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DISSERTATION

SELECTIVE TWO-ELECTRON REDUCTIVE DEFLUORINATION OF
1-Me-CB₁₁F₁₁⁻ AND RELATED ANIONS:
SYNTHESIS AND CHARACTERIZATION OF SALTS OF 1-Me-12-R-CB₁₁F₁₀⁻
AND RELATED ANIONS

Submitted by

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In partial fulfillment of the requirements
For the Degree of Doctor of Philosophy

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Fort Collins, Colorado

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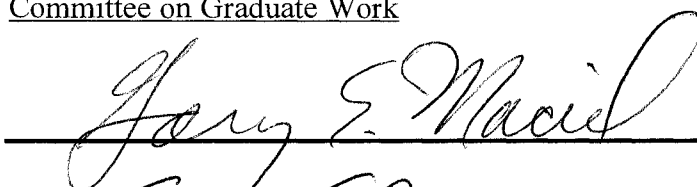
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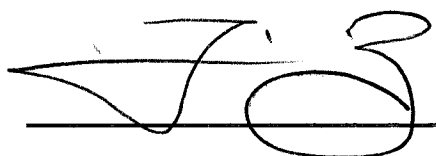
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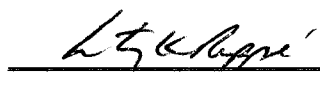
WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY YOSHIHIRO KOBAYASHI ENTITLED *SELECTIVE TWO-ELECTRON REDUCTIVE DEFLUORINATION OF 1-Me-CB₁₁F₁₁⁻ AND RELATED ANIONS: SYNTHESIS AND CHARACTERIZATION OF SALTS OF 1-Me-12-R-CB₁₁F₁₀⁻ AND RELATED ANIONS* BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

SELECTIVE TWO-ELECTRON REDUCTIVE DEFLUORINATION OF 1-Me-CB₁₁F₁₁⁻ AND RELATED ANIONS: SYNTHESIS AND CHARACTERIZATION OF SALTS OF 1-Me-12-R-CB₁₁F₁₀⁻ AND RELATED ANIONS

In this dissertation, a method to selectively defluorinate and functionalize the antipodal B-F bond in 1-R-CB₁₁F₁₁⁻ anion is described. The defluorination reaction mechanism using sodium naphthalenide to form an intermediate anion was investigated by ¹⁹F{¹¹B} NMR, cyclic voltammetry, and computational analysis. By using different molar ratio of sodium naphthalenide, the stoichiometric amount of sodium naphthalenide to reduce 1-Me-CB₁₁F₁₁⁻ was determined to be two. The ¹⁹F{¹¹B} NMR of the intermediate showed that the intermediate is diamagnetic, and the absence of the peak due to the antipodal fluorine atom suggested that the antipodal B-F bond is broken. Cyclic voltammetry of 1-Me-CB₁₁F₁₁⁻ showed a reversible one-electron reduction without the presence of Na⁺. In presence of excess Na⁺, the reduction occurred as an irreversible two-electron process, but at the same potential as the one-electron process. The addition of excess 18-crown-6 restored prevented the two-electron reduction, and restored the reversible one-electron process. This suggested that Na⁺ is probably incorporated in the structure of the intermediate. Based on these results, two structures were proposed, one with B...F...Na⁺ linkage the other with B...Na⁺...F⁻ linkage at the antipodal position. At the NMR time scale, the intermediate did not show electron-exchange between the intermediate and the starting material, 1-Me-CB₁₁F₁₁⁻. This suggested that the structure with B...F...Na⁺ is unlikely. Computational analysis of the

proposed structures predicted that the latter structure is 55 kJ/mol more stable than the former. From these results, the structure of the intermediate was suggested to be $(1\text{-Me-CB}_{11}\text{F}_{11}\cdots\text{Na}^+\cdots\text{F}^-)^{2-}$.

The intermediate was shown to react with various electrophiles, and possible to functionalize the antipodal vertex. For example, when methyl iodide was added to the intermediate solution, the major product was $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$. When SiPh_3Cl was added, the major product was $1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10}^-$. In all cases, one of the isomer, $1\text{-Me-7-X-CB}_{11}\text{F}_{10}^-$ was formed as one of the byproducts, however, the isomeric ratio of the 12-isomer and the 7-isomer was 9:1. Several new compounds were synthesized, and X-ray crystal structures of four new compounds $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$, $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$, and $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ were obtained. The characteristics of each structure are described. One of them, $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$, contained two Ag^+ with different coordination spheres. One of them was the first example of tetrahedral $\text{Ag}(\text{arene})_4^+$.

In order to investigate the effect of substitution on the B12 vertex of $1\text{-Me-CB}_{11}\text{F}_{11}^-$ on the coordinating and ion-pairing abilities of the anions, DFT calculations were performed with $1\text{-Me-CB}_{11}\text{F}_{11}^-$, $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$, and $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$. The calculations predicted that both $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ and $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ had slightly less ion-pairing ability than $1\text{-Me-CB}_{11}\text{F}_{11}^-$. Especially, significant change was observed on the B12-X direction on the ion-pairing ability. The solution conductivities of $\text{N}(n\text{-Bu})_4(1\text{-Me-CB}_{11}\text{F}_{11})$ and $\text{N}(n\text{-Bu})_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ also showed that $\text{N}(n\text{-Bu})_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ is slightly more conductive than $\text{N}(n\text{-Bu})_4(1\text{-Me-CB}_{11}\text{F}_{11})$. The DFT-predicted relative energies of the 12-, 7-, and 2- isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$, $\text{Fe}(\text{Cp})(\text{CO})_2(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, and $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-12-H-CB}_{11}\text{F}_{10})$ were also calculated. For $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$, the 12-isomer was predicted to be the most stable. This suggests that the B12-vertex is the most strongly coordinating. For $\text{Fe}(\text{Cp})(\text{CO})_2(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, substitution of the F12 to CH_3 changes the strongest

coordinating site to the B7-F7 direction, however, the difference between the 12- and 7-isomers was only 1.8 kJ/mol. For $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-12-H-CB}_{11}\text{F}_{10})$, 12-isomer was the most stable, and 7- and 2-isomers were predicted to have much higher energies than the 12-isomer, indicating significant differences in the coordinating ability between the B12-vertex and upper- and lower-belt.

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Chapter 1 Introduction

Introduction to *closo*-monocarborane anions. This dissertation is about the synthesis and properties of derivatives of the 12-vertex *closo*-monocarborane monoanion $\text{CB}_{11}\text{H}_{12}^-$, which was first prepared by Knoth in 1967.¹ The icosahedral structure of this anion, and the numbering of the 12 cage positions, is shown in Figure 1.1. The anion has C_{5v} symmetry, with B12 antipodal to the carbon atom. The five boron atoms bonded to the carbon atom are referred to as upper-belt boron atoms (B_{ub}); the other five boron atoms are referred to as lower-belt boron atoms (B_{lb}).

The use of weakly coordinating anions (WCAs) or "superweak" anions based on the $\text{CB}_{11}\text{H}_{12}^-$ anion was first reported by Reed and coworkers in 1985.² Since that time, many derivatives were prepared by substitution of one or more of the 12 hydrogen atoms with hydrocarbyl groups and/or halogen atoms have been studied as WCAs. Examples include, $\text{CB}_{11}\text{H}_6\text{Br}_6^-$,³ 1-Me- $\text{CB}_{11}\text{Cl}_{11}^-$,⁴ $\text{CB}_{11}\text{Me}_{12}^-$,⁵ and $\text{CB}_{11}(\text{CF}_3)_{12}^-$,⁶ 1-H- $\text{CB}_{11}\text{F}_{11}^-$,⁷ and 1-Me- $\text{CB}_{11}\text{F}_{11}^-$.⁷ A complete list of derivatives of the $\text{CB}_{11}\text{H}_{12}^-$ anion is available in the review by Michl and coworkers.⁸ A selection of these derivatives that are relevant to this dissertation are listed in Table 1.1 (all of them except for 1-H- $\text{CB}_{11}\text{OH}_{11}^-$ have been shown to be useful WCAs).

The applications for which these derivatives have been used include anions for (i) room temperature ionic liquids,⁹ (ii) metallocene polymerization catalysts,¹⁰ (iii) electrolytes for lithium batteries,¹¹ (iv) photoacid generators,¹² and (v) the isolation of reactive cations.¹³⁻¹⁵ Functionalization of the C–H vertex in $\text{CB}_{11}\text{H}_{12-n}\text{X}_n^-$ has been done rather extensively, especially for hydrocarbyl groups. The hydrogen atom in the C–H bond is weakly acidic, and the alkylation of the C–H vertex can simply be done by lithiation with alkyllithium followed by treatment with alkylhalides.^{7,16,17} Compared with the acidic C–H hydrogen atom, the B–H hydrogen atoms are hydridic, therefore B–H vertex can undergo electrophile-induced nucleophilic substitutions.^{6,7,18,19}

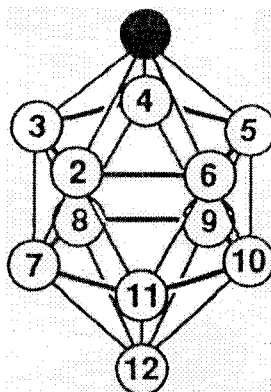


Figure 1.1. Drawing of the CB_{11} -anion showing the numbering order. The black circle is a carbon atom, C1, and white circles are boron atoms. The upper-belt boron and fluorine atoms are B2–B6 and F2–F6, the lower-belt boron and fluorine atoms are B7–B11 and F7–F11.

Table 1.1. Selected derivatives of $\text{CB}_{11}\text{H}_{12}^-$ ^a

anion	synthesis ref.	WCA ^b ref
$\text{CB}_{11}\text{H}_6\text{Br}_6^-$	3	20
$12\text{-CB}_{11}\text{H}_{11}\text{Br}^-$	17	
$\text{CB}_{11}\text{Br}_{12}^-$	4	4
$1\text{-Me-CB}_{11}\text{X}_{11}^-$	$\text{X} = \text{Cl},^{18} \text{Br},^4 \text{I},^4$	4
$\text{CB}_{11}\text{H}_6\text{Cl}_6^-$	17	21
$\text{CB}_{11}\text{H}_6\text{I}_6^-$	22	18
$1\text{-H-CB}_{11}\text{I}_{11}^-$	4	
$\text{CB}_{11}\text{Me}_{12}^-$	5	5
$\text{CB}_{11}(\text{CF}_3)_{12}^-$	23	23
$1\text{-H-CB}_{11}\text{F}_{11}^-$	7	7
$1\text{-Me-CB}_{11}\text{F}_{11}^-$	7	7
$1\text{-H-CB}_{11}(\text{OH})_{11}^-$	24	
$\text{HCB}_{11}(\text{OH})_5\text{Br}_6^-$	25	

^a A complete list of the derivatives of $\text{CB}_{11}\text{H}_{12}^-$ anions is available in a review.⁸

^b Weakly coordinating anion

In order to synthesize more weakly coordinating anions, fluorination of B-H vertices of CB₁₁H₁₂⁻ was achieved in the Strauss Research Group at Colorado State University. Fluorination of CB₁₁H₁₂⁻ with F₂ in liquid anhydrous HF produced the per-B-fluorinated anion 1-H-CB₁₁F₁₁⁻.²⁶ The perfluorinated anion CB₁₁F₁₂⁻ was not observed. Moreover, 1-H-CB₁₁H_{11-n}F_n⁻ intermediates were not observed. However, intermediates of this type were observed when the fluorinating agent was HF in liquid anhydrous HF. Treatment of CB₁₁H₁₂⁻ with liquid HF at 23 °C produced 12-CB₁₁H₁₁F⁻ selectively in high yield (99+% regioselectivity); at 140 °C, 7,12-CB₁₁H₁₀F₂⁻ was the principle product (96% regioselectivity); at 180 °C, 7,9,12-CB₁₁H₉F₃⁻ was the principle product (95+% regioselectivity).²⁷ At even higher temperatures, the principle product was 7,8,9,10,11,12-CB₁₁H₆F₆⁻.²⁷ These results show that the antipodal B12-H12 bond is fluorinated first, followed by fluorination of the five lower-belt B-H bonds. The five upper-belt B-H bonds undergo electrophilic fluorination last.

One of the derivatives of 1-H-CB₁₁F₁₁⁻, 1-Me-CB₁₁F₁₁⁻, has shown to have a great potential as an electrolyte for lithium-ion batteries.²⁸ The conductivities of Li⁺ salts of some of the WCAs including 1-Me-CB₁₁F₁₁⁻, are listed in Table 1.2. Compared with PF₆⁻, which is the electrolyte currently used for some of the commercially available lithium-ion batteries, the dc conductivity of Li(1-Me-CB₁₁F₁₁) was more than two times higher. In addition, it has been previously shown that 1-R-CB₁₁F₁₁⁻ is useful for the isolation of reactive cations. One of the examples for this application is isolation of the (*i*-Pr)₃Si⁺ cation. The X-ray single crystal structure of [(*i*-Pr)₃Si][1-Et-CB₁₁F₁₁] showed that the F12 atom coordinates to the (*i*-Pr)₃Si⁺ cation.²⁹ This structure gave us an idea of synthesizing wider variety of weakly coordinating anions by substituting the B12 vertex with less or non-coordinating substituents.

Selective functionalization of CB₁₁-anion. Selective functionalization of B12 vertex for 12-CB₁₁H₁₂I⁻ has been reported by Michl and coworkers.³⁰ In their method, 12-CB₁₁H₁₂I⁻ was synthesized from CB₁₁H₁₂⁻ and I₂ in AcOH via nucleophilic

substitution, then B–I vertex is alkylated by Kumada coupling using low-valent palladium catalyst such as $\text{PdCl}_2(\text{PPh}_3)_2$. From this method, numbers of 1-R-12-R'- $\text{CB}_{11}\text{H}_{11-n}\text{X}_n^-$ derivatives have been synthesized by further functionalizing the remaining B–H vertices.⁸ However, this method would not work to produce 1-R-12-X-decafluoro-*closo*-carborane anion since the substituent on the B12 vertex may not withstand the reaction condition of the fluorination. The other approach is to selectively defluorinate and alkylate the B12 vertex of the 1-R- $\text{CB}_{11}\text{F}_{11}^-$. Based on DFT calculations, the bond dissociation energies of the B–H and the B–F at the B2 vertex in carborane anions are 103 and 155 kcal/mol, respectively, and for B7 and B12 vertices, the values are smaller, but within 2 kcal/mol.³¹ This result indicates that the B–F bond is strong, and harsh reaction conditions may be required for defluorination. In fact, The 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ anion was shown to be stable indefinitely in 5 M HCl or 5 M H_2SO_4 ⁷ where as $\text{CB}_{11}\text{H}_{12}^-$ undergoes electrophile-induced nucleophilic substitution at the B12 vertex to form a B12–OH bond.³² However, in 3 M KOH, the anion underwent defluorination to form 1-Me- $\text{CB}_{11}(\text{OH})\text{F}_{10}^-$ and 1-Me- $\text{CB}_{11}(\text{OH})_2\text{F}_9^-$ after 24 hours.⁷ In the Strauss group, former postdoctoral fellow Dr. Sergei Ivanov explored the debromination reaction of $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ with excess sodium metal in THF at room temperature. The product mixture contained $\text{CB}_{11}\text{H}_7\text{Br}_5^-$, $\text{CB}_{11}\text{H}_8\text{Br}_4^-$, $\text{CB}_{11}\text{H}_9\text{Br}_3^-$, and $\text{CB}_{11}\text{H}_{10}\text{Br}_2^-$ and did not show selective defluorination on the B12 vertex.³³ On the other hand, when Ivanov performed the defluorination reaction of 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ with excess sodium metal in THF at room temperature for 25 hours, the product mixture contained 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ with 41% conversion. This reaction gave us an insight for B12 functionalization but was not investigated further. Based on this example, we can explore different reducing agents to selectively defluorinate and further functionalize the B12 vertex. The goal for this work was to achieve selective functionalization of the B12 vertex of 1-R- $\text{CB}_{11}\text{F}_{11}^-$ with various substituents with a good conversion and to investigate the effect of the substitution on the properties of anions.

Table 1.2. Conductivities of lithium salt of selected WCAs.

anion	σ mS/cm
CF_3SO_3^-	0.004
PF_6^-	0.073
$\text{CB}_{11}\text{H}_{12}^-$	0.059
$\text{Me}_3\text{NB}_{12}\text{F}_{11}^-$	0.068
1-Me-CB₁₁F₁₁⁻	0.190

10 mM solution in dimethoxyethane at 25 °C

Coordinating ability vs. ion-pairing ability of anions. The choice of a particular "superweak" (i.e., weakly-coordinating) anion for a given chemical task will depend on the relative importance of different attributes of the anions under consideration. Some obvious practical attributes are cost, availability, absolute and batch-to-batch purity, toxicity, and cost of disposal. Other relevant attributes include thermal, chemical, photochemical, and/or electrochemical stability. Additional issues include whether or not salts of the anion tend to be soluble in low-dielectric and/or weakly coordinating solvents and whether or not salts of the anion tend to form crystals suitable for single-crystal X-ray crystallography. Finally, the most important attributes are related to how well the anion actually performs. One might want to know, for example, which anion to use to maximize the activity of a cationic metallocene olefin-polymerization catalyst under a given set of conditions³⁴ or which anion to use for a secondary lithium-ion battery to maximize the conductivity of a lithium salt in a given solvent.^{35,36} In principle, one would like to understand how to control each attribute at the molecular level so that one could design new superweak anions that, first and foremost, give adequate performance and, secondarily, are cost-effective, non-toxic, stable over time, etc. Such understanding might lead to the synthesis of superior superweak anions.

One of the goals of the research described in this dissertation was to further develop an understanding of how to alter the ways in which a particular superweak anion interacts with cations in condensed phases through judicious substitution of one or more moieties on the anion (the more general goal, already discussed, was to discover ways to selectively substitute one or more of the fluorine atoms in the carborane superweak anion 1-Me-CB₁₁F₁₁⁻ with other moieties such as H, Me, I, OH, etc.). Some of the new anions that were prepared in the course of this work are shown in Figure 1.2. The successful synthesis of 1-Me-12-H-CB₁₁F₁₀⁻ and 1,12-Me₂-CB₁₁F₁₀⁻, in particular, allowed two related but different aspects of cation-anion interactions to be addressed: (i) the coordina-

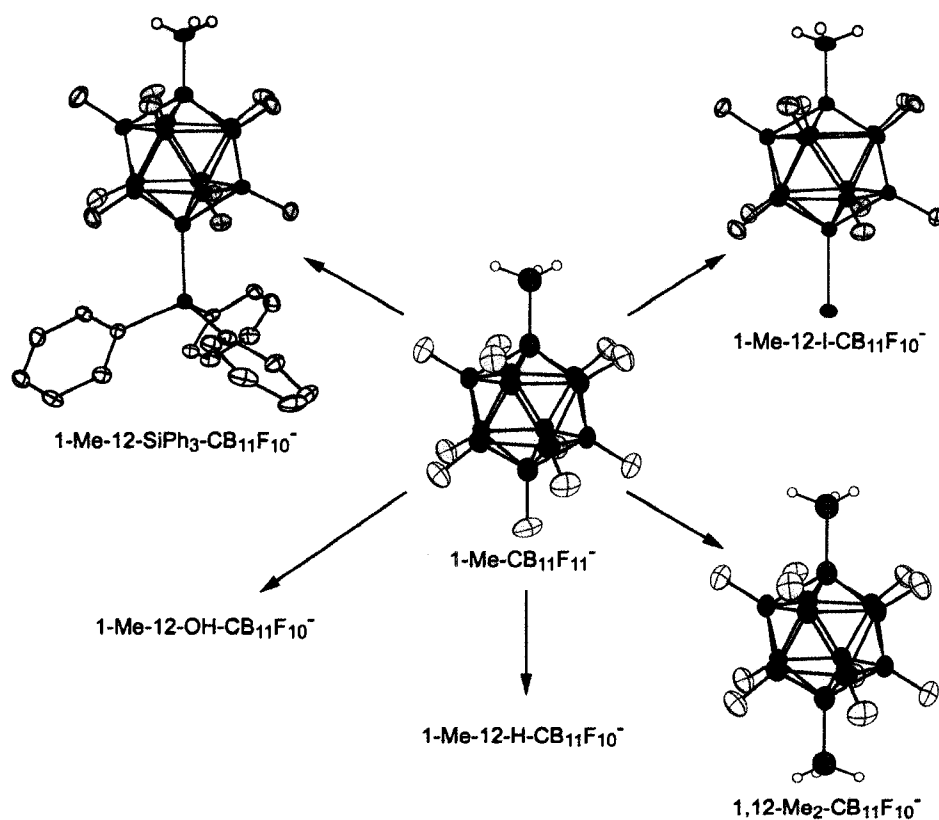
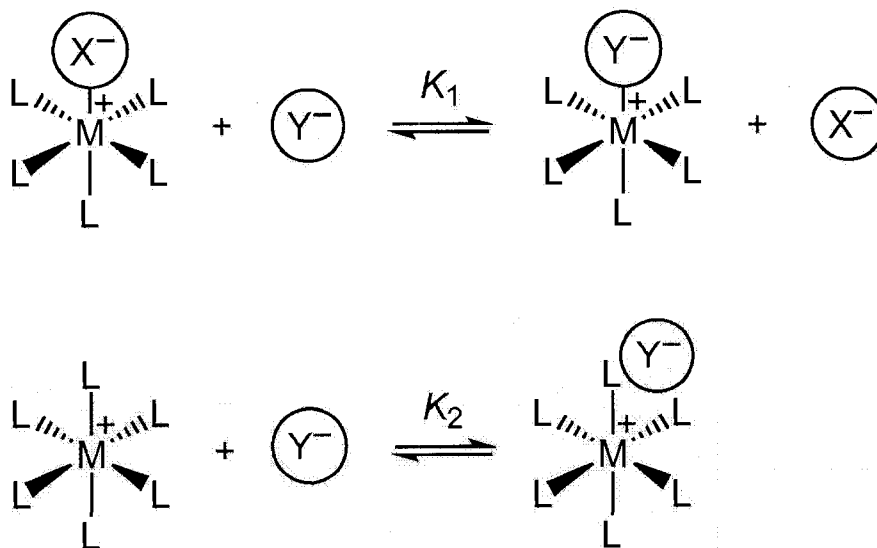


Figure 1.2. Some of the transformations accomplished in the research reported in this dissertation. The synthesis of these and other new carborane anions will be discussed in Chapter 4. The X-ray structures of salts of the anions 1,12-Me₂-CB₁₁F₁₀⁻, 1-Me-12-I-CB₁₁F₁₀⁻, and 1-Me-12-SiPh₃-CB₁₁F₁₀⁻ will be discussed in Chapter 5. (Color coding: yellow, F; green, B; brown, C; purple, I; orange, Si)

ting ability of an anion with respect to a reference cationic Lewis acid in a given solvent; and (ii) the ion-pairing ability of an anion with respect to a reference counteranion in a given solvent.

Consider the equilibria shown in Scheme 1.1. The K_1 equilibrium is the *substitution* of one anionic ligand, X^- , by another, Y^- . The K_1 value is *defined* as the coordinating ability of Y^- relative to X^- *for a given metal complex in a given solvent*. Note that the coordinating ability of an anion is essentially the same as the anion's Lewis basicity towards a given Lewis acid in a given solvent. Note also that the ratio $K_1(Y_1^-)/K_1(Y_2^-)$ can be less than 1 for a L_nM^+ cation in a particular solvent but greater than 1 for a different L_nM^+ cation or in a different solvent (Y_1^- and Y_2^- are two different anions; such reversals are common and well-understood phenomena in Lewis acid-base chemistry³⁷). The important point is that the coordinating ability of an anion is a relative quantity and must always be defined with respect to (i) a specific reference anion, (ii) a specific cation, and (iii) a specific solvent. Furthermore, the K_1 equilibrium shown in Scheme 1 assumes that Y^- is a *free* ion. That is, it ignores the presence of the original counterion of Y^- that was added to the solution, which may interact more or less strongly with Y^- than with X^- . This is particularly problematic in low-donor-number, low-dielectric-constant solvents typically used to study superweak anions. The best that can be done is to use as an *innocent* counteranion as possible, and in most cases that means using the $N(n\text{-Bu})_4^+$ cation.

The K_2 equilibrium is the association of the free ions ML_n^+ and Y^- to form the *outer-sphere ion pair* $\{ML_n^+Y^-\}$, also known as a *contact ion pair*³⁸ or an *intimate ion pair*³⁹ (note that one or more of the ligands L can be solvent molecules; in addition, the cation can be a nonmetal species such as NR_4^+). An anion's K_2 value is *defined* as its ion-pairing ability with respect to a given cation in a given solvent. Individual K_2 values can, in principle, be measured directly, so the ion-pairing ability of an anion can be an absolute quantity, unlike coordinating ability. For example, some K_2 values have been



Scheme 1.1. The displacement of a coordinated anion by another anion. (the K_1 equilibrium) and association of free ions to form contact ion pair (the K_2 equilibrium). The abbreviations used are: M^+ , a metal, metalloid, or nonmetal cation; X^- and Y^- , two anions; L , a generic ligand or substituent attached to M^+ .

determined by analyzing the kinetics of anation reactions of metal complexes in aqueous solution.^{40,41} In general, however, K_2 values are much more difficult to measure than relative K_1 values. In many cases one can only estimate relative K_2 values by measuring the relative conductivities of solutions of salts of the anions. In these cases it is critical that the size and shape of the anions being compared are similar, because conductivities are governed by ion mobilities and solution viscosity as well as by the K_2 equilibrium.

It is instructive to use solid-state structures (or fragments of solid-state structures) as models for species in solution involved in the K_1 and K_2 equilibria. Some examples are shown in Figure 1.3. The molecules $\text{Si}(\text{i-Pr})_3(1\text{-Et-CB}_{11}\text{F}_{11})$ ⁴² and $\text{Li}(\text{DME})(\text{borate})$ ⁴³ are models for anions coordinated to cations (DME = 1,2-dimethoxyethane; borate⁻ = $\text{B}(\text{OC}(\text{2-O-C}_6\text{H}_4)(\text{CF}_3)_2)_2^-$). The $[\text{Ni}(\text{H}_2\text{O})_6][\text{B}_{12}\text{F}_{12}]$ formula unit⁴⁴ is a model for an outer-sphere ion pair in water (in this case the ligands are solvent molecules). Finally, $\text{Si}(\text{i-Pr})_3(\text{CH}_3\text{CN})^+$ and $\text{Li}(\text{DME})_3^+$, taken from the structures of $\text{Si}(\text{i-Pr})_3(\text{CH}_3\text{CN})(\text{CB}_9\text{H}_5\text{Br}_5)$ ⁴⁵ and $\text{Li}(\text{DME})_3(1,1,4,4\text{-tetraphenyl-1,3-butadienide})$,⁴⁶ respectively, are models for "free" (i.e., solvated) cations in acetonitrile and DME, respectively.

Most chemists would probably assume that the equilibrium constant (equilibrium quotient) ratios $K_1(\text{Y}_1^-)/K_1(\text{Y}_2^-)$ and $K_2(\text{Y}_1^-)/K_2(\text{Y}_2^-)$ would both be greater than 1.0, both be less than 1.0, or both be approximately equal to 1.0. In other words, most chemists probably assume that if an anion is more weakly coordinating than another anion, it would also be more weakly ion pairing. The two ratios are both related to how strongly anions interact with cations, *but are the coordinating ability and ion-pairing ability of anions governed by precisely the same attributes of the anions or by different attributes?* There are only two studies in which this fundamental question has been addressed using anions of *nearly identical* size and shape. In the first study, the anions compared were tetrakis(polyfluoroalkoxy)aluminates, $\text{Al}(\text{OR}_f)_4^-$.⁴⁷ The lithium salts of these anions are soluble in aliphatic and aromatic hydrocarbon solvents but display strong Lewis acidity.⁴⁷

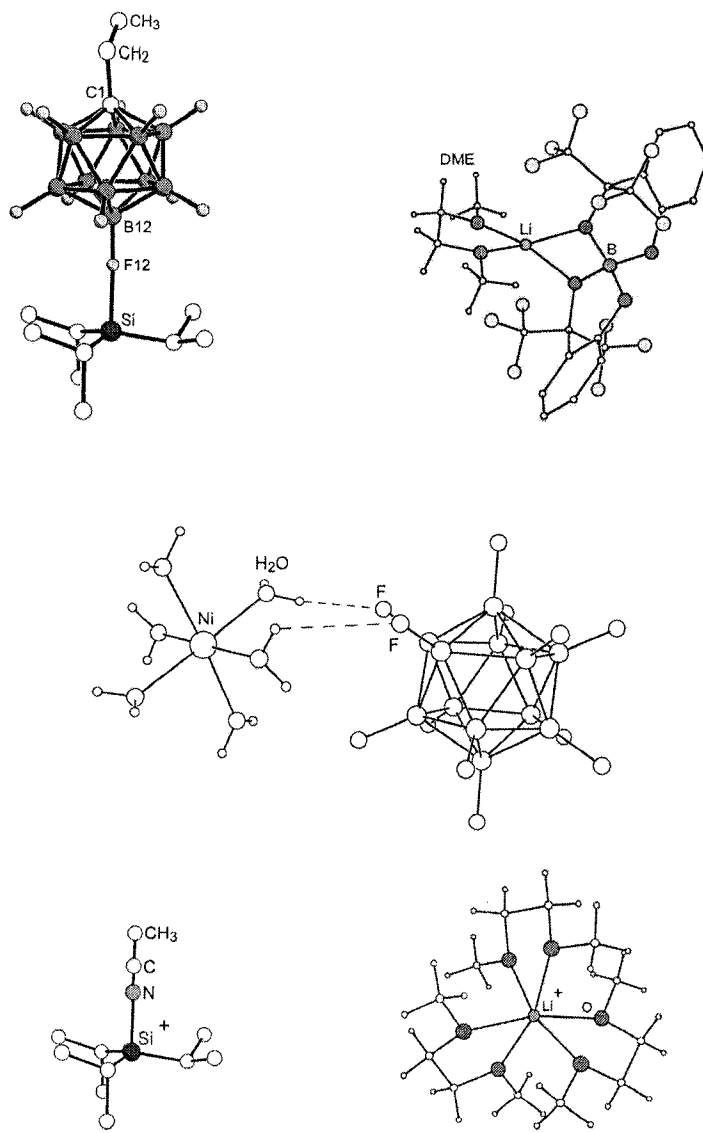


Figure 1.3. Portions of the X-ray structures of $\text{Si}(\text{i-Pr})_3(1\text{-Et-CB}_{11}\text{F}_{11})^{42}$ (top left), $\text{Li}(\text{DME})(\text{Li}(\text{borate})_2)^{43}$ (top right; $\text{DME} = 1,2\text{-C}_2\text{H}_4(\text{OMe})_2$, $\text{borate}^- = \text{B}(\text{OC}(2\text{-O-C}_6\text{H}_4)(\text{CF}_3)_2)_2^-$), and $\text{Ni}(\text{H}_2\text{O})_6(\text{B}_{12}\text{F}_{12})^{44}$ (middle; the separation of the ions is to scale), and the $\text{Si}(\text{i-Pr})_3(\text{NCCH}_3)^+$ cation (bottom left) and $\text{Li}(\text{DME})_3^+$ cation (bottom right) in the X-ray structures of $\text{Si}(\text{i-Pr})_3(\text{NCCH}_3)(\text{CB}_9\text{H}_5\text{Br}_5)^{45}$ and $\text{Li}(\text{DME})_3(1,1,4,4\text{-tetraphenyl-1,3-butadienide})^{46}$ respectively.

One of the lithium salts, with $\text{OR}_f = \text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2$, is an active Lewis-acid catalyst for 1,4-conjugate addition reactions in toluene solution,⁴⁸ and many of the $\text{LiAl}(\text{OR}_f)_4$ salts have sufficiently high conductivities in solvents such as DME and propylene carbonate that they have been considered as electrolytes to replace LiPF_6 in secondary lithium-ion batteries.⁴⁹ X-ray crystal structures of two $\text{LiAl}(\text{OR}_f)_4$ salts with $\text{OR}_f = \text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2$ ($\text{LiAl}(\text{HFPP})_4$)⁴⁸ and $\text{OC}(\text{C}_6\text{H}_{11})(\text{CF}_3)_2$ ($\text{LiAl}(\text{HFCP})_4$)⁵⁰ are shown in Figure 1.4. Not only are the alkoxy groups similar in size and shape, the Li^+ ions have virtually the same environment; both compounds are examples of *penetrated ion pairs*. In both cases, the Li^+ ions have trigonal prismatic LiO_2F_4 coordination spheres with similar Li–O and Li–F bond distances, as shown in Table 1.3.^{47,48,50}

The drawings in Figure 1.4 and the data in Table 1.3 demonstrate that the two $\text{Al}(\text{OR}_f)_4^-$ anions have nearly identical shapes and very similar sizes. Based on the crystal structures, the formula unit volume of $\text{LiAl}(\text{HFCP})_4$ is only 7.2% larger than that of $\text{LiAl}(\text{HFPP})_4$. The $\text{Al}(\text{HFCP})_4^-$ anion coordinates to Li^+ 50 times stronger than the $\text{Al}(\text{HFPP})_4^-$ anion in dichloromethane at 24 °C (the other cation used was $\text{N}(n\text{-Bu})_4^+$; this is an example of a K_1 equilibrium).⁴⁷ This is a sensible result, because the alkoxide $\text{OC}(\text{C}_6\text{H}_{11})(\text{CF}_3)_2^-$ is 32 times more basic towards $\text{H}^+(\text{aq})$ than is the alkoxide $\text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2^-$.⁴⁷ However, in DME solution, it is the $\text{LiAl}(\text{HFCP})_4$ salt, with the *more* basic anion, that has the *higher* conductivity. To reiterate, the Li^+ salt of the more weakly coordinating anion has a lower conductivity than the Li^+ salt of the more strongly coordinating anion, at least in a low dielectric solvent ($\epsilon(\text{DME}, 25\text{ °C}) = 7.2^{51}$). In a higher-dielectric solvent such as acetonitrile ($\epsilon(\text{CH}_3\text{CN}, 25\text{ °C}) = 37.5^{51}$), the conductivities of the two salts are indistinguishable.

In the second study, published in 2003 in *J. Electrochem. Soc.*,⁴³ the eight anions compared were bis(polyfluorodiolato)borates, including $\text{B}(\text{2-O-C}_6\text{H}_4(\text{CO}(\text{CF}_3)_2))_2^-$ and homologs with one, two, or three F atoms on each of the aryl groups). Two of the anions are shown in Figure 1.5. The substitution of aryl H atoms with F atoms was done to

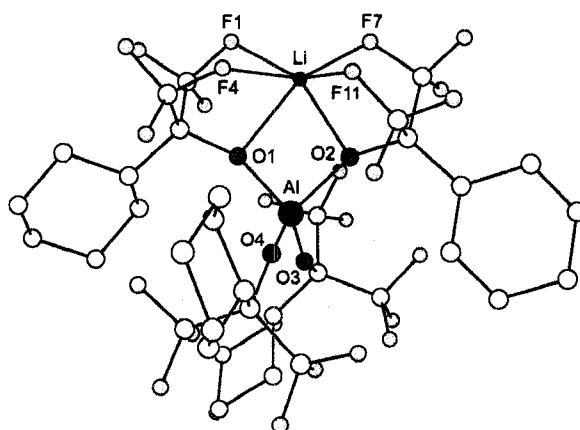
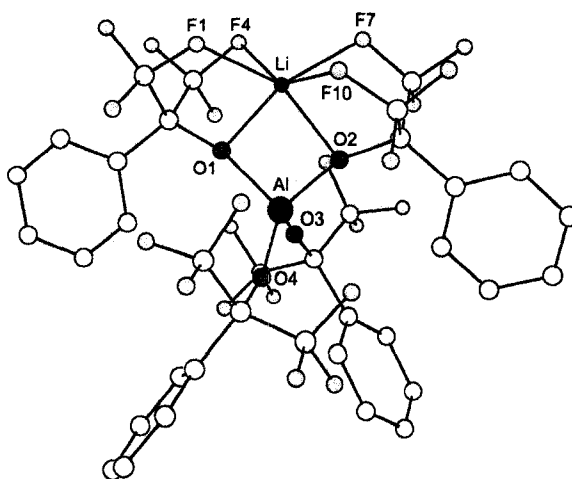


Figure 1.4. Drawings of the structures of $\text{LiAl}(\text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2)_4$ (top)⁴⁸ and $\text{LiAl}(\text{OC}(\text{C}_6\text{H}_{11})(\text{CF}_3)_2)_4$ (bottom).⁵⁰

Table 1.3. Selected structural parameters, relative K_1 values, and solution conductivities for $\text{LiAl}(\text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2)_4$ and $\text{LiAl}(\text{OC}(\text{C}_6\text{H}_{11})(\text{CF}_3)_2)_4$.

