was treated with 10 successive portions of distilled, deionized water (1 mL each). Aqueous fractions 4 and 5 were combined and treated three times with benzene (1 mL each). The benzene layers were combined, and benzene was removed under vacuum. The white solid residue was dissolved in water. Addition of $NHMe_3Cl$ caused the precipitation of AgCl, $[NMe_3H][\mathbf{2}]$, $[NMe_3H][6\text{-}CB_9H_9F]$, and $[NMe_3H][6,8\text{-}CB_9H_8F_2]$. The precipitated solids were washed with acetone. The acetone washings were combined, and acetone was removed under vacuum. The white solid residue was dissolved in water and treated with 1.0 equiv of CsOH (based on an assumed composition of 100% $[NMe_3H][6\text{-}CB_9H_9F]$) to form an aqueous solution of $Cs(6\text{-}CB_9H_9F)$. Removal of water under vacuum afforded 30 mg of purified $Cs(6\text{-}CB_9H_9F)$ (7% based on the original amount of $Cs(\mathbf{2})$). A negative-ion electrospray mass spectrum (NIEMS) and ^{11}B and ^{19}F NMR spectra demonstrated that less than 1% $Cs(\mathbf{2})$ and approximately 2.5% $Cs(6,8\text{-}CB_9H_8F_2)$ were present.

$Cs(6,8\text{-}CB_9H_8F_2)$. A mixture of $Cs(\mathbf{2})$ (0.46 g, 1.8 mmol) and LAHF (15 mL) was stirred at 25°C for 48 h. All volatiles were removed under vacuum, leaving 0.480 g of a white residue. The residue was recrystallized from acetone and then from water to afford 0.35 g of $Cs(6,8\text{-}CB_9H_8F_2)$ (67% yield). The water filtrate contained a significant amount of product. When the filtrate was treated with $N(n\text{-}Bu)_4Cl$, 0.14 g of $[N(n\text{-}Bu)_4][6,8\text{-}CB_9H_8F_2]$ (19% yield) was precipitated. The new compound $Cs(6,8\text{-}CB_9H_8F_2)$ contained approximately 3% $Cs(6,7\text{-}CB_9H_8F_2)$.

$Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$. A mixture of $Cs(6,8\text{-}CB_9H_8F_2)$ and an excess of $AgNO_3$ was treated with benzene and stirred for 24 h. After filtration of the reaction mixture, benzene was removed under vacuum to afford the white solid compound $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$. Crystals of this compound were obtained by cooling a benzene solution to 0 °C.

$Cs(6\text{-}CB_9H_9Cl)$. A solution of $Cs(\mathbf{2})$ (0.089 g, 0.35 mmol) in acetone (1 mL) was treated with a solution of NCS (0.094 g, 0.70 mmol) in acetone (1 mL) and stirred at room temperature for 50 days. The reaction mixture was clear and colorless throughout this period of time. The solvent was removed under vacuum, leaving a white solid residue, which was washed with dichloromethane to remove succinimide and unreacted NCS. A ^{11}B NMR spectrum of the crude product mixture revealed that the following cesium salts were present (approximate relative abundances in parentheses): $Cs(\mathbf{2})$ (1%); $Cs(6\text{-}CB_9H_9Cl)$ (94%); $Cs(10\text{-}CB_9H_9Cl)$ (1%); $Cs(6,8\text{-}CB_9H_8Cl_2)$ (4%). The crude product was recrystallized from distilled, deionized water to yield three crops of colorless crystals (total yield = 79%). A ^{11}B NMR spectrum of purified $Cs(6\text{-}CB_9H_9Cl)$ did not exhibit resonances due to $Cs(\mathbf{2})$ or $Cs(10\text{-}CB_9H_9Cl)$. A small amount (<2%) of $Cs(6,8\text{-}CB_9H_8Cl_2)$ was observed in the NIEMS.

$Cs(CB_9H_8Cl_2)$ (Mixture of Isomers). A solution of $Cs(\mathbf{2})$ (0.089 g, 0.35 mmol) in acetone (2 mL) was heated at 55 °C for a total of 5 days with several portions of NCS (total amount added was 0.163 g, 1.22 mmol, 3.5 equiv). The portions were added at $t = 0$ (2.5 equiv), $t = 3$ days (0.5 equiv), and $t = 4$ days (0.5 equiv). The solvent was removed under vacuum, leaving a white, solid residue which was washed with dichloromethane to remove succinimide and unreacted NCS. The NIEMS of the product mixture revealed that the following cesium salts were present (approximate relative abundances in parentheses): $Cs(CB_9H_9Cl)$ (7%); $Cs(CB_9H_8Cl_2)$ (92%); $Cs(CB_9H_7Cl_3)$ (1%). 1- and 2D ^{11}B NMR spectra indicated that the following three isomers were present: $Cs(6,8\text{-}CB_9H_8Cl_2)$ (68%); $Cs(6,7\text{-}CB_9H_8Cl_2)$ (24%); $Cs(6,10\text{-}CB_9H_8Cl_2)$ (8%).

$Cs(6\text{-}CB_9H_9Br)$. A solution of $Cs(\mathbf{2})$ (0.050 g, 0.20 mmol) in acetone (1 mL) was treated with a solution of NBS (0.037 g, 0.21 mmol) in acetone (1 mL) and stirred at room temperature for 15 h. The reaction mixture was clear and colorless throughout this period of time. The solvent was removed under vaccum, leaving a white solid residue, which was washed with dichloromethane to remove succinimide and unreacted NBS. A ^{11}B NMR spectrum of the crude product mixture revealed that the following cesium salts were present (approximate relative abundances in parentheses): $Cs(6\text{-}CB_9H_9Br)$ (84%); $Cs(10\text{-}CB_9H_9Br)$ (9%); $Cs(CB_9H_8Br_2)$ (7%). The crude product was recrystallized from distilled, deionized water to yield three crops of colorless crystals (total yield = 66%). A ^{11}B NMR spectrum of purified Cs(6-

---

(7) Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022. TPP^{2-} = 5,10,15,20-tetraphenylporphyrinate dianion.

(8) Jelínek, T.; Plešek, J.; Mareš, F.; Heřmánek, S.; Štíbr, B. *Polyhedron* **1987**, *6*, 1981.

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

(10) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(11) Nestor, K.; Štíbr, B.; Kennedy, J. D.; Thornton-Pett, M.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262.

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

(13) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1956**, 3030.

CB_9H_9Br) did not exhibit resonances due to $Cs(10\text{-}CB_9H_9Br)$ or $Cs(CB_9H_8Br_2)$. Less than 2% $Cs(CB_9H_8Br_2)$ was observed in the NIEMS.

$Cs(CB_9H_8Br_2)$ (Mixture of Isomers). A solution of Cs(**2**) (0.054 g, 0.21 mmol) in acetone (1 mL) was treated with a solution of NBS (0.076 g, 0.43 mmol) in acetone (1 mL) and stirred at room temperature for 16 days. The reaction mixture was pale yellow and clear throughout this period of time. The solvent was removed under vaccum, leaving a white solid residue, which was washed with dichloromethane to remove succinimide and unreacted NBS. An NIEMS and a ^{11}B NMR spectrum of the product revealed that the following cesium salts were present (relative abundances in parentheses): $Cs(6\text{-}CB_9H_9Br)$ (10%); $Cs(CB_9H_8Br_2)$ (90%). The ^{11}B NMR spectrum revealed that at least three isomers of $Cs(CB_9H_8Br_2)$ were present (approximate relative abundances in parentheses): $Cs(6,8\text{-}CB_9H_8Br_2)$ (64%); $Cs(6,7\text{-}CB_9H_8Br_2)$ (32%); $Cs(6,10\text{-}CB_9H_8Br_2)$ (4%).

$Cs(6\text{-}CB_9H_9I)$. A solution of Cs(**2**) (0.070 g, 0.28 mmol) in water (1 mL) was treated with solid I_2 (0.071 g, 0.28 mmol) and stirred at room temperature for 2 days. After this time, the reaction mixture was clear and pale yellow (no solid I_2 remained). Crystals were grown directly from this solution. Collection of three separate crops from the reaction mixture gave a 51% total yield of $Cs(6\text{-}CB_9H_9I)$, judged to be >99% pure by ^{11}B NMR and mass spectroscopy.

$Cs(CB_9H_8I_2)$ (Mixture of Isomers). A solution of Cs(**2**) (0.050 g, 0.20 mmol) in water (10 mL) was treated with solid I_2 (0.10 g, 0.40 mmol) and stirred at 35 °C for 19 days. The reaction mixture was dark red and clear throughout this period of time. An NIEMS of the crude product revealed that the following cesium salts were present (relative abundances in parentheses): $Cs(CB_9H_9I)$ (40%); $Cs(CB_9H_8I_2)$ (60%). The ^{11}B NMR spectrum revealed that at least three isomers of $Cs(CB_9H_8I_2)$ were present (approximate relative abundances in parentheses): $Cs(6,8\text{-}CB_9H_8I_2)$ (48%); $Cs(6,7\text{-}CB_9H_8I_2)$ (48%); $Cs(6,10\text{-}CB_9H_8I_2)$ (4%).

