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Regioselective Fluorination of $CB_{11}H_{12}^-$. New Weakly Coordinating Anions

Sergei V. Ivanov,[1a,b] Anthony J. Lupinetti,[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

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The preparation of new weakly coordinating anions (WCAs) is an active endeavor because they are being used to solve important problems in synthesis, catalysis, and materials science.[2] Taking advantage of the "non-stick" properties of highly fluorinated materials, WCAs such as $B(C_6F_5)_4^-$,[2,3] $B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$,[2,3] $B(OTeF_5)_4^-$,[4] $Sb(OTeF_5)_6^-$,[5] $Al(OC(CH_3)(CF_3)_2)_4^-$,[6] and $Nb(OCH(CF_3)_2)_6^-$ [6] have been prepared and studied. On the other hand, some of the most useful and most stable WCAs are the icosahedral carborane anions, including $CB_{11}H_{12}^-$,[7] 12-$CB_{11}H_{11}Br^-$,[8] and 7,8,9,10,11,12-$CB_{11}H_6Br_6^-$.[9] It seemed logical that uninegative fluorinated carborane anions might be superior to other WCAs for some applications, but only one example, 2-$CB_{11}H_{11}F^-$, has been reported.[10] Its method of preparation, the insertion of a "BF" moiety into the *nido* anion 7-$CB_{10}H_{13}^-$, cannot be used to produce more highly fluorinated derivatives.

We report that $CB_{11}H_{12}^-$ and 2-$CB_{11}H_{11}F^-$ can be regioselectively fluorinated in a general way to prepare the following anions: 12-$CB_{11}H_{11}F^-$, 7,12-$CB_{11}H_{11}F^-$, 2,12-$CB_{11}H_{10}F_2^-$, and 7,9,12-$CB_{11}H_9F_3^-$. It was previously found that salts of $B_{12}H_{12}^{2-}$ were fluorinated by treatment with liquid anhydrous HF (LAHF) at temperatures from −20 to 600 °C.[11] A series of anions $B_{12}H_{12-x}F_x^{2-}$, with $x = 2$, 4−8, 10, 12, were characterized (some by X-ray crystallography).[11c] However, under most conditions, mixtures of anions with varying degrees of fluorination were formed.[11] We have found that LAHF will selectively fluorinate salts of $CB_{11}H_{12}^-$ or 2-$CB_{11}H_{11}F^-$ in a stepwise manner at a given temperature, producing salts that have high compositional purity and excellent isomeric purity. Treatment of $[Cs][CB_{11}H_{12}]$[12] (0.286 g) with LAHF (10 mL) for 20 h at 23 °C produced a single pure solid in 96% yield (0.292 g) as well as 1 equiv of a noncondensable gas (H_2). The ^{11}B and ^{19}F NMR spectra of the unrecrystallized product are shown in Figure 1 (there is no detectable $CB_{11}H_{12}^-$ or difluoro derivative).[13,14] The spectra are consistent with monofluoro substitution and C_{5v} symmetry, demonstrating that the most hydridic hydrogen atom of $CB_{11}H_{12}^-$ (i.e., the hydrogen atom farthest removed from the carbon atom) has been replaced by a fluorine atom:

$$[Cs][CB_{11}H_{12}] + HF \xrightarrow[23°C,\ 22\ h]{\text{anhydrous HF}} [Cs][12\text{-}CB_{11}H_{11}F] + H_2$$

Cation exchange reactions have allowed Ag^+, $N(n\text{-}Bu)_4^+$, and NMe_3H^+ salts of 12-$CB_{11}H_{11}F^-$ to be isolated in good yields. For example, extraction of an aqueous solution of [Cs][12-$CB_{11}H_{11}F$] and $AgNO_3$ with benzene, followed by cooling of the benzene solution, yielded crystals of $[Ag(C_6H_6)_2]$[12-$CB_{11}H_{11}F$].[15] The structure (illustrated synopsis; Supporting Information) consists of silver(I) ions coordinated to two benzene ligands in asymmetric η^2 fashion and to two terminal B−H hydrogen atoms of two pseudoicosahedral *closo* 12-$CB_{11}H_{11}F^-$ anions. Significantly, there is no interaction between the silver ion and the fluorine atom: the closest Ag···F interaction is >4.6 Å, more than 1.4 Å longer than the sum of van der Waals radii.[16] In the structure of $[Ag(C_6H_6)]$[12-

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(13) All NMR data are reported for Cs^+ salts in acetone-d_6 unless otherwise noted. Chemical shift standards are $SiMe_4$ (^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F). Some $^1H-^{11}B$ coupling constants could not be determined due to overlapping resonances. Abbreviations: s, singlet; d, doublet; q, quartet; bd, broader than other resonances.