	$\text{Al}(\text{OC}(\text{C}_6\text{H}_5)(\text{CF}_3)_2)_4^-$	$\text{Al}(\text{OC}(\text{C}_6\text{H}_{11})(\text{CF}_3)_2)_4^-$
anion abbreviation	$\text{Al}(\text{HFPP})_4^-$	$\text{Al}(\text{HFCP})_4^-$
Li^+ salt formula unit volume, $\text{\AA}^3$	977.1(2)	1047.6(1)
Li–O distances, $\text{\AA}$	1.966(8), 1.978(8)	1.937(5), 1.950(5)
Li–F distances, $\text{\AA}$	1.98(1), 2.08(1), 2.10(1), 2.35(1)	1.889(5), 2.090(5), 2.206(8), 2.928(8)
$K_1/K_1(\text{Al}(\text{HFPP})_4^-)$	1	50
$\text{p}K_a$ of alcohol (aq. soln.)	8.8	10.3 (32 times less acidic)
conductivity (0.01 M, DME), mS cm^{-1}	0.250(2)	0.283(2)
conductivity (0.01 M, CH_3CN), mS cm^{-1}	0.883(2)	0.883(2)

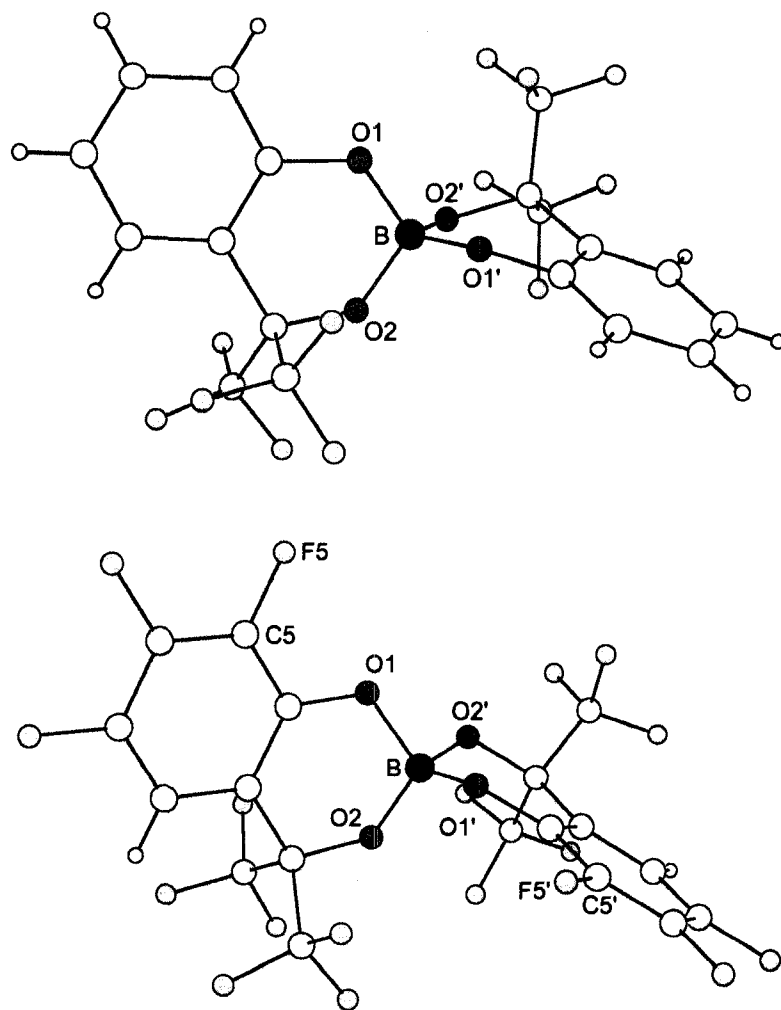


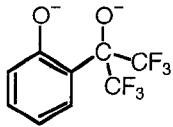
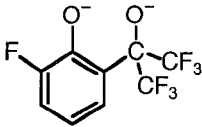
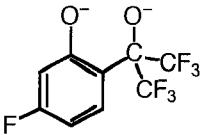
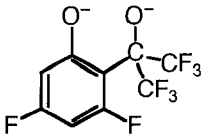
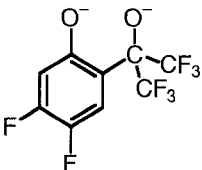
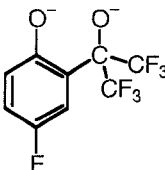
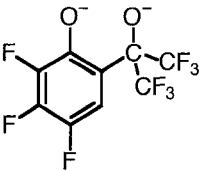
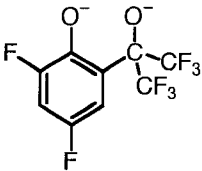
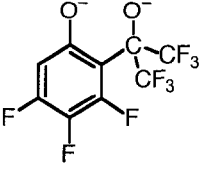
Figure 1.5. Structures of the $\text{B(2-O-C}_6\text{H}_4(\text{CO}(\text{CF}_3)_2))_2^-$ (top) and $\text{B(2-O-3,4,5-F}_3\text{-C}_6\text{H}_4(\text{CO}(\text{CF}_3)_2))_2^-$ (bottom) anions.⁵⁰

change the electronic structure of the anions while keeping their geometric structure (i.e., their shape and size) as constant as possible. In every case (eight examples), adding an F atom to the 4, 5, or 6 position on the aryl group *increased* the conductivity of solutions of the Li^+ salt, but in every case (three examples), adding an F atom to the 3 position of the aryl group *decreased* the conductivity, as shown in Table 1.4 and Figure 1.6. Therefore, changing a C–H bond into a C–F bond in a weakly coordinating anion can result in a more strongly ion pairing anion if the F atom is added in the "wrong" place. Although the coordinating abilities of the eight borate anions were not directly measured, it is likely that the anions with 3-F atoms are more weakly coordinating, not more strongly coordinating, despite the fact that they are more strongly ion-pairing. This is probably true for two reasons. First, the steric hindrance of the 3-F atoms might prevent a metal ion from closely approaching the phenoxide O atom. Second, the gas phase basicity of the 2-fluorophenoxide ion is lower than the gas-phase basicity of the phenoxide, the 3-fluorophenoxide, or the 4-fluorophenoxide ions.⁵² The authors of the *J. Electrochem Soc.* paper concluded "To our knowledge, this is the first example showing that fluorination of an electrolyte can, in some cases, result in a decrease in conductivity. Conductivity is influenced by the positions of the fluorine atoms as well as by the number of fluorine atoms."⁴³

Linkage isomers. The final part of this Introduction is related to an important aspect of the coordination chemistry of weakly coordinating anions. For metal complexes $\text{L}_n\text{M}(\text{solv})^+$ that have only a single site for anion coordination (i.e., the site of binding of the solvent molecule), anions such as the carborane anions in Figure 1.2 can coordinate using an upper-belt F atom, a lower-belt F atom, or the substituent on B12 (F, I, H, CH_3 , or SiPh_3), which leads to the possibility of linkage isomers, in solution if not in the solid state.

A related example for which linkage isomers were actually detected is a complex of $\text{CB}_{11}\text{H}_{12}^-$. The compound that was studied in detail was $\text{CpFe}(\text{CO})_2(\text{CB}_9\text{H}_{10})$,^{53,54}

Table 1.4. Conductivities of $\text{LiB}(\text{O} \text{---} \text{O})_2$ salts (0.5 M in DME)^a

$\text{O} \text{---} \text{O}^{2-}$ formula abbreviation structure	conductivity, 0.5 M DME, mS cm^{-1}	$\text{O} \text{---} \text{O}^{2-}$ formula abbreviation structure	conductivity, 0.5 M DME, mS cm^{-1}
$2\text{-O-C}_6\text{H}_4(\text{CO}(\text{CF}_3)_2)^{2-}$ F_0^{2-} 	5.88	$2\text{-O-3-F-C}_6\text{H}_3(\text{CO}(\text{CF}_3)_2)^{2-}$ 3-F_1^{2-} 	5.39
$2\text{-O-4-F-C}_6\text{H}_3(\text{CO}(\text{CF}_3)_2)^{2-}$ 4-F_1^{2-} 	6.89	$2\text{-O-4,6-F}_2\text{-C}_6\text{H}_2(\text{CO}(\text{CF}_3)_2)^{2-}$ $4,6\text{-F}_2^{2-}$ 	7.55
$2\text{-O-4,5-F}_2\text{-C}_6\text{H}_2(\text{CO}(\text{CF}_3)_2)^{2-}$ $4,5\text{-F}_2^{2-}$ 	7.87	$2\text{-O-5-F-C}_6\text{H}_3(\text{CO}(\text{CF}_3)_2)^{2-}$ 5-F_1^{2-} 	6.57
$2\text{-O-3,4,5-F}_3\text{-C}_6\text{H}(\text{CO}(\text{CF}_3)_2)^{2-}$ $3,4,5\text{-F}_3^{2-}$ 	7.79	$2\text{-O-3,5-F}_2\text{-C}_6\text{H}_2(\text{CO}(\text{CF}_3)_2)^{2-}$ $3,5\text{-F}_2^{2-}$ 	6.39
$2\text{-O-4,5,6-F}_3\text{-C}_6\text{H}(\text{CO}(\text{CF}_3)_2)^{2-}$ $4,5,6\text{-F}_3^{2-}$ 	8.39		

^a The symbol $\text{O} \text{---} \text{O}^{2-}$ represents the diolate(2-) anions shown in the table;
DME = 1,2-dimethoxyethane.

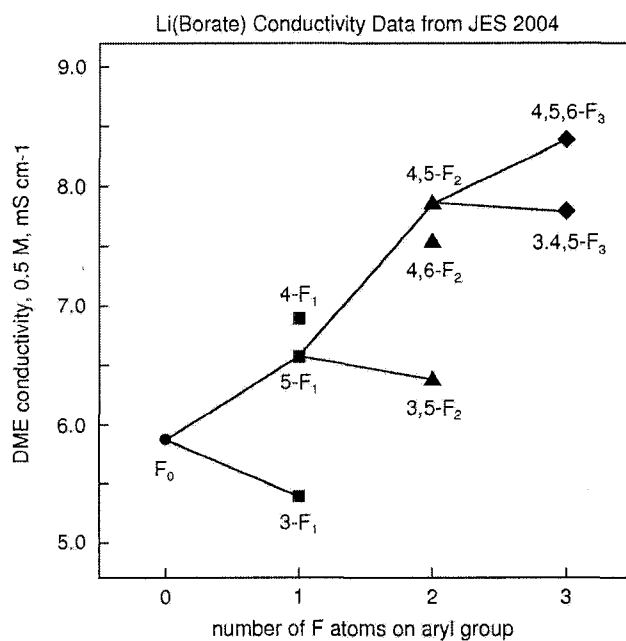


Figure 1.6. Conductivities of the lithium salts listed in Table 1.4 (0.5 M in DME). Note that in every case, adding an additional F atom to the aryl groups can either increase or decrease the conductivity depending on the position of the added F atom.

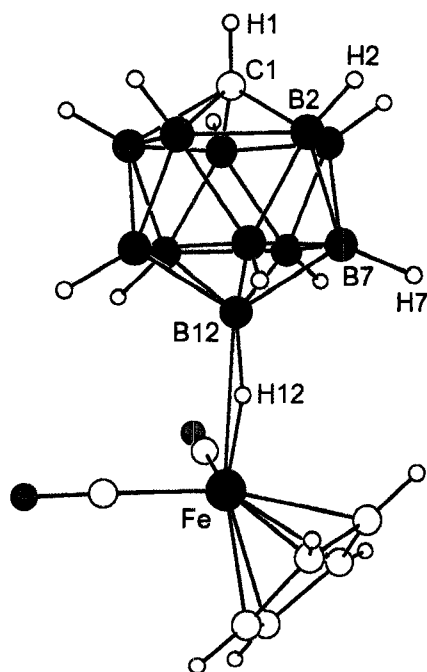


Figure 1.7. Drawing of the structure of $\text{Fe}(\text{Cp})(\text{CO})_2(\text{CB}_{11}\text{H}_{12})$ (coordinates from ref 53; the unlabelled red atoms are O atoms). The Fe–H12, Fe–B12, and B12–H12 distances are 1.56(2), 2.593(2), and 1.18(2) Å, respectively, and the Fe–H12–B12 angle is 141(2)°.

which is shown in Figure 1.7. The Fe atom is coordinated to the B12–H12 sigma bond. This is the H atom that generally coordinates to the metal ion when $\text{CB}_{11}\text{H}_{12}^-$ is a unidentate ligand,^{53,55,56} and this is the H atom that is attacked first in electrophilic substitution reactions of $\text{CB}_{11}\text{H}_{12}^-$.^{27,57-59}

However, *two* linkage isomers were observed in dichloromethane solution, and these were assigned to the solid-state structure (i.e., the Fe–H12 isomer) and to the Fe–H7 isomer. The Fe–H12 isomer was 2.7 times more abundant at 25 °C than the Fe–H7 isomer,⁵⁴ and this was in harmony with the then-generally-accepted understanding that H12 is "the most hydridic" H atom in $\text{CB}_{11}\text{H}_{12}^-$.^{27,57,58} However, quantum mechanical calculations at the DFT level of theory, carried out by Dr. Alexey A. Popov in support of the research described in this dissertation, now show that H12 is *not* the most hydridic H atom in $\text{CB}_{11}\text{H}_{12}^-$. This will be discussed in Chapter 6.

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Chapter 2 Experimental

Inert Atmosphere. Unless otherwise noted, all reactions and sample preparations were carried out with the rigorous exclusion of air and water. For these reactions, glovebox, Schlenk, and high-vacuum techniques were employed, using a purified dinitrogen atmosphere whenever necessary.¹

Solvents. Distilled water was deionized by passing it through a Bardstead Nanopure water treatment system so that the final resistivity was 18 M Ω -cm. This distilled/deionized water will be denoted as d²-H₂O. All solvents used were dried by distillation with an appropriate drying agent. The following solvents were dried with sodium: toluene (Fisher, ACS certified); tetrahydrofuran (THF, Fisher, ACS certified); *n*-pentane (Fisher, ACS certified); hexanes (Fisher, ACS certified); benzene (Fisher, ACS certified). Dimethoxyethane (DME, Acros 99+%) was dried with sodium benzophenone ketyl. The following solvents were dried by distillation over calcium hydride: acetonitrile (Fisher, HPLC grade); acetonitrile-*d*₃ (99.8%, Cambridge Isotope Laboratories); dichloromethane (Fisher, HPLC grade); dichloromethane-*d*₂ (Cambridge Isotope Laboratories, 99.9%). Acetone (Fisher, ACS certified) and acetone-*d*₆ were dried by distillation from activated 4Å molecular sieves.

Reagents. The following reagents were used as received: sodium (Aldrich, 99.95%), potassium (Aldrich, 99.95%), lithium (Aldrich, 99.9%), bis(pentamethylcyclopentadienyl)iron(II) (FeCp*₂, Aldrich, 97%), naphthalene (Aldrich, 99%), 9,10-dihydroanthracene (DHAN, Aldrich, 97%), iodomethane (MeI, Aldrich, 99%), triphenylchlorosilane (SiPh₃Cl, Aldrich, 97%), cesium chloride (Fisher, 99.99%), lithium chloride (Baker, 99.2%), sodium hydroxide (Fisher, ACS certified), silver nitrate (Spectrum, 99.0%), dimethylsulfate (Aldrich, 99+%), trimethylammonium chloride

(NHMe₃Cl, Aldrich, 98%), tetramethylammonium chloride (TMACl) (Aldrich, 98%), tetrabutylammonium chloride (Aldrich, 98%), 1-bromodecane (DcBr, Aldrich 98%), silver tetrafluoroborate (Aldrich, 98%), methyllithium (1.6 M in diethylether, Aldrich), *n*-butyl lithium (2.5 M in hexanes, Aldrich), methyltrifluoromethanesulfonate (Aldrich, ≥99%), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, Aldrich, 99%). Bromoethane (Aldrich, 99+%) was distilled from calcium hydride. The compound 1-iodo-2,2,2-trifluoroethane (Oakwood Products Inc.) was distilled from calcium hydride and stored over copper wire in a Schlenk tube. The compounds 2-chloropropane (*i*-PrCl), 2-bromopropane(*i*-PrBr), and 2-iodopropane (*i*-PrI) (Aldrich, 98%) were distilled from calcium hydride. Allylbromide (Aldrich, 99%) was distilled from calcium hydride. Tetrabutylammonium perchlorate (TBAP, Kodak) was dried with ethylacetate (Fisher, ACS certified) using azeotropic method. Mercury was purified by washing with 10% nitric acid and washing three times by d²-H₂O. After this mercury was dried on a filterpaper.

Spectroscopic Measurements. All samples for NMR spectroscopy were acetonitrile-*d*₃, acetone-*d*₆, dichloromethane-*d*₂, THF, or DME solutions in NMR tubes sealed with Teflon valves. Spectra were recorded on a Varian Inova 300 spectrometer. Chemical shift standards were internal acetonitrile-*d*₃ (δ 1.94), acetone-*d*₆ (δ 2.05) for ¹H NMR, external BF₃•OEt₂ (δ 0) for ¹¹B NMR, and external or internal C₆F₆ (δ -164.9) for ¹⁹F NMR and ¹¹B decoupled ¹⁹F NMR (¹⁹F{¹¹B}). In order to determine the compositional and isomeric ratios, delay was optimized to have enough relaxation time. Samples for the negative-ion electrospray-ionization mass spectrometry (NIES-MS) were acetonitrile solutions and were recorded on a Finnigan LCQ DUO spectrometer.

Cyclic voltammetry. Cyclic voltammograms were recorded with an EG&G Princeton Applied Research Model 263A potentiostat/galvanostat. All measurements

were performed in the glovebox using DME solutions that were ca. 1 mM analyte and 0.1 M TBAP. The experimental reference electrode was Ag wire, the working electrode was a glassy carbon disk with a diameter of 2.5 mm, and the counter electrode was a platinum mesh. All potentials in this dissertation are relative to decamethylferrocenium/decamethylferrocene couple ($\text{FeCp}^*_2^{+/0}$). The decamethylferrocenium/ferrocene reduction potential was achieved by adding an equimolar amount of FeCp^*_2 to the analyte solution as an internal standard.

Preparation of $\text{Cs}(\text{CB}_{11}\text{H}_{12})$ from $\text{NHMe}_3(\text{CB}_{11}\text{H}_{12})$. In a 50 mL round bottom flask, $\text{NHMe}_3\text{CB}_{11}\text{H}_{12}$ (4.87g, 24.0 mmol) was added and suspended in ca. 25 mL of $\text{d}^2\text{-H}_2\text{O}$. To this mixture, NaOH (1.15 g, 28.8 mmol) was added with stirring. As dissolution of the solid proceeded, strong odor due to the formation of trimethylamine was noticed, however, gas evolution was not observed. To this solution, minimum amount of acetone was added to dissolve the solid completely. In order to remove trimethylamine, the solution was heated to 60 to 70°C, and placed under a reduced pressure with a diaphragm pump for 16 hrs. The solution was filtered by a medium-porosity fritted glass filter. To the filtrate, a solution of CsCl (4.04 g, 24.0 mmol) in 5.0 mL of $\text{d}^2\text{-H}_2\text{O}$ was added. A white precipitate was formed immediately. After stirring this suspension for 16 hours, the solid was filtered by a medium-porosity-fritted glass filter to obtain white solid. Yield: 4.36 g $\text{CsCB}_{11}\text{H}_{12}$ (65.9% based on $\text{NHMe}_3(\text{CB}_{11}\text{H}_{12})$).

Preparation of $\text{NHMe}_3(1\text{-H-CB}_{11}\text{F}_{11})$. The fluorination of $\text{Cs}(\text{CB}_{11}\text{H}_{12})$ was achieved by modification of a procedure previously reported by our group.² In a typical reaction, $\text{CsCB}_{11}\text{H}_{12}$ (1.0 g, 3.6 mmol) was dissolved in anhydrous HF (20 mL) in a 300 mL Monel reactor. To this solution, gaseous F_2 (10% F_2 in N_2) was added so that the pressure was 60 psi (57 mmol F_2 , assuming the volume was 280 mL). After 8 hours of stirring at room temperature, the reactor was cooled to -78 °C (acetone/dry ice) and all

the volatiles were removed under vacuum. This F₂ addition and gas removal cycle was repeated five times. After the final cycle, HF was slowly removed and the reactor was put under vacuum for minimum 15 minutes at room temperature. To the reactor, no more than 100 mL of d²-H₂O was added in portions to quantitatively recover the fluorinated product. To this solution, an aqueous solution of 1.2 equivalents of (NHMe₃)Cl was added to form white precipitate. The precipitate was collected by filtration, washed with ca. 3 mL of cold water, and dried under vacuum. Yield: 1.02g of (NHMe₃)(1-H-CB₁₁F₁₁) (69% based on CsCB₁₁H₁₂). ¹⁹F NMR (acetonitrile-*d*₃, δ) -248.3 (s, 1 F), -256 (s, 10 F) NIES-MS; *m/z* 341.3, (calc. *m/z* 341.1)

Synthesis of Cs(1-Me-CB₁₁F₁₁). In a 50 mL Schlenk flask, (777 mg, 1.94 mmol) of NHMe₃(1-H-CB₁₁F₁₁) was added and dissolved in 20 mL of THF. To the solution, 1.6 M methyl lithium in diethylether (2.7 mL, 4.32 mmol) was added by a syringe and stirred for 16 hrs. In order to remove trimethylamine, the volume of the reaction mixture was reduced to approximately 50% (i.e., 50% of the solvent and presumably 100% of the more volatile trimethylamine) under vacuum. To the remaining solution, MeI (300 μL, 4.81 mmol) was added by a syringe and stirred for 1 hr. Then, all volatiles were removed under vacuum to leave a colorless-to-pale-yellow oil. A minimum amount of d²-H₂O (ca. 10 mL), was added to the oil. The product Li(1-Me-CB₁₁F₁₁) was extracted four times with diethylether (4 × 5 mL). The organic layers were combined and the solvent was removed under vacuum to leave a colorless-to-pale-yellow oil, to which d²-H₂O (ca. 10 mL) was added. The cloudy solution that resulted was filtered, and the colorless-to-pale-yellow filtrate was combined with a solution of CsCl (367 mg, 2.18 mmol) in 5 mL of d²-H₂O. The white crystalline precipitate that formed was isolated by filtration, washed two times with cold d²-H₂O (2 × 3 mL), and dried under vacuum for at least eight hours at room temperature. Yield: 534 mg of Cs(1-Me-CB₁₁F₁₁) (71.6% based on NHMe₃(1-H-CB₁₁F₁₁)). NMR: ¹⁹F{¹¹B}, (acetonitrile-*d*₃, δ) -253.5 (s, 1 F), -257.9 (s, 5 F), -259.8 (s,

5 F); ^{11}B , (acetonitrile- d_3 , δ) -7.8 (s, 1 B), -22.8 (s, 10 B); ^1H (acetonitrile- d_3 , δ) 1.5 (s, 3 H). NIES-MS; m/z 355.4 (calc. m/z 354.9).

Defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with metallic sodium. Typical reaction was performed as follows: In a glovebox, Cs(1-Me-CB₁₁F₁₁) (51.1 mg, 1.05×10^{-1} mmol) was placed in a 50 mL or a 100 mL Schlenk flask. Freshly cut sodium metal (0.599 g, 26.1 mol) was added to the flask followed by addition of 10 mL of anhydrous THF. The reaction mixture was stirred with a magnetic stirrer for certain amount of time. The mixture was stirred at room temperature, and samples were collected over certain time period. The samples were analyzed by NMR spectroscopy and mass spectrometry. (The results are discussed in Chapter 3.)

Defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with NaK. Typical reaction was as follows: In a glovebox, Cs(1-Me-CB₁₁F₁₁) (50.5 mg, 0.10 mmol) was added in a 50 mL Schlenk flask and dissolved in 5.0 g of anhydrous DME (for the reaction in presence of DHAN, (19.0 mg, 0.10 mmol) of this compound was added at this point). To the solution, NaK (2:8) was added by a pipette. The mixture was stirred at room temperature, and samples were collected over certain time period. The samples were analyzed by NMR spectroscopy and mass spectrometry. (The results are discussed in Chapter 3.)

Defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with sodium amalgam (NaHg). Typical reaction was performed as follows. In a glovebox, Cs(1-Me-CB₁₁F₁₁) (102.9 mg, 2.11×10^{-1} mmol) was added to a Schlenk flask and dissolved in 50 g of dry DME. This solution was stirred with a glass coated magnetic stir bar. To this solution, NaHg (4.63 g, 1.1 mmol (Na)) was added by a syringe. The solution was vigorously stirred at room temperature. The samples were collected over certain time period. The samples were

analyzed by NMR spectroscopy and mass spectrometry. (The results are discussed in Chapter 3.)

Preparation of Na/Hg (0.56% Na). Sodium amalgam was prepared by the method described in literature.³ Prior to use, Hg was washed with diluted HNO₃ and filtered through a filter paper with a small hole on the bottom. 193.087 g of Hg was measured in a Schlenk flask. Under nitrogen flow, 1.091 g of freshly cut metallic sodium cubes were added carefully. (Formation of amalgam is very vigorous and requires special precaution for spillage.) This amalgam was stored under nitrogen in a Schlenk flask for later use.

Preparation of samarium(II) iodide. In a glovebox, previously purified diiodoethane (233.8 mg, 0.83 mmol) was added to a Schlenk tube. To the tube, samarium powder (137.2 mg, 0.91 mmol) and 3.0 g of dry THF was added. The mixture was stirred for 24 hours at 25°C. At this point, the solution was dark blue and some dark blue crystalline solid was also observed. The solution was collected by filtration in the glovebox. After this, the solvent was removed under vacuum to leave dark blue powder. Yield: 363.9 g (98%) of SmI₂

Defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with samarium(II) iodide. In a glovebox, Cs(1-Me-CB₁₁F₁₁) (25.9 mg, 5.31×10^{-2} mmol) was added in an NMR tube with a Teflon valve. To the NMR tube, ca. 0.5 mL of dry THF was added. In a vial, SmI₂ (21.4 mg, 5.29×10^{-2} mmol) was added and dissolved in ca. 0.3 mL of dry THF. The solution was transferred quantitatively to the NMR tube by rinsing the vial with ca. 0.2 mL of THF. The reaction mixture was stirred at room temperature, and reaction was monitored by ¹⁹F NMR spectroscopy. (The result is discussed in Chapter 3.)

Defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with sodium naphthalenide in presence of 9,10-dihydroanthracene (DHAN). In an NMR tube, Cs(1-Me-CB₁₁F₁₁) (26.6 mg, 5.45×10^{-2} mmol) was added. In the NMR tube, (9.8 mg, 7.64×10^{-2} mmol) of DHAN was added. This mixture was dissolved in dry DME. To this solution, 0.55 mL of previously prepared 0.1 M sodium naphthalenide in DME was added. The reaction was analyzed by ¹⁹F and ¹¹B NMR spectroscopy. (The results are discussed in Chapter 3.)

Synthesis of Cs(1-Et-CB₁₁F₁₁). In a 50 mL Schlenk flask, NHMe₃(1-H-CB₁₁F₁₁) (229.2 mg, 0.57 mmol) was added and dissolved in 20 mL of anhydrous THF. To the solution, (503 μ L, 1.26 mmol) of 2.5 M butyl lithium in hexanes was added by a syringe and stirred for 16 hrs. In order to remove trimethylamine, the volume of the reaction mixture was reduced to 50% by a rotary evaporator. To the remaining solution, bromoethane (140 μ L, 1.87 mmol) was added by a syringe and stirred for 1 hr. Then, THF was removed under vacuum to leave colorless-to-pale-yellow oil. To the oil, a minimum amount (ca. 10 mL) of d²-H₂O, was added. Li(1-Et-CB₁₁F₁₁) was extracted with diethylether (4 $\times$ 5 mL). From the extract, diethylether was removed under vacuum to leave colorless to pale yellow oil. To this oil, ca. 10 mL of d²-H₂O was added and filtered with a glass filter pipette. To the solution, an aqueous solution of CsCl (120 mg, 0.71 mmol) was added to the filtrate to form white crystalline solid. The solid was filtered with medium fritted glass filter, washed with cold water, and dried under vacuum. Yield: 82.5 mg of Cs(1-Et-CB₁₁F₁₁) (28% based on NHMe₃(1-H-CB₁₁F₁₁)). ¹⁹F{¹¹B} NMR (acetonitrile-*d*₃, δ) -253.5 (s, 1 F), -257.9 (s, 5 F), -259.8 (s, 5 F), ¹¹B NMR (acetonitrile-*d*₃, δ) -14.3 (s, 1 B), -22.8 (s, 10 B), ¹H NMR (acetonitrile-*d*₃, δ) 0.8 (s, 3 H), NIES-MS *m/z* 355.4 (calc. *m/z* 354.9)

Synthesis of Cs(1-Bn-CB₁₁F₁₁). In a 50 mL Schlenk flask, NHMe₃(1-H-CB₁₁F₁₁) (211.0 mg, 0.53 mmol) was added and dissolved in 20 mL of anhydrous THF. To the

solution, 2.5 M butyl lithium in hexane (0.5 mL, 1.25 mmol) was added by a syringe and stirred for 16 hrs. To remove NMe₃, the volume of the solvent was reduced to half under vacuum. To the remaining solution, EtBr (121 μ L, 1.06 mmol) was added by a syringe and stirred for one hour. Then, THF was removed under vacuum to leave a pale yellow oil. To the oil, minimum amount (ca. 10 mL) of d²-H₂O, was added. Li(1-Bn-CB₁₁F₁₁) was extracted with diethylether (4 $\times$ 5 mL). From the extract, diethylether was removed under vacuum to leave brown oil. To this oil, ca. 10 mL of d²-H₂O was added and filtered with a glass filter pipette. To the solution, aqueous solution of CsCl (98.2 mg, 0.58 mmol) was added to the filtrate to form white crystalline solid. The solid was filtered with medium porosity fritted glass filter, washed with cold water, and dried under vacuum. Yield: 254.1 mg (85%) of Cs(1-Bn-CB₁₁F₁₁) NIES-MS *m/z* 431.5 (calc. *m/z* 431.1)

Synthesis of Cs(1,12-Me₂-CB₁₁F₁₁) with sodium naphthalenide (NaNaph).

Typical reaction was performed as follows: In a glove box, (20.0 mg 4.10×10^{-2} mmol) of Cs(1-Me-CB₁₁F₁₁) was placed into one side of an H-tube and dissolved in ca. 6 mL of DME (solution A). 1 to 4 equivalent of naphthalene (5.3–21.0 mg) was placed into the other side of the H-tube and dissolved in ca. 6 mL of DME (solution B). To the solution B, excess of freshly cut Na⁰ was added. The H-tube was taken out from the glove box and connected to the Schlenk line. The solvent in the solution A was vacuum transferred to the solution B. After transfer was complete, the solution B was stirred with a glass-coated magnetic stir bar at room temperature for 16 hours yielding dark green solution. After this, the solution B was cooled to –55 °C in acetonitrile/liq. N₂ bath, and transferred to the other side through a medium or fine fritted glass filter while pushing the solution with N₂ gas from one side. The combined solution was kept at –55 °C for 30 minutes and agitated. At this point, the color of the solution changed rapidly. Depending on the amount of sodium naphthalenide added, the color varied from bright red (with 1–2 eq.