Deuteration of $Cs(CB_9H_{10})$, $Cs(6\text{-}CB_9H_9F)$, and $Cs(6\text{-}CB_9H_9I)$. A sample of each of these three compounds was dissolved in 20% DCl in D_2O so that the concentration of the carborane cluster was approximately 0.05 M. The solutions were kept at 25 °C, and ^{11}B NMR spectra were recorded at regular time intervals.

Spectroscopic Measurements. Samples for IR spectroscopy were dichloromethane or toluene solutions in 0.2 mm path length cells with ZnS windows. Spectra were recorded at room temperature on a Nicolet 5PC FTIR spectrometer. Samples for ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy were acetone-d_6, dichloromethane-d_2, or benzene-d_6 solutions in sealed 5-mm glass tubes. Spectra were recorded on a Bruker WP-300 spectrometer. Chemical shifts (δ scale) are relative to external $BF_3{\cdot}OEt_2$ (^{11}B), internal Me_4Si (^{13}C), and internal $CFCl_3$ (^{19}F). Samples for negative-ion electrospray mass spectrometry were solutions in either water, acetonitrile, methanol, or a mixture of these three solvents. Spectra were recorded on a Fisons VG Quattro-SQ mass spectrometer. The sample cone voltage was 75 V, sufficiently high to preclude the formation of ion clusters.[14]

Crystallographic Study. Crystals of $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$ were examined at or below −20 °C using an apparatus previously described.[15] When a suitable crystal was found, it was embedded in Halocarbon 25-5S grease at the end of a glass fiber and quickly placed in the cold nitrogen stream of an LT-2 unit. Details of the crystallographic experiment and subsequent computations are summarized in Table 1.[16]

The diffraction data were obtained using a Siemens P4 diffractometer, and computations were performed with crystallographic software supplied by Siemens[16a] or by Professor G. M. Sheldrick.[16b] Lorentz and polarization corrections were applied to the data, but no absorption correction was applied owing to the low value of the absorption coefficient.

Table 1. Details of the X-Ray Diffraction Study of $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$

molecular formula	$C_{13}H_{20}AgB_9F_2$
fw	419.4
cryst dimens, mm	0.40 × 0.30 × 0.20
unit cell dimens	
a, Å	7.945(2)
b, Å	11.274(2)
c, Å	20.756(4)
unit cell vol, Å^3	1859.2(7)
data collcn temp, °C	−100
crystal system	orthorhombic
space group	$P2_12_12_1$
Z	4
calcd density, g cm^{-3}	1.50
F(000)	832
abs coeff, mm^{-1}	1.09
radiation (λ, Å)	Mo Kα (0.7107)
maximum (sin θ)/λ, Å^{-1}	0.704
scan type	$\theta - 2\theta$
scan speed, deg min $^{-1}$	variable (2−30)
2θ range, deg	4−60
reflns	$h,\pm k,\pm l$
no. of reflns measd	2706
no. of unique reflns	2706
no. of params	221
residual indices[a]	$R_1 = 0.078$ $wR_2 = 0.197$
goodness of fit	0.95
max/min, final ΔF map, e Å^{-3}	+2.95, −2.81

[a] $R_1 = \sum||F_o| - |F_c||/\sum |F_o|$ for 1550 reflections with $F_o > 2.0\sigma(F_o)$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$ for all data.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$[a,b]

Ag−C11	2.52(2)	Ag−C12	2.47(2)
Ag−C21	2.65(1)	Ag−C22	2.49(1)
Ag−H9	2.10[c]	Ag−H10	2.09[c]
Ag···B9	2.62(1)	Ag···B10	2.51(1)
Ag···F1	4.07(2)	Ag···F2	3.82(2)
Ag···F2′	3.19(2)	B6−F1	1.42(2)
B8−F2	1.38(2)	C1−B(ub)	1.54(2)−1.58(2)
B(ub)−B(ub)	1.76(2)-1.82(2)	B(ub)−B(lb)	1.78(2)−1.84(2)
B(lb)−B(lb)	1.81(2)−1.85(2)	B10−B(lb)	1.66(2)−1.71(2)

C11−Ag−C12	32.0(8)	C21−Ag−C22	30.2(4)
C12−C11−Ag	72(1)	C11−C12−Ag	76(1)
C22−C21−Ag	68.2(8)	C21−C22−Ag	81.6(8)
H9−Ag−H10	88.1[b]	B10−B9−H9	118.7[b]
B9−B10−H10	128.9[b]	B(ub)−C1−B(ub)	70(1)-72(1)
B(ub)−C1−B(ub)′	109(1)−110(1)	B(ub)−B(ub)−B(ub)	89(1)-92(1)
B(lb)−B(lb)−B(lb)	89(1)−91(1)	B(lb)−B10−B(lb)	65(1)-68(1)
B(lb)−B10−B(lb)'	101(1), 101(1)		

[a] B(ub) = upper-belt boron atoms = B2−B5; B(lb) = lower-belt boron atoms = B6−B9. [b] All B−B−B angles for triangular faces formed exclusively by upper- and lower-belt boron atoms ranged from 59(1) to 61(1)°. [c] No esd's are given for these values because the hydrogen atoms are in calculated (idealized) positions.

The structure was solved by direct methods and refined using full-matrix least-squares procedures on F^2 for all data. All non-hydrogen atoms were refined anisotropically, with the exception of the carbon atoms of one of the benzene ligands (C11-C16), which was disordered. This ligand was best represented as two coplanar rings offset from one another by approximately 30°. Hydrogen atoms were not included in the disordered benzene ligand. Other hydrogen atoms were included in idealized positions with isotropic thermal parameters 20% larger than the equivalent isotropic *U* value of the atoms to which they were attached.

The correctness of the enantiomorph was confirmed by evaluation of an absolute structure parameter.[16c,d] The highest peak and deepest valley in the final ΔF map were found in the immediate vicinity of the silver atom. Selected interatomic distances and angles are listed in Table 2.

Results and Discussion

Fluorination Reactions. Our earlier work demonstrated that liquid anhydrous hydrogen fluoride (LAHF) will fluorinate the

---

(14) Hop, C. E. C. A.; Saulys, D. A.; Gaines, D. F. *Inorg. Chem.* **1995**, *34*, 1977.

(15) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349.

(16) (a) Sheldrick, G. M. SHELXTL, vers. 5.03 (1994). (b) Sheldrick, G. M. SHELXL-96, vers. 2(β) (1996). (c) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876. (d) Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1985**, *A41*, 500.

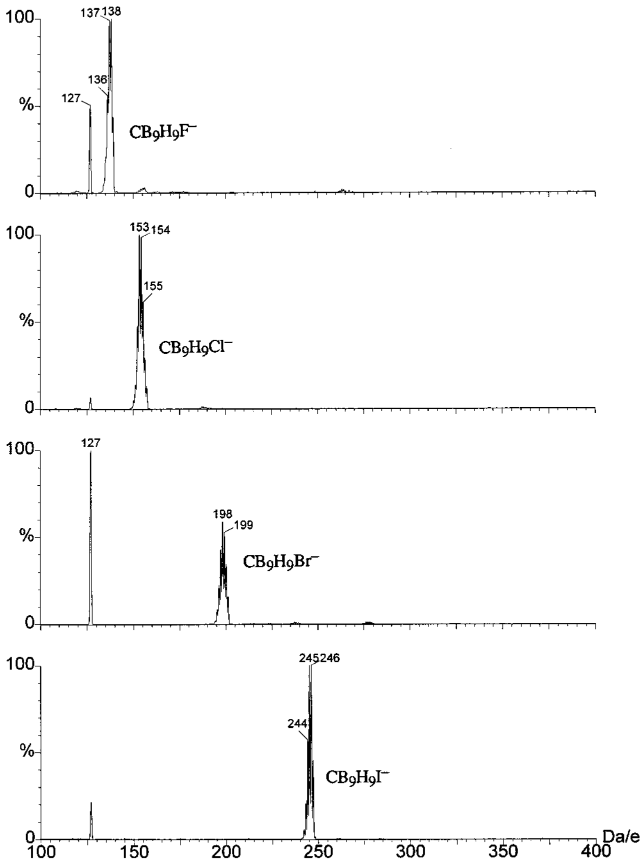


Figure 1. Negative-ion electrospray mass spectra of purified samples of Cs(6-CB_9H_9X) (X = F, Cl, Br, I). The peak at Da/e = 127 is due to I^- added as an internal standard.

12-position of $\mathbf{1}^-$ at 25 °C and the 7- and 12-positions at 140 °C.[4] Therefore, our first attempted fluorination of $\mathbf{2}^-$ involved treating Cs(**2**) with a large excess of LAHF. When Cs(**2**) was treated with LAHF at 20 °C for 2.5 h, a mixture containing Cs(**2**), Cs(6-CB_9H_9F), and Cs(6,8-$CB_9H_8F_2$) was formed:

$$\mathrm{Cs}(\mathbf{2}) + \mathrm{HF} \xrightarrow[20\ ^\circ\mathrm{C},\ 2.5\ \mathrm{h}]{\mathrm{LAHF}} \underset{10\%}{\mathrm{Cs}(\mathbf{2})} + \underset{78\%}{\mathrm{Cs}(6\text{-}\mathrm{CB_9H_9F})} + \underset{12\%}{\mathrm{Cs}(6,8\text{-}\mathrm{CB_9H_8F_2})} + \mathrm{H_2}$$

The preceding equation is not balanced with respect to HF and H_2. The percentages listed were determined from a combination of ^{11}B and ^{19}F NMR spectra and a negative-ion electrospray mass spectrum (NIEMS) of the crude reaction mixture. Variation of the temperature from −18 to +20 °C did not allow for the formation of Cs(6-CB_9H_9F) that was free of Cs(**2**) or Cs(6,8-$CB_9H_8F_2$). The 20 °C reaction mixture can be purified by taking advantage of the differences in solubility of silver salts of these anions in water (see Experimental Section). The NIEMS of purified Cs(6-CB_9H_9F) is shown in Figure 1. The isotope pattern is that expected for an anion with nine boron atoms having natural abundances of 20% ^{10}B and 80% ^{11}B.