(14) For 12-$CB_{11}H_{11}F^-$: $\delta(^{13}C)$ 36.1 (d); $\delta(^{11}B)$ 14.3 (bd s), −14.4 (d, $J_{HB} = 136$ Hz), −18.8 (d, $J_{HB} = 152$ Hz); $\delta(^{19}F)$ −190.4 (q, $J_{BF} = 59$ Hz). For 2-$CB_{11}H_{11}F^-$ (NMe_3H^+ salt): $\delta(^{13}C)$ 51.4 (d); $\delta(^{11}B)$ 4.1 (bd s), −8.2 (d, $J_{HB} = 138$ Hz), −14.4 (d), −15.4 (d, $J_{HB} = 144$ Hz), −17.2 (d), −21.7 (d, $J_{HB} = 135$ Hz); $\delta(^{19}F)$ −208.4 (q, $J_{BF} = 55$ Hz). For $CB_{11}H_{12}^-$: $\delta(^{13}C)$ 51.4 (d); $\delta(^{11}B)$ −6.0 (d, $J_{HB} = 136$ Hz), −12.4 (d, $J_{HB} = 137$ Hz), −15.3 (d, $J_{HB} = 150$ Hz).

(15) Crystals were grown by cooling a benzene solution of [Ag][12-$CB_{11}H_{11}F$]: $C_{13}H_{23}AgB_{11}F$, $M_r = 425.1$, orthorhombic, space group $Pca2_1$, $a = 16.323(3)$ Å, $b = 6.755(1)$ Å, $c = 17.095(3)$ Å, $V = 1884.9(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.498$ g cm^{-3}, $F(000) = 848$, λ(Mo Kα) = 0.710 73 Å, $\mu = 10.7$ cm^{-1}, $T = -100$ °C, crystal dimensions 0.45 × 0.28 × 0.04 mm; Siemens P4 diffractometer, $\theta-2\theta$ scan technique, 2375 independent reflections measured ($4° \le 2\theta \le 55°$); anisotropic refinement (full-matrix least-squares on F^2) for all non-hydrogen atoms, hydrogen atoms in calculated positions, semiempirical absorption correction; final $R(I > 2\sigma(I)) = 0.060$, final R(all data) = 0.076; total number of parameters = 235.

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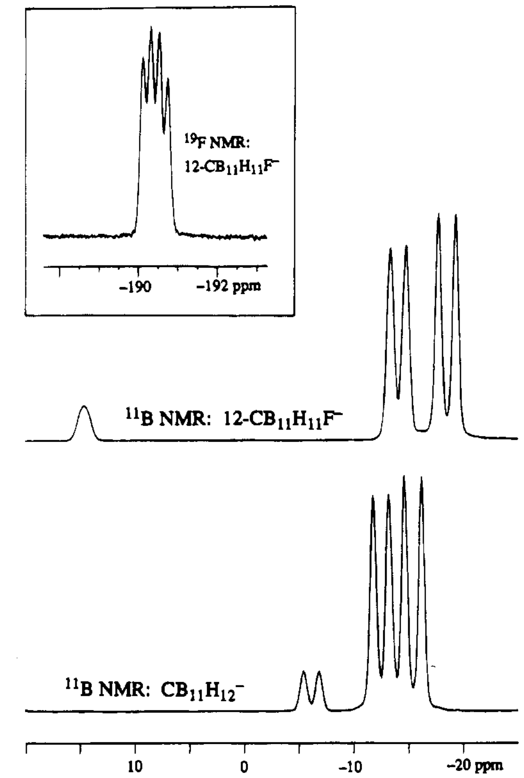

Figure 1. Proton-coupled ^{11}B NMR spectra (96.3 MHz, acetone-d_6) of [Cs][12-$CB_{11}H_{11}F$] (top) and [Cs][$CB_{11}H_{12}$] (bottom). Inset: ^{19}F NMR spectrum (282.4 MHz, acetone-d_6) of [Cs][12-$CB_{11}H_{11}F$].