NaNaph) to dark green with yellow tint (> 2 eq. NaNaph). To this solution, four equivalents (10.2 μL) of methyl iodide were added by a syringe through a septum. The reaction mixture was stirred and kept at $-50\text{ }^{\circ}\text{C}$ for between 30 minutes to an hour until the color turned faintly yellow to colorless. At this point, presence of white solid was noticed. After this, the solution was gradually warmed up to the room temperature. After exposing the solution to air, the precipitate was filtered with glass filter pipettes, and filtrate was collected. After this, the solvent was removed from the filtrate under vacuum to leave white solid. This solid was washed with hexanes to remove residual naphthalene. The remaining solid was dissolved in $\text{d}^2\text{-H}_2\text{O}$, and to this solution, 1.2 equivalents of NHMe_3Cl (4.7 mg, 4.9×10^{-2} mol) was added to form $\text{NHMe}_3(1, 12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ as white solid. ^1H NMR (acetonitrile- d_3 , δ) -0.5 (s, 3 H), 0.8 (s, 3 H), 2.0 (s, 9 H), $^{19}\text{F}\{^{11}\text{B}\}$ NMR (acetonitrile- d_3 , δ) -248.3 (s, 1 F), -256.9 (s, 1 F), $^{11}\text{B}\{^1\text{H}\}$ (acetonitrile- d_3 , δ) -23.2 (s, 1 B), -16.7 , (s, 5 B), -14.6 (s, 5 B), NIES-MS m/z 351.5 (calc. m/z 351.0)

Synthesis $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$. General procedure for this synthesis was same as the one described above. In an H-tube, $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ (20.6 mg, 0.0422 mmol) was placed into one side and dissolve in 10 mL of DME (solution A). In the other side of the H-tube, naphthalene (13.5 mg, 0.105 mmol) was placed and dissolved in 10 mL of DME (solution B). To the solution B, excess amount of freshly cut Na^0 was added. The H-tube was connected to a Schlenk line and solvent in the solution A was transferred to the solution B under vacuum. After transfer was complete, the solution was stirred with a glass coated magnetic stir bar at room temperature for 16 hours. The solution B was cooled to $-55\text{ }^{\circ}\text{C}$, and transferred to the other side through a medium or fine fritted glass filter. The combined solution was kept at $-55\text{ }^{\circ}\text{C}$ for 30 minutes, and excess CH_2ICF_3 was added by a syringe under N_2 flow. The reaction mixture was stirred and kept at $-55\text{ }^{\circ}\text{C}$ for 30 minutes to 1 hour until the color turned pale yellow to colorless. $^{19}\text{F}\{^{11}\text{B}\}$ NMR (acetonitrile- d_3 , δ) -247.5 (s, 5 F), -250.6 (s, 5 F), $^{11}\text{B}\{^1\text{H}\}$ NMR

(acetonitrile- d_3 , δ) -37.5, (s, 1 B), -16.2 (s, 10 B), NIES-MS m/z 463.3 (calc. m/z 462.9)

Synthesis of Li(1,12-Me₂-CB₁₁F₁₀). In a glove box, NHMe₃(1,12-Me₂-CB₁₁F₁₀) (46.9 mg, 0.114 mmol) was added to a 15 mL vial and dissolved in 10 mL of dry THF. To this solution, 60% NaH/mineral oil dispersion (8.3 mg, 0.208 mmol) was added. Immediately after the addition of NaH, evolution of gas, presumably H₂, was observed. After stirring the mixture for 16 hours at room temperature, the solid was removed by vacuum filtration, and solvent removed from the filtrate to leave white solid. This solid was taken out from the glove box, and converted to silver salt by following the procedure reported by Juhasz et al.⁴ In a 15 mL vial, the white solid was dissolved in ca. 3 mL of distilled/deionized H₂O. To this solution, AgNO₃ (33.0 mg, 0.194 mmol) was added and stirred for 30 minutes. To this solution, few drops of acetonitrile was added to form white precipitate. This solution was left without stirring for several hours to form colorless crystals. The crystals were collected by filtration and washed with d²-H₂O (3 $\times$ 1 mL). The crystals were transferred into a 15 mL vial, and ca. 5 mL of d²-H₂O was added to form white suspension. In a separate vial, LiCl (4.8 mg, 0.113 mmol) was added and dissolved in ca. 3 mL of d²-H₂O. To the suspension, solution of LiCl was added quantitatively and stirred for 16 hours. After filtration, H₂O was removed under vacuum to leave white solid. This white solid was dried under vacuum at 120°C. 15 mg (4.19 $\times$ 10⁻² mmol) of dry Li(1,12-Me₂-CB₁₁F₁₀) was collected as white solid. Yield: 36.8 %. ¹⁹F{¹¹B} NMR (acetonitrile- d_3 , δ) -248.3 (s, 1 F), -256.9 (s, 1 F), ¹¹B{¹H} NMR (acetonitrile- d_3 , δ) -22.2 (s, 1 B), -15.6 (s, 5 B), -13.7 (s, 5 B), ¹H NMR (acetonitrile- d_3 , δ), 1.55 (s, 1 H), 0.22 (s, 1 H)

Cs(1-Me-12-decyl-CB₁₁F₁₀). In a glove box, Cs(1-Me-CB₁₁F₁₁) (30.5 mg, 6.25 $\times$ 10⁻² mmol) was added to one side of an H-tube and dissolved in ca. 6 mL of DME

(solution A). In the other side, naphthalene (32.0 mg, 0.250 mmol) of was added and dissolved in ca. 6 mL of DME (solution B). To the solution B, freshly cut Na⁰ (11.1 mg, 0.483 mmol) was added. The H-tube was taken out from the glove box and connected to the Schlenk line. The solvent in the solution A was vacuum transferred to the solution B. After transfer was complete, the solution B was stirred with a glass-coated magnetic stir bar at room temperature for 16 hours yielding dark green solution. After this, the solution B was cooled to -55 °C in acetonitrile/liq. N₂ bath, and transferred to the other side through a medium or fine fritted glass filter while pushing the solution with N₂ gas from one side. The combined solution was kept at -55 °C for 30 minutes and agitated. After this, 1-bromo-decane (55.0 µL, 0.265 mmol) was added by a syringe through a septum. The color of the solution changed from dark green to orange immediately, and eventually it turned cloudy, but colorless. After letting it sit for 30 more minutes with occasional stirring, the H-tube was taken out from the bath. The solution was filtered through a pipette packed with glass filter, and filtrate collected in a 15 mL vial. The solvent was removed under vacuum to leave white solid. This solid was rinsed with hexane to remove residual naphthalene. ¹¹B{¹H} NMR (acetonitrile-*d*₃, δ) -15.2 (s, 5 B), -17.2 (s, 5 B), -23.0 (s, 1 B), ¹⁹F{¹¹B} NMR (acetonitrile-*d*₃, δ) -248.3, (s, 1 F), -256.2 (s, 1 F), ¹H NMR (acetonitrile-*d*₃, δ) 0.88 (t, 3 H), 0.98 (t, 2 H), 1.3 (m, 14 H), 1.5 (t, 2 H), 1.6 (s, 3 H) NIES-MS *m/z* 477.5 (calc. *m/z* 477.3)

Synthesis of (1-Me-12-SiPh₃-CB₁₁F₁₀). Typical reaction was performed as follows: Cs(1-Me-CB₁₁F₁₁) (104.1 mg, 2.13 × 10⁻¹ mmol) of was placed into one side of an H-tube and dissolved in ca. 6 mL of DME (solution A). Naphthalene (69.0 mg, 5.38 × 10⁻¹ mmol) was placed into the other side of the H-tube and dissolved in ca. 6 mL of DME (solution B). To the solution B, excess of freshly cut Na⁰ was added and green color on the surface of Na⁰ indicated instant formation of sodium naphthalenide. The H-tube was connected to a Schlenk line, and the solvent in the solution A was vacuum

transferred to the solution B. After transfer was complete, the solution was stirred with a glass coated magnetic stir bar at room temperature for 16 hours to obtain a dark green sodium naphthalenide solution. The solution B was cooled to $-55\text{ }^{\circ}\text{C}$, and transferred to the other side through a medium or fine fritted glass filter. The combined solution showed instant color change from dark green to dark brown. This solution was kept at $-55\text{ }^{\circ}\text{C}$ for 30 minutes, then SiPh_3Cl (194.3 mg, 6.59×10^{-1} mmol) was added under N_2 flow. As SiPh_3Cl reacted the color of the solution became lighter and white precipitate formed. The reaction mixture was stirred and kept under $-55\text{ }^{\circ}\text{C}$ for 30 minutes to an hour until the color turned pale yellow to colorless. The solution was then warmed up slowly to the room temperature, and the precipitate was filtered with a glass filter filled pipette to collect the filtrate. The solvent was removed under reduced pressure to leave beige solid. The solid was rinsed with hexanes, several times to remove naphthalene. The solid was recrystallized by dissolving in acetone and diffusing hexanes into the solution. $^{11}\text{B}\{^1\text{H}\}$ NMR (acetonitrile- d_3 , δ) -15.0 (s, 5 B), -16.8 (s, 5 B), -32.6 (s 1 B) ^1H NMR (acetonitrile- d_3 , δ) 1.6 (s, 3 H), 7.3 (m, 9 H), 7.6 (m, 6 H) $^{19}\text{F}\{^{11}\text{B}\}$ NMR (acetonitrile- d_3 , δ) -245.3 (s, 1 F), -239.8 (s, 1 F) NIES-MS m/z 595.6 (calc. m/z 595.4)

Preparation of of $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$. In a glove box, $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$ (12.1 mg, 1.66×10^{-2} mmol) was added to a 15 mL vial, and AgBF_4 (3.7 mg, 1.9×10^{-2} mmol) was added in a separate vial. To both vials, ca. 3 mL of dry CH_2Cl_2 was added. $\text{AgBF}_4/\text{CH}_2\text{Cl}_2$ mixture was transferred to the other vial by a pipette. In order to quantitatively transfer AgBF_4 , the vial was rinsed with CH_2Cl_2 (5×3 mL) and the rinsing liquid was transferred to the other vial. The mixture was stirred at room temperature for two days. To the mixture, 5 mL of dry benzene was added to the mixture. The volume was reduced to ca 3 mL under vacuum. The solid was removed by filtration, and the solvent removed under vacuum leaving white to beige solid. To the solid, minimum amount of dry benzene was added and recrystallized by layering dry *n*-

pentane. Yield was not calculated due to the small scale of the reaction. NIES-MS m/z 595.6 (calc. m/z 595.4)

Computational methods. Geometry optimization of all molecules and ions was performed using PBE functional⁵ and PRIRODA quantum-chemical code.^{6,7} The code employed expansion of the electron density in an auxiliary basis set to accelerate evaluation of the Coulomb and exchange-correlation terms.⁶ A TZ2P-quality basis set as implemented in PRIRODA was used for optimization; no symmetry constraints were adopted. Analysis of the spatial distribution of molecular orbitals and electrostatic potential as well as analysis of the atomic charges was performed at the PBE0/6-311G (2d,p) level of theory with the use of PC GAMESS;⁸ PBE/TZ2P-optimized coordinates were employed in these calculations. Testing calculations with the use of 6-311G ++ (2d,p) basis set did not show considerable changes of calculated parameters and hence diffuse function were not used. Optimization of coordinates of two proposed intermediate structures, $(1\text{-Me-CB}_{11}\text{F}_{10}\text{--Na}^+\text{--F}^-)^{2-}$ and $(1\text{-Me-CB}_{11}\text{F}_{11})^{3-}\text{---Na}^+$ ion pairs, was performed at PBE0/aug-cc-pVTZ(-f) level with the use of PC GAMESS⁴ (hereafter "(-f)" denotes that polarization function of f -type were removed from the original cc-pVTZ basis set).

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Chapter 3 Reaction of 1-Me-CB₁₁F₁₁⁻ with different reducing agents

Introduction. Reductive defluorination of B–F bonds has not been as well-studied as the reductive defluorination of C–F bonds. For C–F bonds, reductive defluorination has been accomplished using alkali metals,¹ alkaline earth metals,² sodium-mercury amalgam (NaHg),³ and organic radical anions such as the naphthalenide anion.^{4,5,6} For B–F bonds, the only published example is the report by Köster and Grassberger on the defluorination of ethyldifluoroborane with metallic lithium in THF to produce *nido*- and *closo*-carboranes.⁷

Before this work, there was one unpublished example of the reductive defluorination of any B–F derivatives of the icosahedral C₂B₁₀, CB₁₁, and B₁₂ cages. The one example is the reaction performed by Dr. S. V. Ivanov in the Strauss Research Group at Colorado State University. This reaction, which was not investigated further by Dr. Ivanov, was the starting point for the investigation described in this chapter. The reductive dehalogenation of analogous species with B–X bonds other than X = F are limited to (i) one reaction by Dr. Ivanov of CB₁₁H₆Br₆⁻ with sodium and (ii) the transformation of B–I bonds to B–H bonds by Michl and coworkers.⁸

Results and Discussion

To search for an efficient reducing agent to selectively defluorinate the B12 vertex of 1-R-CB₁₁F₁₁⁻, several reducing agents were examined. These reducing agents include Na⁰, NaK, NaHg, CaH₂, Mg⁰, SmI₂, and sodium naphthalenide. Some of these reducing agents showed little effect or no effect on defluorination. For instance, CaH₂ showed no effect on defluorination of 1-Me-CB₁₁F₁₁⁻ after one week at 85 °C in DME. Another one-electron reducing agent, SmI₂, also did not exhibit defluorination ability for the 1-Me-CB₁₁F₁₁⁻ anion in DME after two days at room temperature. With Mg⁰

(activated by I₂ prior to the reaction and stored in the glovebox), defluorination of Cs(1-Me-CB₁₁F₁₁) in DME did not occur at room temperature. At 85 °C, defluorination was observed by ¹⁹F NMR, but was extremely slow. After 10 days of reflux, only approximately 11% of 1-Me-CB₁₁F₁₁[−] was converted to 1-Me-12-H-CB₁₁F₁₀[−]. Sodium metal, NaK, NaHg, and sodium naphthalenide showed remarkable defluorination ability, and the results are discussed below.

(a) Reductive defluorination of Cs(1-Me-CB₁₁F₁₁) with metallic sodium. Dr. Ivanov investigated defluorination of 1-Me-CB₁₁F₁₁[−] with metallic sodium in THF. This experiment was carried out at room temperature for 25 hours. The negative-ion electrospray-ionization mass spectroscopy (NIES-MS) spectrum of the product mixture showed a new peak at *m/z* 337. This mass corresponds to an anion which underwent mono-defluorination, 1-Me-CB₁₁HF₁₀[−]. The ¹⁹F NMR spectrum of the product mixture showed two new peaks with approximately equal integration at −253.4 and −244.6 ppm. The symmetry of the defluorinated species on the B12 vertex is C_{5v}, which exhibits two peaks with equal intensity. Two isomers, defluorination at B2 or B7 vertex, have C_s symmetry, which would exhibit six peaks with integral ratio of 1:1:2:2:2:2. Based on these data, Dr. Ivanov concluded that the product mixture contained 1-Me-12-H-CB₁₁F₁₀[−]. The conversion of 1-Me-CB₁₁F₁₁[−] to 1-Me-12-H-CB₁₁F₁₀[−], based on the ¹⁹F NMR spectrum, was 41%. The defluorination reaction seemed to be selective to the B12 vertex, however, this reaction was performed only once. In order to investigate further, the reaction was repeated under the same conditions. Figure 3.1 shows the NIES-MS spectrum of the product mixture after 25 hours of reaction. The product mixture contained several defluorinated species with B–H bonds such as 1-Me-CB₁₁H₃F₈[−] (*m/z* 301.5), 1-Me-CB₁₁H₂F₉[−] (*m/z* 319.3), and 1-Me-12-H-CB₁₁F₁₀[−] (*m/z* 337.3). Significantly, the peak of the starting material at *m/z* 355 was absent. In addition to these hydride species, there were several unknown species at *m/z* 352.3, 372.3, 389.4, and

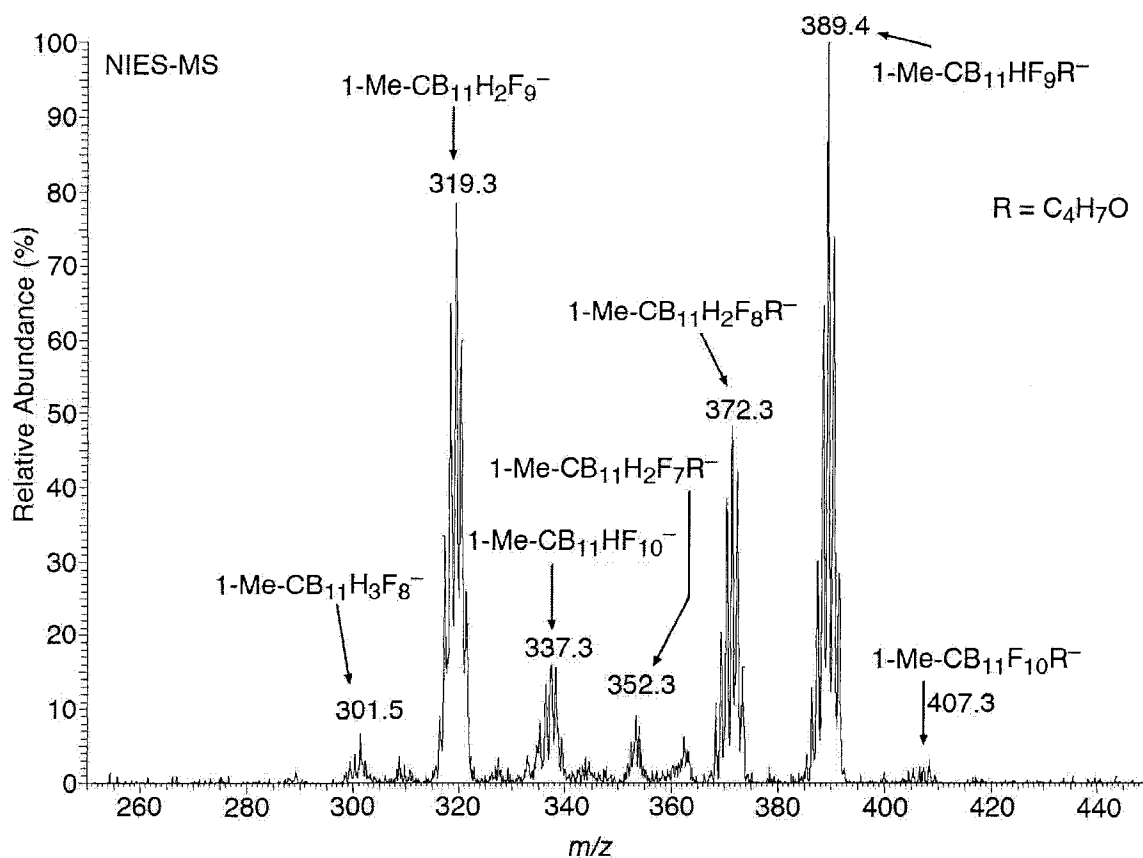


Figure 3.1. The negative-ion electrospray-ionization mass spectrum of the product mixture from reduction of Cs(1-Me-CB₁₁F₁₁) by metallic sodium in THF. The product mixture contained no 1-Me-CB₁₁F₁₁⁻, and contained seven defluorinated species. R = tetrahydrofuryl (C₄H₇O)

407.3. Based on the simulated mass spectra, these peaks are due to 1-Me-CB₁₁F₇H₂(C₄H₇O)[−] (calc. *m/z* 353.1), 1-Me-CB₁₁F₈H₂(C₄H₇O)[−] (calc. *m/z* 371.1) and 1-Me-CB₁₁F₉H(C₄H₇O)[−] (calc. *m/z* 389.1), and 1-Me-CB₁₁F₁₀(C₄H₇O)[−] (calc. *m/z* 407.1). Presumably, the first three anions formed from the hydride abstraction from THF, the latter four anions formed by addition of tetrahydrofuryl group (C₄H₇O) to the CB₁₁ cage. Based on this observation, we propose that the addition reaction to the defluorinated boron atom is radical mechanism.

Figure 3.2 shows the pathways to form these defluorinated anions. The abbreviations are made to show numbers of hydrogen and fluorine atoms, and tetrahydrofuryl groups in the anions. After the first defluorination, products with B–H or B–(C₄H₇O) bonds are formed. This should not be different for the second and the third defluorinations. For instance, the first defluorination of the B–F bond is followed by addition of a hydrogen atom or tetrahydrofuryl group (R) to form 1-Me-CB₁₁HF₁₀[−] (HF₁₀) or 1-Me-CB₁₁F₁₀R[−] (F₁₀R). When the second defluorination occurs to HF₁₀, it will form 1-Me-CB₁₁H₂F₉[−] (H₂F₉) and 1-Me-CB₁₁HF₉R[−] (HF₉R). When the second defluorination occurs to F₁₀R, 1-Me-CB₁₁HF₉R[−] (HF₉R) and 1-Me-CB₁₁F₉R₂[−] (F₉R₂) will form. Table 3.1 shows the total percentages and the percentages with respect to constant number of fluorine atoms (%F_{*n*}) for each anion. The percentages are calculated based on the NIES-MS spectrum. If our speculation for the radical mechanism is correct, the %F_{*n*} for HF₁₀ and F₁₀R should be 50:50. However, the actual percentages are 89 and 11 %, respectively. Presumably, this is due to the different reduction potentials for these two anions. The R group is electron donating compared to a hydrogen atom. This may cause the reduction potential to drop. The %F_{*n*} for the second defluorination products, H₂F₉, HF₉R, and F₉R₂ are 44, 56, and 0%. The higher percentage of HF₉R is due to the two

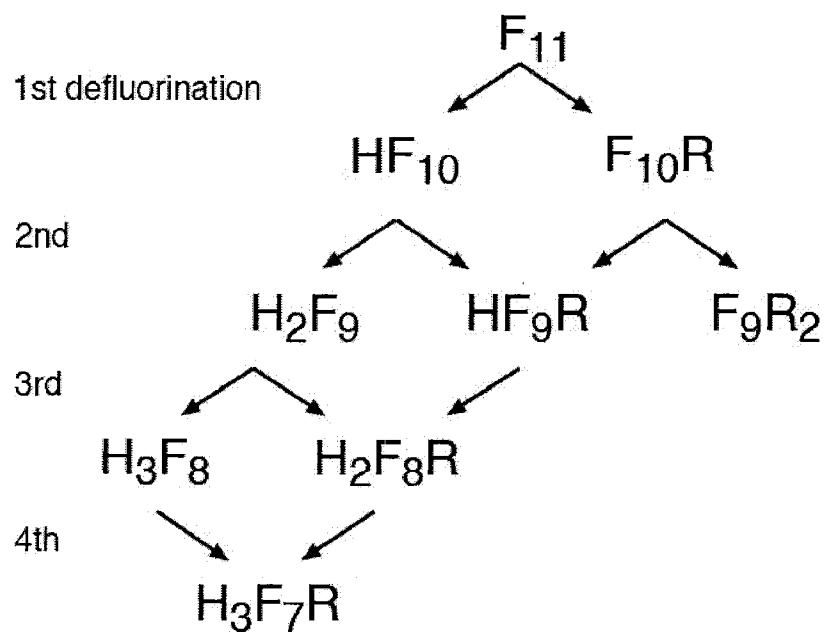


Figure 3.2. Pathways to form different anions. Abbreviations are used to indicate the number of hydrogen and fluorine atoms, and tetrahydrofuryl group (R) in the anions. In other words, 1-MeCB₁₁[−] was omitted from the anions. Each anion form B–H or B–R bond after each defluorination step.

Table 3.1. Percentages of anions for constant number of fluorine atoms and for the total composition. (Values are calculated from the % intensity of each anion in the NIES-MS spectrum.)

	% intensity	% for constant F_n	% of total
HF ₁₀	16	89	6
F ₁₀ R	2	11	1
H ₂ F ₉	79	44	31
HF ₉ R	100	56	40
F ₉ R ₂	0	0	0
H ₃ F ₈	6	11	2
H ₂ F ₈ R	49	89	19

different pathways to form this anion. The HF_9R anion can be formed from both HF_{10} and F_{10}R . Statistically, this should double the amount of HF_9R compared to HF_9R . However, due to the difference in the rate of reduction, HF_9R is easier to be further reduced to form F_8 species. The absence of F_9R_2 can be explained by the steric effect. The tetrahydrofuryl group is relatively bulky, and it may not at all form the second B–R bond. In the third defluorination, the $\%F_n$ for H_3F_8 and $\text{H}_2\text{F}_8\text{R}$ are 11 and 89%, respectively. The significantly small value for H_3F_8 is presumably due to the fact that the only source of this anion is H_2F_9 , which may be hard to reduce.

In order to monitor the reaction over time, a separate experiment was performed. This reaction was done in an NMR tube with Teflon screw cap. Figure 3.3 shows the ^{19}F NMR spectra of the reaction mixture in THF between 13 hours to 35 hours of reaction time. For the first 13 hours, the reaction was done without stirring (Figure 3.3(B)). As expected, the reaction was slow. The reaction occurs only on the surface of the metallic sodium, and the size of the surface area is the limiting factor. There were a set of peaks from $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion at -246.2 and -254.9 ppm, and another set of peaks at -210.2 and -211.6 ppm. In order to speed up the reaction, the mixture was sonicated for 3 hours. The peaks for the $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion did not change significantly, however, the peaks at -210.2 and -211.6 ppm increased (Figure 3.3(C)). These peaks disappeared after exposure to air. This observation suggests that the peaks are probably an intermediate species. More will be discussed about the intermediate below in this chapter. The increase in the peaks of the intermediate, but not the $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion showed that defluorination is a fast reaction, and the formation of $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion from the intermediate is slow under inert atmosphere in THF at room temperature. After 35 hours including total six hours of sonication, the ^{19}F NMR showed that not only the peaks for the intermediate, but the peaks for $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion increased

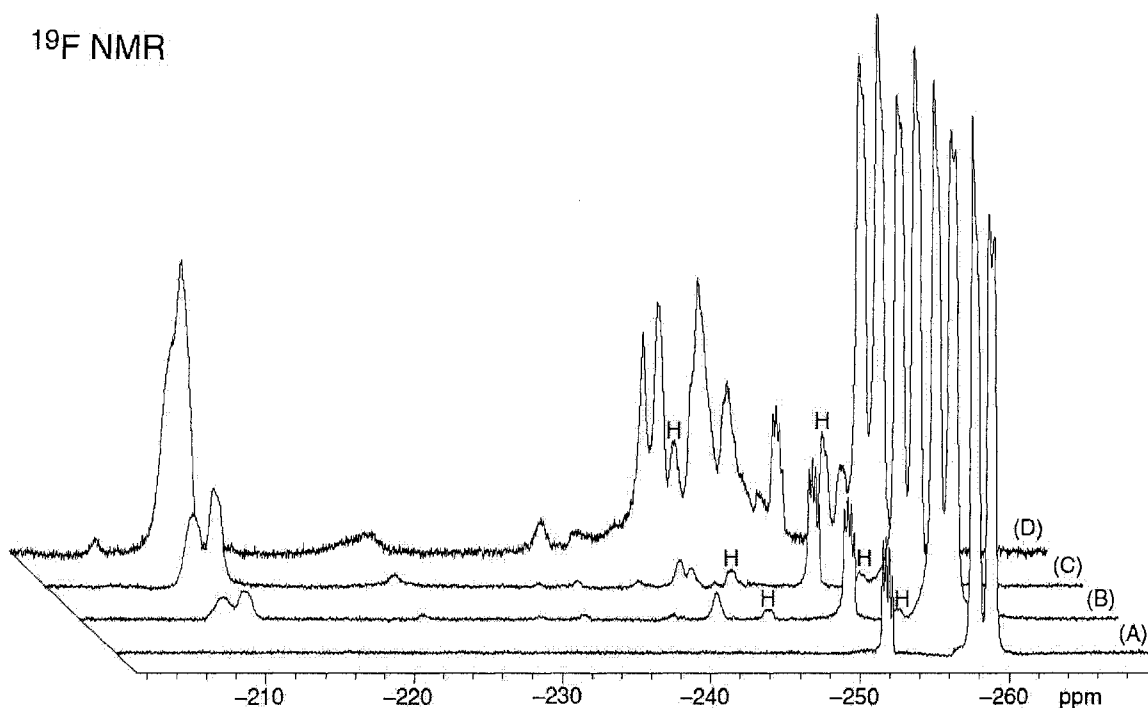
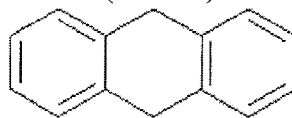


Figure 3.3. The 282.4 MHz ^{19}F NMR spectra of the reaction mixture in THF. The reaction was carried out with $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and metallic sodium in THF at 25°C . All spectra were normalized based on the height of the most intense peak (peaks for the belt fluorine atoms of the $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$). (A) $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ in THF before the reaction. (B) After 13 hours without stirring. (C) After 22 hours including 3 hours of sonication. (D) After 35 hours including total 6 hours of sonication. The peaks at -246.2 and -254.9 ppm are from $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$. The peaks at -210.2 and -211.6 ppm are presumably from the intermediate species. After 35 hours, the multiple peaks appeared and these are probably due to several species of multiple defluorination products. Note that peaks from $1\text{-Me-CB}_{11}\text{F}_{11}^-$ at -251.8 , -257.5 and -258.7 ppm were still present.

significantly (Figure 3.3 (D)). In addition, there were multiple peaks, presumably for products that underwent multiple defluorination, at -242.8 , -243.8 , -246.5 , -248.5 , -251.5 , and -256.0 ppm. Even after 35 hours, the peaks from the starting material, 1-Me- $\text{CB}_{11}\text{F}_{11}^-$, at -251.8 , -257.5 and -258.7 ppm were present.

In order to form the 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ anion more selectively, it is necessary to prevent the formation of the CB_{11} derivatives with the tetrahydrofuryl group. Since the reaction seemed to undergo radical mechanism, addition of an appropriate hydrogen donor into the reaction should aid the selective formation of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$. The choice of the hydrogen donor must be made so that the other radical would not be added to the carborane cage. As hydrogen donors, 1,2,3,4-tetrahydronaphthalene, and decahydronaphthalene are well known and have been used for coal liquifaction,^{9,10} but for our purpose, 9,10-dihydroanthracene (DHAN) was chosen for its size.



9,10-dihydroanthracene (DHAN)

The reaction was carried out with 20 times excess of sodium and five equivalents of DHAN in THF at 25°C . After one hour, the solution turned dark green, indicating the formation of a radical anion, presumably dihydroanthracenide. Figure 3.4 shows the NIES-MS and ^{19}F NMR spectra of the reaction mixture after 25 hours. Based on the NIES-MS spectrum, all starting material reacted to form defluorinated species. The reaction was complete much faster than the reaction without DHAN. This is almost certainly due to the reaction being homogeneous because of the formation of the soluble dihydroanthracenide or anthracenide radical anion. The major product was 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ anion, and significantly, no peaks were found at m/z 372.3 and 389.4, which indicates the absence of the derivatives with the tetrahydrofuryl group. However,

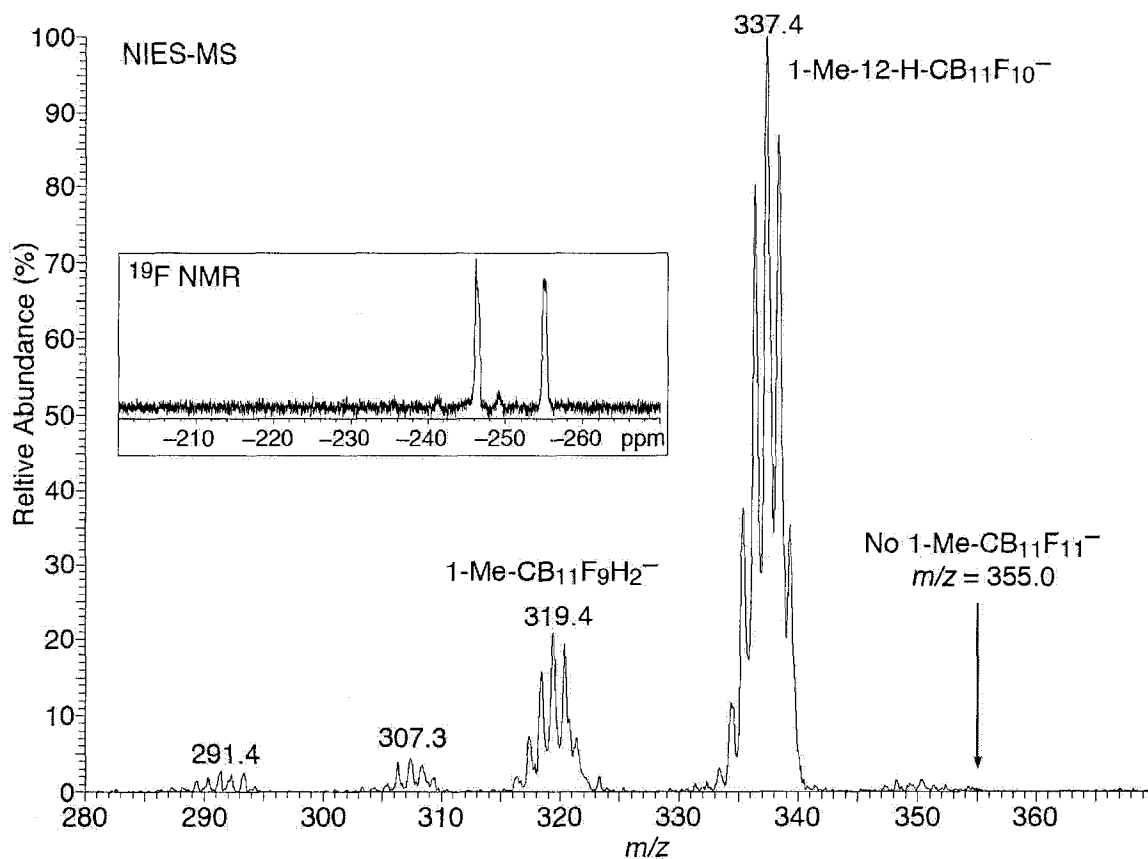


Figure 3.4. The 282.4 MHz ^{19}F NMR (inset) and the negative-ion electrospray-ionization mass spectra showing selective formation of $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$. Note the absence of THF adducts in the mass spectrum and absence of the peaks of the intermediate in the NMR spectrum. Reaction condition: 20 equivalents (based on $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$) of Na^0 and five equivalents of DHAN in THF. Stirred for 25 hours at 25°C . The peak at 307.3 belongs to $1\text{-Me-CB}_{10}\text{F}_9\text{H}^-$ (calc. m/z 307.1), which was formed from defluorination of $1\text{-Me-CB}_{10}\text{F}_{10}^-$, an impurity in the starting material.

approximately 17% of 1-Me-CB₁₁F₉H₂[−], which is a product from multiple defluorination, was present. A possible reason for lower percentage of 1-Me-CB₁₁F₉H₂[−] and absence of further multiple defluorination products such as 1-Me-CB₁₁F₈H₃[−] and 1-Me-CB₁₁F₇H₄[−] is the shorter reaction time. Another notable observation is that in the ¹⁹F NMR spectrum, the peaks from the intermediate were absent. Presumably, this is due to the presence of DHAN which reacted rapidly with the intermediate to produce 1-Me-12-H-CB₁₁F₁₀[−].

Although sodium metal seemed to selectively defluorinate the B12 vertex of the 1-Me-CB₁₁F₁₁[−] anion at the beginning of the reaction, as the reaction proceeded, several species of products which underwent multiple defluorination were formed. This indicates that sodium metal is too strong a reducing agent for selective defluorination of 1-Me-CB₁₁F₁₁[−]. In addition, since the reaction occurs only on the surface of the sodium metal, the precise control of the rate of reaction was difficult.

(b) Defluorination of Cs(1-Me-CB₁₁F₁₁) with NaK. NaK is a versatile reducing agent used in various chemical syntheses.^{11,12,13} It forms low-melting eutectic mixture and is liquid in a wide range of Na:K ratios at room temperature.¹⁴ Although it is stronger reducing agent than metallic sodium due to the presence of potassium (Na: $E^0 = -2.71$ V v.s. K: $E^0 = -2.93$ V), and may cause multiple defluorination of 1-Me-CB₁₁F₁₁[−], control over the rate of reaction may be easier due to its liquid form. In this work, 20:80 wt% NaK was used. The reaction was carried out in DME, in presence of DHAN for 25 hours at room temperature. Figure 3.5 shows the ¹⁹F, ¹¹B, and ¹¹B{¹H} NMR, and NIES-MS spectra of the reaction mixture. Based on the ¹⁹F NMR, no 1-Me-CB₁₁F₁₁[−] was observed in the reaction mixture after 25 hours. We expected that NaK would produce similar products to sodium metal, but surprisingly, ¹⁹F NMR spectra showed two sets of new peaks. One of them is for 1-Me-12-H-CB₁₁F₁₀[−] (−246.2 and −254.9 ppm) as seen in the reaction with Na⁰. The other set at −248.3 and −256.8 ppm was not observed when the reducing agent did not contain potassium. For instance two separate defluorination reactions using metallic sodium as a reducing agent in DME did not contain these peaks.

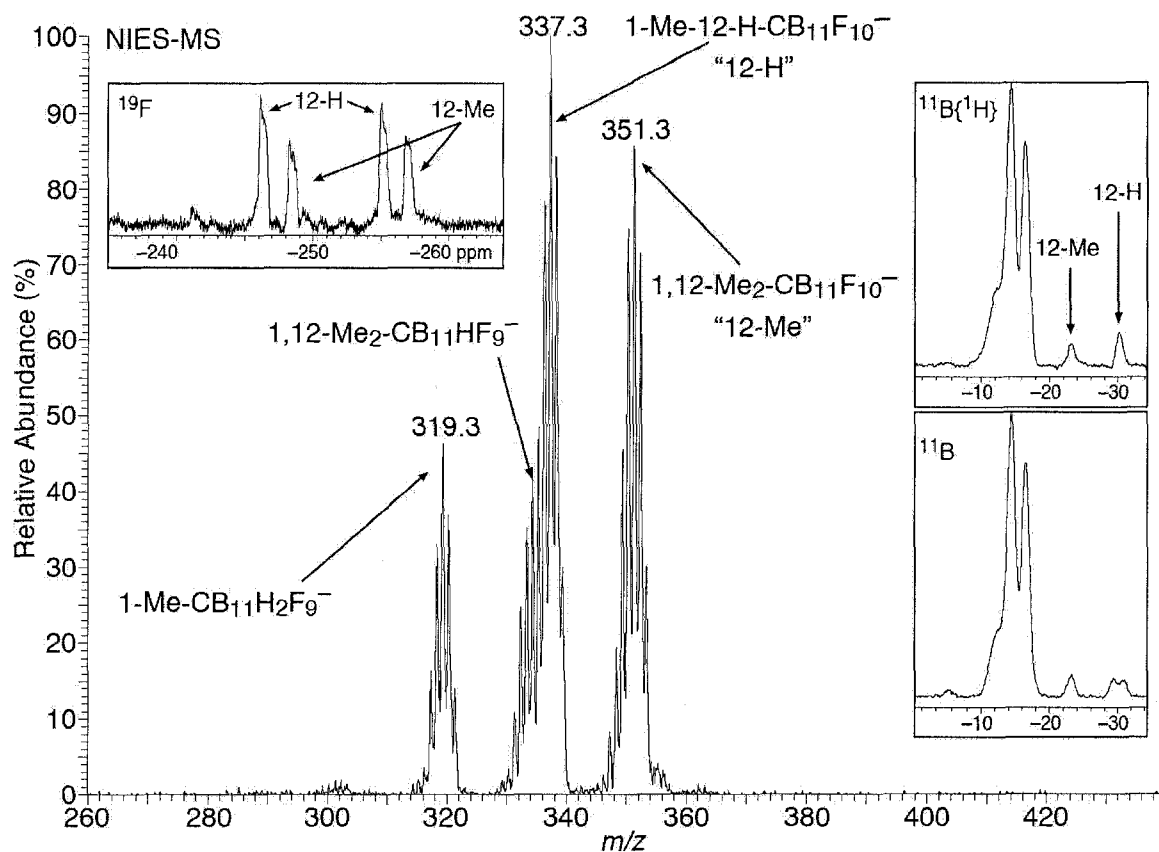


Figure 3.5. The negative-ion electrospray-ionization mass spectrum, 282.4 MHz ^{19}F NMR spectrum (left inset), and 96.3 MHz $^{11}\text{B}\{^1\text{H}\}$ and ^{11}B NMR spectra (right insets) of the product mixture from 25-hour reaction of $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and 1.5 eq. NaK in presence of DHAN in DME. DME was the solvent for all NMR spectra. The mass spectrum shows the presence of $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$, $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$, $1\text{-Me-CB}_{11}\text{H}_2\text{F}_9^-$, and $1,12\text{-Me}_2\text{-CB}_{11}\text{HF}_9^-$. The NMR spectra support the presence of $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ and $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$.

