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# Highly Fluorinated Weakly Coordinating Monocarborane Anions. 1-H-$CB_{11}F_{11}^-$, 1-$CH_3$-$CB_{11}F_{11}^-$, and the Structure of $[N(n\text{-}Bu)_4]_2[CuCl(CB_{11}F_{11})]$

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Monocarborane monoanions, especially derivatives of $CB_{11}H_{12}^-$, are some of the most promising new weakly coordinating anions.[2,3] This is because they are weakly coordinating *and* extraordinarily stable chemically and electrochemically. Important examples include $CB_{11}H_6Cl_6^-$,[4,5] $CB_{11}H_6Br_6^-$,[4−6] $CB_{11}H_6I_6^-$,[5] 1-$CH_3$-$CB_{11}Cl_{11}^-$,[7] and $CB_{11}(CH_3)_{12}^-$.[8]

Of the three hexahalo derivatives listed, $CB_{11}H_6Cl_6^-$ is the least coordinating toward the $Si(i\text{-}Pr)_3^+$ cation.[5] This significant result suggests that fluorinated derivatives of $CB_{11}H_{12}^-$ might be even more weakly coordinating than the corresponding chlorinated, brominated, or iodinated derivatives, at least for some cations. For this reason, we have been developing synthetic strategies for the polyfluorination of $CB_{11}H_{12}^-$ and the related carborane ion $CB_9H_{10}^-$.[9] The use of supercritical HF or F-TEDA[10] has resulted in mixtures of ions of varying composition.[9] For example, $CB_{11}H_{12}^-$ was converted to a mixture of $CB_{11}H_7F_5^-$ (35%), $CB_{11}H_6F_6^-$ (59%), and $CB_{11}H_5F_7^-$ (6%) using anhydrous HF at 390 °C.[9e] Such mixtures were separated, but only after lengthy chromatographic procedures which resulted in relatively low isolated yields.[9e]

We now report that $CB_{11}H_{12}^-$ can be converted to 1-H-$CB_{11}F_{11}^-$ in 74% isolated yield using $F_2$ in HF at room temperature:

$$Cs^+CB_{11}H_{12}^- + 11F_2 \xrightarrow[25\ °C,\ 48\ h]{HF(l)} Cs^+(1\text{-}H\text{-}CB_{11}F_{11})^- + 11HF$$

In a typical preparation, 1.0 g of $CsCB_{11}H_{12}$ (3.6 mmol) dissolved in 50 mL of anhydrous HF was treated with 57 mmol of $F_2$ (10% $F_2$ in $N_2$) in a Monel reactor. After workup with water and precipitation with $(NMe_3H)Cl$, 1.1 g of $(NMe_3H)(1\text{-}H\text{-}CB_{11}F_{11})$ was isolated (74% yield based on $CsCB_{11}H_{12}$, see the Supporting Information for details).[11] The compound $(NMe_3H)(1\text{-}H\text{-}CB_{11}F_{11})$ was readily converted to $(NMe_3H)(1\text{-}CH_3\text{-}CB_{11}F_{11})$ anion in 82% isolated yield by treating a 0.6 M aqueous NaOH solution of $(NMe_3H)(1\text{-}H\text{-}CB_{11}F_{11})$ with an excess of dimethyl sulfate.[12] Note that the isolated yield of $(NMe_3H)(1\text{-}CH_3\text{-}CB_{11}F_{11})$ is 61% after a two-step preparation from commercially available $Cs(CB_{11}H_{12})$. The $N(n\text{-}Bu)_4^+$, $CPh_3^+$, and/or $Ag^+$ salts of 1-H-$CB_{11}F_{11}^-$ and 1-$CH_3$-$CB_{11}F_{11}^-$ can be prepared by simple metathesis reactions using the $Cs^+$ or $NMe_3H^+$ salts.