The proton-decoupled 1D ^{11}B NMR spectrum, 2D $^{11}B-^{11}B$ COSY NMR spectrum, and the 1D ^{19}F NMR spectrum of Cs(6-CB_9H_9F) are shown in Figures 2−4, respectively. Chemical shift and coupling constant data for this compound and other compounds discussed below are listed in Table 3. Note that the 70-Hz boron−fluorine splitting for the B6−F6 moiety in 6-$CB_9H_9F^-$ is not resolved in the 1D ^{11}B spectrum but is reasonably well resolved in the ^{19}F spectrum. This value may be compared with J_{BF} values of 55 and 59 Hz, respectively, for 2-$CB_{11}H_{11}F^-$ [3d] and 12-$CB_{11}H_{11}F^-$,[4] respectively. The shape of the ^{19}F pattern for 6-$CB_9H_9F^-$ is consistent with the superposition of two patterns due to $^{11}B-F$ (80%, J_{BF} = 70 Hz) and $^{10}B-F$ (20%, J_{BF} = 23 Hz) isotopomers and with a small boron isotope effect on $\delta(^{19}F)$.[17] Note that a B−F splitting of approximately 150 Hz, which is clearly related to but is not equal to J_{BF}, is observed in the 2D $^{11}B-^{11}B$ COSY NMR spectrum of Cs(6-CB_9H_9F). This behavior was also observed in the 2D spectra of 2-$CB_{11}H_{11}F^-$ [3d] and 12-$CB_{11}H_{11}F^-$.[4]

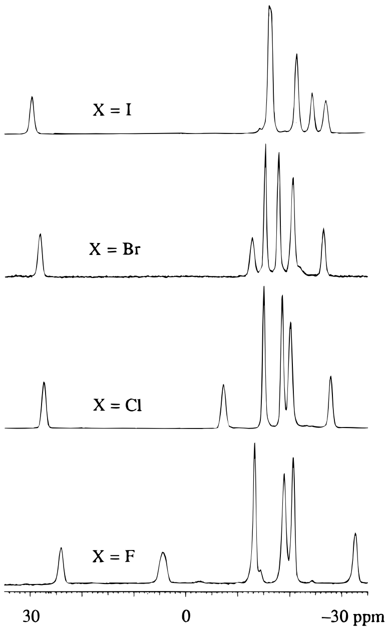


Figure 2. 96.3 MHz proton-decoupled ^{11}B NMR spectra of Cs(6-CB_9H_9X) in acetone-d_6 (X = F, Cl, Br, I). The peak on the left side of all four spectra is assigned to B10. The second peak from the left is assigned to B6 for X = F, Cl, and Br. The peak on the right side of the X = I spectrum is assigned to B6.

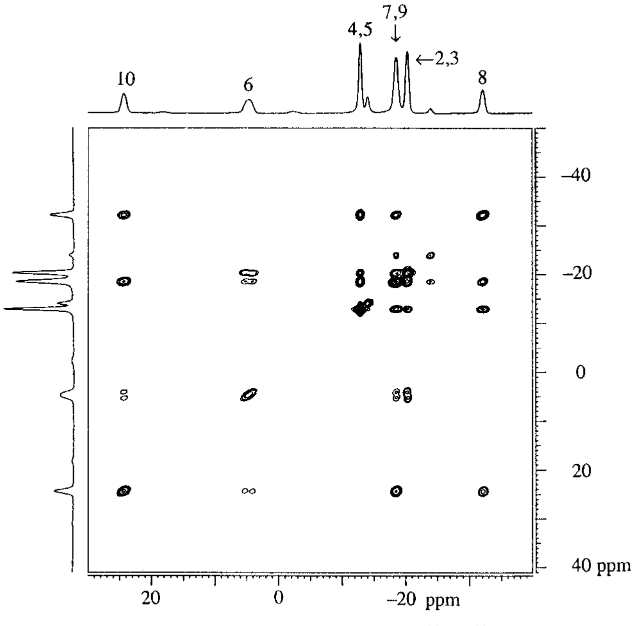


Figure 3. 96.3 MHz proton-decoupled 2D $^{11}B-^{11}B$ COSY NMR spectrum of Cs(6-CB_9H_9F) in acetone-d_6. Note the presence of a trace of Cs(CB_9H_{10}) and a few percent of Cs(6,8-$CB_9H_8F_2$).

There is little doubt that B6, not B10 or B2, is the first boron atom to be fluorinated. The 1D and 2D ^{11}B NMR spectra are consistent with a cluster having C_s symmetry, such as 6-$CB_9H_9F^-$, and are inconsistent with a C_{4v} cluster, such as 10-$CB_9H_9F^-$. It is also clear that the alternative C_s product, 2-$CB_9H_9F^-$, can be ruled out because the 2D spectrum clearly shows that the

---

(17) Bacon, J.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3063.

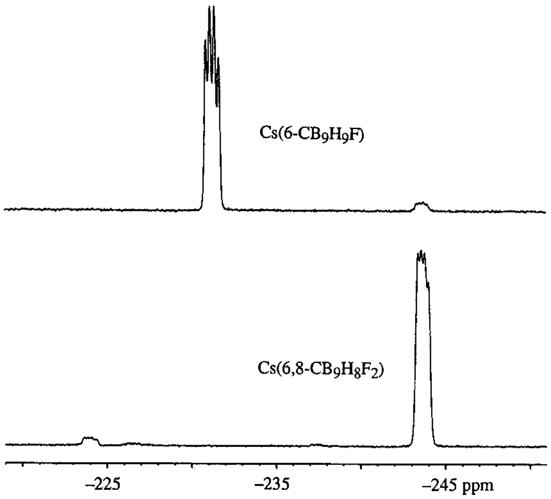


Figure 4. 282.4 MHz ^{19}F NMR spectra (acetone-d_6) of Cs(6-CB_9H_9F) (top) and Cs(6,8-$CB_9H_8F_2$) (bottom). Note that the sample of Cs(6-CB_9H_9F) contains a few percent of Cs(6,8-$CB_9H_8F_2$) and that the sample of Cs(6,8-$CB_9H_8F_2$) contains a few percent of Cs(6,7-$CB_9H_8F_2$).

fluorinated boron atom is correlated with B10. The assignments indicated on the 2D spectrum are completely consistent with the structure of 6-$CB_9H_9F^-$: 10 is correlated with 8, {7,9}, and 6; 8 is correlated with 10, {7,9}, and {4,5}; {7,9} is correlated with 10, 8, 6, {4,5}, and {2,3}. However, an important question remains: Is 6-$CB_9H_9F^-$ the thermodynamically most stable isomer or a kinetic product of the reaction of $CB_9H_{10}^-$ with LAHF?

The reaction of Cs(**2**) with LAHF for 48 h at 25 °C produced, in good yield (67%), an isomeric mixture of new compounds having the formula Cs($CB_9H_8F_2$). As above, the reaction was regioselective:

$$\mathrm{Cs}(\mathbf{2}) + 2\mathrm{HF} \xrightarrow[25\ ^\circ\mathrm{C},\ 48\ \mathrm{h}]{\mathrm{LAHF}} \underset{97\%}{\mathrm{Cs}(6,8\text{-}\mathrm{CB_9H_8F_2})} + \underset{3\%}{\mathrm{Cs}(6,7\text{-}\mathrm{CB_9H_8F_2})} + 2\mathrm{H_2}$$

The compositional purity can be judged from the NIEMS of the mixture of isomeric cesium salts, which is shown in Figure 5. The structural assignments for the two isomers, 6,8-$CB_9H_8F_2^-$ and 6,7-$CB_9H_8F_2^-$, are based on the 2D ^{11}B−^{11}B NMR spectrum and the ^{19}F NMR spectrum of the product mixture, which are shown in Figures 6 and 4, respectively. (Although the resonances for {7,9} and {2−5} are accidentally isochronous in Figure 6, they are observed as separate peaks in spectra of other salts; see below.) Note that the much more abundant 6,8-isomer has a higher symmetry (C_{2v}) than the 6,7-isomer (C_s), even though both isomers contain a pair of symmetry-related fluorine atoms. The ^{19}F NMR spectrum does show a trace amount of at least one other fluorine-containing species at δ −226.5 and −237.5. Therefore, trace amounts of 2,6-$CB_9H_8F_2^-$, 4,6-$CB_9H_8F_2^-$, and/or 6,10-$CB_9H_8F_2^-$ may be present.