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum also showed two peaks from two separate B12 atoms at -23.3 and -30.5 ppm. The peak at -30.5 ppm showed ^1H coupling, but the peak at -23.3 ppm did not show coupling in the ^{11}B NMR spectrum. This means that the peak at -30.5 ppm is the B12 vertex of the $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion. In the NIES-MS spectrum, there were four sets of peaks, two of them are for $1\text{-Me-CB}_{11}\text{H}_2\text{F}_9^-$ (m/z 319.3) and $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ (m/z 337.3), and two new peaks at m/z 333.3 and 351.3.

Based on their isotopic patterns and the masses, the two new peaks in the mass spectrum were concluded to be anions with a methyl group on the B12 vertex, $1,12\text{-Me}_2\text{-CB}_{11}\text{HF}_9^-$ (calc. m/z 333.0) and $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ (calc. m/z 351.0). The $1,12\text{-Me}_2\text{-CB}_{11}\text{HF}_9^-$ anion has C_s symmetry and would exhibit five peaks with integral ratio of 1:2:2:2:2, but would not have intense peaks in neither ^{19}F nor $^{11}\text{B}\{^1\text{H}\}$ NMR at this concentration. Therefore, the peak at -23.3 ppm in the ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR was concluded to be B12 in the $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ anion. The presence of B12-methyl derivatives gave rise to questions; (i) the origin of the methyl group; (ii) why it was not seen when sodium metal was used as a reducing agent. In the reaction mixture, there are two possible sources: the DME molecule and the methyl group on C1 vertex of the anion. The methyl group on the C1 vertex is unlikely to be the source of the methyl cation simply because $1,12\text{-H}_2\text{-CB}_{11}\text{F}_{10}^-$ was not seen at all in the mass spectrum. Therefore the source of the methyl group is certainly from the DME molecules. The product mixture from a separate defluorination experiment with potassium metal in DME without DHAN, showed predominantly $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$. Unlike the reaction with sodium metal in THF, the reaction with potassium in DME did not show any evidence of the formation of a B12-(OCH₂CH₂OMe) or a B12-(OCH₂CH₂O)-B12 bonds. Therefore the addition mechanism is not a radical mechanism. A possible explanation for the absence of B12-Me derivatives in the reaction with sodium metal could be due to the difference in the strength of the metal/solvent coordination. Coordination of the metal to the DME

molecule should affect the C–H and C–O bond strength. This means that depending on the coordination strength, DME may undergo methyl or hydride abstraction.

NaK seemed to be an interesting reducing agent because it produced 1,12-Me₂-CB₁₁F₁₀[–] without addition of a methylating agent, but it also produced significant amount of multiple defluorination products and therefore it was not an efficient reagent for the selective defluorination reaction of 1Me-CB₁₁F₁₁[–].

(c) Defluorination of Cs(1-Me-CB₁₁F₁₁) with NaHg. NaHg is a milder reducing agent than metallic sodium and used for organic syntheses,^{15,16} and the reduction of organometallic complexes.^{17,18} The advantage of using NaHg is that depending on the concentration, the reduction potential will be different, therefore the reducing ability may be adjusted. In our experiment, in order to achieve better selectivity in defluorination, 0.5–1.0% NaHg was used. Fig 3.6 shows the ¹⁹F NMR spectra of the reaction mixture between 10 hours to 5 days from the first addition of two equivalents of NaHg. As it was expected, defluorination was slow, but selective. Based on the integration, the spectrum showed that only 4.5% of 1-Me-CB₁₁F₁₁[–] anion was converted to 1-Me-12-H-CB₁₁F₁₀[–] anion during the first 10 hours. Between 24 hours to 48 hours, the conversion increased gradually, and after 48 hours, the reaction became much slower. It took five days to convert 12.5% of the starting material. Presumably, the reaction became slower due to the decrease in concentration of Na in Hg which will cause significant increase in the reduction potential.

In order to obtain the 1-Me-12-H-CB₁₁F₁₁[–] in high yield, consecutive addition of NaHg was studied. Figure 3.7 shows the ¹⁹F{¹¹B} NMR spectra of the reaction mixture from this experiment. After addition of five equivalents of NaHg (Figure 3.7A), nearly 50% of 1-Me-CB₁₁F₁₁[–] was converted to 1-Me-12-H-CB₁₁F₁₀[–] in one week. After another addition of five equivalents of NaHg, the conversion was nearly 80% in one week (Figure 3.7B). For the third addition, large excess (168 eq.) of NaHg was added. After one week,

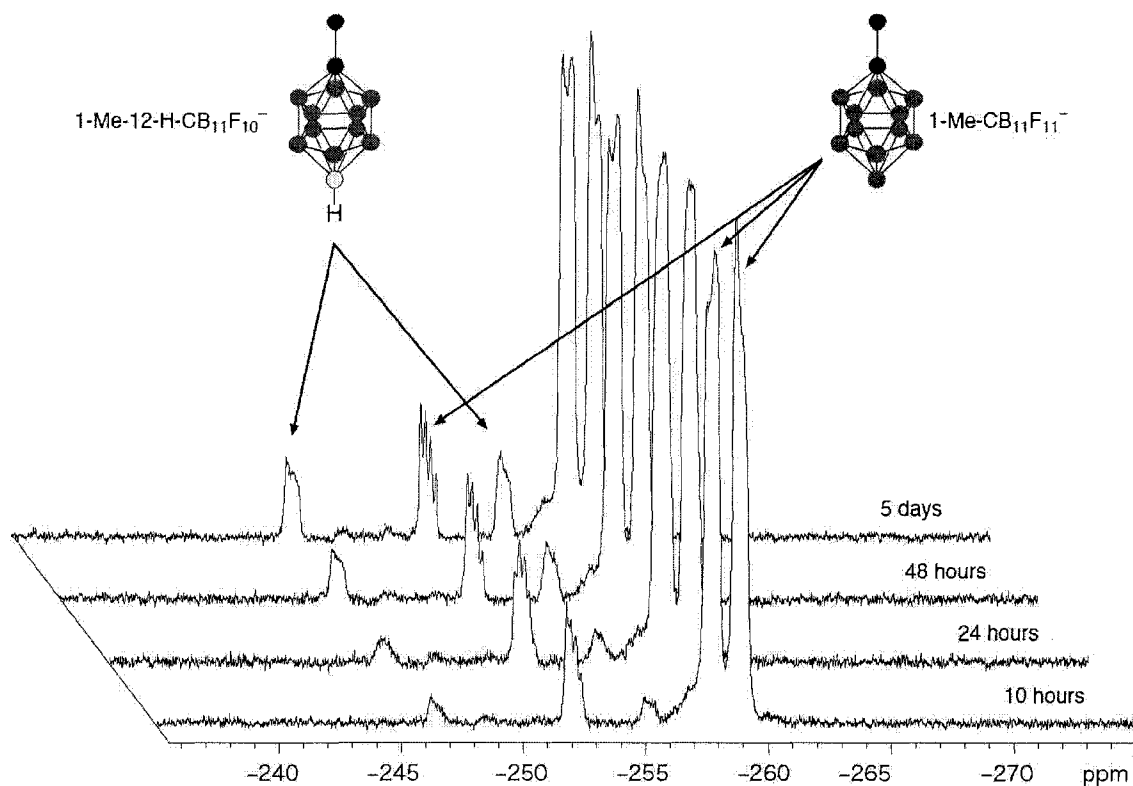


Figure 3.6. 282.4 MHz ^{19}F NMR spectra of reaction mixture from the time period between 10 hours to 5 days after the addition of two equivalents (based on Na^0) of NaHg. The intensities of the peaks are normalized to the most intense peak. From the spectra, it can be seen that $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ anion can be produced selectively. There was no multiply defluorinated species.

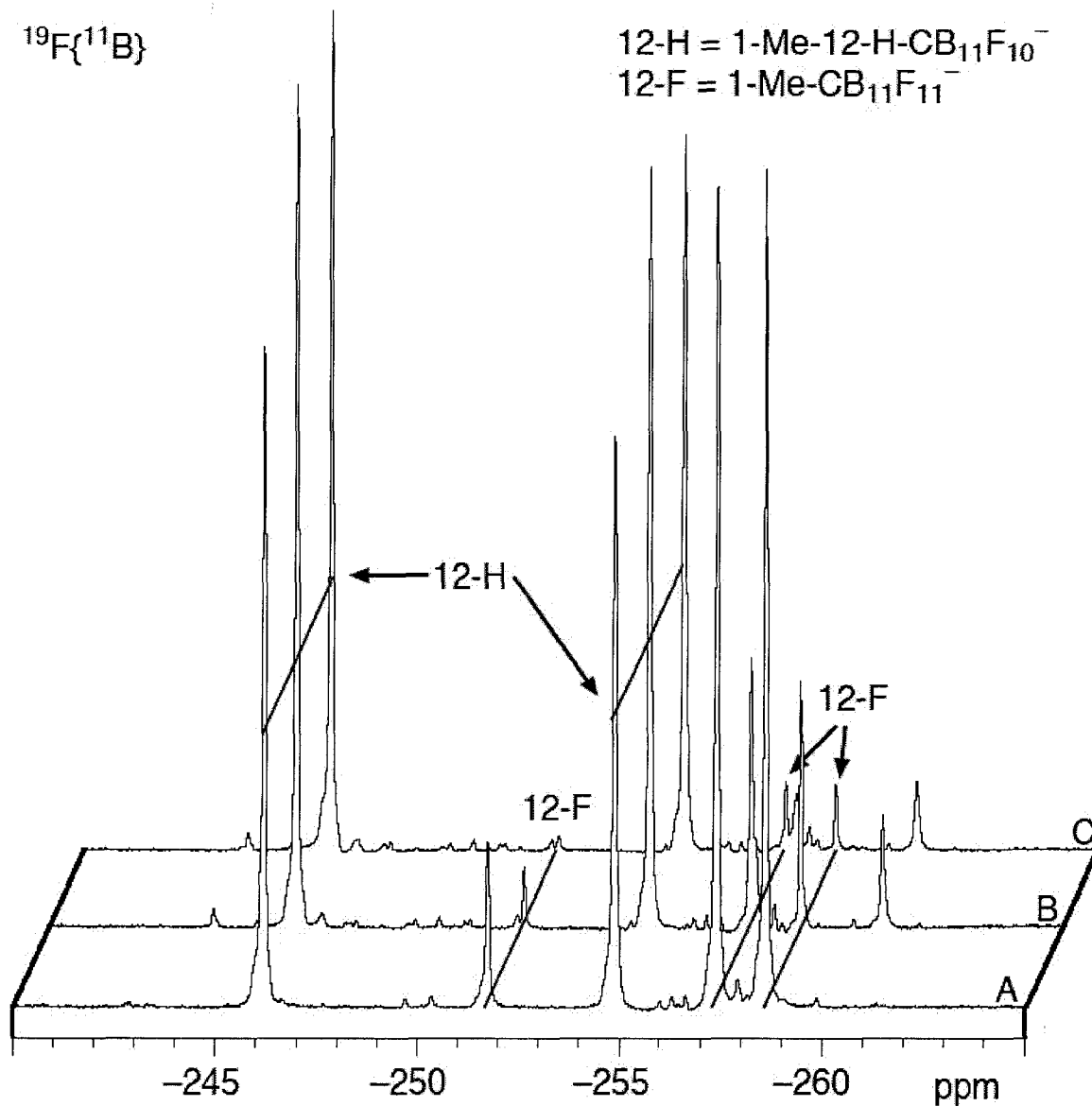


Figure 3.7. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of reaction mixtures from consecutive addition of NaHg in DME. A: 1 week after the first addition of five equiv. of NaHg. B: 1 week after the second addition of five equiv. of NaHg. C: 1 week after the third addition of large excess of NaHg. The peaks that are marked as 12-H and 12-F are for 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ and 1-Me- $\text{CB}_{11}\text{F}_{11}^-$, respectively. In each spectrum, the intensities of the peaks are normalized to the most intense peak.

the conversion reached 93% without formation of significant amount of byproducts such as multiple defluorination products and 1-Me-X-H-CB₁₁F₁₁⁻ (X ≠ 12).

In addition to the defluorination reaction carried out in DME, two separate experiments showed that 12-H product could also be formed when diethylether or toluene was used as a solvent. In case of toluene, Cs(1-(ω-decenyl)-CB₁₁F₁₁) (this compound was used instead of Cs(1-Me-CB₁₁F₁₁) simply because it is not soluble in toluene) was reduced with NaHg to form 1-(ω-decenyl)-CB₁₁F₁₀⁻ anion with more than 90% conversion.

By using NaHg as a reducing agent, alkylation of the B12 vertex was attempted by addition of MeI as an alkylating agent. However, in presence of NaHg, MeI simply reacted with NaHg and no defluorination was observed. In order to explore the possibility of synthesizing various 1-Me-12-X-CB₁₁F₁₀⁻ derivatives and to investigate the reactivity of the intermediate, several reactions were performed in an NMR tube. For alkylation, MeI was used as an alkylating agent. First, Cs(1-Me-CB₁₁F₁₁) was reacted with NaHg in DME in a Schlenk flask. A small portion of the reaction mixture was transferred to an NMR tube with a Teflon screw cap. As shown in Figure 3.8 (top), the ¹⁹F{¹¹B} NMR spectrum of the reaction mixture before the addition of MeI showed intense peaks from the intermediate at -210 and 211 ppm, 1-Me-12-H-CB₁₁F₁₀⁻ at -246.2 and -254.9 ppm, and 1-Me-CB₁₁F₁₁⁻ at -251.8, -257.7–258.7 ppm. (The presence of the intermediate after removal of NaHg gave the idea about the formation of 1-Me-12-H-CB₁₁F₁₀⁻. At room temperature, the intermediate reacts with the solvent slowly. This means that by lowering the temperature, the formation of 1-Me-12-H-CB₁₁F₁₀⁻ may be slowed down. The effect of the reaction temperature on the formation of 1-Me-12-H-CB₁₁F₁₀⁻ will be discussed later in this chapter.) After addition of excess MeI to this mixture, the peaks from the intermediate completely disappeared and two new peaks at -248.2 and -256.6 ppm for 1,12-Me₂-CB₁₁F₁₀⁻ were observed. This result suggested that it is possible to produce a variety of 1-Me-12-R-CB₁₁F₁₁⁻ using different alkylating agents.

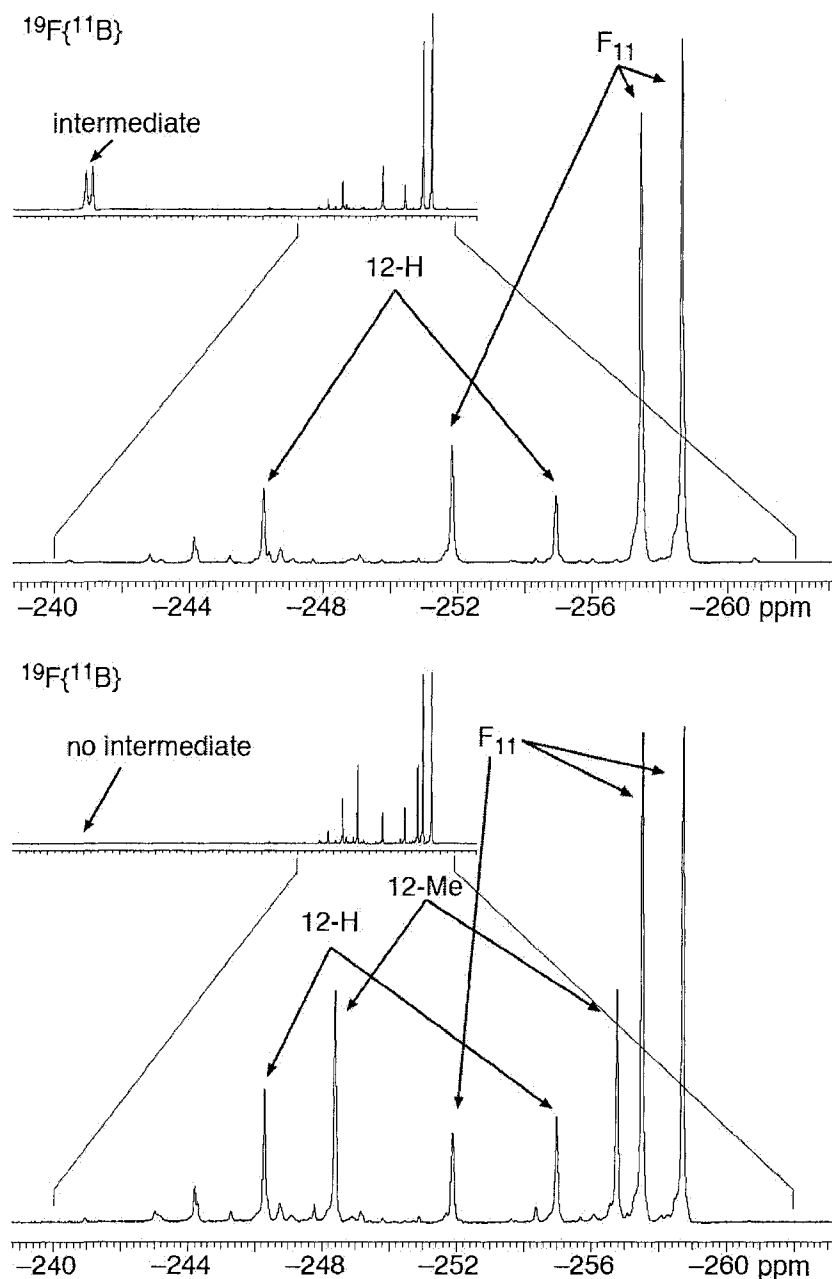


Figure 3.8. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR of the reaction mixture obtained from the reaction between Cs(1-Me-CB₁₁F₁₁) and NaHg in DME (top), and the mixture after addition of excess MeI (bottom). After the addition of MeI, the peaks from the intermediate completely disappeared and two new peaks at -248.2 and -256.6 ppm appeared due to the formation of 1,12-Me₂-CB₁₁F₁₀⁻. (12-H = 1-Me-12-H-CB₁₁F₁₀⁻, F₁₁ = 1-Me-CB₁₁F₁₁⁻, 12-Me = 1,12-Me₂-CB₁₁F₁₀⁻)

By employing the same method which was used for the reaction between the intermediate and MeI, the effect of the addition of excess dry oxygen gas was also examined. For this experiment, oxygen gas was dried by passing through a trap filled with glass fiber at $-196\text{ }^{\circ}\text{C}$ and added to the intermediate solution in an NMR tube. Figure 3.9 shows the $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of the reaction mixture before and after the addition of oxygen. The color of the mixture before the addition of oxygen gas was orange. Presumably, this is due to the large amount of the intermediate. In fact, after the addition of oxygen, the color faded and turned colorless in seconds, and white precipitate was formed. The disappearance of the intermediate was also confirmed with the $^{19}\text{F}\{^{11}\text{B}\}$ NMR. The spectrum of the mixture after the addition of oxygen showed that the intermediate was completely consumed. The spectrum also showed that there were two new peaks at -255.3 and -260.5 ppm. The integration of the peaks before and after the addition of oxygen showed that 77% of the intermediate was converted to the new species, and 23% was converted to 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$. When the mixture containing the new species was exposed to air or water, the peaks due to the new species completely disappeared and formed two different new peaks at -256.5 and -257.6 ppm (Figure 3.10). The mass spectrometric analysis of this mixture shown in Figure 3.10, showed two sets of peaks at m/z 337.3 and 354.3. The peaks which has the maximum at 337.3 is from 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$, and the peaks which have the maximum at 354.3 corresponds to two overlapped peaks from 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ (m/z 355) and 1-Me-12-OH- $\text{CB}_{11}\text{F}_{10}^-$ (m/z 353). (The intensities of these peaks in the mass spectrum do not match with the intensities in the NMR spectrum. This is due to different sensitivities of the instrument towards these anions.)

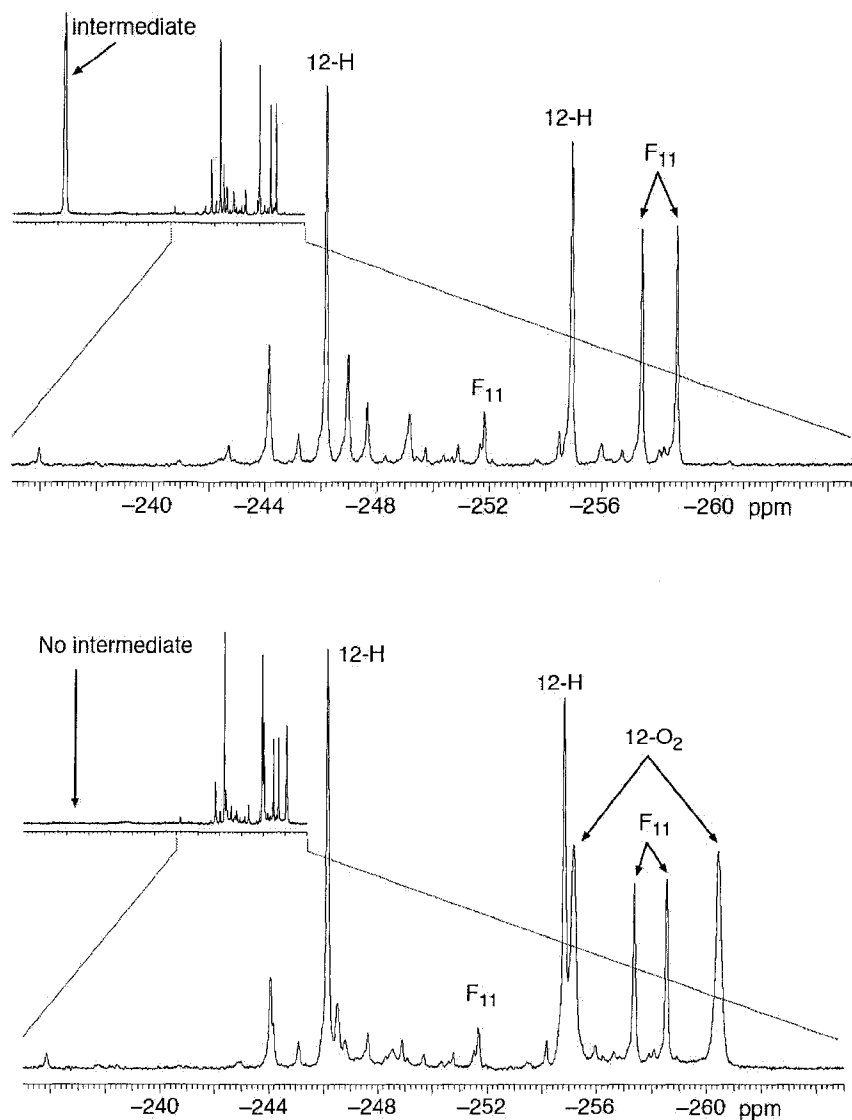


Figure 3.9. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of the reaction mixture obtained from the reaction between Cs(1-Me-CB₁₁F₁₁) and NaHg in DME (top), and the mixture after the addition of excess dry oxygen gas (bottom). After the addition of oxygen, the peaks from the intermediate disappeared and two new peaks at -255.3 and -260.5 ppm appeared. The identity of these peaks have not been determined, however, it may be due to 1-Me-12-O₂-CB₁₁F₁₀²⁻.

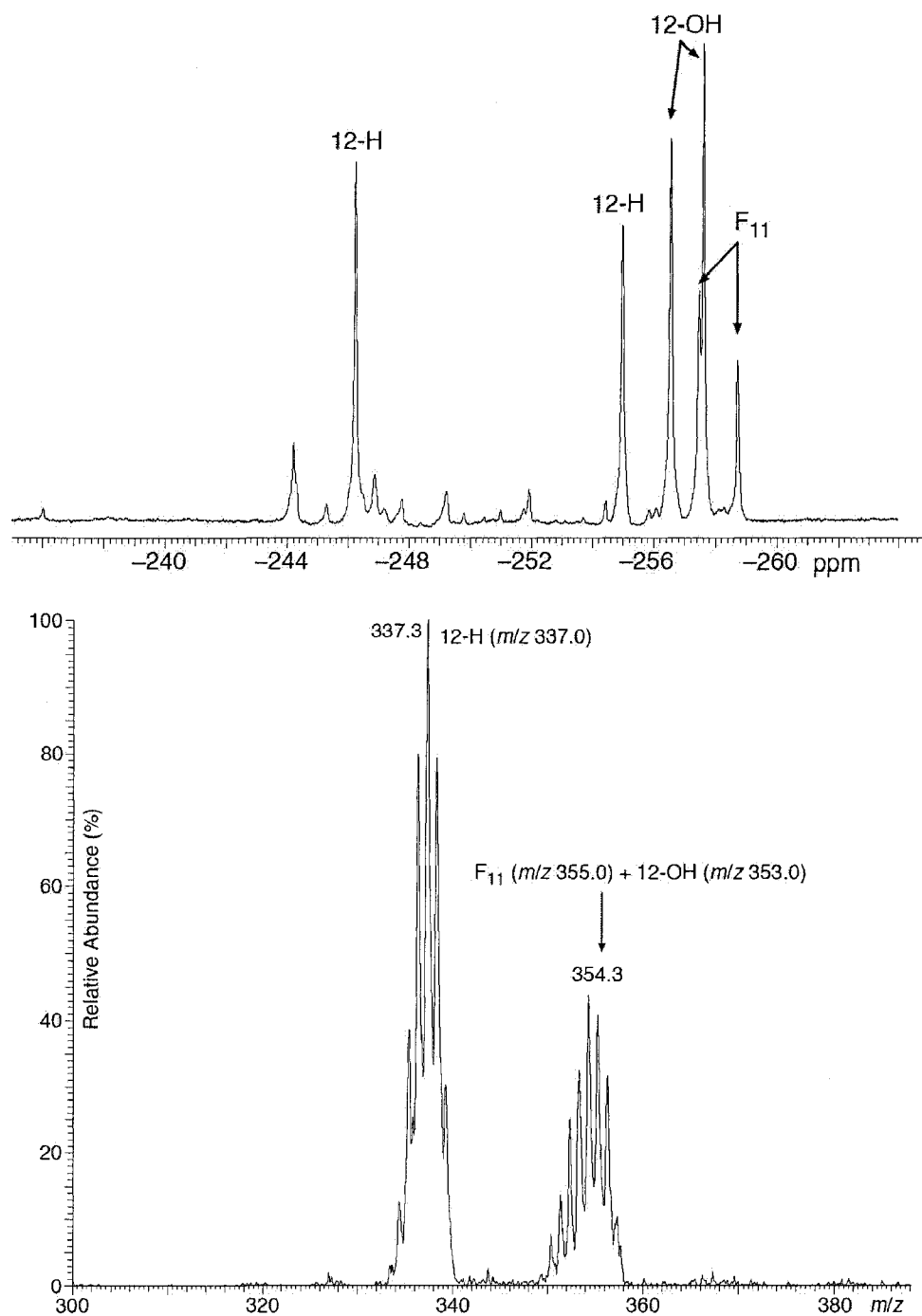


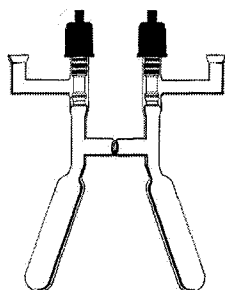
Figure 3.10. Top: 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum of the mixture after addition of water. Bottom: negative-ion electrospray-ionization mass spectrum of the mixture. The mass spectrum indicate the presence of 1-Me-12-OH- $\text{CB}_{11}\text{F}_{10}^-$, which presumably is the origin of the peaks at -256.5 and -257.6 ppm in the NMR spectrum.

In summary, NaHg appeared to be a good reducing agent to selectively defluorinate the B12 vertex without formation of products from multiple defluorination. However, the reaction was extremely slow and consecutive addition of NaHg was necessary to completely defluorinate the given amount of 1-Me-CB₁₁F₁₁⁻. Further functionalization of the B12 vertex was possible by separating the intermediate solution from NaHg and addition of functionalizing agent such as MeI and oxygen followed by water. However, because of the slow defluorination process, generation of 1-Me-12-H-CB₁₁F₁₀⁻ in the intermediate solution was inevitable.

(d) Defluorination of Cs(1-Me-CB₁₁F₁₁) with sodium naphthalenide. The defluorination reaction of Cs(1-Me-CB₁₁F₁₁) with Na in presence of DHAN gave us an idea of homogeneous reducing agents. Also, the results describe above, using the intermediate as a precursor to synthesize 1-Me-12-R-CB₁₁F₁₀⁻, indicated a possibility of one-pot synthesis of a variety of 12-R derivatives. In order to choose an appropriate reducing agent, the reduction potential of Cs(1-Me-CB₁₁F₁₁) was measured. Figure 3.11a shows the cyclic voltammogram of an equimolar solution of Cs(1-Me-CB₁₁F₁₁) and bis(pentamethylcyclopentadienyl) iron(II) (FeCp^{*}₂) in 0.1 M TBAP/DME at 25 °C. The voltammogram demonstrated reversible redox peaks, and a cathodic current as large as the current for FeCp^{*}₂, which indicates one-electron reduction ($E_{p,a} = -2.6$ V vs. FeCp^{*}₂^{+ / 0}). Figure 3.11b shows the cyclic voltammogram of naphthalene with equimolar FeCp^{*}₂ in 0.1 M TBAP/DME at 25 °C. It shows that the reduction of naphthalene to form naphthalenide radical occurs at -2.7 V, which is just below the reduction potential of Cs(1-Me-CB₁₁F₁₁). This demonstrated that an alkali metal salt of naphthalenide would be a promising reducing agent for selective defluorination of 1-Me-CB₁₁F₁₁⁻.

In order to explore defluorination reactions quantitatively, all reactions using sodium naphthalenide (NaNaph) were performed in an H-tube, unless otherwise noted.

By using an H-tube, DME solution of NaNaph is generated in one side of the vessel, from a certain equivalent(s) (with respect to the amount of Cs(1-Me-CB₁₁F₁₁)) of naphthalene and excess sodium metal. This solution was transferred to the other side, which was filled with a DME solution of Cs(1-Me-CB₁₁F₁₁), by filtration. In addition, when using this apparatus, the temperature can be controlled from the beginning to the end of defluorination/alkylation with a simple setup.



H-tube

The ratio of carborane anion and the reducing agent must be very important to understand the reductive defluorination mechanism, and to avoid multiple defluorination. To study the effect of the amount of NaNaph and 1-Me-CB₁₁F₁₁[−] anion, several separate reactions were performed with various amount of NaNaph. The reaction temperature was kept at −20 °C to examine the possibility of suppressing the formation of 1-Me-12-H-CB₁₁F₁₀[−]. Figure 3.12 shows the ¹⁹F{¹¹B} NMR spectrum of the reaction mixture obtained from the reduction of Cs(1-Me-CB₁₁F₁₁) with one, two, or four equivalents of NaNaph followed by MeI addition. The conversions of 1-Me-CB₁₁F₁₁[−] to form 1,12-Me₂-CB₁₁F₁₀[−] anion for one, two, and four equivalents of NaNaph were 21, 86, and 99%, respectively. Although the H-tube is an excellent apparatus to transfer and mix solutions relatively quantitatively, small amount of the NaNaph solution will still remain in the other side of the H-tube. Considering this loss, it was found that two equivalents of NaNaph is necessary to reduce all 1-Me-CB₁₁F₁₁[−] anion. In fact, a separate experiment

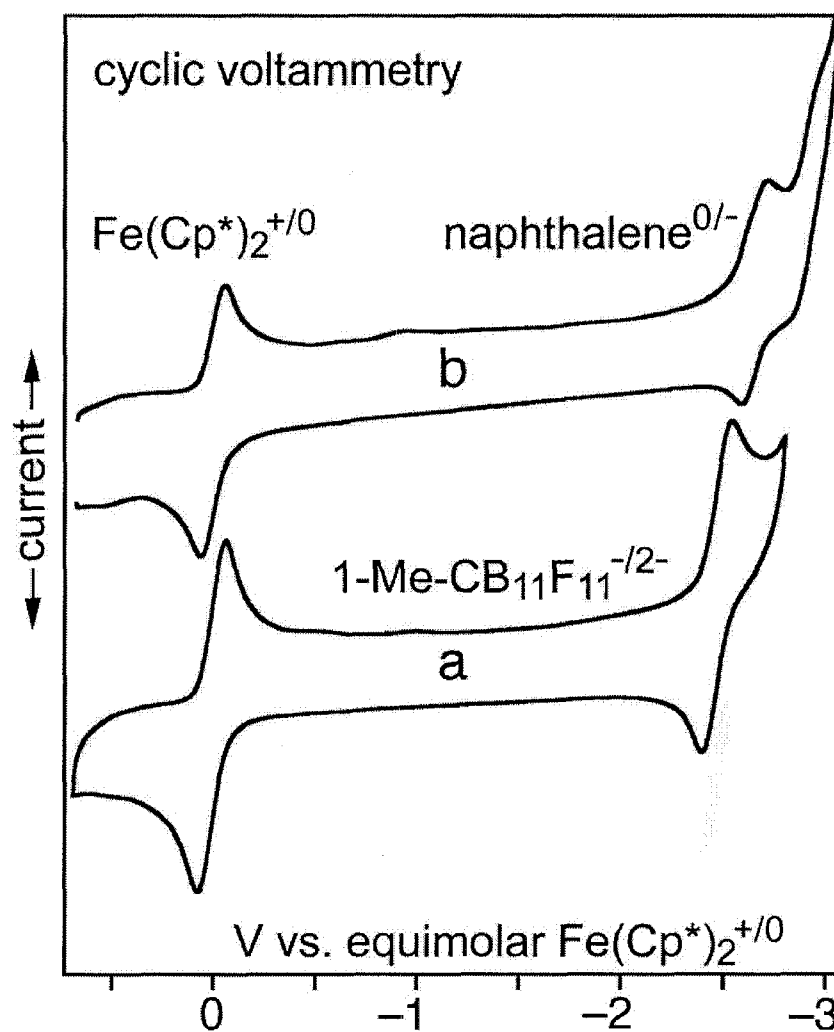


Figure 3.11. Cyclic voltammograms of $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ (a), and naphthalene (b) in the presence of equimolar FeCp^*_2 in 0.1 M TBAP in DME at 25 °C.

