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Synthesis and Structure of Ag(1-Me-12-SiPh$_3$-CB$_{11}$F$_{10}$): Selective F12 Substitution in 1-Me-CB$_{11}$F$_{11}$$^-$ and the First Ag(arene)$_4$$^+$ Tetrahedron

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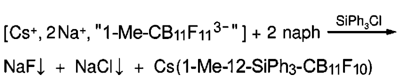
The selective substitution of the antipodal F atom in 1-Me-CB$_{11}$F$_{11}$$^-$ with a SiPh$_3$ moiety led to the isolation and structure determination of the cesium(I) and silver(I) salts of the 1-Me-12-SiPh$_3$-CB$_{11}$F$_{10}$$^-$ anion. The silver salt contains both a nearly trigonal-planar Ag(arene)$_3$$^+$ cation and the first example of a Ag(arene)$_4$$^+$ cation.

In 2004 we reported the first example of a rigorously planar Ag(arene)$_3$$^+$ complex.[1] The structure consisted of layers of $\{\mathrm{Ag(CHPh_3)^+}\}_\infty$ polycations with weakly coordinating[2−5] 1-Me-CB$_{11}$F$_{11}$$^-$ anions filling trigonal prismatic holes of six Ag$^+$ ions from successive $\{\mathrm{Ag(CHPh_3)^+}\}_\infty$ layers, with no Ag···F contacts shorter than 3.3 Å. In order to (i) prepare new superweak anions by selective defluorination of 1-Me-CB$_{11}$F$_{11}$$^-$ (**I**$^-$) and (ii) extend silver(I)−arene chemistry[6] to the as-yet-unknown Ag(arene)$_4$$^+$ cation, we have prepared 1-Me-12-SiPh$_3$-CB$_{11}$F$_{10}$$^-$ (**II**$^-$), one of a new family of 1-R-12-X-CB$_{11}$F$_{10}$$^-$ anions we are studying, and have determined the structures of its cesium(I) and silver(I) salts. The silver(I) salt has a tetrahedral Ag(arene)$_4$$^+$ cation as well as a Ag(arene)$_3$$^+$ cation. Our interest in the 12-SiPh$_3$ anion was not that it might be a superior weakly coordinating anion, because it would not, but that it would be easier to purify, crystallize, and characterize than anions with other 12-X substituents. More relevant anions with 12-H, -I, and -CH$_3$ groups have also been prepared (see Supporting Information) but will be reported later because their purity and yield have not yet been optimized.

Scheme 1. Synthesis of Cs(1-Me-12-SiPh$_3$-CB$_{11}$F$_{11}$) (Cs(**II**)) from Cs(1-Me-CB$_{11}$F$_{11}$) (Cs(**I**); naph$^-$ is the naphthalenide radical anion)[a]



$$\mathrm{Cs(1\text{-}Me\text{-}CB_{11}F_{11})} + 2\,\mathrm{Na^+(naph^-)} \xrightarrow[-55\ ^\circ\mathrm{C}]{\mathrm{DME}}$$

$$[\mathrm{Cs^+}, 2\mathrm{Na^+}, \text{"}\mathrm{1\text{-}Me\text{-}CB_{11}F_{11}{}^{3-}}\text{"}] + 2\ \mathrm{naph} \xrightarrow{\mathrm{SiPh_3Cl}}$$

$$\mathrm{NaF}\downarrow + \mathrm{NaCl}\downarrow + \mathrm{Cs(1\text{-}Me\text{-}12\text{-}SiPh_3\text{-}CB_{11}F_{10})}$$

[a] The putative 2e$^-$ reduced intermediate depicted as “1-Me-CB$_{11}$F$_{11}$$^{3-}$” is almost certainly not the 1-Me-CB$_{11}$F$_{11}$$^{3-}$ trianion (**I**$^{3-}$). The composition and structure of the intermediate is not known at this time.