The cesium salt was converted to the silver salt by treatment of a mixture of solid Cs(6,8-$CB_9H_8F_2$) and excess solid $AgNO_3$ with benzene:

$$\mathrm{Cs}(6,8\text{-}\mathrm{CB_9H_8F_2})(\mathrm{s}) + \mathrm{AgNO_3}(\mathrm{s}) \xrightarrow{\mathrm{C_6H_6}} \mathrm{Ag}(6,8\text{-}\mathrm{CB_9H_8F_2}) + \mathrm{CsNO_3}(\mathrm{s})$$

The accidental degeneracy of ^{11}B resonances for the {B7,B9} and the {B2−B5} sets of symmetry-equivalent boron atoms for Cs(6,8-$CB_9H_8F_2$) dissolved in acetone-d_6 is broken for Ag(6,8-$CB_9H_8F_2$) dissolved in benzene-d_6 (see Table 3). The structure of Ag(C_6H_6)$_2$(6,8-$CB_9H_8F_2$), shown in Figure 7, consists of discrete molecules with no significant intermolecular interactions. The closest intermolecular Ag···H(B) distance is >4.5 Å. The closest Ag···F distance of any type is 3.19(1) Å (to F2 in another molecule), which happens to be the sum of van der Waals radii for silver and fluorine.[18] The 6,8-$CB_9H_8F_2^-$ anion consists of a 10-vertex bicapped square antiprism, with the unique carbon atom in one of the two lower-connectivity axial (polar) positions. Note that the connectivity of the carbon atom has not changed after the conversion of $CB_9H_{10}^-$ to 6,8-$CB_9H_8F_2^-$. The axial position of the carbon atom in unsubstituted $CB_9H_{10}^-$, long known from spectroscopic data, was confirmed recently by X-ray crystallography,[11] and is in accord with electron-counting formalisms.[19] The only other structurally characterized CB_9 derivative, **3**$^-$, also exhibits an axial carbon atom.[3e,f] Both the upper-belt and the lower-belt boron atoms in 6,8-$CB_9H_8F_2^-$ form square arrays that are planar to within 0.008 Å (the angles of the two squares vary from 89(1) to 92-(1)°; the upper belt consists of B2−B5, and the lower belt consists of B6−B9). These two square planes are nearly parallel, forming an interplane angle of 0.3°. As in the structures of **2**$^-$ and **3**$^-$, there are three different cluster bond types having distinct bond length ranges: C−B(eq), 1.55(2)−1.58(2) Å (eq = equatorial = upper or lower belt); B(eq)−B(eq), 1.76(2)−1.85(2) Å; B(eq)−B(ax), 1.66(2)−1.72(2) Å (ax = axial; B(ax) = B10). Relatively shorter B(eq)−B(ax) bonds were also observed in the structure of $B_{10}H_{10}^{2-}$.[20]

The two fluorine atoms are bonded to two nonadjacent lower-belt boron atoms in 6,8-$CB_9H_8F_2^-$. The B−F distances of 1.38-(2) and 1.42(2) Å can be compared with the B−F distance of 1.37(1) Å in the related compound Ag(C_6H_6)$_2$(12-$CB_{11}H_{11}F$).[4] The perpendicular distances of F6 and F8 from the least-squares plane formed by the four atoms B6−B9 are 0.44 and 0.46 Å, respectively. This results in the two B−F bonds being tilted 19° with respect to the B6−B9 plane. For comparison, the B(eq)−Br bonds in Ag($C_6H_5CH_3$)(**3**) are tilted 21−25° with respect to the B6−B9 plane.[3f]

The silver ion is coordinated to two benzene molecules in an asymmetric bidentate fashion. The Ag−C21 and Ag−C22 distances are 2.66(1) and 2.49(1) Å, respectively. The Ag−C21−C22 fragment forms an idealized 30−60−90 right triangle. The C21−Ag−C22, Ag−C21−C22, and Ag−C22−C21 angles are 30.4(4), 67.9(8), and 81.7(8)°, respectively. The disorder present in the other benzene molecule precludes a meaningful discussion of the analogous distances and angles for the Ag−C11−C12 fragment. Asymmetric bidentate coordination of arene ligands is common for d^{10} metal ions such as Ag$^+$.[21]

The silver ion is also coordinated to a single bidentate 6,8-$CB_9H_8F_2^-$ anion through its B9−H9 and B10−H10 bonds. The Ag−H9 and Ag−H10 distances are 2.10 and 2.09 Å, respectively. The H9−Ag−H10 bite angle is 88.1°. The five-membered chelate ring formed by Ag, H9, H10, B9, and B10 is coplanar to within 0.04 Å. This is the first example of

---

[18] (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 257.

[19] (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

[20] (a) Dobrott, R. D.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 1779. (b) Fuller, D. J.; Kepert, B. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 2097.

[21] (a) Taylor, I. F., Jr.; Hall, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 5745. (b) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1991**, *93*, 3167. (c) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 4307. (d) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

Table 3. NMR Spectral Data for $CB_9H_{10-n}X_n^-$ Compounds[a]

anion	$\delta(^{13}C)$	$\delta(^{11}B)$, int, pattern (assignt)[b]	$J(^{11}B-^1H)$, Hz[c]
$CB_9H_{10}^-$	53.4	30.6, 1, d (B10)	151
		−18.7, 4, d (B2−B5)	150
		−24.2, 4, d (B6−B9)	137
$CB_9H_{10}^-$		23.3, 1, d (B10)	145
(20% DCl in D_2O)		−23.3, 4, d (B2−B5)	151
		−28.9, 4, d (B6−B9)	133
6,7,8,9,10-$CB_9H_5D_5^-$		23.0, 1, s (B10)	
(20% DCl in D_2O)		−23.3, 4, d (B2−B5)	151
		−29.1, 4, s (B6−B9)	
6-$CB_9H_9F^-$ [d]	48.5	24.1, 1, d (B10)	150
		4.4, 1, bd s (B6)	
		−13.1, 2, d (B4, B5)	150
		−18.8, 2, d (B7, B9)	141
		−20.6, 2, d (B2, B3)	147
		−32.5, 1, d (B8)	139
6-$CB_9H_9F^-$ [e]	48.5	7.8, 1, d (B10)	137
(Ag^+ salt, C_6D_6)		3.9, 1, bd s (B6)	
		−12.9, 2, d (B4, B5)	156
		−20.8, 2, d (B7, B9)	n.o.
		−20.8, 2, d (B2, B3)	n.o.
		−35.8, 1, d (B8)	126
6,8-$CB_9H_8F_2^-$ [f]	44.2	17.8, 1, d (B10)	150
		−2.5, 2, bd s (B6, B8)	
		−14.3, 6, d (B2−B5, B7, B9)	n.o.
6,8-$CB_9H_8F_2^-$ [g]		4.0, 1, d (B10)	126
(Ag^+ salt, C_6D_6)		−3.3, 2, bd s (B6, B8)	
		−14.1, 4, d, (B2−B5)	158
		−16.5, 2, d (B7, B9)	127
6,7-$CB_9H_8F_2^-$ [h]		16.7, 1, d (B10)	n.o.
		6.9, 2, bd s (B6, B7)	
		−7.7, 1, d (B5)	150
		−14.9, 2, d (B2, B4)	n.o.
		−22.3, 1, d (B3)	n.o.
		−27.9, 2, d (B8, B9)	141
6-$CB_9H_9Cl^-$	51.8	27.5, 1, d (B10)	155
		−7.0, 1, s (B6)	
		−14.8, 2, d (B4, B5)	151
		−18.3, 2, d (B2, B3)	156
		−19.9, 2, d (B7, B9)	145
		−27.6, 1, d (B8)	139
6,8-$CB_9H_8Cl_2^-$		24.3, 1, d (B10)	
		−10.7, 2, s (B6, B8)	
		−14.3, 4, d (B2−B5)	
		−16.3, 2, d (B7, B9)	
6,7-$CB_9H_8Cl_2^-$		24.2, 1, d (B10)	
		−4.6, 2, s (B6, B7)	
		−14.5, 2, d (B2, B4)	
		−17.9, 1, d (B3)	
		n.o. (B5)	
		−23.3, 2, d (B8, B9)	
6,10-$CB_9H_8Cl_2^-$		34.4, 1, s (B10)	
		−7.3, 1, s (B6)	
		−19.7, 2, d (B7, B9)	
		−17.8, 1, d (B4, B5)	
		n.o. (B2, B3)	
		−26.7, 1, d (B8)	
6-$CB_9H_9Br^-$	52.8	28.2, 1, d (B10)	155
		−12.7, 1, s (B6)	
		−15.2, 2, d (B4, B5)	152
		−17.8, 2, d (B2, B3)	158
		−20.6, 2, d (B7, B9)	144
		−26.5, 1, d (B8)	136
6-$CB_9H_9I^-$	54.5	29.7, 1, d (B10)	156
		−16.3, 2, d (B2, B3)	~150
		−16.6, 2, d (B4, B5)	~150
		−21.6, 2, d (B7, B9)	141
		−25.6, 1, d (B8)	145
		−27.2, 1, s (B6)	
$CB_9H_{10}^-$		30.3, 1, d (B10)	151
($N(n\text{-}Bu)_4^+$ salt, CD_2Cl_2)		−18.4, 4, d (B2−B5)	150
		−23.9, 4, d (B6−B9)	135
Fp(10-CB_9H_{10})[i]		5.6, 1, d (B10)	86
(CD_2Cl_2)		−17.5, 4, d (B2−B5)	~160
		−19.2, 4, d (B6−B9)	~150
Fp(6-CB_9H_{10})[i]		26.5, 1, d (B10)	169
(CD_2Cl_2)		−24.1, 2, d (B7, B9)	140
		n.o. (B4, B5)	n.o.
		n.o. (B2, B3)	n.o.
		n.o. (B8)	n.o.
		−34.5, 1, d (B6)	76