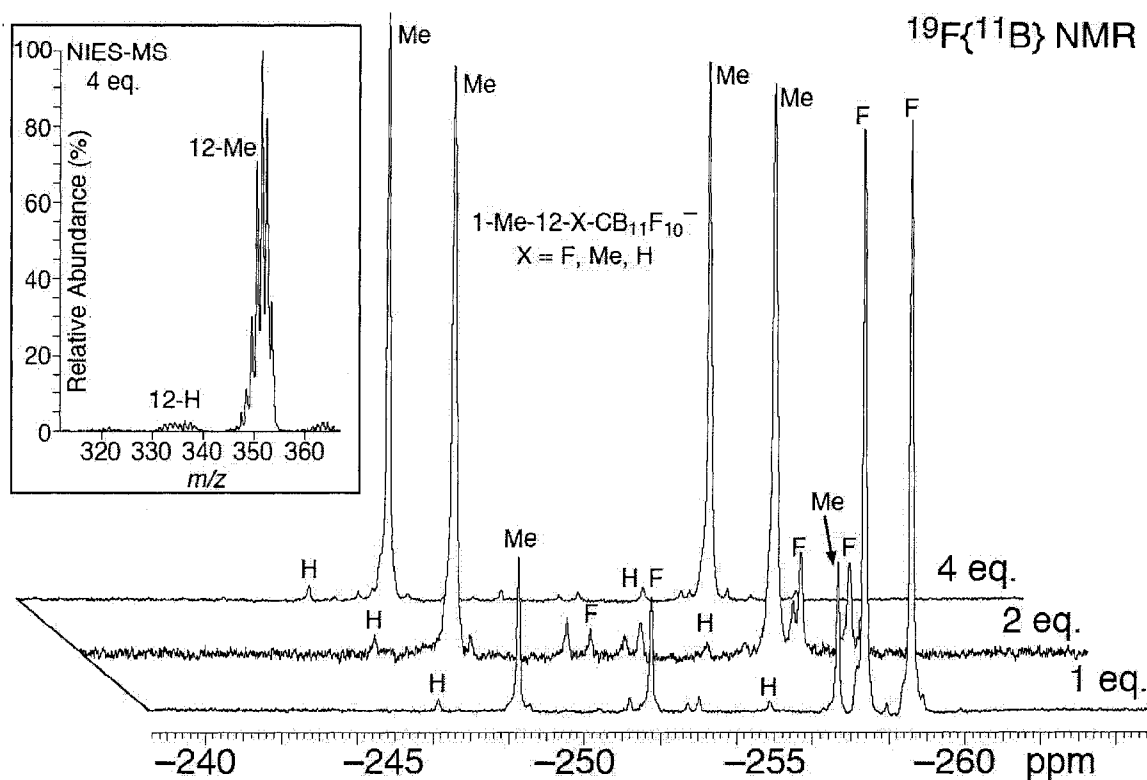


Figure 3.12. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of reaction mixtures in DME from one, two, or four equivalents of NaNaph followed by MeI addition, and the negative-ion electrospray-ionization mass spectrum (inset) of the reaction product (the temperature was kept at $-20\text{ }^{\circ}\text{C}$ during the entire reaction). It is evident that one equivalent of NaNaph is not enough to reduce all $1\text{-Me-CB}_{11}\text{F}_{11}^-$. The mass spectrum shows that the reaction is not enough to reduce all $1\text{-Me-CB}_{11}\text{F}_{11}^-$. The mass spectrum shows that the reaction with four equivalents of NaNaph produces mainly $1\text{-Me-CB}_{11}\text{F}_{10}^-$ without multiple-defluorination products. In addition, by carrying out the reaction at $-20\text{ }^{\circ}\text{C}$, the formation of $1\text{-Me-12-H-CB}_{11}\text{F}_{11}^-$ was suppressed dramatically.

with 2.5 equivalents of NaNaph did not have any starting material left in the product mixture. Another important observation is that even with four equivalents of NaNaph, there is no sign of multiple defluorination in NIES-MS spectrum (m/z for two of the multiple defluorinated species are 347.0 (1-Me-CB₁₁F₉Me₂⁻), and 333.0 (1,12-Me₂-CB₁₁HF₉⁻)). Another important result is that by lowering the reaction temperature to -20 °C, the formation of 1-Me-12-H-CB₁₁F₁₁⁻ was suppressed dramatically.

The reactions using an H-tube showed another useful fact. When one equivalent of NaNaph was used, the reaction mixture turned reddish orange rapidly (seconds) after mixing the NaNaph solution and the carborane solution. When two equivalents of NaNaph were used, the color of the mixed solution was more intense. With four equivalents, the solution was dark green with slightly brown tint. The red color is certainly due to the formation of the intermediate. These observations strongly support that two equivalents of NaNaph are necessary to defluorinate all starting materials. In all cases, after addition of excess (with respect to the amount of NaNaph) MeI, the solution turned cloudy, but colorless or faintly yellow. Presumably, the precipitation was due to the formation of NaI and NaF, and the color change was due to disappearance of the intermediate. Similar color change was observed when the reaction was performed at room temperature without addition of an alkylating agent. Figure 3.13 shows the color change of the reaction mixture obtained from mixing Cs(1-Me-CB₁₁F₁₁) and 2.5 equivalents of NaNaph in DME. The photographs were taken between one minute to 13 days after mixing the NaNaph and the carborane solutions. Figure 3.13 A shows the dark green color of the NaNaph solution due to the naphthalenide radical anion. Figure 3.13 B shows the reaction minute after mixing the two solutions at -55 °C. This color of the reaction mixture changed from dark green to red (in seconds) indicating the formation of the intermediate is a fast reaction. After mixing the solutions, the temperature was gradually raised to room temperature. After 18 hours, the formation of precipitate

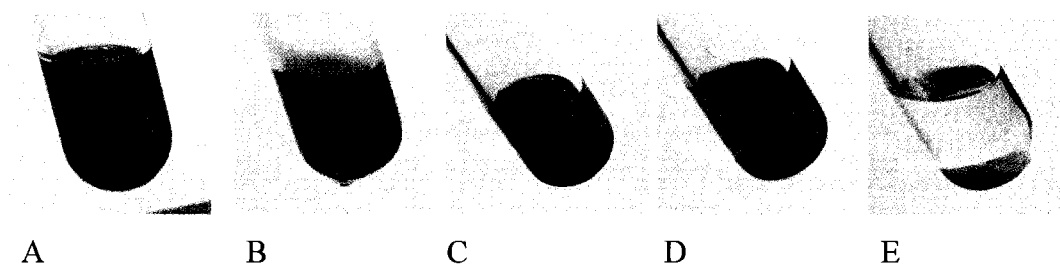


Figure 3.13. Photographs of the color changes observed for defluorination of Cs(1-MeCB₁₁F₁₁) in DME with 2.5 eq. of sodium naphthalenide. The defluorination reaction was performed at $-55\text{ }^{\circ}\text{C}$, and after mixing the carborane and NaNaph, the temperature was raised to the ambient temperature gradually. A: NaNaph in DME, B: 1 minute after mixing Cs(1-MeCB₁₁F₁₁) and NaNaph, C: 18 hours after mixing, D: 40 hours after mixing, E: 13 days after mixing.

was observed (Figure 3.13 C). After 13 days, the solution became colorless (Figure 3.13 E).

Figure 3.14 shows the NIES-MS and $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of the product mixture from this experiment. Based on the spectra, the major product was 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ with 73% compositional purity. The byproducts were 1-Me- $\text{CB}_{11}\text{H}_2\text{F}_9^-$, 1-Me- $\text{CB}_{11}\text{RF}_{10}^-$ ($\text{R} = \text{C}_4\text{H}_9\text{O}_2$), and undetermined CB_{11} derivative which has m/z value of 349.5. The presence of 1-Me- $\text{CB}_{11}\text{H}_2\text{F}_9^-$ confirmed that the temperature control is an important factor to prevent multiple defluorination. As described above, when the reaction temperature was kept at $-20\text{ }^\circ\text{C}$ until the addition of an alkylating agent, multiple defluorination did not occur even with four equivalents of NaNaph. These results indicated that at low temperature, multiple defluorination can be prevented. Assuming that the formation of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ has a radical mechanism, the amount of 1-Me- $\text{CB}_{11}\text{RF}_{10}^-$ was much smaller than 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$, and this is probably due to the sterics of R group. The structure of $\text{C}_4\text{H}_9\text{O}_2$ is probably not $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, but $\text{CH}_3\text{OCHCH}_2\text{OCH}_3$. The radical of the former structure is less stable than the latter, and the latter is bulkier.

In summary, by using NaNaph, selective defluorination/alkylation of 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ was successfully achieved using two or more equivalents of NaNaph. By lowering the reaction temperature to $-20\text{ }^\circ\text{C}$, the formation of 1-Me-1-H- $\text{CB}_{11}\text{F}_{10}^-$ was significantly suppressed. This allowed us to selectively synthesize new 1-Me-12-R- $\text{CB}_{11}\text{F}_{10}^-$ anions in high yield.

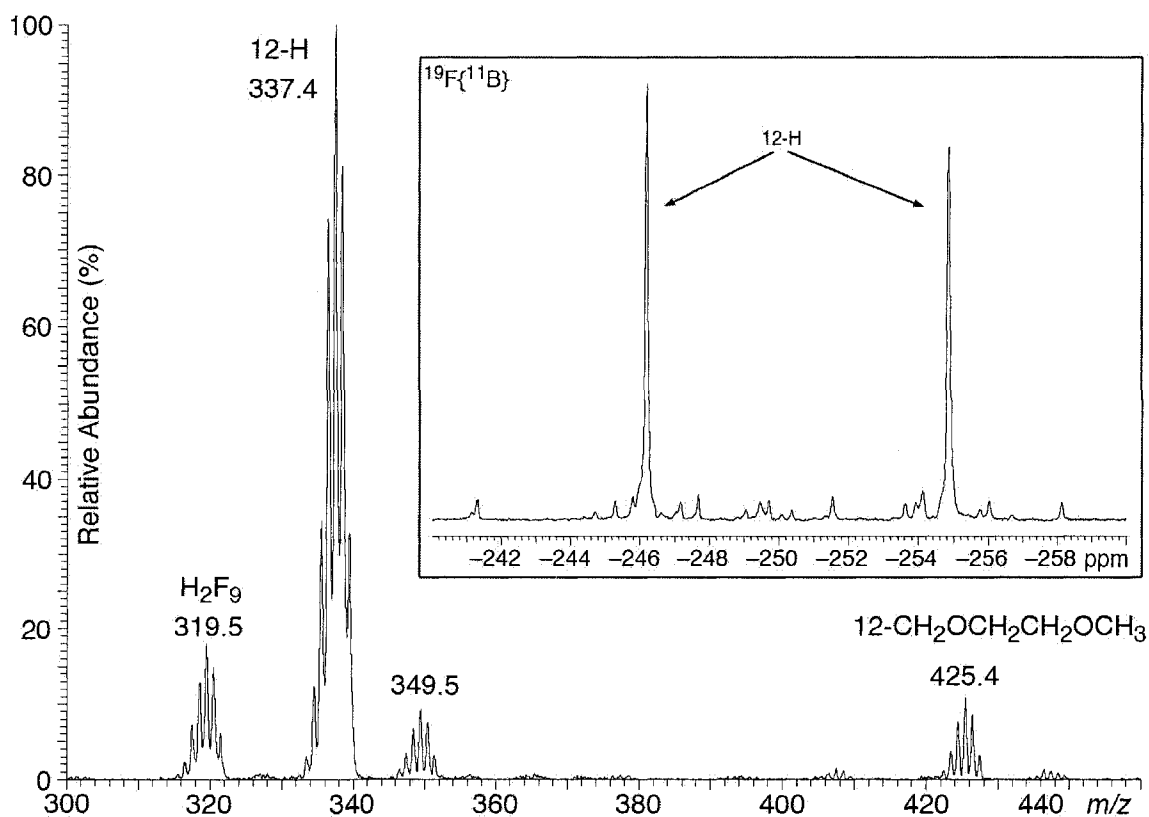


Figure 3.14. Negative-ion electrospray-ionization mass spectrum and 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum of the product mixture obtained from the reaction of $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and 2.5 equivalents of NaNaph at room temperature. The product mixture contained $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ (12-H), $1\text{-Me-CB}_{11}\text{H}_2\text{F}_9^-$ (H_2F_9), $1\text{-Me-CB}_{11}\text{RF}_{10}^-$ (RF_{10}), and an undetermined product at m/z 349.5.

(e) The reaction intermediate and the possible reaction mechanism. As described above, during the defluorination reaction with NaHg or NaNaph, an intermediate species which has ^{19}F NMR chemical shifts at ca. $\delta -210$ was observed. It was evident from the visual observation of the reaction, and the spectrometric analysis of the product, that in order to reduce 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ quantitatively, two equivalents of NaNaph are required. From these results, it is reasonable to assume that the intermediate maybe an anion with 3- charge. The $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum of the intermediate solution in DME, shown in Figure 3.15, showed two peaks, at -210.3 and -211.1 ppm, with an intensity ratio that is approximately 1:1. These peaks were significantly broadened when no ^{11}B decoupling was used. These observations suggest that these fluorine atoms are bonded to the belt boron atoms and are on the upper and lower belts. In the $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum, the fluorine peak from B12-F12 was not observed, however, the visual observation of the reaction did not show precipitation before addition of an alkylating agent. Therefore it is reasonable to assume that in the intermediate, the fluorine atom on the B12 vertex is somehow bonded.

Another reason to believe that the intermediate has a 3- charge is that based on the DFT calculation, 1-Me- $\text{CB}_{11}\text{F}_{11}^{3-}$ is diamagnetic. The DFT calculations performed by Dr. Alexey A. Popov in Moscow State University indicated that LUMO of 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ is singly degenerate. If the intermediate has 2- charge, it would be paramagnetic. The $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum, shown in Figure 3.15, showed that the intermediate is not paramagnetic.

To investigate the identity of the intermediate and the reductive-defluorination reaction mechanism, the reaction was performed electrochemically. Figure 3.16 shows the series of cyclic voltammograms obtained at room temperature in 0.1 M TBAP/DME. The cyclic voltammogram of equimolar $\text{Fe}(\text{Cp}^*)_2$ and $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ in 0.1 M TBAP/DME solution, shown in Figure 3.16B, exhibited a reversible one-electron

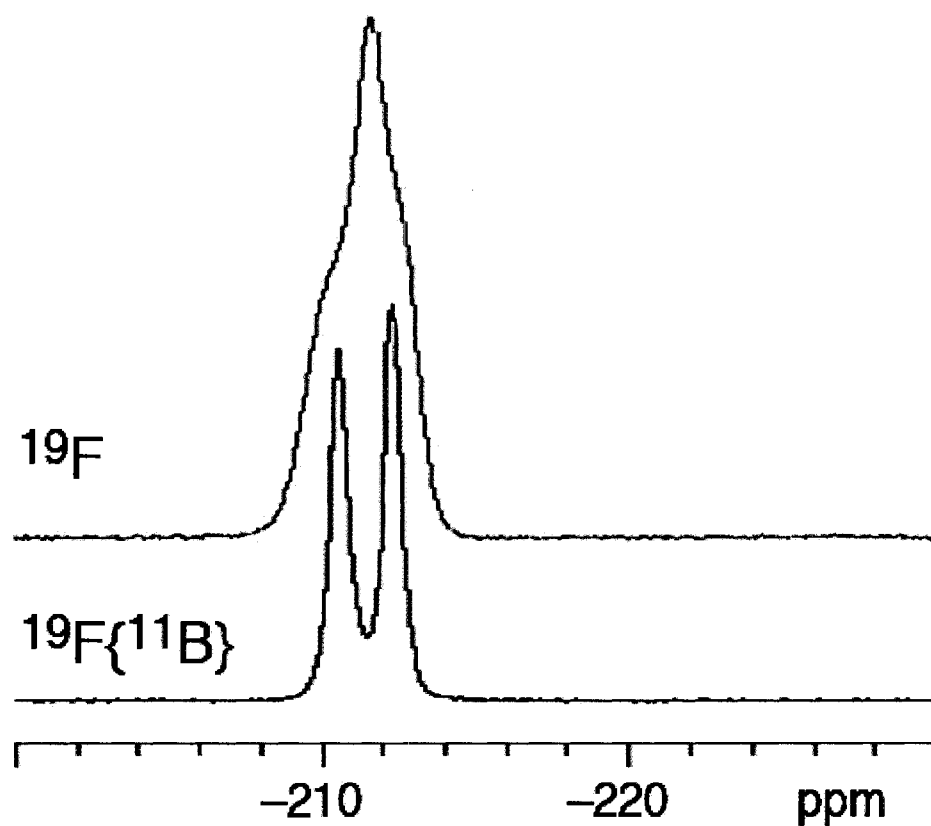
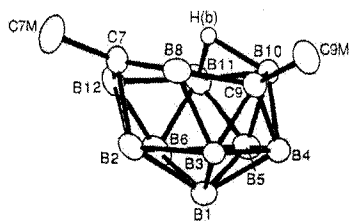


Figure 3.15. 282.4 MHz ^{19}F and $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of the intermediate solution in DME. The ^{19}F NMR spectrum shows broadening of the peaks due to the ^{19}F - ^{11}B coupling.

reduction at -2.6 V vs. $\text{Fe}(\text{Cp}^*)_2$, presumably forming a $1\text{-Me-CB}_{11}\text{F}_{11}^{2-}$ radical anion. This result contradicts the assumption based on H-tube reactions. In order to make the conditions close to the actual H-tube reactions, excess Na^+ ions were added as NaClO_4 . Interestingly, the height of the peak for reduction of $1\text{-Me-CB}_{11}\text{F}_{11}^-$ is doubled the height of the reduction peak for equimolar $\text{Fe}(\text{Cp}^*)_2$, this means that the presence of excess Na^+ ions induced irreversible *two-electron* reduction at the same potential as reversible one-electron reduction (Figure 3.16C). Moreover, additions of excess Li^+ or K^+ ions showed the same effect. Interestingly, when excess 18-crown-6 was added to the solution containing $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and excess NaClO_4 , the reversible one-electron reduction was restored (Figure 3.16D). These results suggest that the intermediate is, in fact, the 3- anion. Also, to produce the intermediate, strong electrophiles, such as Li^+ , Na^+ , and K^+ ions, but not Cs^+ ion, are necessary. (A separate electrochemical experiment with $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ excess Cs^+ as $\text{Cs}(\text{CB}_{11}\text{H}_{12})$ did not exhibit two-electron reduction, but showed one-electron irreversible reduction at -2.8 V. Another interesting fact obtained from the electrochemical experiment is that reduction of $1\text{-Me-CB}_{11}\text{F}_{11}^-$ anion does not undergo a cage-opening rearrangement. Although the cluster electron count of the 12-vertex-*closo*- $\text{CB}_{11}\text{F}_{11}^{3-}$ cluster ($2n + 4 e^- = 28 e^-$; $n = 12$) is the same as the kinetic¹⁹ and thermodynamic²⁰ isomers of 12-vertex *nido*-7,9- $\text{Me}_2\text{-7,9-C}_2\text{B}_{10}\text{H}_{11}^-$, which are formed by two-electron reduction of *closo*- $\text{Me}_2\text{-C}_2\text{B}_{10}\text{H}_{10}$ followed by protonation,²¹ the ^{19}F NMR spectrum of $\text{CB}_{11}\text{F}_{11}^{3-}$ and the structures of salts of $1\text{-Me-12-R-CB}_{11}\text{F}_{10}^-$ ($\text{R} = \text{H}, \text{Me}$), described above, leave no doubt that $\text{CB}_{11}\text{F}_{11}^{3-}$ is a 12-vertex-*closo* trianion.



nido-7,9- $\text{Me}_2\text{-7,9-C}_2\text{B}_{10}\text{H}_{11}^-$

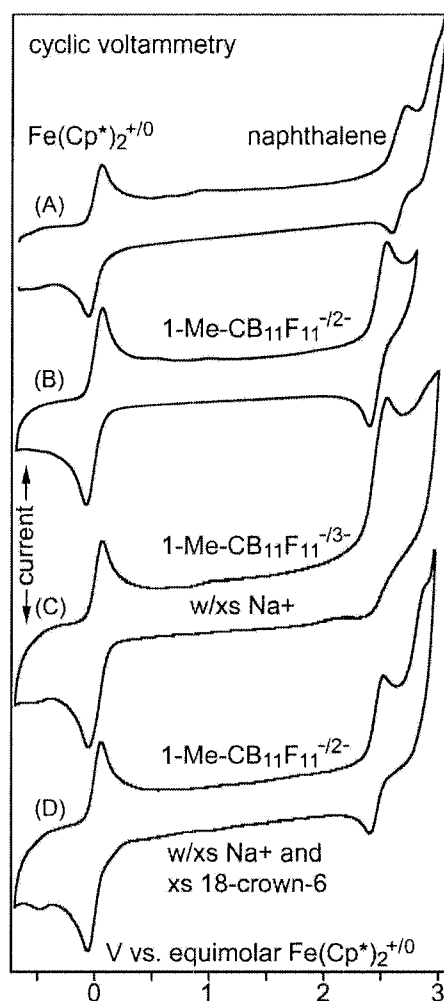


Figure 3.16. The cyclic voltammograms of (A): naphthalene and Fe(Cp*)₂; (B): 1:1 molar ratio of Fe(Cp*)₂ and Cs(1-Me-CB₁₁F₁₁); (C): excess NaClO₄ added to (B); (D): excess 18-crown-6 added to (C). All measurements were performed in 0.1 M TBAP/DME. After addition of excess Na⁺, it clearly shows an irreversible two-electron reduction process. The addition of 18-crown-6 to the solution containing Na⁺ restored the reversible one-electron reduction.

The irreversible reduction of the 3- anion suggests that the B12-F12 bond is cleaved. If the B12-F12 bond were still present, outer-sphere electron transfer between 1-Me-CB₁₁F₁₁³⁻ and a ferrocenium cation oxidant should occur. In order to examine if the outer-sphere electron transfer occurs, the intermediate was treated with 1,1',3,3'-tetrakis-(2-methyl-2-hexyl)ferrocenium nitrate (DEC⁺NO₃⁻).²² When the ferrocenium salt was added to the intermediate solution in DME, the red color from the intermediate disappeared rapidly. The ¹⁹F{¹¹B} NMR of the product mixture showed no sign of the outer-sphere electron transfer. The disappearance of the color was due to formation of 1-Me-12-H-CB₁₁F₁₀⁻. We speculate that 1-Me-12-H-CB₁₁F₁₀⁻ was formed by proton abstraction from the DEC⁺ cation. The 1-Me-12-H-CB₁₁F₁₀⁻ anion was also formed when TBAP was added to the intermediate solution. The reaction occurred rapidly, based on the color change and ¹⁹F{¹¹B} NMR spectrum. In this case, presumably, proton was abstracted from the alkyl groups of the TBA⁺ cation the mechanism of which is similar to the Hofmann degradation of NR₄⁺ cations.²³

To summarize the observations with the intermediate; (i) use of 1.0 equivalent of NaNaph led to the formation of only 0.5 equivalent of Cs(1,12-Me₂-CB₁₁F₁₀); (ii) the intermediate is diamagnetic; (iii) treatment of the intermediate with more than two equivalents of the one-electron oxidizing agent DEC⁺NO₃⁻, led not to the recovery of 1-Me-CB₁₁F₁₁⁻, but to the rapid (seconds) formation of 1-Me-12-H-CB₁₁F₁₀⁻; (iv) the intermediate reacted only slowly (days) with DME to form primarily 1-Me-12-H-CB₁₁F₁₀⁻; (v) the cyclic voltammogram of an equimolar solution of 1-Me-CB₁₁F₁₁⁻ and FeCp*₂ in the presence of several equivalents of NaClO₄ exhibited a cathodic current for 1-Me-CB₁₁F₁₁⁻ that was twice as large as for the FeCp*₂⁺⁰ couple, indicating of an irreversible two-electron reduction; (vi) addition of excess TBAP to the intermediate induced the rapid (seconds) formation of 1-Me-12-H-CB₁₁F₁₀⁻; (vii) no precipitate was observed upon generation of the intermediate. Based on these results, we propose the structure of the intermediate to be B12-F12 cleaved, but the fluorine atom is connected

with the carborane structure with $\text{B12-F}\cdots\text{Na}^+$ or $\text{B12}\cdots\text{Na}^+\cdots\text{F}^-$ bond. The drawings of the structures are shown in Figure 3.17. With these structures, the absence of the peak from the fluoride ion in ^{19}F NMR can be explained as a result of the broadening of the peak caused by ^{23}Na – ^{19}F coupling. The structure B, shown in Figure 3.17 is probably not the case. If this is the correct structure, re-oxidation by outer-sphere electron transfer should occur in the presence of DEC^+ . The DFT calculated energy also showed that the structure with the $\text{B}\cdots\text{Na}^+\cdots\text{F}^-$ linkage, the DFT optimized geometry of which is shown in Figure 3.17 C, is 55 kJ/mol more stable compared to the structure with the $\text{B-F}\cdots\text{Na}^+$ linkage, the DFT optimized geometry is shown in Figure 3.17 D. However, the DFT calculation was performed with no involvement of DME molecules, therefore, more detailed computational analysis is necessary.

Another DFT calculation showed that HOMO of $1\text{-Me-CB}_{11}\text{F}_{10}^{2-}$, in which B12 does not have a fluorine atom, has the large electron distribution on the *p* orbital of the B12 vertex. The drawing of the HOMO of $1\text{-Me-CB}_{11}\text{F}_{10}^{2-}$ is shown in Figure 3.18. This result demonstrates that Na^+ can coordinate strongly using the electron rich *p* orbital on the B12 vertex, and probably this is more likely to form compared to the structure with $\text{B-F}\cdots\text{Na}^+$ linkage.

In order to identify the actual structure by the single-crystal X-ray crystallography, attempts to obtain single crystals of the intermediate were made in DME solution layered with benzene or pentane at $-15\text{ }^\circ\text{C}$. However, in both cases a dark brown oil was formed.

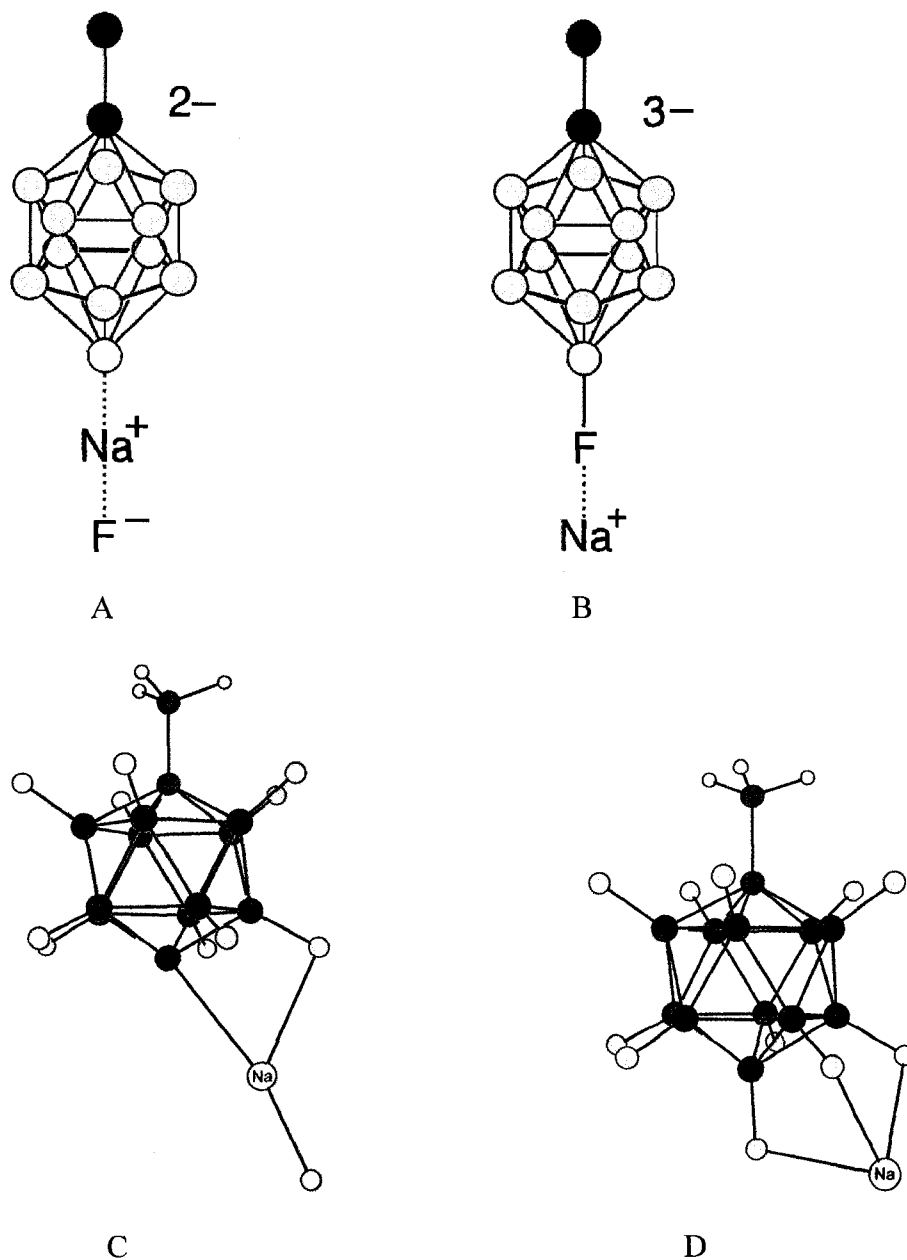
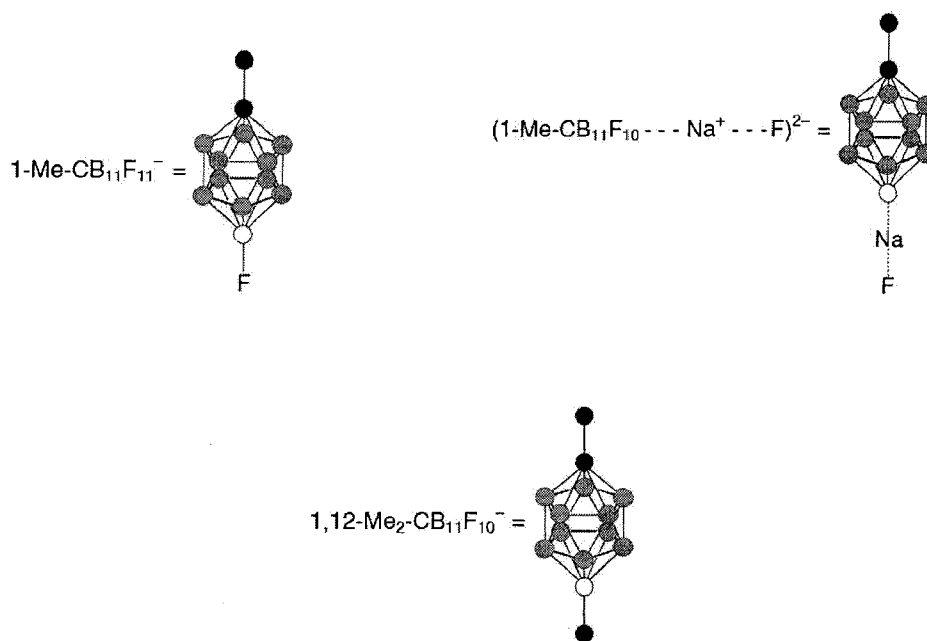
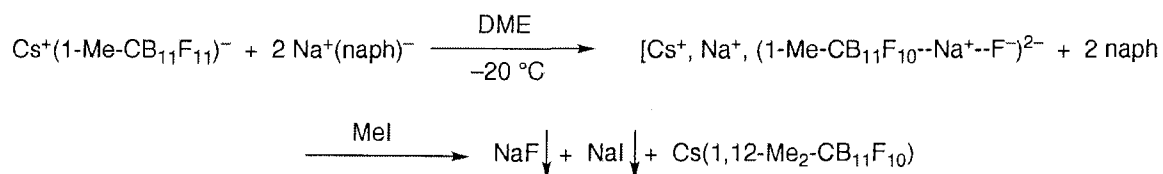


Figure 3.17. The proposed structures of the intermediate $\{\text{Na}^+1\text{-Me-CB}_{11}\text{F}_{11}\}^{3-}$ and the drawings obtained from the DFT calculations. Drawing C and D are the DFT optimized geometries for A and B, respectively. The sodium ion was placed as shown in drawings A and B prior to the optimization. The calculation showed that geometry C is 55 kJ/mol more stable than geometry D.

From all the observations described above, we propose the stoichiometric reaction equation for the defluorination/alkylation reaction to be as shown in Scheme 3.1.

In summary, of all the reducing agents examined, none of the alkali metals were appropriate for the selective defluorination of 1-Me-CB₁₁F₁₁⁻ due to the formation of product(s) from multiple defluorination. NaHg was more selective than alkali metals, however, the reaction was extremely slow, and consecutive addition of NaHg was necessary to complete the selective defluorination. With a discovery of an optimized condition, NaNaph showed the best performance. Reactions with NaNaph revealed that the defluorination reaction required at least two equivalents of the reducing agent, and enable to add an alkyl group to the B12-vertex by addition of an alkylating agent to the reaction mixture. By using the synthetic method described in this chapter, we synthesized or generated novel 1-R-12-R'-CB₁₁F₁₀⁻ anions, the results will be described in Chapter 4.



Scheme 3.1. The proposed stoichiometric reaction scheme for the two electron-reductive defluorination of Cs(1-Me-CB₁₁F₁₁) in DME. The structures of the anions are shown without the charges, and hydrogen atoms. (black: carbon; gray: B–F; white: B)

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Chapter 4 Synthesis or generation of 1-R-12-R'-CB₁₁F₁₀[−] anions

In this chapter, synthesis of 1-R-12-R'-CB₁₁F₁₀[−] (R = Me, R' = H, Me, decyl, SiPh₃, and I) are described. These anions were obtained in high selectivity (> 90%), and when possible, isolated, and the yields were obtained. In addition, NMe₄⁺, Cs⁺, or Ag⁺ salts of 1,12-Me₂-CB₁₁F₁₀[−], 1-Me-12-SiPh₃-CB₁₁F₁₀[−], and 1-Me-12-I-CB₁₁F₁₀[−], were characterized by X-ray single crystal crystallography. The detailed analyses of the crystal structures are described in Chapter 5. Some of the 1-R-12-R'-CB₁₁F₁₀[−] anions (R = Me, Et, or Bn, R' = Me, Et, or *i*-Pr) were generated, but not isolated. For these anions, the reaction condition and the spectroscopic data of the product mixture will be described. All the reactions were carried out in an H-tube at either −20 or −55 °C in DME with at least 2.5 equivalents of NaNaph as a reducing agent unless otherwise noted.

(a) Synthesis of Cs(1,12-Me₂-CB₁₁F₁₀). Since the discovery of the synthetic method to produce 1-Me-12-R-CB₁₁F₁₁[−], which was described in Chapter 3, the most extensively studied anion was 1,12-Me₂-CB₁₁F₁₀[−] because of its potential to possess lower charge asymmetry which may lead to weaken the coordinating ability. The preliminary experiments which were carried out in an NMR tube using the intermediate obtained from reduction of 1-Me-CB₁₁F₁₁[−] by NaHg showed that both MeI and methyl trifluoromethanesulfonate can be used as an alkylating agent to produce 1,12-Me₂-CB₁₁F₁₀[−] effectively. For the larger scale synthesis, MeI was used simply because it is more stable and easy to purify. The visual observation of the larger scale reaction showed rapid color change from red to colorless within several seconds and the formation of white precipitate after addition of MeI. In Figure 4.1, NIES-MS, and ¹⁹F{¹¹B} and ¹¹B{¹H} NMR spectra of the product mixture before the purification are shown. In the mass spectrum, the largest peak was seen at *m/z* 351.5, and the isotopic pattern of this peak shows good match with the simulated mass spectrum of 1,12-Me₂-CB₁₁F₁₀[−] (Figure

4.1 bottom). Along with this anion, approximately 5% (based on the integral ratio in the $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum) of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ at m/z 337.0 was also formed. The $^{19}\text{F}\{^{11}\text{B}\}$ NMR showed two major signals from upper and lower belt fluorine atoms on 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ at -248.3 and -256.8 ppm. The peaks from 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ were also seen at -246.2 and -255.0 ppm. In addition, there were six small peaks at -248.8, -251.2, -252.8, -253.7, -257.2, and -259.0 ppm. Based on the integral ratio of these signals, which is 1:2:1:2:2:2, these peaks are almost certainly for the 1,7-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ isomer that has C_s symmetry. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum showed three large peaks at -14.2, -16.4, and -23.3 ppm for 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$, and one peak at -30.5 ppm for the B12 vertex of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$, and one peak at -6.8 for 1,7-Me₂- $\text{CB}_{11}\text{F}_{10}^-$. The peaks for the B_{ub} and B_{lb} for 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ are probably overlapped and hidden behind the peaks for the B_{ub} and B_{lb} of 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$. Based on the $^{19}\text{F}\{^{11}\text{B}\}$ NMR, the relative amounts of 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$, 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$, and 1,7-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ is 92, 1.4, and 6.6%, respectively. The isomeric purity of 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ and 1,7-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ is 94 and 6%, respectively.