$CB_{11}H_{11}Br$].[8] There is strong Ag−Br interaction of 2.642(1) Å. In harmony with hard and soft acid/base principles, the silver(I)−halogen interaction is lost on changing from the 12-bromo to the 12-fluoro carborane anion: the Ag−Br bond in [$Ag(C_6H_6)$][12-$CB_{11}H_{11}Br$] is replaced by an additional arene ligand in [$Ag(C_6H_6)_2$][12-$CB_{11}H_{11}F$]. This suggests that $CB_{11}H_{12-x}F_x^-$ anions may be more weakly coordinating than $CB_{11}H_{12-x}Br_x^-$ anions for a given value of x, at least for soft metal centers.

The average ν(CO) values for a series of Fe(Cp)(X)$(CO)_2$ compounds in toluene show a steady rise from 2016 cm^{-1} (I^-) to 2049 cm^{-1} ($CB_{11}H_{12}^-$) to 2052 cm^{-1} (SbF_6^-) to 2108 cm^{-1} ($CB_{11}H_6Br_6^-$).[9b] This trend was interpreted as indicating that the coordinating ability of these anions decreases monotonically from I^- (the strongest) to $CB_{11}H_6Br_6^-$ (the weakest).[9b] When [Ag][12-$CB_{11}H_{11}F$] and Fe(Cp)(I)$(CO)_2$ were mixed in toluene, a white precipitate (AgI) slowly formed, leaving an orange solution that exhibited ν(CO) bands at 2068 and 2031 cm^{-1} (average 2049.5 cm^{-1}). On this basis, we conclude that 12-$CB_{11}H_{11}F^-$ is similar in coordinating ability to $CB_{11}H_{12}^-$ and more strongly coordinating than $CB_{11}H_6Br_6^-$. We expect that the hexafluoro anion $CB_{11}H_6F_6^-$, if it can be prepared, will be more weakly coordinating than 12-$CB_{11}H_{11}F^-$.

Two difluoro and one trifluoro derivatives of $CB_{11}H_{12}^-$ were prepared using higher reaction temperatures.[17] Treatment of [Cs][$CB_{11}H_{12}$] with LAHF for 44 h at 140 °C produced [Cs][7,12-$CB_{11}H_{10}F_2$] in high compositional purity. (NMR spectra (Supporting Information) indicate that the product also contained ca. 1% 12-$CB_{11}H_{11}F^-$ and ca. 3% 7,9,12-$CB_{11}H_9F_3^-$. The 7,-12 assignment (C_s symmetry) is based on the 1:1:2:2:2:2:1 ^{11}B NMR intensity pattern and the 1:1 ^{19}F NMR intensity pattern.[13,18] Significantly, no other difluoro isomer was detected in the NMR spectra (ignoring CF-containing isomers, there are six possible $CB_{11}H_{10}F_2^-$ isomers). Thin-layer chromatographic experiments indicate that a mixture of N(n-Bu)$_4^+$ salts of 7,-12-$CB_{11}H_{10}F_2^-$ (R_f = 0.47), 12-$CB_{11}H_{11}F^-$ (R_f = 0.50), and 7,9,12-$CB_{11}H_9F_3^-$ (R_f = 0.44) can be separated on silica using 90:10 (v/v) chloroform/acetonitrile.

The C_s symmetry 2,12-$CB_{11}H_{10}F_2^-$ isomer was formed regioselectively when [NMe_3H][2-$CB_{11}H_{11}F$][10] was treated with LAHF for 16 h at 42 °C.[17] It exhibited 1:1:2:2:2:2:1 ^{11}B NMR and 1:1 ^{19}F intensity patterns similar to but clearly different from those of the 7,12-isomer.[13,18] The NMR spectra (Supporting Information) clearly show that, although there is ca. 2% 2-$CB_{11}H_{11}F^-$ in the product, there is no other difluoro isomer.