The anion **II**$^-$ was prepared by treating Cs(**I**) dissolved in DME at −55 °C with 2.2 equiv of sodium naphthalenide. The dark brown solution was treated with SiPh$_3$Cl, and upon workup, colorless crystals of Cs(**II**) were obtained in 74% yield (based on 1-Me-CB$_{11}$F$_{11}$$^-$), as shown in Scheme 1. The ^{19}F NMR spectrum and a negative-ion electrospray mass spectrum of Cs(**II**) are shown in Figure 1. We propose that the *dark red* (see below) intermediate is at the formal oxidation level of the **I**$^{3-}$ ion but is a species in which the B−F bond antipodal to the carborane C atom (i.e., B12−F12) bond has already been cleaved. This proposal is based on the following observations: (i) use of 1.0 equiv of Na$^+$(naph$^-$) led to a dark red solution and the formation of only 0.5 equiv of Cs(**II**); (ii) the intermediate is diamagnetic (see ^{19}F NMR data in the Supporting Information); (iii) treating the intermediate with 2.2 equiv of the “one-electron oxidizing agent” 1,1′,3,3′-tetrakis-(2-methyl-2-hexyl)ferrocenium nitrate[7] led not to the recovery of **I**$^-$ but to the rapid (seconds) formation of 1-Me-12-H-CB$_{11}$F$_{10}$$^-$ (plus a small amount of the 7-H isomer, see below); (iv) the intermediate reacted only slowly (days) with DME at 25 °C to form primarily 1-Me-12-H-CB$_{11}$F$_{10}$$^-$; (v) the cyclic voltammogram (CV) of an equimolar solution of **I**$^-$ and Fe(Cp*)$_2$ in the presence of several equivalents of NaClO$_4$ exhibited a cathodic current for **I**$^-$ that was twice as large as the current for the Fe(Cp*)$_2$$^{+/0}$ couple, indicative of an irreversible “two-electron” reduction ($E_{\mathrm{p,a}} = -2.6$ V vs Fe(Cp*)$_2$$^{+/0}$; see below); and (vi) addition of excess N(*n*-Bu)$_4$ClO$_4$ to the intermediate induced the rapid (seconds) formation of 1-Me-12-H-CB$_{11}$F$_{10}$$^-$.

The high regioselectivity of the reaction sequence in Scheme 1, ca. 88%, is demonstrated by the ^{19}F{^{11}B} NMR

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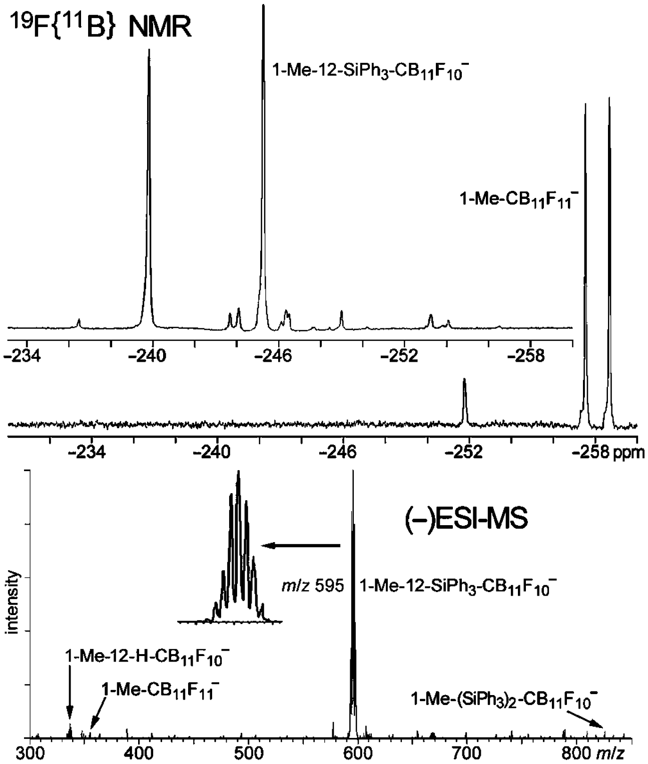