(b) Generation of 1-Me-12-Et- $\text{CB}_{11}\text{F}_{10}^-$. The synthesis of 1-Me-12-Et- $\text{CB}_{11}\text{F}_{10}^-$ was carried out by using EtI as an alkylating agent. By using four equivalents of NaNaph, the intermediate was produced and the color of the reaction mixture turned to clear to dark green with brown tint. Upon addition of four equivalents of EtI, the mixture turned colorless within several seconds and the formation of white precipitate was observed. The $^{19}\text{F}\{^{11}\text{B}\}$ NMR and NIES-MS spectra of the reaction mixture before purification are shown in Figure 4.2. Based on the mass spectrum, the formation of 1-Me-12-Et- $\text{CB}_{11}\text{F}_{10}^-$ was confirmed. Other peaks observed in the spectrum belong to 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (calc. m/z 337), 1-Me-2-OMe-12-H- $\text{CB}_{11}\text{F}_9^-$ (calc. m/z 349) and 1-Me-2-OMe-12-Et- $\text{CB}_{11}\text{F}_9^-$ (calc. m/z 377). The latter two anions are formed from defluorination of the impurity 1-Me-2-OMe- $\text{CB}_{11}\text{F}_{10}^-$, contained in the starting material. The precursor of this

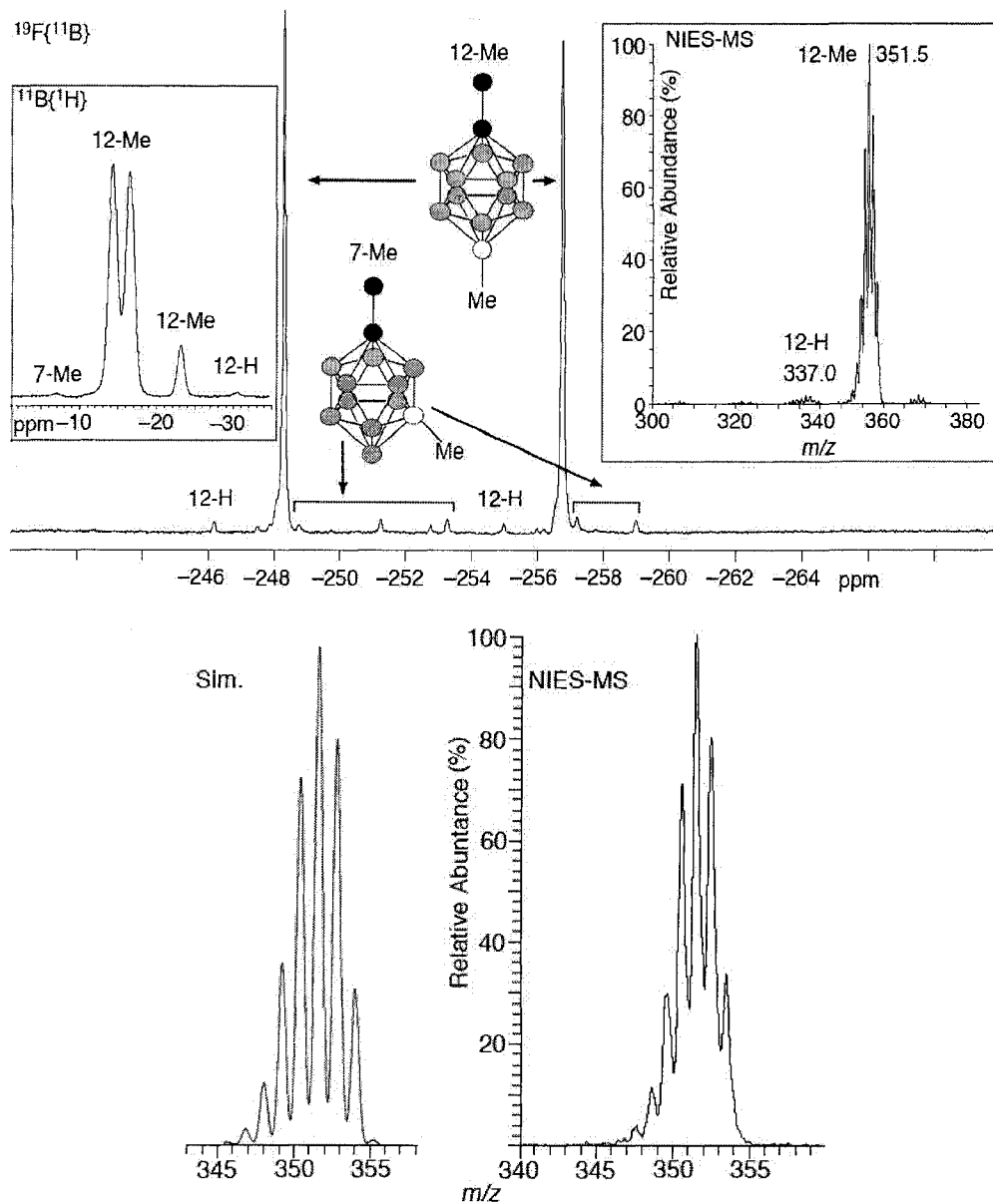


Figure 4.1. Top: 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum (dimethoxyethane), 96.3 MHz $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (left inset; DME), and negative-ion electrospray-ionization mass spectrum (right inset) of the neat product mixture obtained from defluorination of 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ with four equivalents of NaNaph followed by addition of four equivalents of MeI in DME at -55°C . Bottom: Simulated mass spectrum of 1,12-Me $_2$ - $\text{CB}_{11}\text{F}_{10}^-$ (left) and actual NIES-MS spectrum. (right)

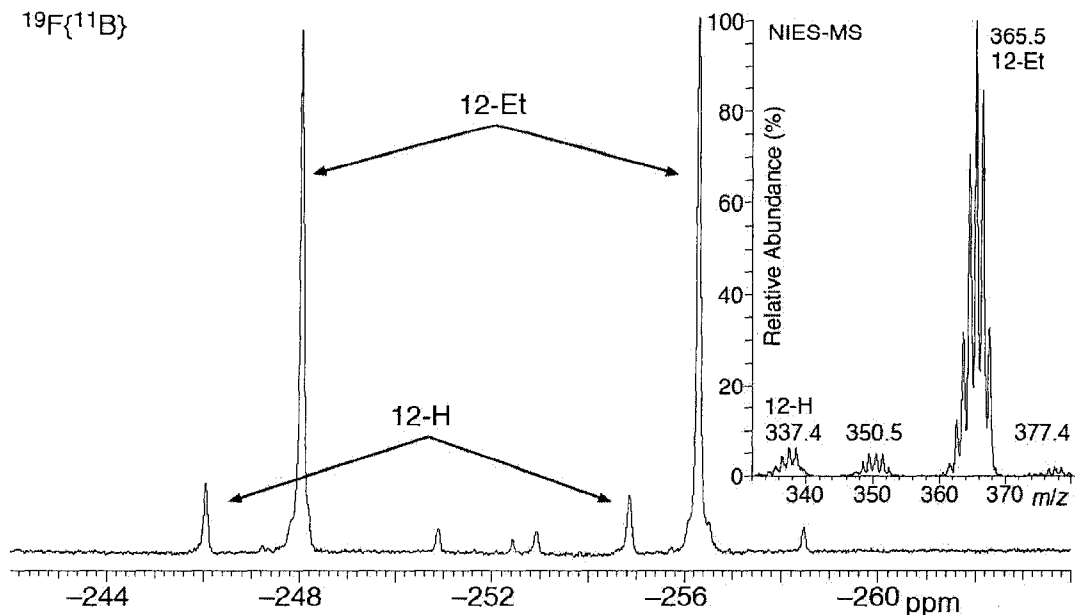


Figure 4.2. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR (dimethoxyethane) and negative-ion electrospray-ionization mass spectra of the reaction mixture before purification. The NMR shows two peaks from belt-fluorine atoms of 1-Me-12-Et- $\text{CB}_{11}\text{F}_{10}^-$ (12-Et) at -248.1 and -256.4 ppm, and two peaks from belt-fluorine atoms of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (12-H) at -246.1 and -254.9 ppm, and five peaks from the impurities at -251.0, -252.5, -253.0, -256.6, and -258.5 ppm. Based on the mass spectrum, the impurities are 1-Me-2-OMe-12-H- $\text{CB}_{11}\text{F}_9^-$ (calc. m/z 349) and 1-Me-2-OMe-12-Et- $\text{CB}_{11}\text{F}_9^-$ (calc. m/z 377). Based on the NMR spectrum the relative amounts of 1-Me-12-Et- $\text{CB}_{11}\text{F}_{10}^-$ and 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ are 88.5 and 11.5%, respectively.

anion 1-H-2-OH-CB₁₁F₁₀[−] was formed during the fluorination of CB₁₁H₁₂[−]. During the synthesis of 1-Me-CB₁₁F₁₁[−], 1-H-2-OH-CB₁₁F₁₀[−] was converted to 1-Me-2-OMe-CB₁₁F₁₀[−]. The NMR spectrum shows two peaks from belt-fluorine atoms of 1-Me-12-Et-CB₁₁F₁₀[−] at −248.1 and −256.4 ppm, and two peaks from belt-fluorine atoms of 1-Me-12-H-CB₁₁F₁₀[−] (12-H) at −246.1 and −254.9 ppm, and five peaks from the impurities at −251.0, −252.5, −253.0, −256.6, and −258.5 ppm. Based on the NMR spectrum, the relative amounts 1-Me-12-Et-CB₁₁F₁₀[−] and 1-Me-12-H-CB₁₁F₁₀[−] are 88.5 and 11.5%, respectively (1-Me-2-OMe-12-H-CB₁₁F₉[−] and 1-Me-2-OMe-12-Et-CB₁₁F₉[−] are not included).

(c) Generation of 1-Me-12-(*i*-Pr)-CB₁₁F₁₀[−]. The substitution on the B12 vertex with a sterically bulky alkyl group was attempted with *t*-BuCl and neopentyl chloride in two separate experiments, but neither of these alkylating agents produced B12-R products. In both cases the major product was 1-Me-12-H-CB₁₁F₁₀[−]. Presumably, these alkyl groups are too large for B12-substitution. In fact, attempt to substitute the C1 vertex which is as sterically hindered as the B12 vertex, with *t*-BuCl or neopentyl group failed to yield C1-substituted product. The most sterically bulky alkyl group which could substitute the B12 vertex was *i*-Pr group. However, when *i*-PrCl was used as an alkylating agent, no B12-substitution occurred. (Similar to this result, it was unable to substitute C1 vertex with *i*-Pr group when *i*-PrCl was used.) Presumably, this is because the chloride is not a good leaving group. This was proven by use of *i*-PrBr or *i*-PrI. Separate experiments using these alkylating agents independently showed the formation of 1-Me-12-(*i*-Pr)-CB₁₁F₁₀[−]. Figure 4.3 shows the NIES-MS spectrum and ¹⁹F{¹¹B} NMR of the reaction mixture obtained from the reaction between Cs(1-Me-CB₁₁F₁₁) and four equivalents of NaNaph followed by addition of excess *i*-PrBr. In the mass spectrum, the formation of 1-Me-12-(*i*-Pr)-CB₁₁F₁₀[−] was confirmed, but contained significant amount of byproducts. These byproducts were 1-Me-12-H-CB₁₁F₁₀[−] and unknown singly charged anion with *m/z* 363.5. The NMR spectrum showed two peaks from the belt-fluorine

atoms of 1-Me-12-(*i*-Pr)-CB₁₁F₁₀[−] at −248.3 and −255.4 ppm, two peaks from 1-Me-12-H-CB₁₁F₁₀[−], and 10 peaks from other byproducts. This unknown product has the similar mass as 1-Me-12-vinyl-CB₁₁F₁₀[−], however the ¹H-NMR of the product mixture did not show any *sp*² protons. The relative amounts of 1-Me-12-H-CB₁₁F₁₀[−] and 1-Me-12-*i*-Pr-CB₁₁F₁₀[−] were approximately 20 and 80% for both reactions with *i*-PrBr and *i*-PrI. The percentage of 1-Me-12-H-CB₁₁F₁₀[−] was constant with these alkylating agents, and the relative amounts was larger than any other alkylation reactions (for MeI, EtI, and DcBr the relative amounts of 1-Me-12-H-CB₁₁F₁₀[−] were within the range of 3–12%), 1-Me-12-H-CB₁₁F₁₀[−] may have formed not only from the solvent, but from hydrogen abstraction or deprotonation from *i*-Pr group.

(d) Generation of 1-Me-12-Bn-CB₁₁F₁₀[−]. The 1-Me-12-Bn-CB₁₁F₁₀[−] anion was generated by using benzylchloride (BnCl) as an alkylating agent. The NIES-MS and ¹⁹F{¹¹B} NMR spectra of the product mixture before purification are shown in Figure 4.4. The mass spectrum showed three sets of peaks at *m/z* 337.5, 371.5, and 427.6. The set of peaks at *m/z* 337.5 is due to 1-Me-12-H-CB₁₁F₁₀[−], and *m/z* 427.6 is from 1-Me-12-Bn-CB₁₁F₁₀[−]. Based on the simulated isotopic distribution and the mass, the set of the peaks at 371.5 belongs to 1-Me-12-Cl-CB₁₁F₁₀[−] (calc. *m/z* 371.4). The NMR spectrum showed two peaks from 1-Me-12-Bn-CB₁₁F₁₀[−] at −248.3 and −255.8 ppm, two peaks from 1-Me-12-H-CB₁₁F₁₀[−], and two peaks from 1-Me-12-Cl-CB₁₁F₁₀[−] at −252.0 and −255.5 ppm. Other small peaks found in the NMR spectrum are presumably the 1-Me-7-X-CB₁₁F₁₀[−] isomers of the three anions. Based on the NMR spectrum, the relative amounts of 1-Me-12-Bn-CB₁₁F₁₀[−], 1-Me-12-H-CB₁₁F₁₀[−], and 1-Me-12-Cl-CB₁₁F₁₀[−] were 50, 10, and 28%, respectively. Since we could not synthesize 1-Me-12-Bn-CB₁₁F₁₀[−] with a good selectivity using BnCl, this reaction system was not investigated further and the mechanism for the formation of 1-Me-12-Cl-CB₁₁F₁₀[−] is not clear at this point.

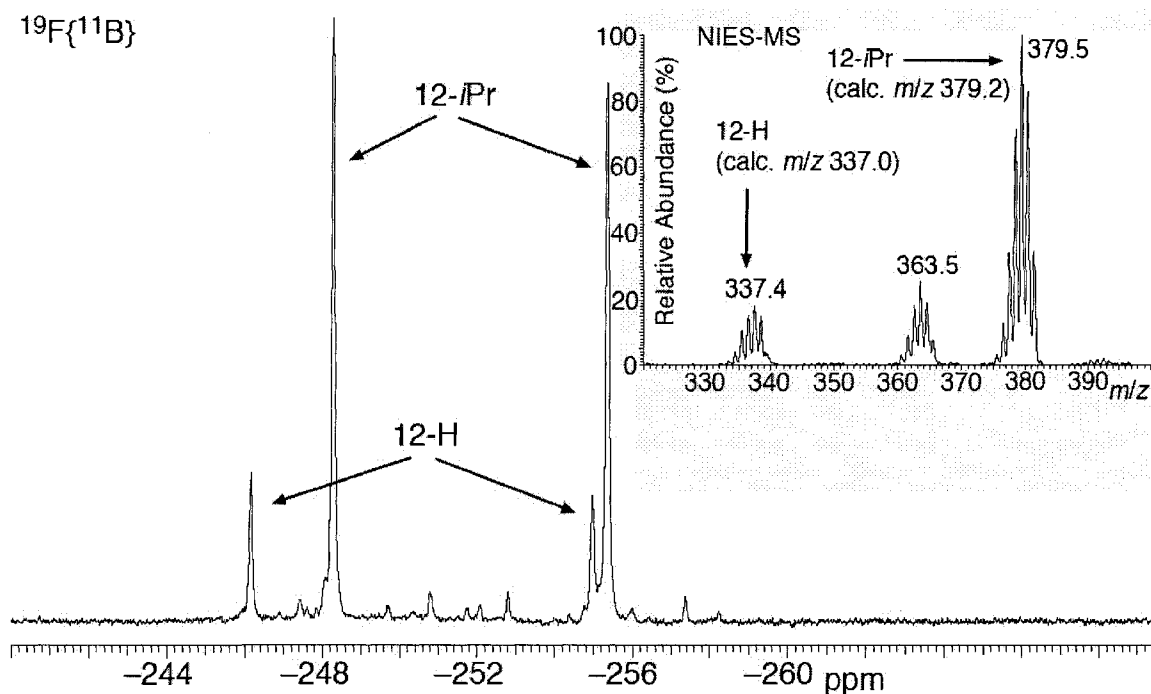


Figure 4.3. 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR (dimethoxyethane) and negative-ion electrospray-ionization mass spectra of the reaction mixture obtained from the defluorination/alkylation reaction of $\text{Cs}(\text{1-Me-CB}_{11}\text{F}_{11})$ with four equivalents of NaNaph and excess $i\text{-PrBr}$. The formation of $\text{1-Me-12-(}i\text{-Pr)-CB}_{11}\text{F}_{10}^-$ was confirmed with the mass spectrum, however, significant amount of $\text{1-Me-12-H-CB}_{11}\text{F}_{10}^-$ and an unknown singly-charged byproduct (m/z 363.5) was also formed.

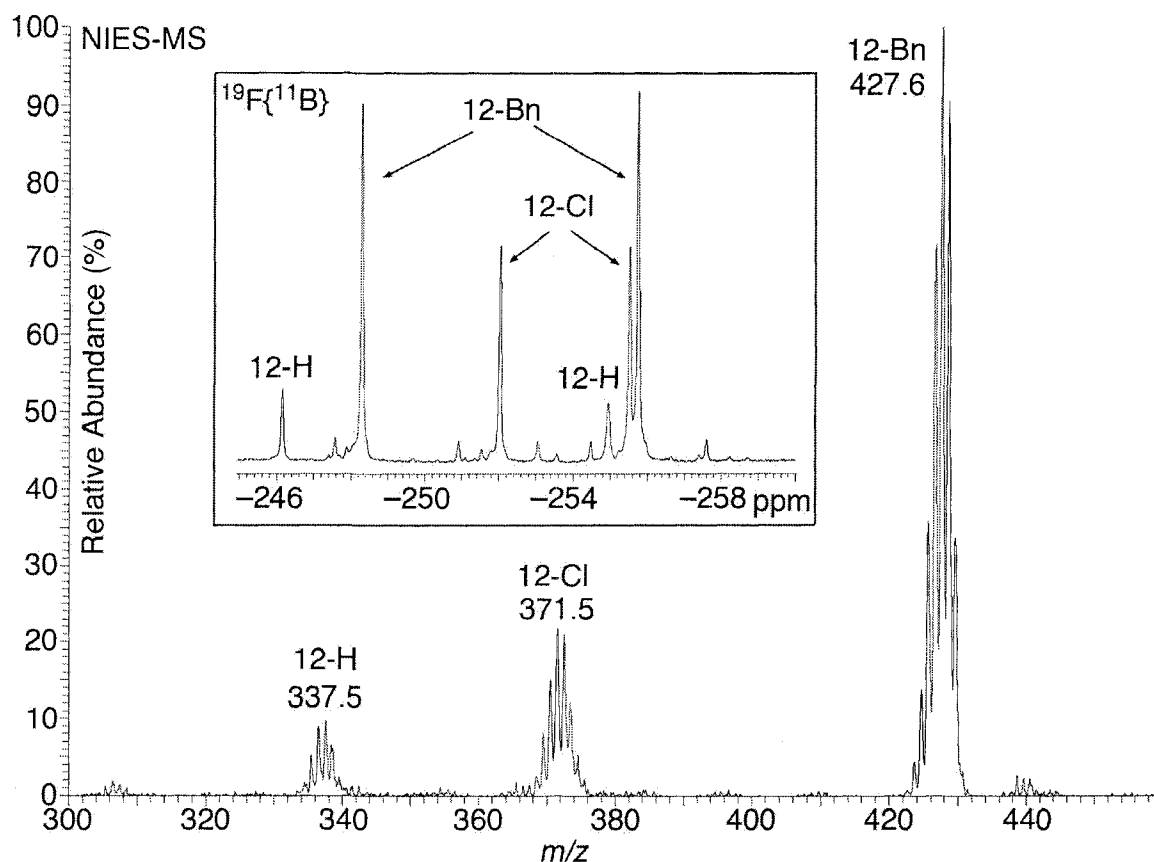


Figure 4.4. Negative-ion electrospray-ionization mass spectrum and 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum (inset: dimethoxyethane) of the product mixture from the reaction between the intermediate and benzylchloride. The small peaks in $^{19}\text{F}\{^{11}\text{B}\}$ NMR may be due to the isomers 1-Me-7-Bn- $\text{CB}_{11}\text{F}_{10}^-$ and 1-Me-7-Cl- $\text{CB}_{11}\text{F}_{10}^-$. The relative amounts of the product anion is approximately 50% for 1-Me-12-Bn- $\text{CB}_{11}\text{F}_{10}^-$ (12-Bn), 10% for 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (12-H), 28% for 1-Me-12-Cl- $\text{CB}_{11}\text{F}_{10}^-$ (12-Cl), and 12% for 1-Me-7-X- $\text{CB}_{11}\text{F}_{10}^-$ isomers.

(e) Generation of 1-Me-12-Dc-CB₁₁F₁₀⁻. In order to synthesize CB₁₁-anion with longer chain of the B12 vertex, addition of decyl group was examined. For the alkylating agent, 1-bromodecane (DcBr) was used. Compared to other alkylating agents, 1-bromodecane (DcBr) took longer to complete the alkylation reaction based on the color change of the reaction mixture. When MeI or EtI was used as an alkylating agent, the reaction mixture changed the color in few second after addition of the alkylating agent, however, in case of DcBr, it took approximately 20 minutes for the reaction mixture to turn from dark green to colorless. Figure 4.5 shows the NIES-MS and ¹⁹F{¹¹B} spectra of the reaction mixture before purification. The mass spectrum showed one intense peak at *m/z* 477.5 that belongs to 1-Me-12-Dc-CB₁₁F₁₀⁻ (calc. *m/z* 477.2). There were also small amounts of 1-Me-12-H-CB₁₁F₁₀⁻ in the mixture. In the NMR spectrum, two large peaks from the belt-fluorine atoms of 1-Me-12-Dc-CB₁₁F₁₀⁻ at -248.8 and -256.7 ppm were observed. Two of other peaks are from 1-Me-12-H-CB₁₁F₁₀⁻, and the small peaks at -249.1, -251.5, -253.4, -254.1, -256.4, and -258.9 are almost certainly from 1-Me-7-Dc-CB₁₁F₁₀⁻ based on the number of the signals and their integral ratio which is 1:2:1:2:2:2. Based on the integral ratio of the peaks, the relative amounts of 1-Me-12-Dc-CB₁₁F₁₀⁻, 1-Me-12-H-CB₁₁F₁₀⁻, and 1-Me-7-Dc-CB₁₁F₁₀⁻ are 88, 3, and 9%, respectively. The isomeric purities of 1-Me-12-Dc-CB₁₁F₁₀⁻ and 1-Me-7-Dc-CB₁₁F₁₀⁻ are 91% and 9%, respectively.

Recrystallization of the tetrabutylammonium salt of 1-Me-12-Dc-CB₁₁F₁₀⁻ was attempted from acetone solution by slow diffusion of hexanes, but this salt formed waxy solid at room temperature.

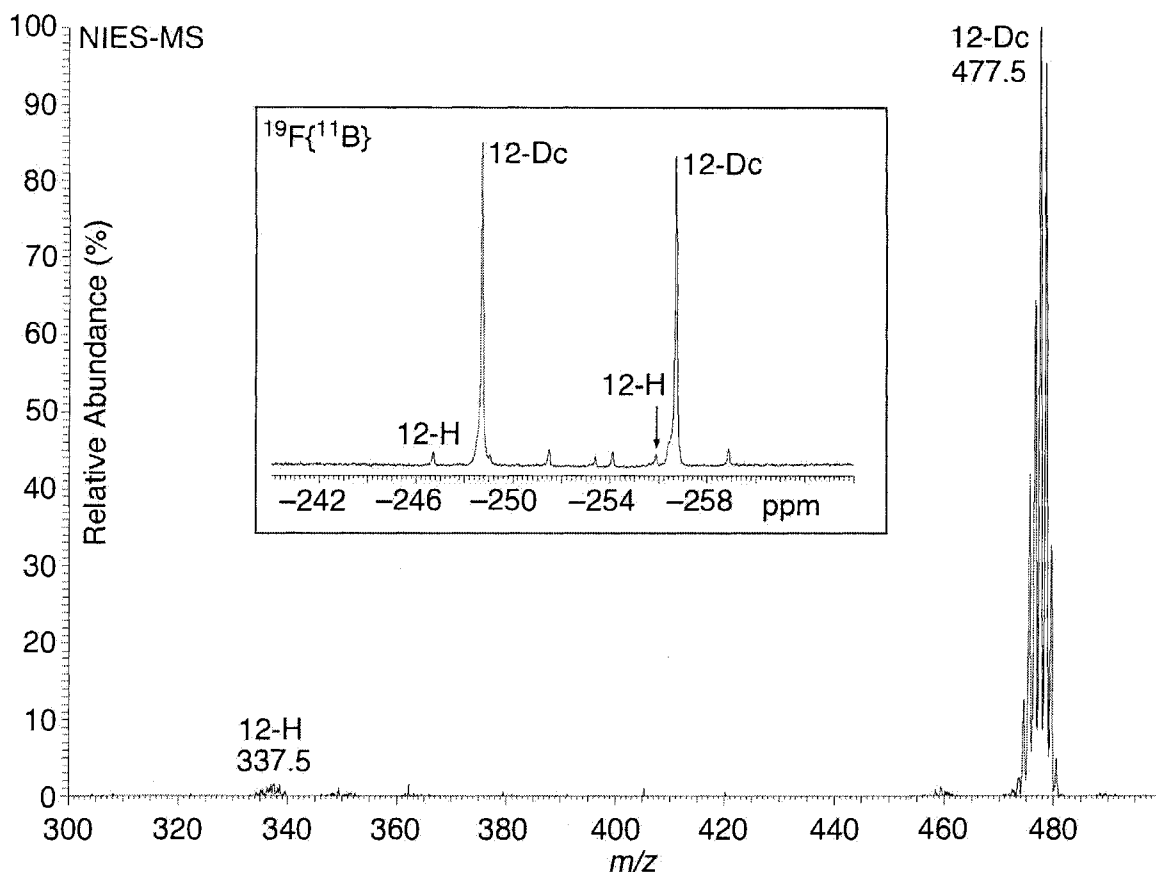


Figure 4.5. Negative-ion electrospray-ionization mass spectrum and 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum (inset: acetonitrile- d_3) of the product mixture obtained from the reaction between $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and three equivalents of NaNaph followed by addition of four equivalents DcBr at $-50\text{ }^{\circ}\text{C}$. The mass spectrum shows the presence of $1\text{-Me-12-Dc-CB}_{11}\text{F}_{10}^-$ (12-Dc) at m/z 477.5, and $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ (12-H) at 337.5. The NMR spectrum shows a set of two peaks from $1\text{-Me-12-Dc-CB}_{11}\text{F}_{10}^-$ (δ -248.8 and -256.7), a set of two peaks from $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ (δ -246.7 and -255.5), and a set of six peaks from $1\text{-Me-7-Dc-CB}_{11}\text{F}_{10}^-$ (δ -249.1 , -251.5 , -253.4 , -254.1 , -256.4 , and -258.9). The relative amounts of $1\text{-Me-12-Dc-CB}_{11}\text{F}_{10}^-$, $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$, and $1\text{-Me-7-Dc-CB}_{11}\text{F}_{10}^-$ are 88, 3, and 9%, respectively. The isomeric purities of $1\text{-Me-12-Dc-CB}_{11}\text{F}_{10}^-$ and $1\text{-Me-7-Dc-CB}_{11}\text{F}_{10}^-$ are 91 and 9%, respectively.

(f) **Synthesis of Cs(1-Me-12-I-CB₁₁F₁₀)**. As mentioned in the introduction, selective substitution of the B12 vertex for several CB₁₁-anions has been reported. These anions were synthesized by substitution of B–I bond to B–R bond by Kumada coupling.¹ Therefore once 1-Me-12-I-CB₁₁F₁₀[–] is isolated, it may be used as a starting material for a variety of 1-Me-12-R-CB₁₁F₁₀[–] derivatives. With our method of defluorination of the B12 vertex followed by iodination, 1-Me-12-I-CB₁₁F₁₀[–] could be obtained in high selectivity. For the preliminary experiment, the intermediate was synthesized in an NMR tube with a Teflon screw cap with excess NaNaph at room temperature. After addition of I₂ to this solution, the color change was observed from dark green to dark red due to the excess I₂. Figure 4.6 shows the NIES-MS and ¹⁹F{¹¹B} NMR spectra of the product mixture before the purification. Based on the NMR spectrum, the product mixture contained approximately 61% of 1-Me-12-I-CB₁₁F₁₀[–], and 18% of 1-Me-12-H-CB₁₁F₁₀[–]. Based on the mass spectrum, 1-Me-CB₁₁H₂F₉[–] (calc. *m/z* 318.2) and 1-Me-CB₁₁HI F₉[–] (calc. *m/z* 444.9) were present in the mixture. In addition to these anions, there was a peak at *m/z* 425.2 due to presumably 1-Me-12-(CH(OCH₃)CH₂OCH₃)-CB₁₁F₁₀[–] (calc. *m/z* 425.1). Since the reaction was performed at room temperature and with excess NaNaph, the presence of 1-Me-12-H-CB₁₁F₁₀[–] and the products from multiple defluorination is reasonable. Nonetheless, this experiment showed that 1-Me-12-I-CB₁₁F₁₀[–] can be produced in reasonably high relative amounts.

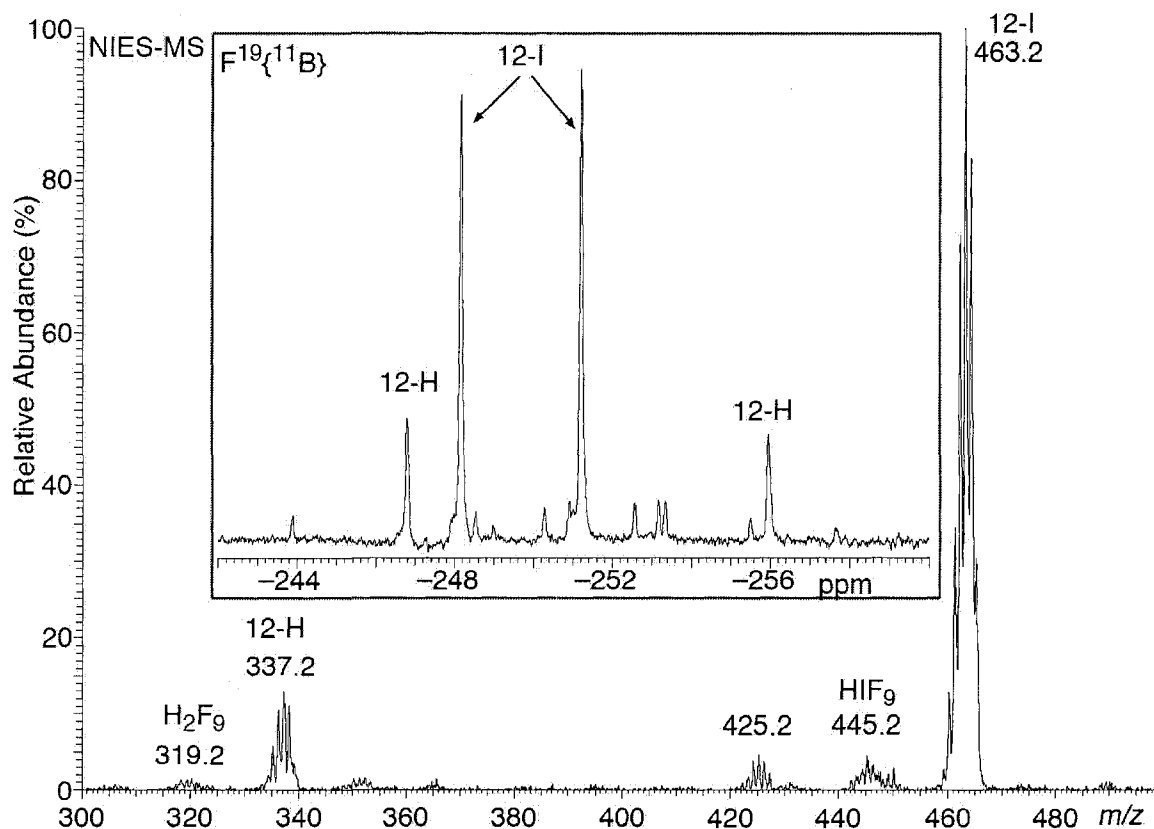


Figure 4.6. Negative-ion electrospray-ionization mass spectrum and 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectrum (inset: acetonitrile- d_3) of the product mixture obtained from the reaction of the intermediate and I_2 . Based on the NMR spectrum, the product mixture contained approximately 61% of 1-Me-12-I- $\text{CB}_{11}\text{F}_{10}^-$ (12-I) and approximately 18% of 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (12-H). There were also some byproducts, which are multiple defluorination products, 1-Me- $\text{CB}_{11}\text{H}_2\text{F}_9^-$ (H_2F_9) (calc. m/z 319.0), 1-Me- $\text{CB}_{11}\text{HIF}_9^-$ (HIF_9) (calc. m/z 444.9), and 1-Me- $(\text{CH}(\text{OCH}_3)\text{CH}_2\text{OCH}_3)\text{-CB}_{11}\text{F}_{10}^-$ (calc. m/z 425.1).

The 1-Me-12-I-CB₁₁F₁₀⁻ anion was also obtained from the reaction with the three equivalents of NaNaph and excess CF₃CH₂I. The preliminary purpose to use this reagent was to produce 1-Me-12-(CF₃CH₂)-CB₁₁F₁₀⁻. The NIES-MS spectrum of the product mixture before purification is shown in Figure 4.7. Although the product mixture contained 1-Me-12-(CF₃CH₂)-CB₁₁F₁₀⁻, which can be seen at *m/z* 419.4, the relative amounts of this anion was only 6.3%. The major product was seen at *m/z* 463.3, which belongs to 1-Me-12-I-CB₁₁F₁₀⁻. The relative amounts of this anion was 66.1%. A possible explanation for this result is that due to the electronegativity of fluorine atoms, the iodine atom in CF₃CH₂I become more electropositive than CF₃CH₂ group. Therefore, the intermediate reacted with the CF₃CH₂I molecule and formed 12-I as a major product. The product mixture also contained significant amount (relative amounts 21.8%) of 1-Me-12-H-CB₁₁F₁₀⁻ and a small amount of 1-Me-12-(CH(OCH₃)CH₂OCH₃)-CB₁₁F₁₀⁻ (*m/z* = 425.5). From an aqueous solution of this product mixture, Cs(1-Me-12-I-CB₁₁F₁₀) was isolated as white opaque crystals. The crystal of Cs(1-Me-12-I-CB₁₁F₁₀) was analyzed by the single-crystal X-ray crystallography, and its crystal structure is described in Chapter 5.