[a] All spectra at 25 °C; C_s^+ salts in acetone-d_6 unless otherwise noted; $\delta(^{13}C)$ for $SiMe_4 = 0$; $\delta(^{11}B)$ for $BF_3{\cdot}OEt_2 = 0$; $\delta(^{19}F)$ for $CFCl_3 = 0$; ^{19}F NMR resonances were multiplets with unequal intensities; in cases where quartets were observed, reported $J(^{11}B-^{19}F)$ values represent the peak-to-peak separations. [b] int = integrated intensity; assignt = assignment; d = doublet, bd s = broad singlet (unresolved multiplet). [c] n.o. = not observable due to poor signal/noise or overlapping resonances. [d] $\delta(^{19}F) = -231.4$, $J(^{11}B-^{19}F) \sim 70$ Hz. [e] $\delta(^{19}F) = -227.2$, $J(^{11}B-^{19}F)$ = n.o. [f] $\delta(^{19}F) = -243.6$, $J(^{11}B-^{19}F) = 59$ Hz. [g] $\delta(^{19}F) = -240.1$, $J(^{11}B-^{19}F)$ = n.o. [h] $\delta(^{19}F) = -223.9$, $J(^{11}B-^{19}F)$ = n.o. [i] $Fp^+ = [Fe(Cp)(CO)_2]^+$; Cp = η^5-C_5H_5.

bidentate chelation by two hydrogen atoms of a *closo*-carborane anion. In the structures of $Ag(C_6H_6)(CB_{11}H_{12})$,[21d] $Ag(C_6H_6)(12\text{-}CB_{11}H_{11}Br)$,[3c] and $Ag(C_6H_6)_2(12\text{-}CB_{11}H_{11}F)$,[4] two hydrogen atoms from two different carborane anions coordinate to the silver ions. Bidentate chelation by two bromine atoms and tridentate chelation by three bromine atoms of **3**$^-$ have been observed,[20f] as has tridentate chelation by three hydrogen atoms of $CB_{11}H_{12}^-$.[22]

Other Halogenation Reactions. The reaction of Na(**2**) with excess Cl_2 in aqueous acetonitrile was reported to yield the pentachloro 6,7,8,9,10-$CB_9H_5Cl_5^-$ anion.[9] In order to determine which boron atom is the first to be chlorinated with an electrophilic chlorinating reagent, reactions of Cs(**2**) with limited amounts of *N*-chlorosuccinimide (NCS) at 25 °C were monitored by NIEMS and ^{11}B NMR spectroscopy. The results are listed in Table 4. When NCS was recrystallized from dichloromethane, it was much less active as a chlorinating agent for **2**$^-$ (cf. experiments 1 and 2 in Table 4). The unrecrystallized material may contain an acidic impurity due to adventitious hydrolysis of the N−Cl bond. This is consistent with the observation that a small amount of CF_3COOH catalyzed the chlorination reaction when recrystallized NCS was used (cf. experiments 2−4). Acid catalysis of reactions of NCS with organic substrates has been reported.[23]

As in the fluorination of **2**$^-$ with LAHF, there was a high degree of regioselectivity for NCS chlorination of a lower-belt boron atom relative to B10 or to an upper-belt boron atom.

---

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

(23) (a) Jung, F.; Tin, K. C.; Durst, T. *Int. J. Sulfur Chem.* **1973**, *8*, 1. (b) Radhakrish-Namurti, P. S.; Sahu, N. C. *Indian J. Chem.* **1981**, *20A*, 269.

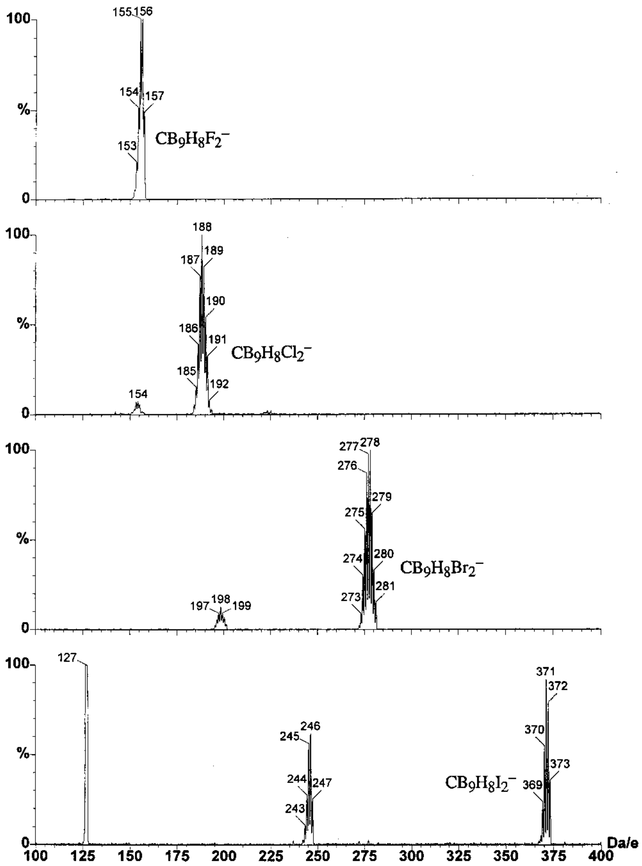


Figure 5. Negative-ion electrospray mass spectra of samples containing one or more isomers of $Cs(CB_9H_8X_2)$ (X = F, Cl, Br, I). The peak at Da/e = 127 in the bottom spectrum is due to I^- added as an internal standard. Note that the X = Cl, Br, and I samples contain varying amounts of the monohalo anions and that the X = Cl sample contains a trace amount of the trichloro derivative.

Because of this, a reasonably pure sample of $Cs(6\text{-}CB_9H_9Cl)$ could be prepared. The reaction of 2.0 equiv of NCS with Cs(**2**) at 25 °C in acetone for 50 days produced a crude product containing 1% Cs(**2**), 94% $Cs(6\text{-}CB_9H_9Cl)$, 1% $Cs(10\text{-}CB_9H_9Cl)$, and 4% $Cs(6,8\text{-}CB_9H_8Cl_2)$. Recrystallization from water afforded a 79% yield of $Cs(6\text{-}CB_9H_9Cl)$ containing less than 2% $Cs(6,8\text{-}CB_9H_8Cl_2)$. The NIEMS and ^{11}B NMR spectrum of purified $Cs(6\text{-}CB_9H_9Cl)$ are shown in Figures 1 and 2, respectively. A mixture of dichloro derivatives having the empirical formula $Cs(CB_9H_8Cl_2)$ was prepared by combining 3.5 equiv of NCS with Cs(**2**) at 55 °C in acetone for 5 days. The NIEMS of this mixture is shown in Figure 5, and ^{11}B NMR results are listed in Table 3. The 1D and 2D ^{11}B NMR spectra (not shown) indicate that the mixture consists of 68% $Cs(6,8\text{-}CB_9H_8Cl_2)$, 24% $Cs(6,7\text{-}CB_9H_8Cl_2)$, and 8% $Cs(6,10\text{-}CB_9H_8Cl_2)$. Note that considerably more of the $6,7\text{-}CB_9H_8X_2$ isomer was produced for X = Cl than for X = F.

In contrast to the case of NCS, *N*-bromosuccinimide (NBS) was not less active when recrystallized and was not more active in the presence of CF_3COOH. The reaction of 1.0 equiv of NBS with Cs(**2**) at 25 °C in acetone for 15 h produced a crude product containing 84% $Cs(6\text{-}CB_9H_9Br)$, 9% $Cs(10\text{-}CB_9H_9Br)$, and 7% $Cs(CB_9H_8Br_2)$. Recrystallization from water afforded a 66% yield of $Cs(6\text{-}CB_9H_9Br)$ containing less than 2% $Cs(CB_9H_8Br_2)$. The NIEMS and ^{11}B NMR spectrum of purified $Cs(6\text{-}CB_9H_9Br)$ are shown in Figures 1 and 2, respectively. A mixture of dibromo derivatives having the empirical formula $Cs(CB_9H_8Br_2)$ was prepared by combining 2.0 equiv of NBS with Cs(**2**) at 25 °C in acetone for 16 days. The NIEMS of this mixture is shown in Figure 5. The 1D and 2D ^{11}B NMR spectra (not shown) indicate that the mixture of dibromo isomers consists of 64% $Cs(6,8\text{-}CB_9H_8Br_2)$, 32% $Cs(6,7\text{-}CB_9H_8Br_2)$, and 4% $Cs(6,10\text{-}CB_9H_8Br_2)$. The ratio of the 6,7- to the 6,8-isomer is larger than the corresponding ratio for $Cs(CB_9H_8Cl_2)$, but the ratio of the 6,10- to the 6,8-isomer is smaller than the corresponding ratio for $Cs(CB_9H_8Cl_2)$.