Figure 1. Negative-ion electrospray-ionization mass spectrum of Cs(**II**) (bottom) and the 282.4 MHz $^{19}F\{^{11}B\}$ NMR spectra of Cs(**I**) and Cs(**II**) (top; CD_3CN). The small peaks in the NMR spectrum of Cs(**II**) may be due to a small amount of the byproduct 1-Me-12-H-$CB_{11}F_{10}^-$ and the isomer 1-Me-7-$SiPh_3$-$CB_{11}F_{10}^-$. The compositional purity of the product anion is 96% 1-Me-*x*-$SiPh_3$-$CB_{11}F_{11}$ and 4% 1-Me-12-H-$CB_{11}F_{11}$ and the isomeric purity is 88% for $x = 12$ and 12% for $x = 7$.

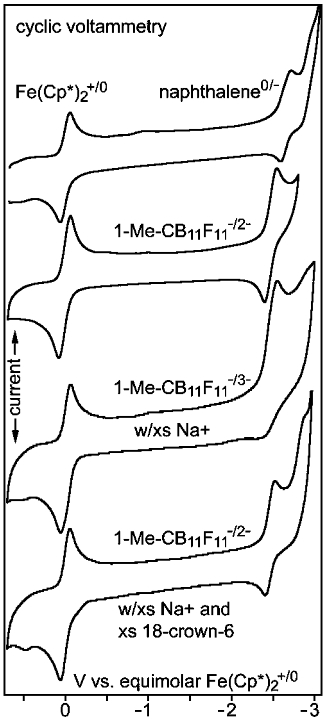

Figure 2. Cyclic voltammograms of naphthalene (top CV) and Cs(**I**) (0.1 M $TBA^+ClO_4^-$ in DME) in the presence of $Fe(Cp^*)_2$.

Table 1. DFT-Optimized Distances (Å) for 1-Me-$CB_{11}F_{11}^{n-}$ ($n = 1-3$)

bond	$n- = 1-$	$n- = 2-$	$n- = 3-$
B12−F12	1.379	1.410	1.438
$B_{\text{lower belt}}-F_{\text{lower belt}}$	1.380	1.409	1.434
$B_{\text{upper belt}}-F_{\text{upper belt}}$	1.374	1.401	1.422
$B12-B_{\text{lower belt}}$	1.812	1.801	1.795
$B_{\text{lower belt}}-B_{\text{lower belt}}$	1.821	1.801	1.791
$B_{\text{lower belt}}-B_{\text{upper belt}}$	1.789	1.783	1.781
$B_{\text{upper belt}}-B_{\text{upper belt}}$	1.796	1.785	1.781
$B_{\text{upper belt}}-C1$	1.735	1.732	1.731

spectrum in Figure 1: the major product, with two resonances, is pseudo-C_{5v}-symmetric **II**$^-$; the minor product is almost certainly the C_s isomer 1-Me-7-$SiPh_3$-$CB_{11}F_{10}^-$. When other electrophiles XY were added instead of $SiPh_3Cl$, other 1-Me-12-X-$CB_{11}F_{11}^-$ anions were formed with high regioselectivity, including X = I (XY = I_2), X = CH_3 (XY = CH_3I), and X = *n*-Dc (XY = *n*-DcBr). The X = H anion was generated by protonation of the two-electron reduced intermediate; a small amount of the 12-H anion was a ubiquitous byproduct in all reactions. Preliminary X-ray structures of (NMe_3H)(1,12-Me_2-$CB_{11}F_{11}$) and Cs(1-Me-12-I-$CB_{11}F_{11}$) are shown in the Supporting Information. Further details about the synthesis and properties of the X = H, I, CH_3, and *n*-Dc anions will be reported in the full paper.