The reaction of [Cs][$CB_{11}H_{12}$] with LAHF at 180 °C for 70 h produced [Cs][7,9,12-$CB_{11}H_9F_3$] in excellent compositional and isomeric purity.[17] The 7,9,12 assignment (C_s symmetry) is based on its 1:2:1:2:2:1:2 ^{11}B NMR intensity pattern, its 1:2 ^{19}F NMR intensity pattern, and its 2D ^{11}B−^{11}B NMR pattern (Supporting Information).[13,18] The NMR spectra are inconsistent with any other isomer, including the C_s-symmetry 7,8,12-isomer (ignoring CF-containing isomers, there are 34 possible $CB_{11}H_9F_3^-$ isomers). One or two percent of a BF-containing impurity is present, but it is not any of the above-mentioned anions. Therefore, the regioselectivity of this reaction is at least 98%. Higher reaction temperatures have resulted in mixtures of 7,9,-12-$CB_{11}H_9F_3^-$ and what appears to be a single isomer of $CB_{11}H_8F_4^-$. Conditions have not yet been optimized for the preparation of relatively pure samples of the tetrafluoro anion.

In summary, the data suggest that the reaction of $CB_{11}H_{12}^-$ or 2-$CB_{11}H_{11}F^-$ and liquid anhydrous HF proceeds by stepwise, regioselective attack of HF on the anion. Whether the reactions are under kinetic or thermodynamic control remains to be seen. The first few members of the $CB_{11}H_{12-x}F_x^-$ class of anions are robust, are stable in aqueous acid (1 M H_2SO_4) and base (1 M NaOH), and promise to be extremely weakly coordinating. Equally important, as far as their use as WCAs is concerned, is the fact that they can be prepared in high compositional purity and excellent isomeric purity.

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Supporting Information Available: Text giving synthetic details, ^{11}B and ^{19}F NMR spectra of salts of 2,12-$CB_{11}H_{10}F_2^-$, 7,12-$CB_{11}H_{10}F_2^-$, and 7,9,12-$CB_{11}H_9F_3^-$, the ^{11}B−^{11}B 2D (COSY) NMR spectrum of [Cs][7,9,12-$CB_{11}H_9F_3$], tables of crystal data and structure refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters for [$Ag(C_6H_6)_2$][12-$CB_{11}H_{11}F$], and a drawing of the structure of [$Ag(C_6H_6)_2$][12-$CB_{11}H_{11}F$] (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) Synthetic details are given in the Supporting Information.

(18) For 7,12-$CB_{11}H_{10}F_2^-$: δ(^{13}C) 32.7 (d); δ(^{11}B) 12.3 (bd s), 7.5 (bd s), −15.9 (d), −16.9 (d), −19.9 (d, J_{HB} = 152 Hz), −22.6 (d, J_{HB} = 154 Hz), −26.5 (d, J_{HB} = 155 Hz); δ(^{19}F) −194.4 (q, J_{BF} = 59 Hz), −212.0 (q, J_{BF} = 56 Hz). For 2,12-$CB_{11}H_{10}F_2^-$ (NMe_3H^+ salt): δ(^{13}C) 35.8 (d); δ(^{11}B) 12.8 (bd s), 1.4 (bd s), −16.0 (d), −16.9 (d, J_{HB} = 128 Hz), −18.5 (d), −20.8 (d), −23.4 (d, J_{HB} = 143 Hz); δ(^{19}F) −193.8 (q, J_{BF} = 59 Hz), −211.8 (q, J_{BF} = 60 Hz). For 7,9,12-$CB_{11}H_9F_3^-$: δ(^{13}C) 28.2 (d); δ(^{11}B) 9.9 (intensity = 1, bd s), 5.1 (intensity = 2, bd s), −17.2 (d), −18.4 (d, J_{HB} = 128 Hz), −23.7 (d, J_{HB} = 154 Hz), −26.9 (d), −28.2 (d, J_{HB} = 141 Hz); δ(^{19}F) −198.1 (intensity = 1, q, J_{BF} = 62 Hz), −216.0 (intensity = 2, q, J_{BF} = 56 Hz).