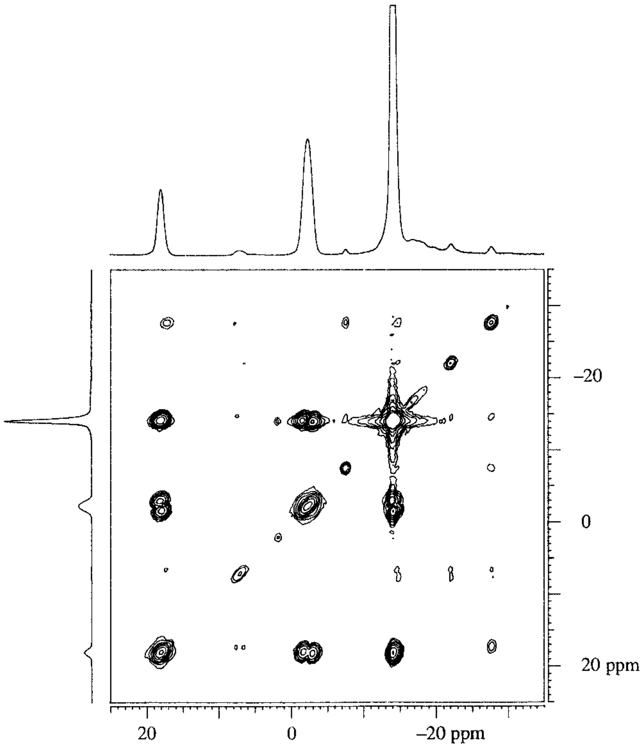


Figure 6. 96.3 MHz proton-decoupled 2D $^{11}B-^{11}B$ COSY NMR spectrum of $Cs(6,8\text{-}CB_9H_8F_2)$ in acetone-d_6. The 1D spectrum at the top has been greatly expanded in the vertical direction to show the presence of 3% $Cs(6,7\text{-}CB_9H_8F_2)$. For the $6,8\text{-}CB_9H_8F_2^-$ isomer, the resonances for the {B7,B9} and {B2,B3,B4,B5} sets of boron atoms are accidentally isochronous.

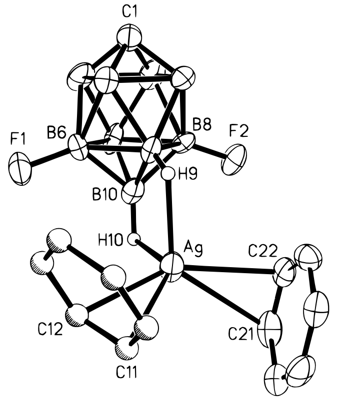


Figure 7. Drawing of $[Ag(C_6H_6)_2][6,8\text{-}CB_9H_8F_2]$ (50% probability ellipsoids except for the carbon atoms of the disordered benzene ligand, C11–C16, which are shown as spheres of arbitrary size) hydrogen atoms have been omitted for clarity except for H9 and H10, which were placed in idealized positions. Selected distances (Å) and angles (deg): Ag–C11, 2.52(2); Ag–C12, 2.47(2); Ag–C21, 2.65(1); Ag–C22, 2.49(1); Ag–H9, 2.10; Ag–H10, 2.09; H9–Ag–H10, 88.1; B6–F1, 1.42(2); B8–F2, 1.38(2); closest Ag···F contact, 3.19(1) (to F2 in another molecule).

Molecular iodine was used to prepare iodinated derivatives of $\mathbf{2}^-$. The reaction of 1.0 equiv of I_2 with Cs(**2**) at 25 °C in water for 2 days produced $Cs(6\text{-}CB_9H_9I)$ in very high compositional and isomeric purity:

$$Cs(CB_9H_{10}) + I_2 \xrightarrow{H_2O,\ 25\ ^\circ C} Cs(6\text{-}CB_9H_9I) + HI$$

Table 4. Products of the Chlorination of $Cs(CB_9H_{10})$ with *N*-Chlorosuccinimide at 25 °C in the Presence or Absence of CF_3COOH[a]

expt	equiv of NCS[b]	purity of NCS[c]	equiv of CF_3COOH	reacn time, days	observed % of anions in product mixture[d]			
					$CB_9H_{10}^-$	$6\text{-}CB_9H_9Cl^-$	$10\text{-}CB_9H_9Cl^-$	$6,8\text{-}CB_9H_8Cl_2^-$
1	1.0	unrecryst	0	7	23	77	0	0
2	1.0	recryst	0	10	97	3	0	0
3	1.0	recryst	0	51	24	74	2	0
4	2.0	recryst	0	49	1	94	1	4
5	1.0	recryst	0.5	1	14	84	1	1
6	1.0	recryst	0.5	16	14	84	1	1

[a] Acetone solution, 25 °C, unless otherwise noted. [b] NCS = *N*-chlorosuccinimide. [c] unrecryst = used as received; recryst = recrystallized from dichloromethane. [d] Determined by negative-ion electrospray mass spectrometry and ^{11}B NMR spectroscopy; values listed are probably no better than ±2%.

Less than 2% of the C_{4v} isomer $10\text{-}CB_9H_9I^-$ was produced, and this was easily removed from the bulk of the material by crystallization. The NIEMS and ^{11}B NMR spectrum of purified $Cs(6\text{-}CB_9H_9I)$ are shown in Figures 1 and 2, respectively. Note that a modest amount of 10-monohalo isomer is produced for X = Cl, Br, and I. This is in contrast to the monofluoro derivative, for which there was no observable amount of 10-monofluoro isomer. This behavior is consistent with the results of monohalogenation of $CB_{11}H_{12}^-$: only the 12-monohalo isomers are produced when the halogen is fluorine,[4] chlorine,[3c] or bromine,[3c] but both 7- and 12-monoiodo isomers are produced in the reaction of $CB_{11}H_{12}^-$ with I_2.[3a] The regioselectivity for monohalogenation of $CB_{11}H_{12}^-$ is apparently greater than that of $CB_9H_{10}^-$.

Prolonged treatment of Cs(**2**) with 2.0 equiv of I_2 in water at 35 °C produced a mixture of mono- (~40%) and diiodo derivatives (~60%). The NIEMS of this mixture is shown in Figure 5. As observed for dichlorination and dibromination, diiodination resulted in the formation of three isomers, $6,8\text{-}CB_9H_8I_2^-$ (~48%), $6,7\text{-}CB_9H_8I_2^-$ (~48%), and $6,10\text{-}CB_9H_8I_2^-$ (~4%). Note that the $(6,8\text{-}CB_9H_8X_2)$:$(6,7\text{-}CB_9H_8X_2)$ ratio decreased in the order 32:1, 3:1, 2:1, and 1:1 for X = F, Cl, Br, and I, respectively.

Analysis of NMR Spectra. The ^{11}B chemical shift data for the $6\text{-}CB_9H_9X^-$ anions provide a rare opportunity to examine the NMR trends of a series of *closo*-heteroborane clusters for which all four halogenated derivatives are available. The behavior of $\delta(^{11}B)$ as a function of halogen electronegativity is shown in Figure 8 for B10 and the three different types of lower-belt boron atoms of $6\text{-}CB_9H_9X^-$. It is now apparent that the trends previously observed for heavier halogen derivatives of *closo*-borane and -heteroborane clusters can be reliably extrapolated to unknown fluoro derivatives.

The slopes of the approximately linear plots are similar in sign and magnitude to those of the plots for the neutral molecular clusters $6\text{-}SB_9H_8Cl$, $6\text{-}SB_9H_8Br$, and $6\text{-}SB_9H_8I$ (the monofluoro derivative of SB_9H_9 is not known).[24] This was expected on the basis of a set of geometry- and symmetry-dependent rules for predicting ^{11}B NMR spectra.[25−27] One rule predicts that iodo substitution should shield the resonance for B6 relative to its value in $CB_9H_{10}^-$ but that substitution by other halogens should deshield the B6 resonance, with the magnitude of the shielding effect increasing as the electronegativity of the halogen increases. This is precisely what is observed for the set of clusters $CB_9H_9X^-$ (X = F, Cl, Br, I). Another rule predicts that when B6 is substituted with an electronegative substituent, the rhomboidal effect on B8 should be twice as large as, and opposite in sign to, the neighbor effect on B7 and B9. The slopes of the least-squares lines for the B8 and {B7,B9} data are −5.4 and +2.0 ppm, respectively.

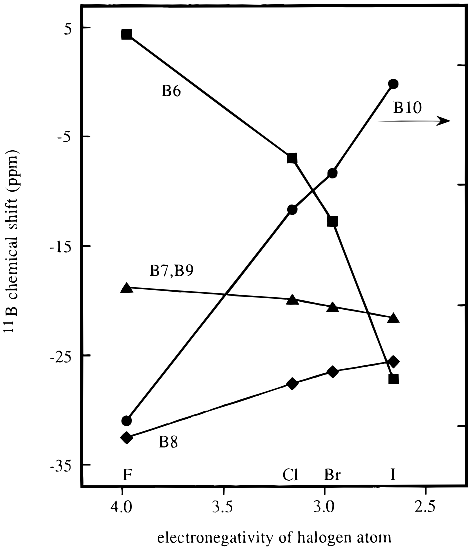
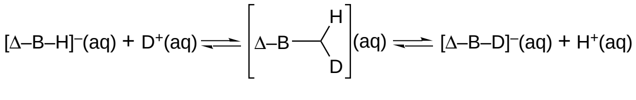


Figure 8. Plots of ^{11}B chemical shifts for the antipodal (B10) and lower-belt (B6−B9) boron atoms in $6\text{-}CB_9H_9X^-$ anions (X = F, Cl, Br, I) vs the Pauling electronegativity of the halogen atom (Cs^+ salts; acetone-d_6, 25 °C). The *y* values for the {B6,B8} and {B7,B9} plots are shown at the left. The *y* values for the B10 plot are shown at the right.