In the absence of Na^+ ions, the 25 °C CV of Cs(**II**) exhibited a *reversible* 1e$^-$ reduction at the same potential as the irreversible 2e$^-$ reduction in the presence of Na^+ (i.e., the cathodic peak potentials were the same), as shown in Figure 2. Furthermore, when excess 18-crown-6 was added to the solution of Cs(**II**) plus excess $NaClO_4$, the *reversible 1e$^-$ reduction* of **I**$^-$ to **I**$^{2-}$ was restored. It appears that an electrophile stronger than Cs^+, such as Na^+, is necessary to promote the 2e$^-$ reduction (i.e., to promote formation of the 2e$^-$ reduced intermediate, presumably by assisting in the cleavage of a cage B−F bond). Note that the putative 12-vertex-*closo* **I**$^{3-}$ cluster would have the same cluster-electron count as the kinetic[8] and the thermodynamic[9] isomers of 12-vertex *nido*-7,9-Me_2-7,9-$C_2B_{10}H_{11}^-$ ($2n + 4$ e$^-$ = 28 e$^-$; $n = 12$), which are formed by 2e$^-$ reduction of *closo*-Me_2-$C_2B_{10}H_{10}$ followed by protonation.[10] The ^{19}F NMR spectrum of the 2e$^-$ reduced intermediate and the X-ray structures of salts of **II**$^-$ (see below) leave no doubt that that intermediate is a 12-vertex-*closo* CB_{11} cluster that has not undergone cage-opening rearrangment.

DFT calculations[11−13] reveal that adding one and two electrons to **I**$^-$ progressively shortens the cluster B−B and B−C bonds and lengthens the exohedral B−F bonds. These results are shown in Table 1. The LUMO, SOMO, and HOMO for **I**$^-$, **I**$^{2-}$, and **I**$^{3-}$, respectively, are very similar in size and shape (see Supporting Information). The DFT calculations also reveal that removing F12 as an F^- ion from **I**$^{3-}$ is less endothermic by 13 or 22 kJ mol^{-1} than removing F7 or F2 as an F^- ion, respectively, and this may explain

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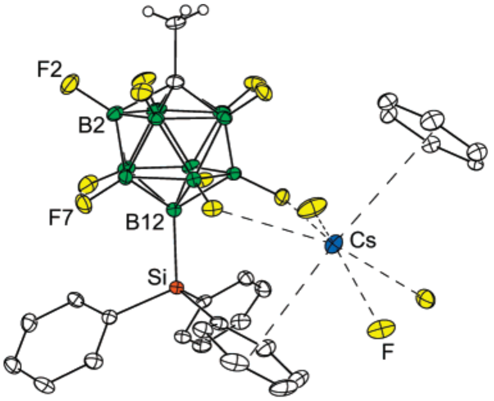

Figure 3. X-ray structure of Cs(**II**) (50% probability ellipsoids; H atoms shown as spheres of arbitrary size for the CH_3 group and omitted from Ph groups for clarity). The range of Cs−C(Ph) distances is 3.600(3)−4.021(3) Å (each one of the coordinated Ph groups is from a different $\mathbf{II}^-$ anion; most of the second $\mathbf{II}^-$ anion has been omitted for clarity).

the observed regioselectivity in the $2e^-$ induced transformation of $\mathbf{I}^-$ into $\mathbf{II}^-$.

The structure of Cs(**II**) is shown in Figure 3.[14] Distances and angles within the carborane cage and the $SiPh_3$ moiety are normal (the B−Si distance is 2.045(3) Å).[1,15] The Cs^+ cation is sandwiched between nearly coplanar Ph groups (interplane angle = 14.4°), one from each of two $\mathbf{II}^-$ anions, and is also coordinated to five F atoms that are contributed by three carborane anions (the range of Cs•••F distances is 2.896(1)−3.237(1) Å).

The silver(I) salt of $\mathbf{II}^-$ was prepared by metathesis of $AgBF_4$ and Cs(**II**).[16] The structure contains two formula units of the salt. The distances and angles within the carborane cages and the $SiPh_3$ moieties are normal (the B−Si distances are 2.021(3) and 2.034(3) Å). The coordination spheres of one of the Ag^+ ions (Ag1) is trigonal planar and will not be discussed further (see Supporting Information for details).