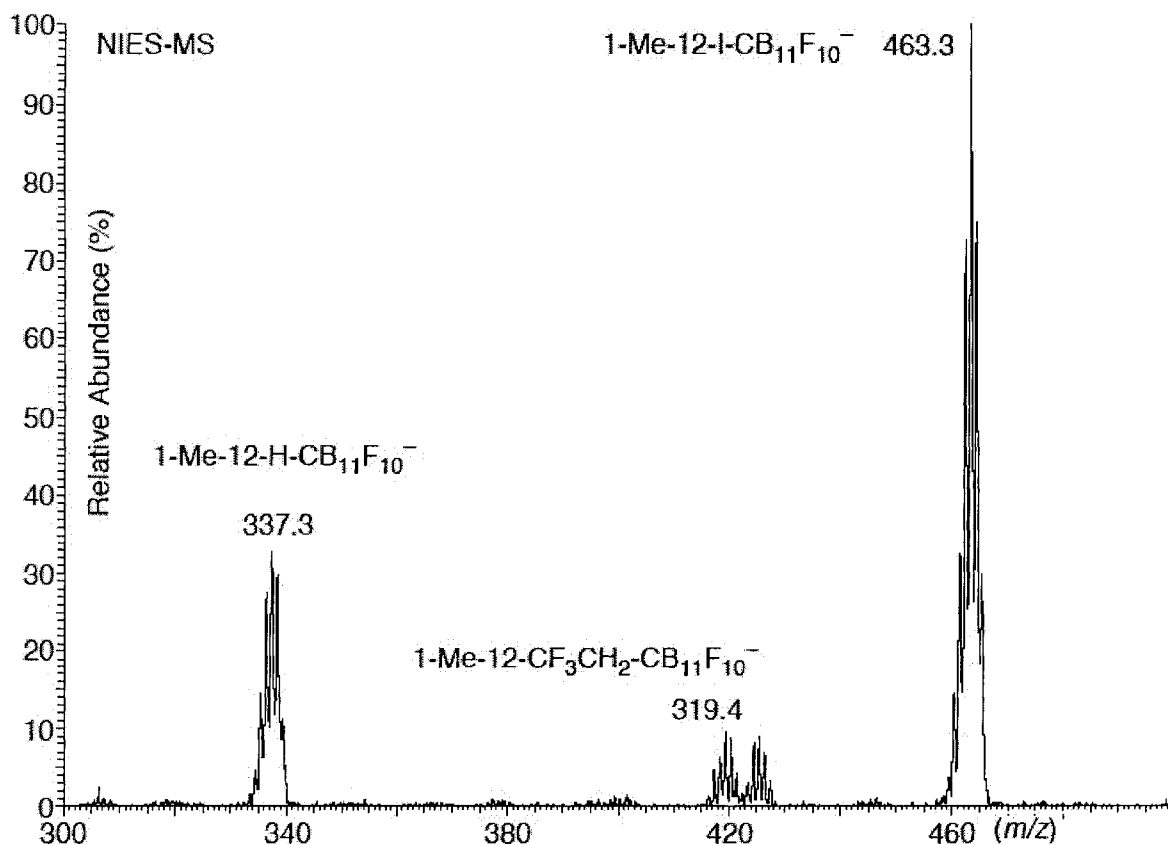


Figure 4.7. Negative-ion electrospray-ionization mass spectrum of the product mixture obtained from the reaction between the intermediate and CF₃CH₂I. The product mixture contained 1-Me-12-H-CB₁₁F₁₀⁻, 1-Me-12-CF₃CH₂-CB₁₁F₁₀⁻, 1-Me-12-I-CB₁₁F₁₀⁻, and 1-Me-12-(CH(OCH₃)CH₂OCH₃)-CB₁₁F₁₀⁻ (calc. *m/z* 425.1). The relative amounts of the product anion is 21.8% for 1-Me-12-H-CB₁₁F₁₀⁻, 6.3% for 1-Me-12-CF₃CH₂-CB₁₁F₁₀⁻, and 66.1% for 1-Me-12-I-CB₁₁F₁₀⁻.

(g) Synthesis of Cs(1-Me-12-SiPh₃-CB₁₁F₁₀)⁻. Our interests to synthesize the 1-Me-12-SiPh₃-CB₁₁F₁₀⁻ anion were to functionalize the B12-vertex with non-alkyl group, and to make the purification, recrystallization, and characterization easier than other B12-substituted anions. Although we were unable to substitute the B12-vertex with bulky alkyl groups, such as *t*-Bu group, SiPh₃ group should be able to substitute the B12-vertex without having the steric problem because of the large size of the silicon atom. For the SiPh₃ source, SiPh₃Cl was chosen simply because it was readily available. For the optimized reaction condition, 2.5 equivalents of NaNaph, and three equivalents of SiPh₃Cl were used. The visual observation of the reaction was the same compared with the reaction for 1,12-Me₂-CB₁₁F₁₀⁻ synthesis, except for the longer duration of the color change. Since SiPh₃Cl was added as solid, it took longer to dissolve completely at -55 °C, therefore the color change was slower than for MeI. The NIES-MS and ¹⁹F{¹¹B} NMR spectra of the product mixture are shown in Figure 4.8. The mass spectrum of the resulting mixture proved that there was no unreacted starting material, the peak of which would be at *m/z* = 355, however, a small amount of 1-Me-12-H-CB₁₁F₁₀⁻ was present in the product mixture. The ¹⁹F{¹¹B} NMR spectra showed the presence of an isomer which is almost certainly 1-Me-7-SiPh₃-CB₁₁F₁₀⁻. Based on the ¹⁹F{¹¹B} NMR spectrum, the relative amounts of 1-Me-*x*-SiPh₃-CB₁₁F₁₀⁻ is 96%, and 4% 1-Me-12-H-CB₁₁F₁₀⁻. The isomeric purity of 1-Me-12-SiPh₃-CB₁₁F₁₀⁻ was 88% with 12% of 1-Me-7-SiPh₃-CB₁₁F₁₀⁻.

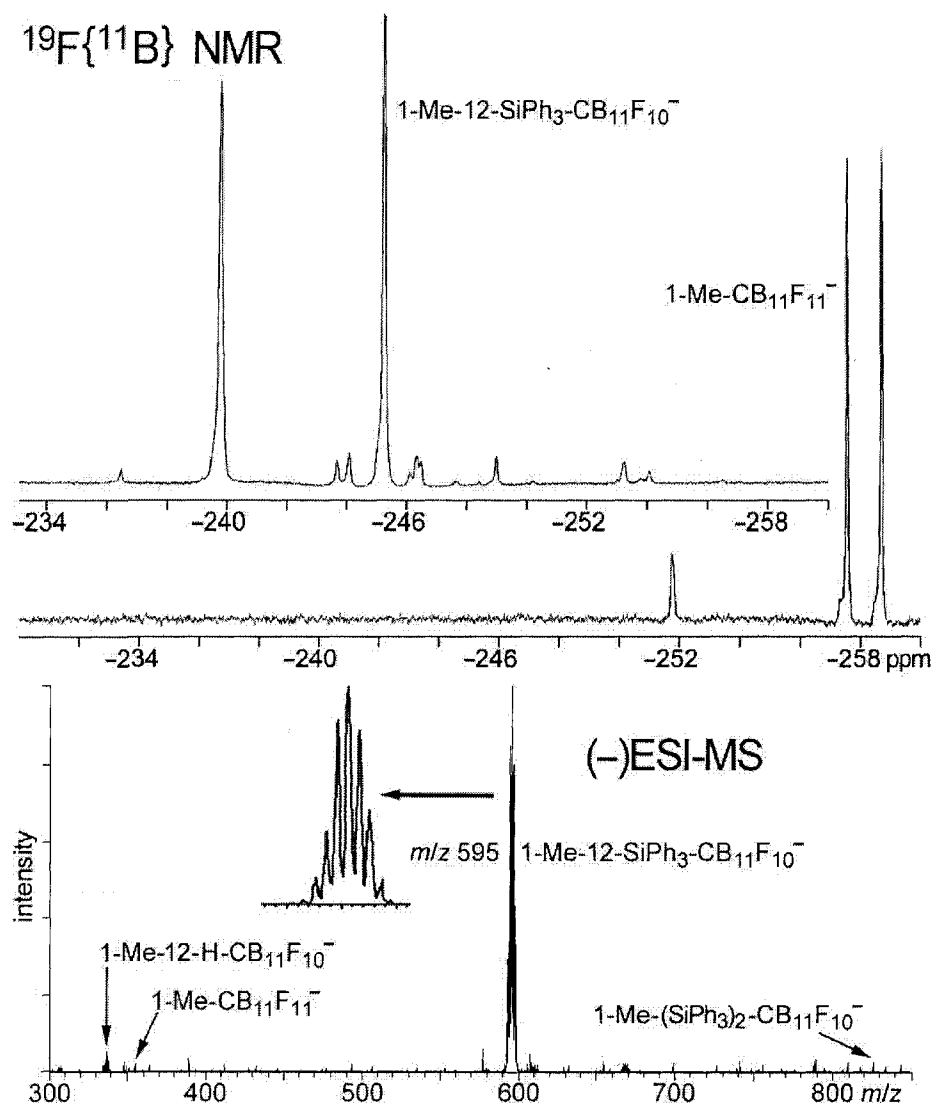


Figure 4.8. Negative-ion electrospray-ionization mass spectrum of $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$ (bottom) and the 282.4 MHz $^{19}\text{F}\{^{11}\text{B}\}$ NMR spectra of $\text{Cs}(1\text{-Me-CB}_{11}\text{F}_{11})$ and $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$ (top; CD_3CN). The small peaks in the NMR spectrum of $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$ may be due to a small amount of the byproduct $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$ and the isomer $1\text{-Me-7-SiPh}_3\text{-CB}_{11}\text{F}_{10}^-$. The relative amounts of the product anion is 96% $1\text{-Me-}x\text{-SiPh}_3\text{-CB}_{11}\text{F}_{10}^-$ with 4% of byproduct ion $1\text{-Me-12-H-CB}_{11}\text{F}_{10}^-$. The isomeric purity is 88% for $x = 12$ and 12% for $x = 7$.

(h) Generation of 1-Bn-12-Me-CB₁₁F₁₀[−]. As described above, the selective functionalization of the B12 vertex in 1-Me-CB₁₁F₁₁[−] with various functional groups was successful. In order to confirm the usefulness of the selective defluorination/alkylation reaction, CB₁₁-anions with different alkyl groups such as benzyl and ethyl groups on the C1 vertex were examined. The Cs(1-Bn-CB₁₁F₁₁) was reacted with 2.5 equivalents of NaNaph followed by excess MeI at −50 °C. The color of the reaction mixture changed from greenish brown to colorless within seconds. The NIES-MS spectrum of the product mixture after removal of insoluble product and volatiles is shown in Figure 4.9. The spectrum showed three sets of peaks at *m/z* 413.5, 427.5, and 431.5 which are 1-Bn-12-H-CB₁₁F₁₀[−] (calc. *m/z* 413.1), 1-Bn-12-Me-CB₁₁F₁₀[−] (calc. *m/z* 427.1), and 1-Bn-CB₁₁F₁₁[−] (calc. *m/z* 431.0), respectively. Although the mass spectrometry does not provide accurate data on relative composition of the mixture, it is clear that the major product of this reaction is 1-Bn-12-Me-CB₁₁F₁₀[−].

(i) Generation of 1-Et-12-Me-CB₁₁F₁₀[−]. The defluorination/alkylation of Cs(1-Et-CB₁₁F₁₁) was also examined using 2.5 equivalents of NaNaph and excess dimethylsulfonate (Me₂SO₄) at −50 °C. After addition of Me₂SO₄, the reaction mixture changed the color from greenish brown to colorless within seconds. Figure 4.10 shows the NIES-MS spectrum of the product mixture after removal of the precipitate (presumably Na₂SO₄) and volatiles. The spectrum showed three sets of peaks at *m/z* 347.5, 350.4, and 365.5. The set of low-intensity peaks at *m/z* 350.4 is due to the presence of 1-Et-12-H-CB₁₁F₁₀[−] (calc. *m/z* 351.0), and the most abundant peak at *m/z* 365.5 is from 1-Et-12-Me-CB₁₁F₁₀[−] (calc. *m/z* 365.0). The other set of low-intensity peaks at *m/z* 347.5 may be due to 1-Et-CB₁₁F₉HMe[−] (calc. *m/z* 347.0). 1-Et-12-Me-CB₁₁F₁₀[−] was formed in high selectivity, in this reaction of one assumes that relative abundances of the impurities are not severely underrepresented in the mass spectra.

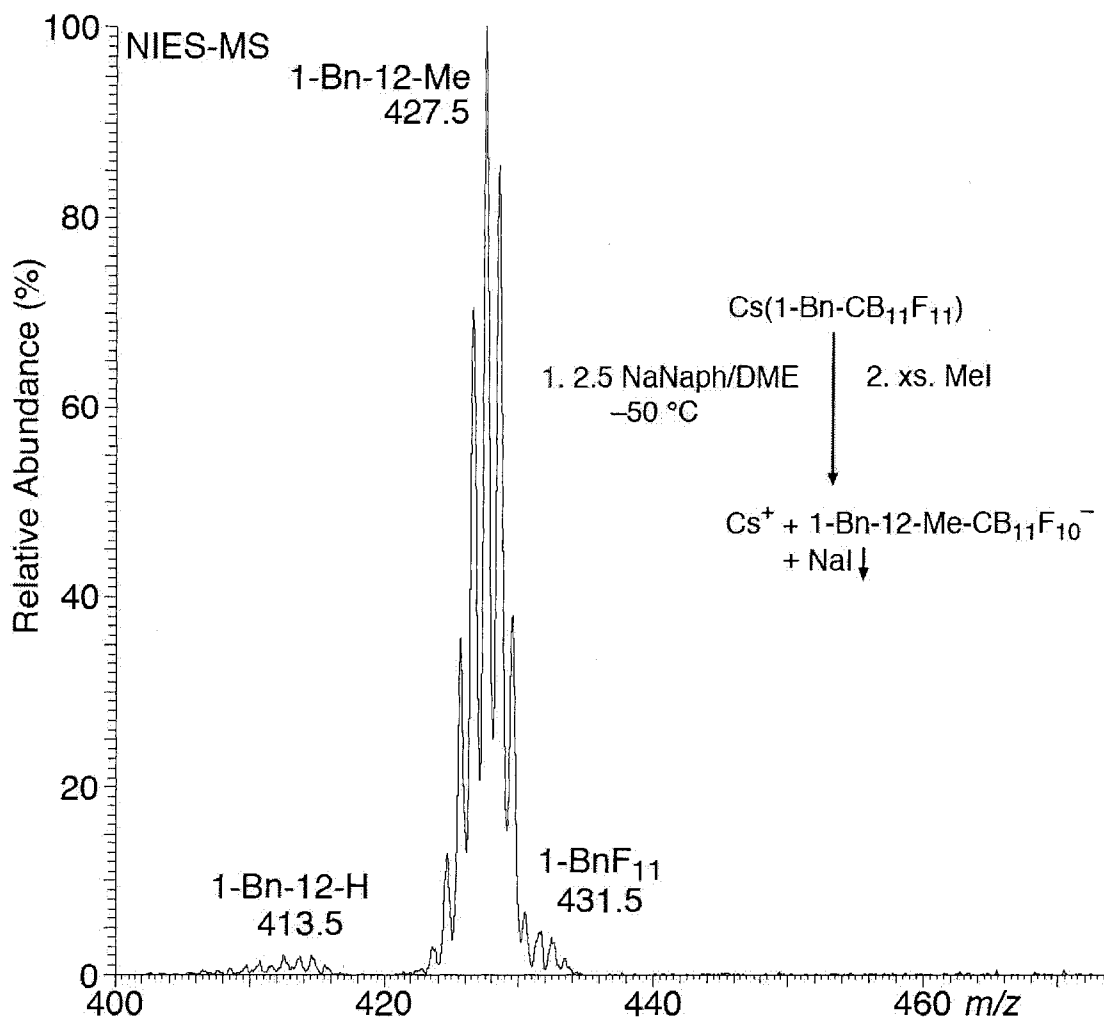


Figure 4.9. Negative-ion electrospray-ionization mass spectrum of the product mixture obtained from the reaction between $\text{Cs(1-Bn-CB}_{11}\text{F}_{11})$ and 2.5 equivalents of NaNaph followed by excess MeI. The three sets of peaks at m/z 413.5, 427.5, and 431.5 are 1-Bn-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (calc. m/z 413.1), 1-Bn-12-Me- $\text{CB}_{11}\text{F}_{10}^-$ (calc. m/z 427.1), and 1-Bn- $\text{CB}_{11}\text{F}_{11}^-$ (calc. m/z 431.0), respectively. From his spectra, it can be concluded that 1-Bn- $\text{CB}_{11}\text{F}_{11}^-$ can also be selectively defluorinated and alkylated using more than two equivalents of NaNaph and excess MeI.

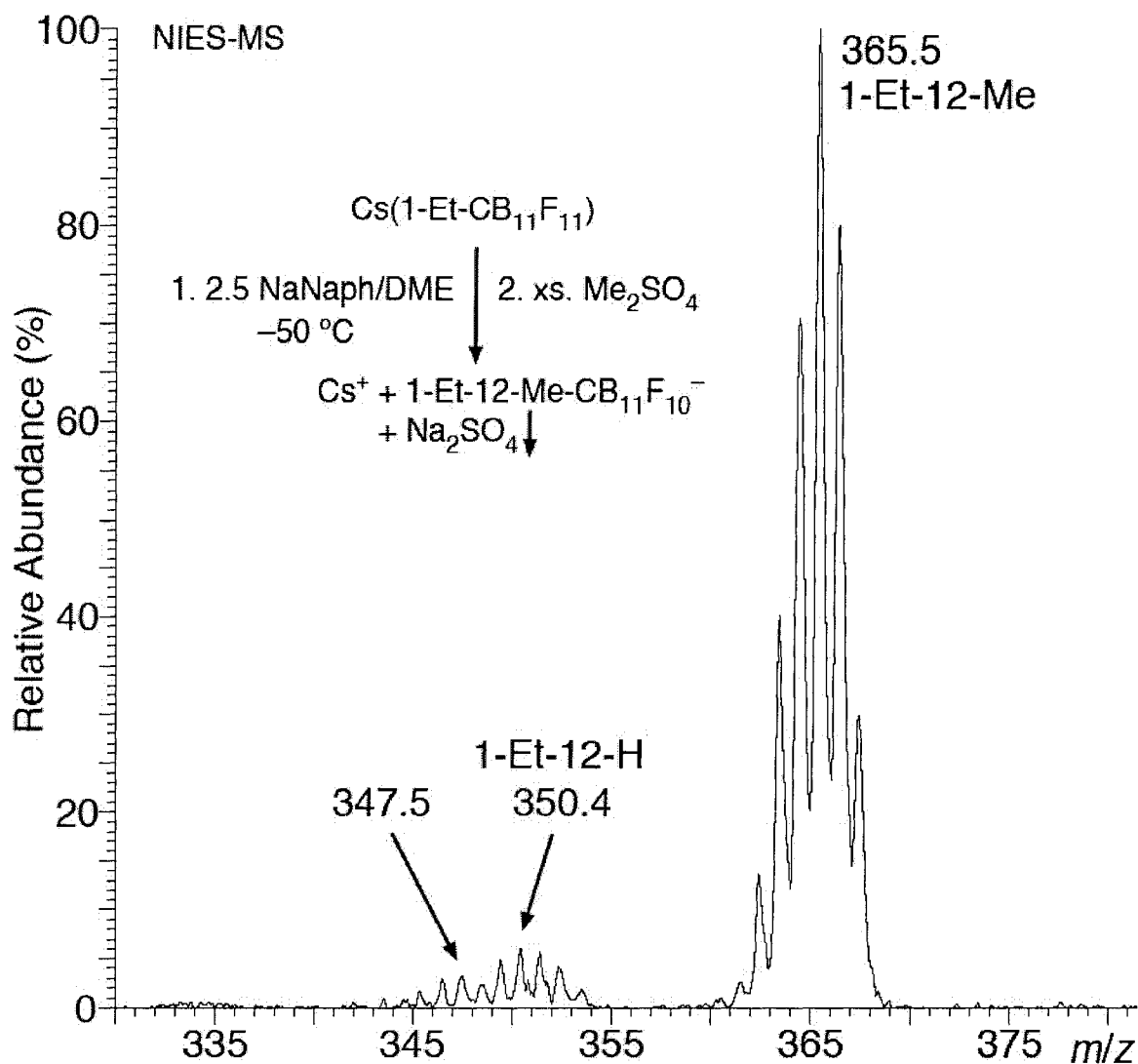


Figure 4.10. Negative-ion electrospray-ionization mass spectrum of the product mixture obtained from the reaction between $\text{Cs(1-Et-CB}_{11}\text{F}_{11})$ and 2.5 equivalents of NaNaph followed by excess dimethylsulfate. The mixture contained 1-Et-12-H- $\text{CB}_{11}\text{F}_{10}^-$ (1-Et-12-H) (calc. m/z 351.0), 1-Et-12-Me- $\text{CB}_{11}\text{F}_{10}^-$ (calc. m/z 365.0), and 1-Et- $\text{CB}_{11}\text{F}_9\text{HMe}^-$ (calc. m/z 347.0).

References

- (1) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374-4376.

Chapter 5 X-ray Crystallography

Three of the five X-ray structures determined in this research by the chemistry X-ray Lab at CSU have been published. These are $(N(n\text{-Bu})_4)_4\text{B}_{24}\text{F}_{22}$,¹ $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$,² and $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$.² The other two are $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$ and $\text{NMe}_4(1,12\text{-CB}_{11}\text{F}_{10})$. The molecular structures of the cation/anion formula units and the cation-anion packing in each of the five structures will be discussed below.

Experimental Section

Crystals of $(N(n\text{-Bu})_4)_4\text{B}_{24}\text{F}_{22}$ were grown by several recrystallizations from acetone/toluene. Crystals of $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ and $\text{Cs}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})$ were grown by slow diffusion of hexanes into an acetone solution. Crystals of $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$ and $\text{Ag}(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})\cdot 0.5\text{C}_6\text{H}_6$ were grown by slow evaporation of saturated aqueous and benzene solutions, respectively.

X-ray diffraction data were recorded on either a Bruker SMART or a Bruker Kappa APEX2 CCD diffractometer using $\text{MoK}\alpha$ radiation (graphite monochromator). Selected details related to the crystallographic experiments are listed in Table 5.1. Unit cell parameters were obtained from least-squares fits to the angular coordinates of all reflections, and intensities were integrated from a series of frames (ω and ϕ rotations) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied by using SADABS.³ The structures were solved by using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least-squares process. All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined by using a riding model. Standard Bruker control (SMART, APEX2) and integration (SAINT, APEX2) software was employed, and Bruker SHELXTL software⁴ was used for structure solution, refinement, and graphics.

Table 5.1. Crystal data and structure refinement parameters^a

compd	(TBA) ₄ B ₂₄ F ₂₂	NMe ₄ (1,12-Me ₂ F ₁₀)	Cs(1-Me-12-I-CB ₁₁ F ₁₀)	CsY	Ag ₂ Y ₂ ·C ₆ H ₆
formula	C ₆₄ H ₁₄₄ B ₂₄ F ₂₂ N ₂	C ₇ H ₁₈ B ₁₁ F ₁₀ N	C ₂ H ₃ B ₁₁ CsF ₁₀	C ₂₀ H ₁₈ B ₁₁ CsF ₁₀ Si	C ₄₆ H ₄₂ Ag ₂ B ₂₂ F ₂₀ Si ₂
formula weight	1647.28	425.13	595.76	728.25	1,484.54
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group, Z	<i>Pbcn</i> , 4	<i>C2/c</i> , 4	<i>P2₁/c</i> , 4	<i>P2₁/n</i> , 4	<i>P2₁/c</i> , 4
cell dimens. <i>a</i> , Å	14.622(1)	18.240(4)	11.0168(5)	9.4773(3)	18.4204(6)
<i>b</i> , Å	34.858(3)	11.086(4)	11.9656(5)	20.3255(7)	19.1497(7)
<i>c</i> , Å	17.594(1)	10.913(3)	11.6033(5)	14.7167(5)	19.1230(7)
α, deg	90	90	90	90	90
β, deg	90	126.35(1)	94.933(2)	92.217(2)	117.838(2)
γ, deg	90	90	90	90	90
temperature, K	100(1)	173(2)	100(1)	100(2)	100(2)
final <i>R</i> indices,	<i>R</i> ₁ = 0.051,	<i>R</i> ₁ = 0.062,	<i>R</i> ₁ = 0.048,	<i>R</i> ₁ = 0.045,	<i>R</i> ₁ = 0.045,
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.122	<i>wR</i> ₂ = 0.174	<i>wR</i> ₂ = 0.127	<i>wR</i> ₂ = 0.075	<i>wR</i> ₂ = 0.095
GOOF on <i>F</i> ²	1.029	1.356	1.139	1.006	0.961

^a All of the crystals were colorless. TBA⁺ = N(*n*-Bu)₄⁺. Y⁻ = 1-Me-12-SiPh₃F₁₀⁻

Results and Discussion

Structures of individual compounds. (a) The structure of $(N(n\text{-Bu})_4)_4B_{24}F_{22}$.

The name for this compound, following a combination of nomenclature rules recommended by the IUPAC⁵ and CAS,⁶ is tetra(*n*-butyl)ammonium(1+) docosafluoro-1:1'-bi[(12v)[*I*_h-1551- Δ^{20} -*clos*o]tetracosaborate](4-). This salt crystallized in the orthorhombic space group *Pbcn*. The C_2 -symmetric $B_{24}F_{22}^{4-}$ anion, shown in Figure 5.1, consists of two $B_{12}F_{11}^{2-}$ icosahedra with a B–B single bond connecting their respective B1 atoms. Selected interatomic distances and angles are listed in Table 5.2, which also lists the corresponding distances and angles for the DFT optimized $B_{24}F_{22}^{4-}$ anion and the $(N(n\text{-Bu})_4)_4B_{24}F_{22}$ (the DFT calculations (PBE functional; TZ2P {6,1,1,1,1,1/4,1,1/1,1} basis set), which were performed by Dr. Alexey A. Popov, are taken from ref. 1). There is good agreement between the X-ray and DFT bond distances except for the 2c-2e B1–B1' bond distance, which is 0.05 Å shorter than predicted (see below). The 1.725(4) Å B1–B1' distance can be compared with the 2c-2e B–B distances linking B_{12} icosahedra in rhombohedral α -boron (1.71(1) Å),⁷ in $Al_{2.1}C_8B_{51}$ (1.774(3) Å),⁸ in $NaAlB_{14}$ (1.756(3) and 1.773(2) Å),⁹ and in $MgAlB_{14}$ ((1.75 Å).¹⁰ As would be expected, the B1–B1' bond is considerably longer than the 1.576(5) Å B–N bond in $Me_3NB_{12}F_{11}^-$.¹¹

The mean B–F distance in $B_{24}F_{22}^{4-}$, 1.387(2) Å, is marginally longer than the mean fluorocarborane anion B–F distance of 1.365(3) Å in $Cu(CO)_4(1\text{-Et-CB}_{11}F_{11})$,¹² as shown in Figure 5.2, and the same as the mean B–F distances of 1.386(5)¹³ and 1.384(5) Å¹¹ in the $B_{12}F_{12}^{2-}$ and $Me_3NB_{12}F_{11}^-$ anions, respectively (in all four cases the number in parentheses is the estimated standard deviation for individual B–F distances). The reason for this may be that the 2- charge of the $B_{12}X_{12}$ cages (including $Me_3NB_{12}F_{11}^-$, which can be thought of as a zwitterion with a 1+ charge on the N atom and a 2- charge on the $B_{12}F_{11}$ cluster) leads to greater F...F repulsion than for the 1-Et- $CB_{11}F_{11}^-$ anion. It is not because there is stronger B–B bonding within the B_{12} cages relative to the CB_{11} cage. The data presented in Figure 5.2 show that there is no significant difference between the B–B

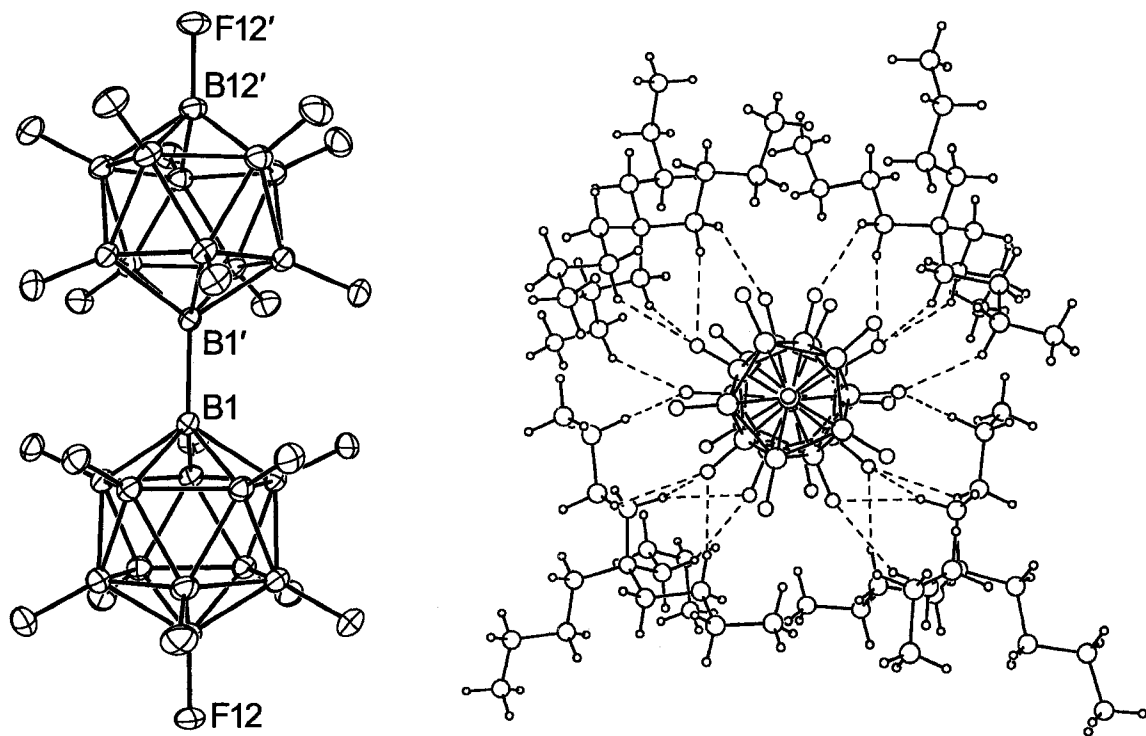


Figure 5.1. Left. The molecular structure of the $B_{24}F_{22}^{4-}$ anion in $(N(n-Bu)_4)_4B_{24}F_{22}$ (50% probability ellipsoids). Right. End-on view of the $B_{24}F_{22}^{4-}$ anion surrounded by its four $N(n-Bu)_4^+$ cations (all atoms are shown as spheres of arbitrary size). Some, but not all, of the $CH \cdots FB$ hydrogen bonds are shown.

Table 5.2. Selected interatomic distances (Å) and angles (deg) for the B₂₄F₂₂⁴⁻ anion^a

parameter	X-ray ^b	DFT B ₂₄ F ₂₂ ⁴⁻	DFT [N(<i>n</i> -Bu) ₄] ₄ [B ₂₄ F ₂₂]
B1–B1'	1.725	1.792	1.745
B1–B _{ub}	1.796–1.808	1.836	1.816
B _{ub} –B _{ub}	1.771–1.784	1.800	1.787
B _{ub} –B _{lb}	1.795–1.807	1.817	1.802
B _{lb} –B _{lb}	1.796–1.808	1.795	1.783
B _{lb} –B12	1.788–1.794	1.799	1.787
B _{ub} –F	1.378–1.389	1.403	1.405–1.409
B _{lb} –F	1.386–1.393	1.419	1.397–1.403
B12–F12	1.392	1.423	1.388
B12⋯B1–B1'	177.7	180	178.7
F12–B12⋯B1	179.7	180	179.5
F _{<i>n</i>} ⋯B1–B1'⋯F _{<i>n</i>} '	26.2°–26.8°	36°	29.5°–29.7°

^a B_{ub} = upper-belt boron atoms connected to B1 (i.e., B2–B6); B_{lb} = lower-belt boron atoms connected to B12 (i.e., B7–B11); *n* = 2–6. ^b The estimated standard deviations are 0.004 Å for B1–B1', 0.003 Å for other B–B bonds, 0.002 Å for all B–F bonds, and 0.1° for the bond angles. ^c The DFT calculations (PBE functional; TZ2P {6,1,1,1,1,1/4,1,1/1,1} basis set) were reported in ref. 1.

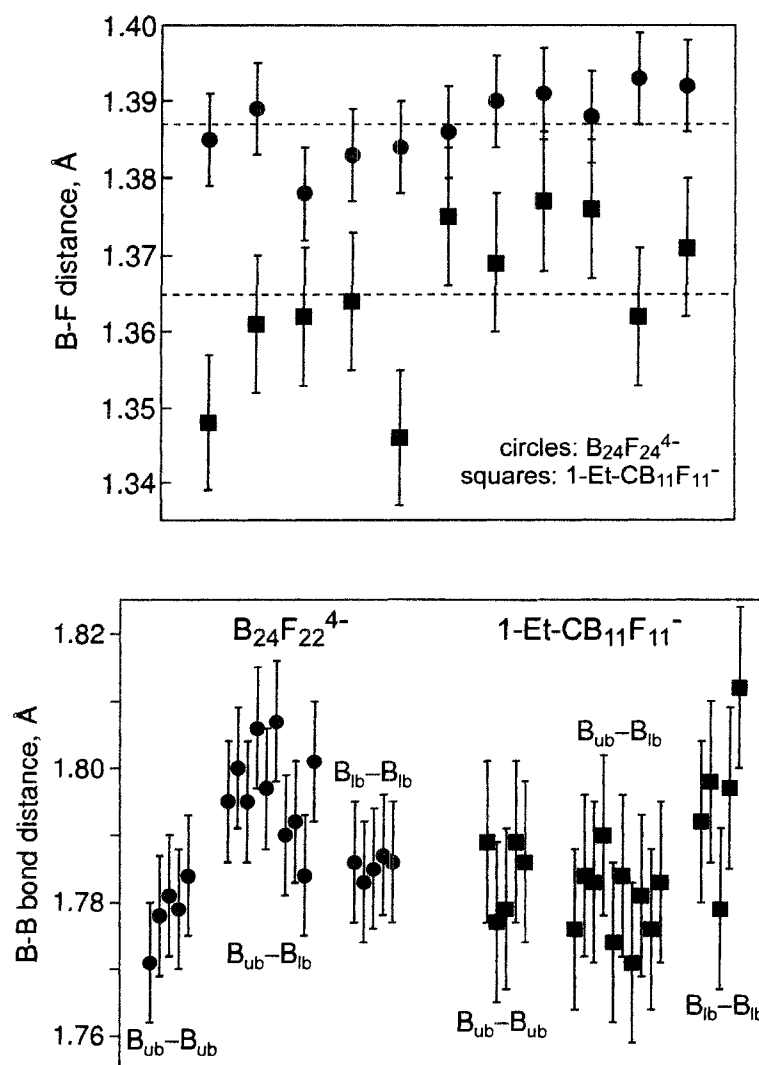


Figure 5.2. (Top) Individual and average (dotted lines) B–F distances (top) and individual B–B distances involving upper-belt (ub) and lower-belt (lb) B atoms (bottom) in $B_{24}F_{24}^{4-}$ (this work) and $1\text{-Et-CB}_{11}F_{11}^{-}$ (ref 12). In both plots the errors shown are at the $\pm 3\sigma$ level of confidence.

distances involving upper-belt and lower-belt B atoms in the $B_{24}F_{22}^{4-}$ and the 1-Et- $CB_{11}F_{11}^-$ anions.