The coordination of Ag^+ to anionic heteroborane cluster B−H bonds deshields the ^{11}B resonances and decreases J_{BH} values for those bonds. The B10−H10 and B8−H8 J_{BH} values for $Cs(6\text{-}CB_9H_9F)$ dissolved in acetone-d_6 are 150 and 139 Hz, respectively, but are only 137 and 126 Hz, respectively, for $Ag(6\text{-}CB_9H_9F)$ dissolved in benzene-d_6. Consistent with this, the B10−H10 J_{BH} value is 150 Hz for $Cs(6,8\text{-}CB_9H_8F_2)$ dissolved in acetone-d_6 but is only 126 Hz for $Ag(6,8\text{-}CB_9H_8F_2)$ dissolved in benzene-d_6. Note also that antipodal and lower-belt J_{BH} values, but not upper-belt J_{BH} values, decrease for $Cs(CB_9H_{10})$ on going from acetone-d_6 to the strongly hydrogen-bonding medium 20% aqueous DCl.

H/D Exchange of $CB_9H_{10}^-$, $6\text{-}CB_9H_9F^-$, and $6\text{-}CB_9H_9I^-$. The deuteration of Cs(**2**) at 25 °C using 20% DCl in D_2O was monitored over time by ^{11}B NMR spectroscopy. The H/D exchange probably occurred in reversible steps such as the following (Δ = cluster minus one B−H vertex):[26]



$$[\Delta\text{–B–H}]^-(aq) + D^+(aq) \rightleftharpoons \left[\Delta\text{–B}\langle{}^{H}_{D}\right](aq) \rightleftharpoons [\Delta\text{–B–D}]^-(aq) + H^+(aq)$$

It was anticipated that the pattern of electrophilic deuteration would lead to a better understanding of the pattern of electrophilic halogenation, since a straightforward correlation had been found earlier for $CB_{11}H_{12}^-$ ($\mathbf{1}^-$). As stated above, monoflu-

---

(24) Smith, W. L.; Meneghelli, B. J.; Thompson, D. A.; Klymko, P.; McClure, N.; Bower, M.; Rudolph, R. W. *Inorg. Chem.* **1977**, *16*, 3008.

(25) Teixidor, F.; Viñas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339.

(26) Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325 and references therein.

(27) A recent application of the Fenske−Hall MO method to the calculation of ^{11}B NMR chemical shifts: Fehlner, T. P.; Czech, P. T.; Fenske, R. F. *Inorg. Chem.* **1990**, *29*, 3103.

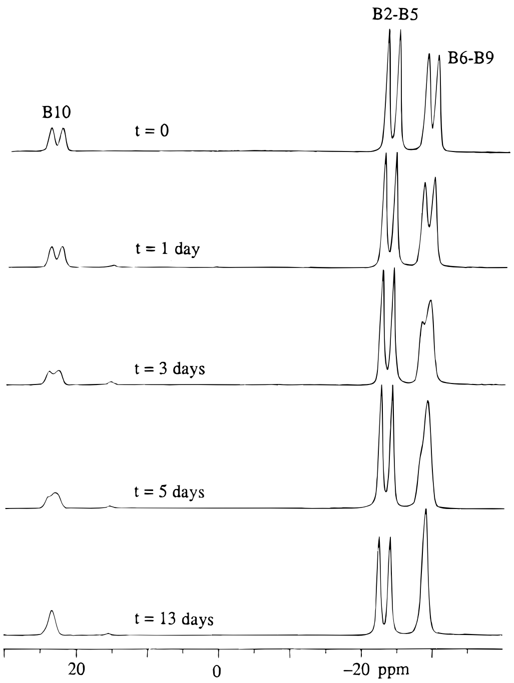


Figure 9. Time-dependent 96.3 MHz proton-coupled ^{11}B NMR spectra of Cs(CB_9H_{10}) in 20% aqueous DCl.

orination, -chlorination, and -bromination of **1**$^-$ occur exclusively at B12, the boron atom antipodal to the more electronegative carbon atom, and monoiodination occurs almost exclusively at B12. This was attributed to the expected greater negative charge on H12 relative to the other B−H hydrogen atoms (i.e., electrophilic halogenation occurs at the "most hydridic" B−H bond). Consistent with this, deuteration of **1**$^-$ with DCl/D_2O occurs significantly faster at B12 than at B7−B11 (deuteration did not occur at all at B2−B6).[8] Recent MNDO calculations provide justification for the observed deuteration pattern: the isomer of gaseous H($CB_{11}H_{12}$) with the additional proton attached to B12 (i.e., forming a 3c-2e$^-$ $\overline{\text{B12}-\text{H}-\text{H}}$ moiety) is 3.6 kcal mol^{-1} more stable than the corresponding $\overline{\text{B7}-\text{H}-\text{H}}$ isomer and 11.7 kcal mol^{-1} more stable than the $\overline{\text{B2}-\text{H}-\text{H}}$ isomer.[28]

Figure 9 displays ^{11}B NMR spectra over time for a solution of Cs(**2**) in 20% aqueous DCl. The B10 and B6−B9 doublets (J_{BH} = 145 and 133 Hz, respectively) both evolve into apparent singlets at the same rate (the J_{BD} coupling is too small to be resolved). After 13 days, it is apparent that the sample of $CB_9H_{10}^-$ has been converted to 6,7,8,9,10-$CB_9H_5D_5^-$. (Note the small isotope effect on δ values: the resonances for B10 and B6−B9 in 6,7,8,9,10-$CB_9H_5D_5^-$ are slightly deshielded from their respective values in the natural-abundance isotopomer.) Therefore, the rates of B6 deuteration and of B10 deuteration are nearly equal. This result clearly does not correlate with the very different relative rates of B6 and B10 halogenation noted above.

The deuteration of Cs(6-CB_9H_9F) at 25 °C using 20% DCl in D_2O was also monitored over time by ^{11}B NMR spectroscopy. The spectra (see Supporting Information) clearly show that B8 is deuterated more than twice as fast as B10 (the deuteration of B8 is nearly complete after 13 days whereas the deuteration of B10 is nearly complete after 38 days). The deuteration of B7 and B9 is even slower (less than 50% complete after 31 days).

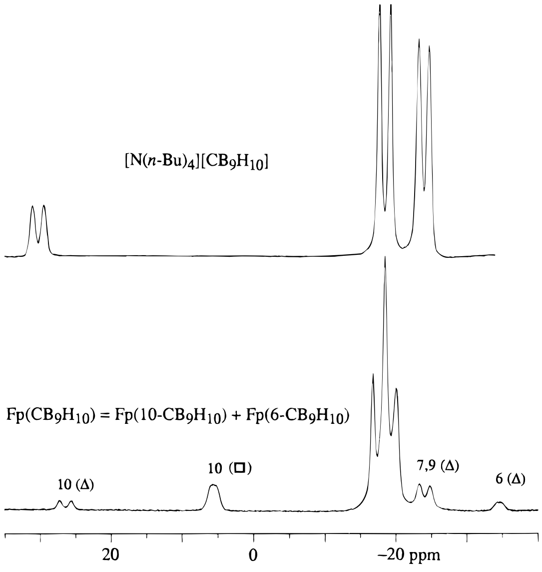
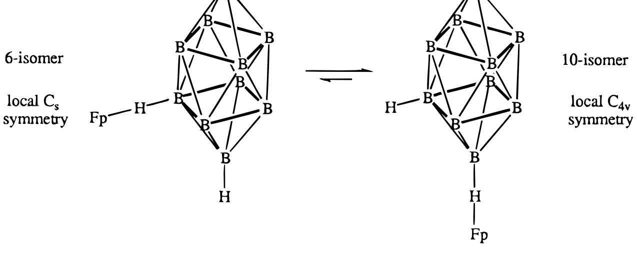


Figure 10. 96.3 MHz proton-coupled ^{11}B NMR spectra of [N(*n*-Bu)$_4$]-[CB_9H_{10}] and Fp(CB_9H_{10}) in dichloromethane-d_2. Resonances for the two isomers Fp(10-CB_9H_{10}) and Fp(6-CB_9H_{10}) are indicated respectively by a square and by triangles in parentheses.

Clearly, the introduction of a single fluorine atom at B6 significantly alters the electronic structure of $CB_9H_{10}^-$, although it leaves the reactivity of B8 nearly the same. The observation that B8 in Cs(6-CB_9H_9F) is deuterated nearly as quickly as B8 in Cs(CB_9H_{10}) is consistent with the difficulty encountered in preparing pure samples of Cs(6-CB_9H_9F): the rate of fluorination of Cs(6-CB_9H_9F) by LAHF is competitive with the rate of fluorination of the parent compound Cs(CB_9H_{10}). The relatively rapid deuteration of the B8−H8 moiety in 6-$CB_9H_9F^-$ is also consistent with the formation of 33 times more 6,8-$CB_9H_8F_2^-$ than 6,7-$CB_9H_8F_2^-$. Interestingly, when Cs(6-CB_9H_9I) was dissolved in 20% DCl in D_2O at 25°C, no deuterium exchange was detected, even after 31 days.