The tetrahedral coordination sphere of the other Ag^+ ion, shown in Figure 4, is the first example of an $Ag(arene)_4^+$ complex of any geometry. There are no contacts between Ag2 and any F atom shorter than 4.7 Å. The Ag^+ ion is coordinated to each of the four phenyl groups via η^1 interactions[6,17−19] with one of the ortho C atoms from each ring, forming what are essentially 30−60−90° AgC_2 right triangles (the four $Ag-C_{ortho}-C_{ipso}$ angles range from 90.8° to 92.2°). The four Ag−C bond distances range from 2.452(2) to 2.511(2) Å. These are compared with other Ag−C(arene) distances in the Supporting Information. The six tetrahedral C−Ag−C angles range from 102.0(1)° to 122.2(1)° (their sum is 655.8(6)°, whereas the ideal sum is 657.0°). The angles between the least-squares planes of the phenyl groups of the two chelating $SiPh_2$ moieties are 96.4° and 96.9°, which requires the two "grab" angles (defined by Kochi and co-workers as the complement of the angle between the arene planes) to be 83.6° and 83.1°, which in turn requires that the shortest distance from Ag2 to each arene plane is to a point outside of the six-membered ring.

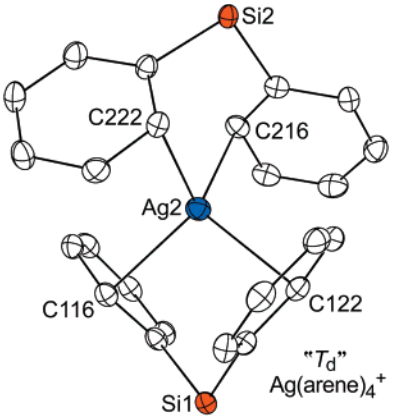

Figure 4. Ag2 coordination sphere in the structure of Ag(**II**)•$0.5C_6H_6$ (50% probability ellipsoids; H atoms omitted for clarity). Selected distances (Å) and angles (deg): Ag2−C116, 2.452(2); Ag2−C122, 2.511(2); Ag2−C216, 2.463(2); Ag2−C222, 2.495(2); Ag2−C116−C111, 91.7(2); Ag2−C122−C121, 90.9(2); Ag2−C216−C211, 91.8(1); Ag2−C222−C221, 92.2(2); C116−Ag2−C122, 102.1(1); C116−Ag2−C216, 122.2(1); C116−Ag2−C222, 110.3(1); C122−Ag2−C216, 114.8(1); C122−Ag2−C222, 104.4(1); C216−Ag2−C222, 102.0(1).

In ongoing work, we are studying the chemical and electrochemical reduction of other $1\text{-R-CB}_{11}F_{11}^-$ anions and of $1\text{-R-12-X-CB}_{11}F_{10}^-$ anions in order to prepare a variety of new anionic fluorocarborane species by one or more selective B−F → B−X transformations.

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Supporting Information Available: Synthetic details, X-ray structural data for Cs(**II**) and Ag(**II**), NMR spectra, and drawings of DFT-predicted MOs and the $1,12\text{-Me}_2\text{-CB}_{11}F_{11}^-$ and $1\text{-Me-12-I-CB}_{11}F_{11}^-$ anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystals of Cs(**II**) were grown by slow diffusion of hexanes into an acetone solution: 0.05 × 0.07 × 0.22 mm^3; monoclinic; $P2_1/n$; a = 9.4773(3) Å, b = 20.3255(7) Å, c = 14.7167(5) Å, β = 92.127(2)°; 2832.9(2) $Å^3$ (Z = 4); ρ_{calcd} = 1.707 Mg m^{-3}; θ_{max} = 33.14°; $-14 < h < 14$, $-30 < k < 30$, $-22 < l < 22$; λ = 0.71073 Å; T = 100(2) K; no. of reflns = 10 763; no. of independent reflns = 7064; restraints/params = 0/388; full-matrix least-squares refinement on F^2; semi-empirical absorption correction from equivalents; μ = 0.143 mm^{-1}; final R indices ($I > 2\sigma(I)$) are R1 = 0.0452 and wR2 = 0.0748; largest diff. peak and hole = 0.502 and −0.319 e $Å^{-3}$.

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