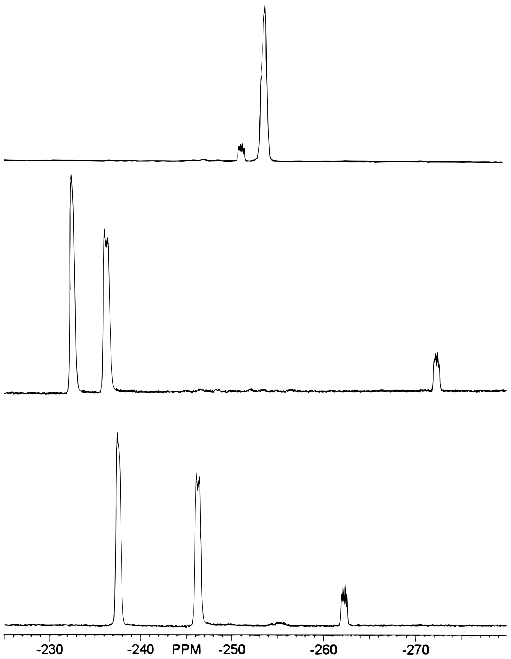

**Figure 1.** Fluorine-19 NMR spectra (282 MHz, $CFCl_3$ external reference ($\delta$ 0) in acetone-$d_6$): top, $Cs^+(1\text{-}H\text{-}CB_{11}F_{11})^-$ in 5 M aqueous DCl (note that the resonances for the upper-belt and lower-belt fluorine atoms are accidentally isochronous); middle, $Na_2(CB_{11}F_{11})$ in 3 M aqueous NaOD after 0.5 h; bottom, $[N(n\text{-}Bu)_4]_2[CuCl(CB_{11}F_{11})]$ in acetone-$d_6$.

NMR (Figure 1) and mass spectra (Supporting Information) demonstrate that 1-H-$CB_{11}F_{11}^-$ is stable indefinitely in aqueous acid (5 M HCl or 5 M $H_2SO_4$) and is moderately stable in aqueous base (no observable decomposition in 3 M KOH after 0.5 h; ∼30% conversion to a mixture of 1-H-$CB_{11}(OH)F_{10}^-$ and 1-H-$CB_{11}(OH)_2F_9^-$ after 24 h). The NMR spectra also indicate that the anion is significantly deprotonated to $CB_{11}F_{11}^{2-}$ in strong aqueous base: there is significant deshielding of F12, the fluorine atom antipodal to the carbon atom, and significant shielding of the upper- and lower-belt fluorine atoms relative to the $^{19}F$ chemical shifts in aqueous acid. The spectra also demonstrate that 1-$CH_3$-$CB_{11}F_{11}^-$ is stable indefinitely in 5 M aqueous acid but is less stable than 1-H-$CB_{11}F_{11}^-$ in 3 M aqueous base, probably because 1-$CH_3$-$CB_{11}F_{11}^-$ cannot be deprotonated to form a 2− anion. The 2− charge of $CB_{11}F_{11}^{2-}$ presumably makes this cluster less prone to nucleophilic attack by $OH^-$ than the 1-H-$CB_{11}F_{11}^-$ and 1-$CH_3$-$CB_{11}F_{11}^-$ clusters. This hypothesis is being explored.

In addition to the stability in aqueous acid and base, 1-H-$CB_{11}F_{11}^-$ and 1-$CH_3$-$CB_{11}F_{11}^-$ were found to be stable when

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[10] F-TEDA = 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate).

[11] For $(NMe_3H)(1\text{-}H\text{-}CB_{11}F_{11})$: negative-ion MS peaks consistent with 11 B atoms (most intense peak at *m/e* 341.2; calcd 341.1); NMR resonances (acetone-$d_6$) at $\delta(^1H)$ 3.93, $\delta(^{11}B)$ −7.8 (1×), −15.9 (5×), −17.4 (5×), $\delta(^{19}F)$ −251.3 (1×), −255.0 (5×), −255.7 (5×).

[12] For $(NMe_3H)(1\text{-}CH_3\text{-}CB_{11}F_{11})$: negative-ion MS peaks consistent with 11 B atoms (most intense peak at *m/e* 355.4; calcd 355.3); NMR resonances (acetone-$d_6$) at $\delta(^1H)$ 1.51, $\delta(^{11}B)$ −8.4 (1×), −16.3 (sh, 5×), and −17.2 (5×), $\delta(^{19}F)$ −250.2 (1×), −255.4 (5×), −256.8 (5×).

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treated with a ≥20-fold excess of triethylaluminum in a mixture of toluene and dichloromethane. There were no changes in $^1$H, $^{11}$B, or $^{19}$F NMR spectra of these solutions, even after several days. It is significant that the C−H proton in 1-H-$CB_{11}F_{11}^-$, although weakly acidic, is not sufficiently acidic to cleave the highly reactive aluminum−carbon bonds in triethylaluminum under these conditions.