Isomers of Fp(CB_9H_{10}) and Fp($CB_{11}H_{12}$). Another indicator of the charge distribution in **1**$^-$ is thought to be the solid-state structure of Fp(**1**), in which the "most hydridic" hydrogen atom, H12, coordinates to the iron atom of the Fp$^+$ electrophile (Fp$^+$ = CpFe(CO)$_2^+$).[3b] On the basis of observed regioselectivity for the deuteration of **1**$^-$ and **2**$^-$, we anticipated that Fp(**2**) might exist as two isomers, with Fp$^+$ coordinated to H6 as well as to H10. This was found to be the case. The ^{11}B NMR spectrum of Fp(**2**) in dichloromethane is shown in Figure 10 (see also Table 3). At 24 °C, the 10-isomer is 3 times more abundant than the 6-isomer (the assignments follow from the 2D ^{11}B−^{11}B COSY NMR spectrum (not shown)). When the spectrum was recorded at 44 °C, the ratio changed from 75:25 to 71:29. The 75:25 ratio was restored when the sample was cooled back to 25 °C (no decomposition was observed). Therefore, the two isomers are in mobile equilibrium:



The symmetry number of the 6-isomer is less than the symmetry number of the 10-isomer, so it is reasonable to assume that the equilibrium shifts to the left as the temperature is raised. Note

---

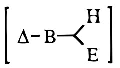
(28) Harchevnikova, N. V.; Diachkov, P. N.; Zubin, A. S.; Solntsev, K. A.; Kuznetsov, N. T.; Ivanov, S. V.; Strauss, S. H. *Dokl. Akad Nauk SSSR*, in press.

that Fp^+ coordination lowers J_{BH} (relative to $[N(n\text{-}Bu)_4][CB_9H_{10}]$ dissolved in dichloromethane-d_2) from 151 to 86 Hz for B10−H10 and from 135 to 76 Hz for B6−H6. A similar spectrum was recorded for Fp(**2**) dissolved in toluene-d_8, indicating that the two isomers are also present in this solvent.

The carbon−oxygen stretching frequencies of Fp^+X^- complexes in toluene solution have been proposed as a measure of the coordinating ability of the anion X^-: the weaker the $Fp^+\cdots X^-$ interaction, the higher the $\nu(CO)$ values.[3f] Solution IR spectra of Fp(**2**) in dichloromethane and in toluene exhibited only one set of symmetrically-shaped peaks (i.e., $\nu_{sym}(CO)$ and $\nu_{asym}(CO)$), indicating that the different isomers have very similar $\nu(CO)$ values. In dichloromethane, the $\nu(CO)$ values were 2071 and 2031 cm^{-1}. In toluene, the $\nu(CO)$ values were 2069 and 2028 cm^{-1} (lit.[3f] 2070, 2030 cm^{-1}). Although infrared spectroscopy is a useful technique for estimating the overall coordinating ability of an anion, the present data indicate that it is not sufficiently sensitive to detect coordination isomers of weakly coordinating carborane anions.

Interestingly, the ^{11}B NMR spectrum of Fp(**1**) in dichloromethane at 25°C (not shown) also showed the presence of two isomers. In this case, the 12-isomer was 2.7 times more abundant than the 7-isomer. Although X-ray crystallography can provide valuable, detailed structural information, it can (as in this case) lead to an incomplete understanding of the relative stabilities of different isomers in solution. The phenomenon of multiple isomers of metal complexes of $\mathbf{1}^-$, $\mathbf{2}^-$, and their halogenated derivatives in solution deserves further study.

Do Thermodynamic or Kinetic Factors Control the Site of Halogenation? Heřmánek and co-workers have suggested that when an electrophile E^+ attacks a deltahedral borane or heteroborane cluster, Δ−B−H, intermediates such as the following may be formed:[26]



$$\left[\Delta\text{-}B\text{-}\!\!<\begin{matrix}H\\E\end{matrix}\right]$$

These intermediates can lose H^+ (e.g., when E^+ is Cl^+, Br^+, or I^+) or can lose molecular H_2 and add a nucleophile (e.g., when $E^+ = H^+$ and the nucleophile is F^-). While this is a plausible concept, the kinetics and mechanisms of halogenation of $\mathbf{1}^-$ and $\mathbf{2}^-$ have not yet been studied in detail. Furthermore, there are no experimental or theoretical data available on the relative thermodynamic stabilities of the various halogenated isomers. In addition, although the relative stabilities of the 2-, 6-, and 10-isomers of $H(CB_{11}H_{12})$ have been determined by MNDO calculations (see above), similar information is not yet available for $H(CB_9H_{10})$. Nevertheless, we will attempt to draw some tentative conclusions from the experimental results so that a working hypothesis based on all available data may be formulated and subsequently tested.

The substitution of one $(B-H)^{2-}$ vertex of the parent clusters $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ with a heteroatomic moiety such as $(C-H)^-$ or $(S)^0$ induces a charge asymmetry.[29] The negative end of the cluster is the antipodal B−H bond. In accordance with this principle, H12 has been referred to as the "most hydridic" hydrogen atom in $CB_{11}H_{12}^-$.[3a−c,4,12] It is certainly the most reactive hydrogen atom. As discussed above, metal ions preferentially (although not exclusively) interact with H12, aqueous D^+ preferentially exchanges with H12, and electrophilic halogenating reagents preferentially react with the B12−H12 bond. However, a number of factors may control these preferences, not just the amount of negative charge on the cluster hydrogen atoms. These factors could include the B−H bond enthalpy, the magnitude of the B−H bond dipole moment, and the overall cluster dipole moment in addition to the H atom charge.

The preferences observed in this work for $CB_9H_{10}^-$ are not as singular as those for $CB_{11}H_{12}$. The Fp^+ cation does preferentially interact with H10, but aqueous D^+ exchanges H6 (and its symmetry-equivalent atoms) and H10 at the same rate. Most significantly, it is B6, not B10, that is the preferred site of monohalogenation. In addition, two lower-belt boron atoms are the preferred sites of dihalogenation. Clearly, the presumed greater negative charge on H10 relative to the four lower-belt hydrogen atoms cannot explain the halogenation results, let alone the deuteration result.

Our halogenation results are consistent with the electrophilic alkylation of SB_9H_9 (axial sulfur atom), which produced 6-SB_9H_8R rather than 10-SB_9H_8R.[30] When 6-SB_9H_8R was heated, it rearranged to 10-SB_9H_8R, presumably the more stable isomer.[30] Our results are also consistent with the electrophilic halogenation of SB_9H_9.[24] Here again, the 6-monohalo derivatives were the predominant products, and they rearranged to the 10-monohalo derivatives upon heating.[24] If B10 is also the thermodynamically preferred site for halogenation of $CB_9H_{10}^-$, then the anions 6-$CB_9H_9X^-$, 6,8-$CB_9H_8X_2^-$, and 6,7-$CB_9H_8X_2^-$ are kinetic products, not thermodynamic products (X = F, Cl, Br, I).

The coupling constant data in Table 3 allow an interesting correlation to be made. For $Cs(CB_9H_{10})$, note that J_{BH} is *smaller* for B6−H6 (137 Hz) than for B10−H10 (151 Hz), and B6 receives the first halogen atom. Therefore, one of the factors that gives rise to the kinetic control of the halogenation reactions may be the relative B−H bond enthalpies, as probed (albeit equivocally) by J_{BH} values. Charge distribution may not be the only factor, or even the most important factor, in electrophilic substitution of *closo*-borane and -heteroborane clusters. We note that this correlation of J_{BH} values with relative rates of monohalogenation also follows for SB_9H_9. For this compound, which is halogenated preferentially at B6, J_{BH} values for B6−H6 and B10−H10 are 152 and 171 Hz, respectively.[31]

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-9628769, CHE-9308583, CHE-8103011, and CHE-9107593). We also thank Akzo Nobel, Inc., for financial support, Callery Chemical Co. for a gift of $B_{10}H_{14}$, Ms. Christine M. Gaudinski for assistance with crystallographic computations, Mr. Donald L. Dick for his expertise with mass spectrometry, and Professor C. A. Reed and Dr. T. Jelínek for valuable discussions and suggestions.

Supporting Information Available: Time-dependent ^{11}B NMR spectra of $Cs(6\text{-}CB_9H_9F)$ in 20% DCl in D_2O, ^{11}B NMR spectrum of $Fp(CB_{11}H_{12})$, and a fully labeled ORTEP diagram and tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for $Ag(C_6H_6)_2(6,8\text{-}CB_9H_8F_2)$ (12 pages). See any current masthead page for ordering information.

IC960859A

---

(29) Štíbr, B. *Chem. Rev.* **1992**, *92*, 225 and references therein.

(30) Meneghelli, B. J.; Rudolph, R. W. *J. Organomet. Chem.* **1977**, *133*, 139.

(31) Pretzer W. R.; Rudolph, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 931.