We probed the weakly coordinating nature of 1-$CH_3$-$CB_{11}F_{11}^-$ by generating Si(*i*-Pr)$_3$(1-$CH_3$-$CB_{11}F_{11}$) in toluene following the procedure of Reed and co-workers:[13,14]

$$\text{xs SiH}(i\text{-Pr})_3 + [\text{CPh}_3][1\text{-CH}_3\text{-CB}_{11}\text{F}_{11}] \xrightarrow{\text{toluene}} \text{Si}(i\text{-Pr})_3(1\text{-CH}_3\text{-CB}_{11}\text{F}_{11}) + \text{CHPh}_3$$

Within a period of 20 h at 25 °C, the $^{29}$Si resonance for SiH(*i*-Pr)$_3$ at $\delta$ 12.1 decreased in intensity and a new $^{29}$Si resonance appeared at $\delta$ 120.0. Significantly, $^{11}$B and $^{19}$F NMR spectra demonstrated that 1-$CH_3$-$CB_{11}F_{11}^-$ did not decompose in the presence of the highly electrophilic, cationic silicon center; there was no evidence for transfer of F$^\bullet$ or F$^-$ from boron to silicon. The NMR peak for F12 was shifted and broadened, however, indicating that F12, and not one of the lower-belt fluorine atoms, is coordinated to the silicon atom. This is in contrast to the coordination of $CB_{11}H_6Cl_6^-$, $CB_{11}H_6Br_6^-$, and $CB_{11}H_6I_6^-$ to the Si(*i*-Pr)$_3^+$ moiety; in these three cases, a lower-belt halogen atom was found to form the bond to the cationic silicon center.[5]

The $\delta(^{29}\text{Si}) = 120$ value for Si(*i*-Pr)$_3$(1-$CH_3$-$CB_{11}F_{11}$) is considerably more positive than $\delta(^{29}\text{Si}) = 97.9$ for Si(*i*-Pr)$_3$($CB_9H_5Br_5$) in toluene[13] and is even more positive than $\delta(^{29}\text{Si}) = 115$ for Si(*i*-Pr)$_3$($CB_{11}H_6Cl_6$) in the solid state.[5] Since the magnitude of $\delta(^{29}\text{Si})$ has been widely adopted as a measurement of silylium-ion character,[15] 1-$CH_3$-$CB_{11}F_{11}^-$ may be the weakest X$^-$ anion used to date for Si(*i*-Pr)$_3$X derivatives. It remains to be seen whether the solid-state $\delta(^{29}\text{Si})$ value of Si(*i*-Pr)$_3$(1-$CH_3$-$CB_{11}F_{11}$) is more positive than the solid-state value of Si(*i*-Pr)$_3$($CB_{11}H_6Cl_6$). Nevertheless, the prospects for using 1-$CH_3$-$CB_{11}F_{11}^-$ and 1-H-$CB_{11}F_{11}^-$ as robust, weakly coordinating anions in a wide variety of applications appear to be very good.

The facile deprotonation of 1-H-$CB_{11}F_{11}^-$ with strong bases provided the opportunity to begin to examine the properties of the $CB_{11}F_{11}^{2-}$ dianion as a ligand for d-block metal complexes. Treatment of [Cu(mesityl)]$_n$[16] with 1 equiv [N(*n*-Bu)$_4$][1-H-$CB_{11}F_{11}$] and one equiv N(*n*-Bu)$_4$Cl in dichloromethane resulted in protonolysis of the Cu−C(mesityl) bond and formation of [N(*n*-Bu)$_4$]$_2$[CuCl($CB_{11}F_{11}$)].[17] Interestingly, there was no reaction between [Cu(mesityl)]$_n$ and [N(*n*-Bu)$_4$][1-H-$CB_{11}F_{11}$] in the absence of N(*n*-Bu)$_4$Cl, which is consistent with the stability of the 1-H-$CB_{11}F_{11}^-$ anion in the presence of $AlEt_3$. The structure of the [CuCl($CB_{11}F_{11}$)]$^{2-}$ dianion is shown in Figure 2.[18] The Cu$^+$ ion exhibits a nearly linear two-coordinate geometry (the C1−Cu−Cl bond angle is 176.0(2)°). There are no intra- or intermolecular contacts between the Cu$^+$ ion and any of the fluorine atoms of the $CB_{11}F_{11}^{2-}$ ligand. The Cu−C and Cu−Cl bond distances of 1.917(5) and 2.136(1) Å can be compared with the analogous distances of 1.906(2) and 2.113(1) Å in CuCl(C(PPh$_3$)$_2$),[19] the only other example of a two-coordinate copper(I) complex with a C−Cu−Cl framework. Other Cu−C bond distances for two-coordinate copper(I) complexes include 2.027(7) Å in [Cu(C(SiMe$_3$)$_2$)$_2$]$^-$,[20] 1.915(9) Å in [Cu(mes)$_2$]$^-$ (mes = mesityl),[21] and 1.935(8) Å in [Cu(CH$_3$)$_2$]$^-$.[22]

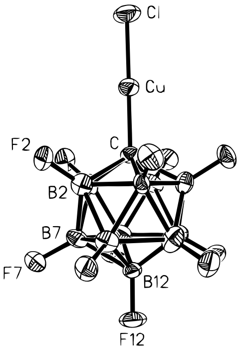

**Figure 2.** Drawing of the [CuCl($CB_{11}F_{11}$)]$^{2-}$ complex in [N(*n*-Bu)$_4$]$_2$[CuCl($CB_{11}F_{11}$)] (50% ellipsoids). Selected bond distances (Å) and angles (deg): Cu−C1, 1.917(5); Cu−Cl, 2.136(1), C1−Cu−Cl, 176.0(2); C1−B, 1.688(8)−1.723(8); B−B, 1.749(9)−1.807(10); B−F, 1.367(7)−1.383(6); closest Cu···F, 3.25 Å.

Although there are many examples of the incorporation of transition metal ions into carborane cages to form *closo*- and *nido*-metallacarboranes,[23] there are few structurally characterized examples[24] of *closo*-carboranes with exo carbon−transition-metal bonds. Furthermore, these few examples are *closo*-dicarboranes, for which the parent dicarborane cluster is a neutral compound. The complex [CuCl($CB_{11}F_{11}$)]$^{2-}$ is the first structurally characterized example of a *closo*-monocarborane with an exo carbon−transition-metal bond. However, the greater significance of the structure of [CuCl($CB_{11}F_{11}$)]$^{2-}$ is that it demonstrates that the coordination chemistry of *closo*-monocarboranes is even richer than originally anticipated.[2,3] Monoanionic derivatives with 12 nonmetal exo substituents such as $CB_{11}H_6X_6^-$, $CB_{11}(CH_3)_{12}^-$, 1-$CH_3$-$CB_{11}Cl_{11}^-$, 1-H-$CB_{11}F_{11}^-$, and 1-$CH_3$-$CB_{11}F_{11}^-$ may be the best weakly coordinating anions for a variety of applications. In addition, carborane dianions with 11 nonmetal substituents, such as $CB_{11}F_{11}^{2-}$, may be valuable as new ligands because they neutralize two equivalents of positive charge on a metal ion but coordinate to the metal ion with the apparent strength of a monoanion.

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**Supporting Information Available:** Synthetic details and selected NMR and mass spectra for new compounds and tables of X-ray parameters and results for [N(*n*-Bu)$_4$]$_2$[CuCl($CB_{11}F_{11}$)] (18 pages, print/PDF)). See any current masthead page for ordering and Web access instructions.

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[18] Crystal data for [N(*n*-Bu)$_4$]$_2$[CuCl($CB_{11}F_{11}$)]: monoclinic, $P2_1/n$, $a = 11.0438(2)$ Å, $b = 31.0643(6)$ Å, $c = 14.1535(3)$ Å, $\beta = 97.478(1)°$, $V = 4814.3(2)$ Å$^3$, $Z = 4$. Data were collected at −108(2) °C on a Siemens SMART System with MoKα radiation to a maximum $2\theta = 56.61°$, giving 11 569 unique reflections; the structure was solved by direct methods (Sheldrick, G. M. SHELXTL, version 5.03, 1994) with full-matrix least-squares refinement on $F^2$, yielding $R_1 = 0.077$ ($I > 2\sigma(I)$), w$R_2 = 0.235$ (all data).

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