The pseudo C_5 axes of the symmetry-related $B_{12}F_{11}^{2-}$ moieties in $B_{24}F_{22}^{4-}$ are nearly co-linear (the $F_{12}-B_{12}\cdots B_1$ and $B_{12}\cdots B_1-B_1'$ angles are 179.7° and 177.7° , respectively). Therefore, the $B_{24}F_{22}^{4-}$ anion has idealized D_5 symmetry. The three unique $F_n\cdots B_1-B_1'\cdots F_n'$ torsion angles are $26.5^\circ \pm 0.3^\circ$ ($n = 2-6$). The DFT-predicted symmetry for the isolated $B_{24}F_{22}^{4-}$ anion, which was not intentionally fixed, is D_{5d} , with all $F_n\cdots B_1-B_1'\cdots F_n'$ torsion angles equal to exactly 36° . The B_{12} cores in the X-ray and DFT $B_{24}F_{22}^{4-}$ anions are both distorted from idealized icosahedral symmetry by elongation of the antipodal $B_1\cdots B_{12}$ vector, as shown in Figure 5.3. The $B_1\cdots B_{12}$ distance in $B_{24}F_{22}^{4-}$, 3.463(3) Å, is significantly longer than the other five antipodal $B\cdots B$ distances, 3.390(3)–3.409(3) Å. Figure 5.3 also shows that a similar, but smaller, axial distortion was observed for the $Me_3NB_{12}F_{11}^-$ anion¹¹ and, as expected, was not observed for the $B_{12}F_{12}^{2-}$ and $B_{12}H_{12}^{2-}$ anions.^{13,14} In addition, Figure 5.3 reveals that the size of the icosahedral B_{12} core in $B_{12}F_{12}^{2-}$ was not affected by the substitution of the twelve hydrogen atoms in $B_{12}H_{12}^{2-}$ for twelve fluorine atoms to produce $B_{12}F_{12}^{2-}$.

Given the current interest in intermolecular/interionic $CH\cdots X$ hydrogen bonding ($X = O, N, \text{halogen}$),¹⁵⁻²² a relevant aspect of the structure of $[N(n\text{-Bu})_4]_4[B_{24}F_{22}]$ is the nature of the cation-anion interactions. Figure 5.1 shows one $B_{24}F_{22}^{4-}$ with four nearest-neighbor $N(n\text{-Bu})_4^+$ cations that form 22 $CH\cdots FB$ hydrogen bonds. There are four other cations that are almost as close as the four shown, and together the eight cations form a sheath of C–H bonds in which the anion is suspended. There are a total of 34 $CH\cdots FB$ hydrogen bonds which range in distance from 2.26 to 2.55 Å. For each $B_{12}F_{11}^{2-}$ moiety, only two F atoms do not form a $CH\cdots FB$ hydrogen bond shorter than 2.6 Å. The $C-H\cdots F$ angles range from 168.4° ($H\cdots F = 2.26$ Å) to 112.8° ($H\cdots F = 2.54$ Å). These distances and angles are similar to those observed or calculated for $CH\cdots F(B,P)$ interactions involving the fluoroanions BF_4^- and PF_6^- .^{23,24}

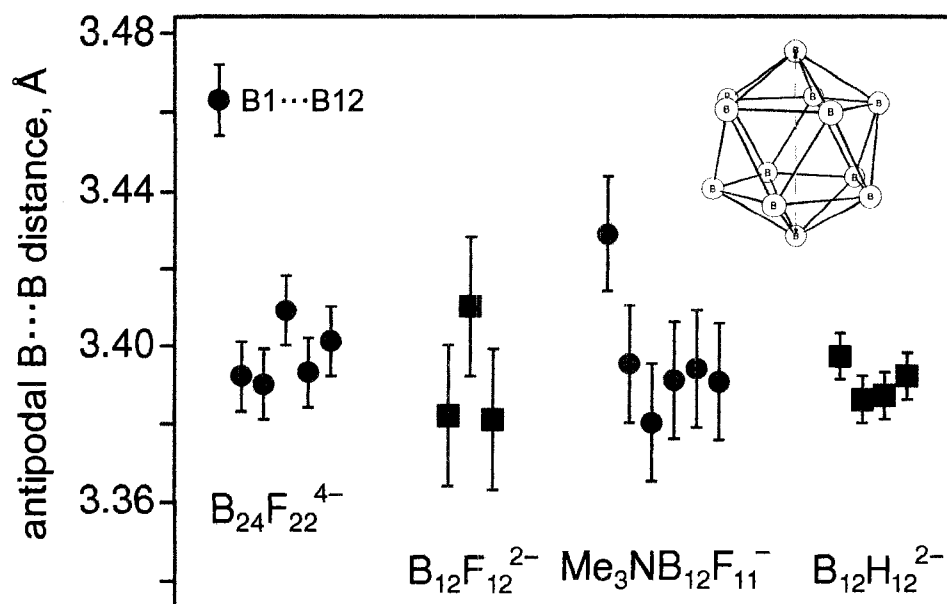


Figure 5.3. Individual antipodal B–B distances in $B_{24}F_{22}^{4-}$ (this work), $B_{12}F_{12}^{2-}$ (ref. 13), $Me_3NB_{12}F_{11}^{-}$ (ref. 11), and $B_{12}H_{12}^{2-}$ (ref. 14). The errors shown are at the $\pm 3\sigma$ level of confidence.

The $B_{24}F_{22}^{4-}$ anion is not the first structurally characterized $[closo-B_nX_{n-1}]_2^{4-}$ tetraanion. In 1992 Hawthorne and co-workers reported the structures of two isomers of $B_{20}H_{18}^{4-}$, each of which consisted of two $B_{10}H_9^{2-}$ moieties joined by a 2c-2e B–B bond (various hydrates of potassium salts of an equatorial-equatorial and an axial-axial isomer were studied by single-crystal X-ray diffraction).²⁵ The protonated trianion $B_{20}H_{19}^{3-}$ ²⁶ and different isomers of the two-electron oxidized dianion $B_{20}H_{18}^{2-}$ ^{27,28} have also been structurally characterized. This well-studied system stands in sharp contrast to the homologous $B_{24}H_{22}^{4-}/B_{24}H_{23}^{3-}/B_{24}H_{22}^{2-}$ system, about which much less is known. Electrochemical oxidation of $B_{12}H_{12}^{2-}$ in acetonitrile was reported to yield the $B_{24}H_{23}^{3-}$ trianion,^{29,30} but the structure of this species has never been unequivocally determined (i.e., even an unambiguous spectroscopic characterization of this species has not appeared in the last 30+ years). The same is true for the putative monohydroxy derivative, $B_{24}H_{22}OH^{3-}$.³¹ Similarly, a number of tetraanions with the formula $B_{24}H_{22-n}X_n^{4-}$ were reported in 1969 ($X = Cl, Br, I$), but neither their composition nor their isomeric purity were established (only elemental analysis, IR spectra, and ^{11}B NMR spectra consisting of one or two broad bands were reported).³² Finally, the dianion $B_{24}H_{20}I_2^{2-}$ has also been reported but, apparently, has never been characterized by modern spectroscopic techniques.³³

(b) The structure of $NMe_4(1,12-Me_2-CB_{11}F_{10})$. The IUPAC name of this compound is tetramethylammonium(1+) 1,12-dimethyl-1-carba-*closo*-dodecaborate(1-)). This salt crystallized in the monoclinic space group $C2/c$. The carborane anion is centered on a crystallographic inversion center and therefore has pseudo- D_{5d} symmetry instead of pseudo- C_{5v} symmetry. This requires a disorder that interchanges (i) C1 and B12 and the CH_3 groups attached to them and (ii) the five pairs of mutually antipodal B atoms and the F atoms attached to them (i.e., upper- and lower-belt B and F atoms are interchanged by the inversion disorder). A drawing of the structure of the anion is shown in Figure 5.4 and selected interatomic distances and angles are listed in Table 5.3. The observed

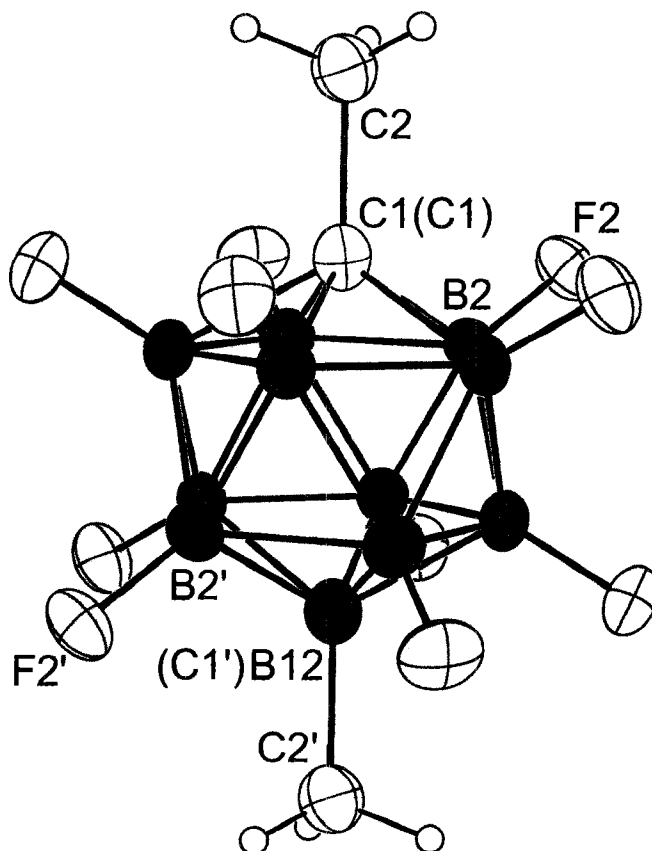


Figure 5.4. The inversion-disordered structure of the 1,12-Me₂CB₁₁F₁₀⁻ anion in NMe₄(1,12-Me₂-CB₁₁F₁₀) (50% probability ellipsoids except for H atoms which are shown as spheres of arbitrary size). This drawing shows C1 and B12 as separate atoms so that the idealized *C*_{5v} symmetry of the anion (ignoring the H atoms) can be appreciated, but C1 and B12 are actually indistinguishable (i.e., the anion has idealized *D*_{5d} symmetry if the H atoms are ignored). (Color coding: yellow, F; green, B; large white, C; small white, H)

Table 5.3. Selected interatomic distances (Å) and angles (deg) for the 1,12-Me₂-CB₁₁F₁₀[−], 1-Me-12-I-CB₁₁F₁₀[−], and 1-Me-12-SiPh₃-CB₁₁F₁₀[−] anions^a

parameter ^a	1,12-Me ₂ - ^b	1-Me-12-I- ^c	1-Me-12-SiPh ₃ - (Cs ⁺ salt) ^d	1-Me-12-SiPh ₃ - (Ag ⁺ salt) ^e
C1-CH ₃		1.525(2)	1.509(4)	1.522(4)-1.524(4)
C1-B _{ub}	1.725	1.724(3)-1.733(3)	1.715(4)-1.749(4)	1.713(4)-1.731(4)
B _{ub} -B _{ub}	1.786(3)-1.808(3)	1.796(3)-1.806(3)	1.777(4)-1.789(4)	1.779(4)-1.807(4)
B _{ub} -B _{lb}		1.774(3)-1.791(3)	1.774(4)-1.790(4)	1.770(4)-1.789(1)
B _{lb} -B _{lb}		1.815(3)-1.829(3)	1.797(4)-1.812(4)	1.792(4)-1.817(4)
B _{lb} -B12		1.788(3)-1.791(3)	1.801(4)-1.809(4)	1.794(4)-1.805(4)
B _{ub} -F	1.357(2)-1.369(2)	1.349(2)-1.360(2)	1.355(3)-1.367(3)	1.349(3)-1.361(3)
B _{lb} -F		1.359(2)-1.366(2)	1.366(3)-1.385(3)	1.360(3)-1.381(3)
B12-X		2.154(2)	2.044(3)	2.021(3), 2.034(3)

^a All data from this work; B_{ub} = upper-belt boron atoms; B_{lb} = lower-belt boron atoms.

^b NMe₄(1,12-Me₂-CB₁₁F₁₀); all B-B and B-F distances involving the upper-belt and lower-belt B atoms are listed in the B_{ub}-B_{ub} and B_{ub}-F rows. ^c Cs(1-Me-12-I-CB₁₁F₁₀).

^d Cs(1-Me-12-SiPh₃-CB₁₁F₁₀). ^e Ag₂(1-Me-12-SiPh₃-CB₁₁F₁₀)₂·C₆H₆.

C1–CH₃ distance is 1.555(3) Å. For comparison, the C1–CH₃ distance in the 1-Me-CB₁₁F₁₁[–] anion in the structure of (Ag(CHPh₃))(1-Me-CB₁₁F₁₁) is 1.518(9) Å³⁴ and the C1–CH₃ and B12–CH₃ distances in the structure of (C₆H₅NHMe₃)(CB₁₁Me₁₂)·MeOH are 1.520(5) and 1.601(6) Å, respectively.³⁵ Note that the average of 1.52 and 1.60 Å is 1.56 Å. The B–F bond distances in 1,12-Me₂-CB₁₁F₁₀[–] anion are unexceptional. They range from 1.359(2) to 1.370(2) Å. For comparison, the B–F bond distances in the 1-Me-CB₁₁F₁₁[–] and 1-Et-CB₁₁F₁₁[–] anions range from 1.348(8) to 1.380(9) Å and from 1.348(3) to 1.375(3) Å, respectively.^{12,34}

Since the NMe₄⁺ cation is disordered in such a way that there are eight C atoms at 50% occupancy bonded to the N atom instead of only four C atoms at 100% occupancy, a discussion of the CH···FB hydrogen bonding in this compound is not warranted.

(c) The structure of Cs(1-Me-12-I-CB₁₁F₁₀). This compound's IUPAC name is cesium(I) 1-methyl-12-triphenylsilyl-decafluoro-1-carba-*closo*-dodecaborate(1–). This salt crystallized in the monoclinic space group *P*2₁/*c*. However, the unit cell is only slightly distorted from an idealized cube, with cell lengths of 11.01, 11.97, and 11.60 Å and cell angles of 90, 94.9, and 90 deg. This is a relevant observation because the structure consists of a distorted cubic close-packed (ccp) array of carborane anions (i.e., ABCABC... packing) with the cesium ions filling all of the pseudo-octahedral holes. (The packing of cations and anions will be discussed later in this chapter.) A thermal ellipsoid plot of the anion is shown in Figure 5.5 and selected interatomic distances and angles are listed in Table 5.3. The C–B, B–B, and B–F distances are normal. The B–I distance of 2.154(2) Å can be compared with the 2.180(2) and 2.169(2) Å and B–I distances of in some iodo- and diiodo-*meta*-dicarba-*closo*-dodecaboranes.³⁶

The Cs⁺ ions in Cs(1-Me-12-I-CB₁₁F₁₀) are surrounded by eight F atoms in a distorted cubic array, as also shown in Figure 5.5. The Cs–F distances range from 3.011(1) to 3.673(2) Å (the mean and median Cs–F distances are 3.190 and 3.064(1)/3.099(1) Å, respectively). There are also two Cs–I distances of 4.0227(2) and

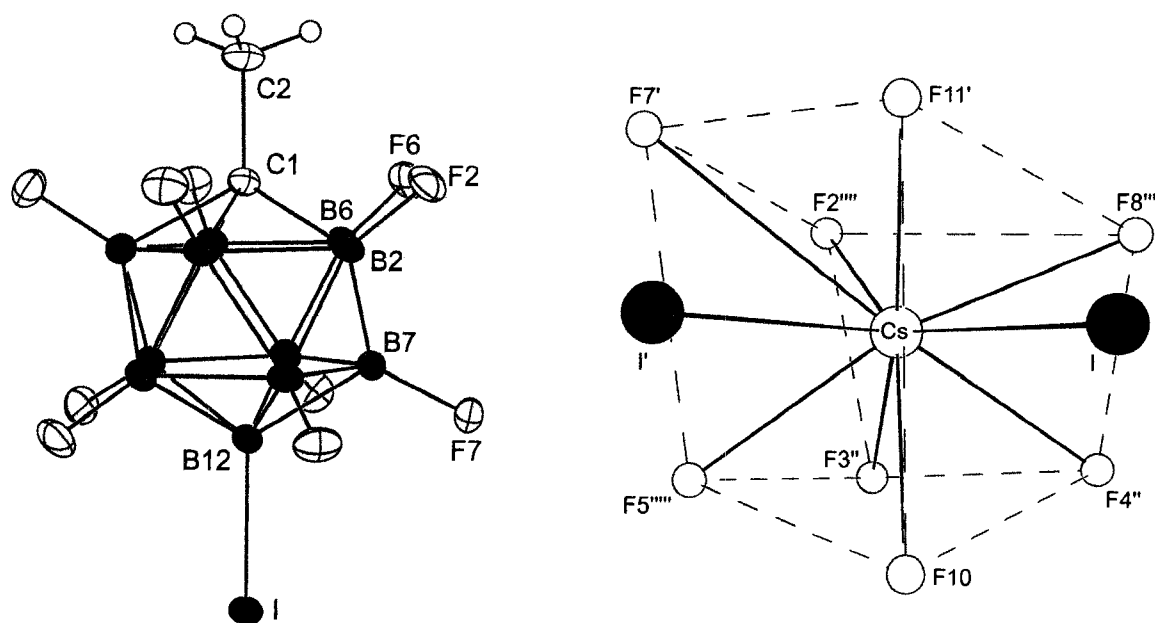


Figure 5.5. Thermal ellipsoid plot of the 1-Me-12-I-CB₁₁F₁₀⁻ anion (left; 50% probability ellipsoids except for H atoms which are shown as spheres of arbitrary size) and the coordination sphere of the Cs⁺ cation in Cs(1-Me-12-I-CB₁₁F₁₀) (right; spheres of arbitrary size). (Color coding: yellow, F; green, B; large white, C; small white, H; purple, I)

4.1409(2) Å (the I atoms can be thought of as capping two adjacent "square" faces of the CsF₈ cube). These distances can be analyzed using the *bond-valence* approach popularized by I. D. Brown.³⁷⁻³⁹ In the modern version of bond-valence calculations, the contribution, *s*, to the bond-valence sum of an element in a crystal is given by:

$$s = \exp[(R_0 - R)/0.37]$$

where *R*₀ is a parameter unique to the two elements that comprise the bond, and *R* is the observed bond distance. For a monpositive cation such as Cs⁺, the sum of the individual bond valence contributions should equal 1.000 (i.e., the valence of Cs⁺ is +1). The *R*₀ parameters for Cs–F and Cs–I bonds are 2.33 and 3.18 Å, respectively.⁴⁰ (An *R*₀ value for a 1+ cation and 1- anion can be thought of as the bond distance of a gas phase diatomic molecule that would give an *s* value of 1.000. For comparison, the equilibrium bond distances for the gas-phase diatomics CsF and CsI are 2.3453 and 3.3150 Å, respectively.⁴¹) The *s* values for the 10 Cs–X distances in Cs(1-Me-12-I-CB₁₁F₁₀) are:

		bond valence, <i>s</i>
Cs–F8'''	3.011(1) Å	0.159
Cs–F11'	3.045(1)	0.145
Cs–F5'''''	3.044(1)	0.145
Cs–F2D	3.064(1)	0.138
Cs–F10	3.099(1)	0.125
Cs–F4''	3.307(2)	0.071
Cs–F3''	3.273(2)	0.078
Cs–F7'	3.673(2)	0.027
Cs–I	4.0227(2)	0.102
Cs–I'	4.1409(2)	0.074
		sum = 1.064

Therefore, the sum of bond valences for Cs(1-Me-12-I-CB₁₁F₁₀) is within 6.4% of the expected value of 1.000. For comparison, the bond valence sums for crystalline CsF (six 3.005 Å distances⁴¹) and CsI (eight distances 3.950 Å⁴¹) are 0.968 and 0.998, respectively.

(d) The structure of Cs(1-Me-12-SiPh₃-CB₁₁F₁₀). The IUPAC name for this salt is cesium(I) 1-methyl-12-triphenylsilyl-decafluoro-1-carba-*clos*o-dodecaborate(1-). This compound crystallized in the monoclinic space group $P2_1/n$. A thermal ellipsoid plot of the formula unit is shown in Figure 5.6 and selected interatomic distances and angles are listed in Table 5.3. The C–B, B–B, and B–F distances are normal.

The Cs⁺ ion is positioned between two nearly parallel phenyl groups from different anions, with 12 Cs–C distances that range from 3.600(3) to 4.021(3) Å (all but three of them are less than or equal to 3.788(3) Å). The Cs⁺ is also coordinated by five F atoms from three anions that form a pentagonal belt around Cs⁺ (these five F atoms are not coplanar; the range of out-of-plane displacements from the least-squares plane of the five F atoms is +0.66 to –0.86 Å). The bond valences for the Cs–F contacts are:

		bond valence, <i>s</i>
Cs–F10	3.238(2) Å	0.086
Cs–F11	3.134(2)	0.114
Cs–F2'	3.201(2)	0.095
Cs–F9'	3.028(2)	0.152
Cs–F7''	2.896(2)	0.217
		sum = 0.664

This means that only 66% of the total bond valence for Cs⁺ in this compound is due to the five Cs–F contacts, and therefore that ca. 34% is due to the Cs–C(arene) contacts (no published R_0 value is available for Cs–C bonds).

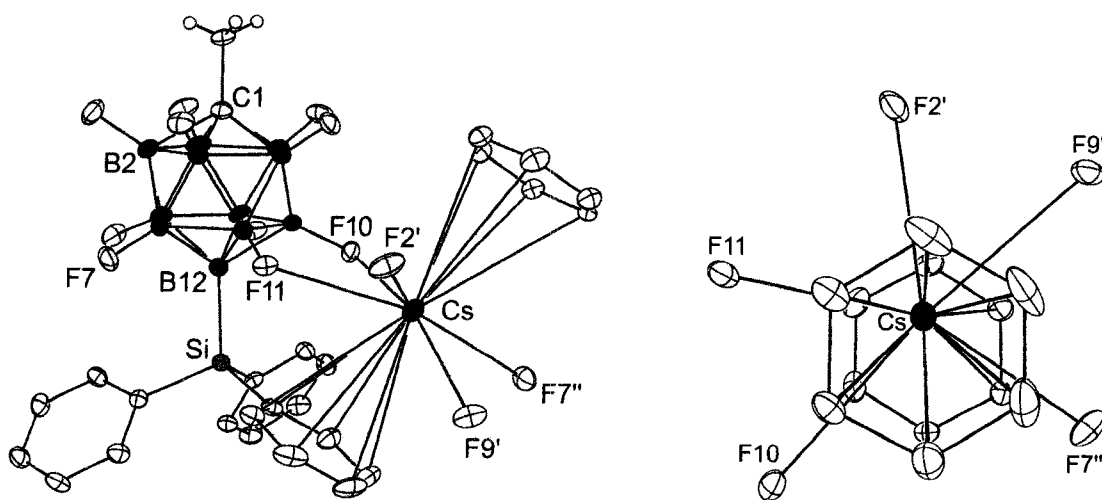


Figure 5.6. Thermal ellipsoid plot of the 1-Me-12-SiPh₃-CB₁₁F₁₀ anion in Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) (left; 50% probability ellipsoids except for H atoms on the CH₃ group which are shown as spheres of arbitrary size; H atoms on the Ph groups have been omitted for clarity) and the coordination sphere of the Cs⁺ cation in Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) (right; 50% probability ellipsoids). (color coding: yellow, F; green, B; large white, C; small white, H; blue, Cs; orange, Si)

There are regions in the structure of Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) in which several phenyl groups interact with one another in an *edge-face* fashion,⁴²⁻⁴⁴ similar to the interaction of two benzene molecules in the gas-phase⁴⁵⁻⁴⁷ or in crystalline benzene. Figure 5.7 shows this region for a set of four cations and six anions. The apparent face-to-face π - π interactions between phenyl groups in this drawing are actually more than 8 Å apart and therefore are not significant. Figure 5.8 shows three close-up views of the central edge-face region in Figure 5.7. One of the edge-face interactions, between rings **a** and **b**, has a centroid-to-centroid distance of 4.91 Å, a vertical displacement of one centroid from the least-squares plane of the other ring of 4.82 Å, and an interplane angle of 61.4°. The interaction between rings **a** and **c** has centroid-to-centroid distance of 5.33 Å, a vertical displacement of one centroid from the least-squares plane of the other ring of 5.22 Å, and an interplane angle of 79.7°.

In a 2007 *J. Phys. Chem. A* paper by Kim and co-workers, the most stable conformations of the benzene dimer were predicted to be edge-face conformations, and these have centroid-to-centroid distances of 4.89–4.93 Å and vertical displacements of one centroid from the least-squares plane of the other C₆ ring of 4.81–4.87 Å. In a 2007 *Chem. Phys. Lett.* paper by Head-Gordon and co-workers, one of the most stable edge-face conformations of the benzene dimer was predicted to have a centroid-to-centroid distance of 4.75 Å, a vertical displacement of one centroid from the least-squares plane of the other ring of 4.68 Å, and an interplane angle of 90°. ⁴⁶ This latter conformation is compared with one of the edge-face interactions in Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) in Figure 5.9.

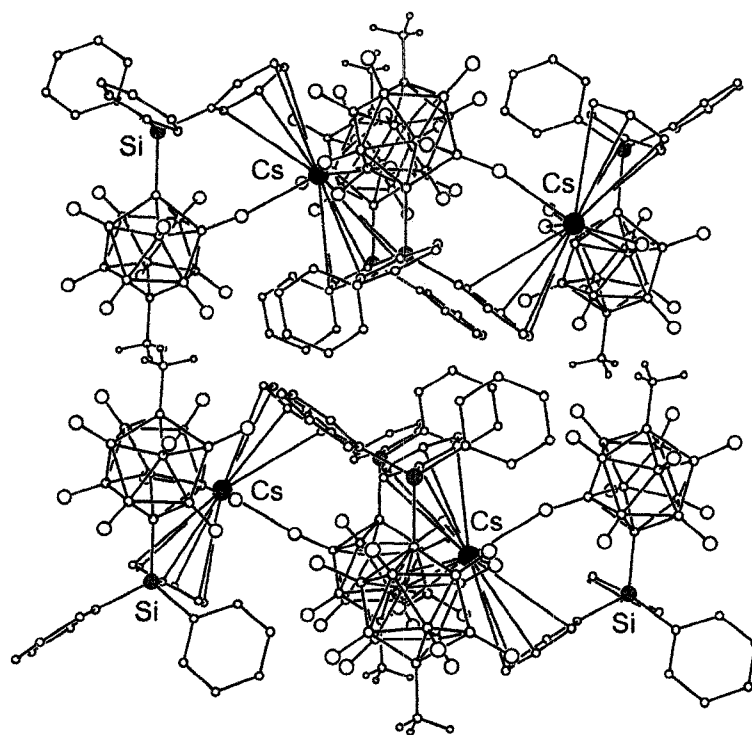


Figure 5.7. A portion of the structure of Cs(1-Me-12-SiPh₃-CB₁₁F₁₀), showing four Cs⁺ cations (blue spheres) and six 1-Me-12-SiPh₃-CB₁₁F₁₀⁻ anions (Si atoms are depicted as orange spheres). Note the central region of the diagram in which multiple phenyl groups from different anions interact with one another in an edge-face motif.

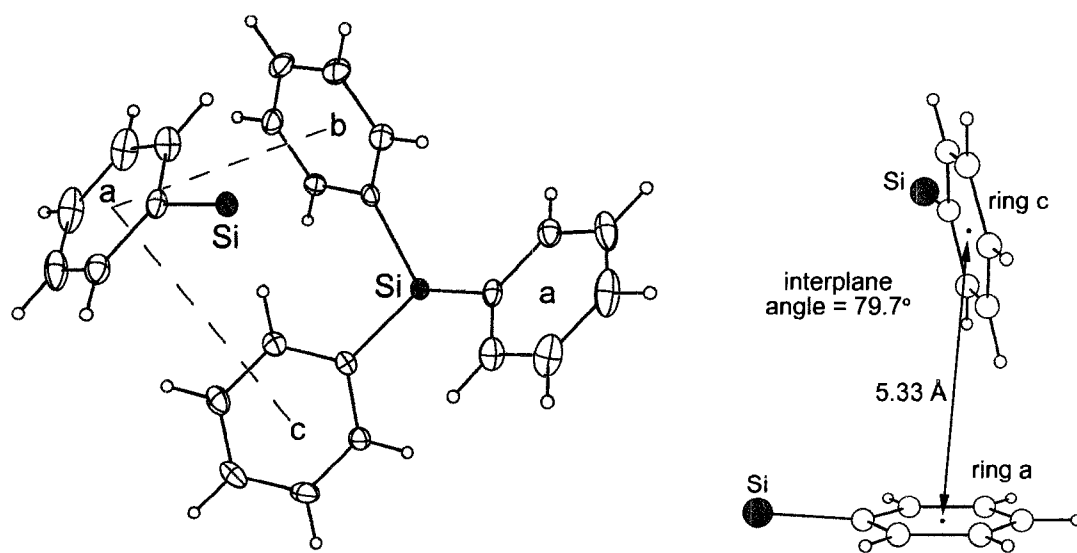


Figure 5.8. Two close-up views of the central region of the diagram in Figure 5.7. The drawing on the left shows the two edge-face interactions between aromatic rings **a** and **b** and rings **a** and **c** (the Cs^+ cations are coordinated to rings **a** and **b**). The drawing on the right shows the edge-face interaction between rings **a** and **c** in a different orientation for clarity, with the ring centroid-to-centroid distance and interplane angle indicated.

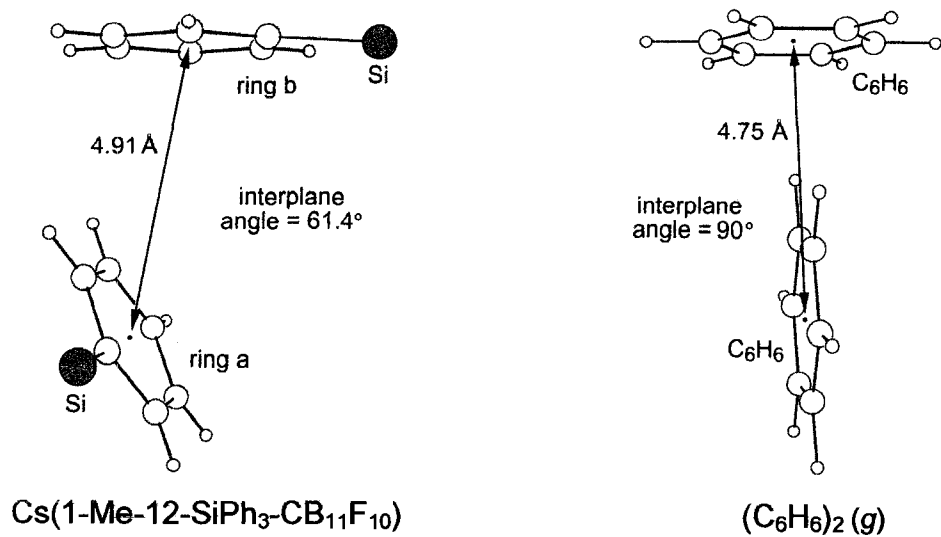


Figure 5.9 One of the edge-face phenyl-phenyl interactions in Cs(1-Me-12-SiPh3-CB11F10) (left) and one of the theoretically most stable edge-face conformations of the gas-phase benzene dimer (coordinates from ref.46).

(e) **The structure of $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$.** The IUPAC name for this salt is silver(I) 1-methyl-12-triphenylsilyl-decafluoro-1-carba-*closo*-dodecaborate-(1-) hemibenzene solvate. It crystallized in the monoclinic space group $P2_1/c$. A ball and stick drawing of the formula unit is shown in Figure 5.10 and thermal ellipsoids plots of the Ag1 and Ag2 coordination spheres are shown in Figure 5.11. 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).

Silver(I) arene chemistry has been of interest to structural chemists since the pioneering work of Amma.⁴⁸⁻⁵⁰ A recent, thorough analysis of the Cambridge Crystallographic Database by Kochi and co-workers showed that rather narrow ranges of several structural parameters are observed for a variety of $\text{Ag}(\text{arene})_{2,3}^+$ moieties.⁵¹ In every case, these moieties were also bonded to one or more atoms of the counterion and occasionally to another ligand such as 1,2- $\text{C}_6\text{H}_4\text{I}_2$ or H_2O . The first "free" $\text{Ag}(\text{arene})_3^+$ moiety, with a trigonal-planar coordination geometry, was reported in 2004 (the compound was $\text{Ag}(\text{CHPh}_3)(1\text{-Me-CB}_{11}\text{F}_{11})^{34}$). No $\text{Ag}(\text{arene})_4^+$ moiety of any kind had been reported before this work.

The Ag1 cation is strongly coordinated to a phenyl group from each anion and to the lattice benzene molecule, and is weakly bonded to an F atom from one anion. The $\text{Ag}\cdots\text{F107}$ distance is 2.706(3) Å; the next closest $\text{Ag}\cdots\text{F}$ contact is 3.200(3) Å to F211'. The Ag1-C135-C134 and Ag1-C235-C236 angles are 80.2(2) and 83.0(2)°, respectively. The C1-Ag1-C135 , C1-Ag1-C235 , and C135-Ag1-C235 angles are 123.3(1), 123.7(1), and 113.0(1)°, and their sum is 360.0(3)°, demonstrating that the $\text{Ag1}(\text{arene})_3^+$ coordination unit is essentially trigonal planar (Ag1 is displaced by only 0.05 Å from the C1–C135–C235 least-squares plane towards F107). The Ag–C distances involving Ag1 and other trigonal $\text{Ag}(\text{arene})_3^+$ coordination units are shown in in Figure 5.12 (Ag2–C distances are included for comparison).^{34,52,53}

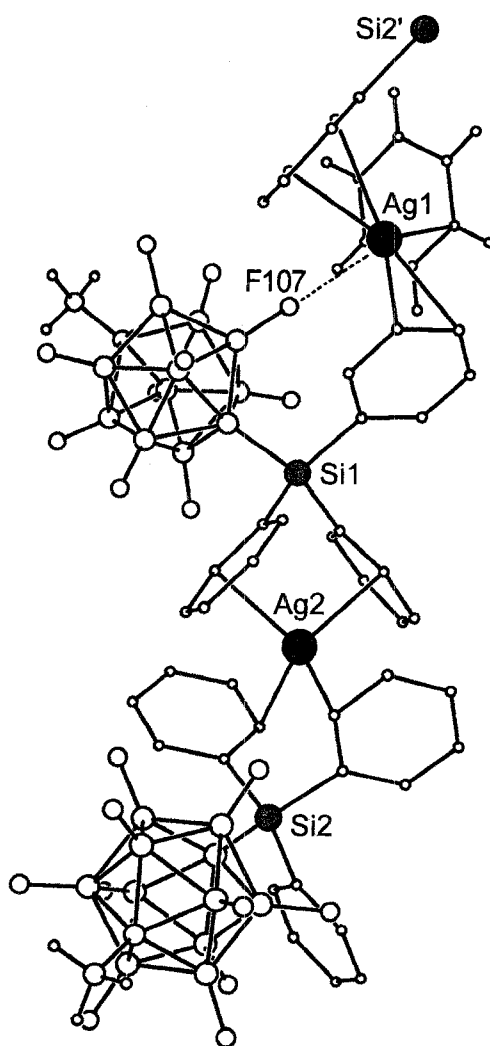


Figure 5.10. Ball and stick drawing of the $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ formula unit. The C atoms of the phenyl groups and the benzene solvate have been drawn as smaller than usual spheres for clarity, and the H atoms of the phenyl groups (but not the benzene solvate) have been omitted for clarity

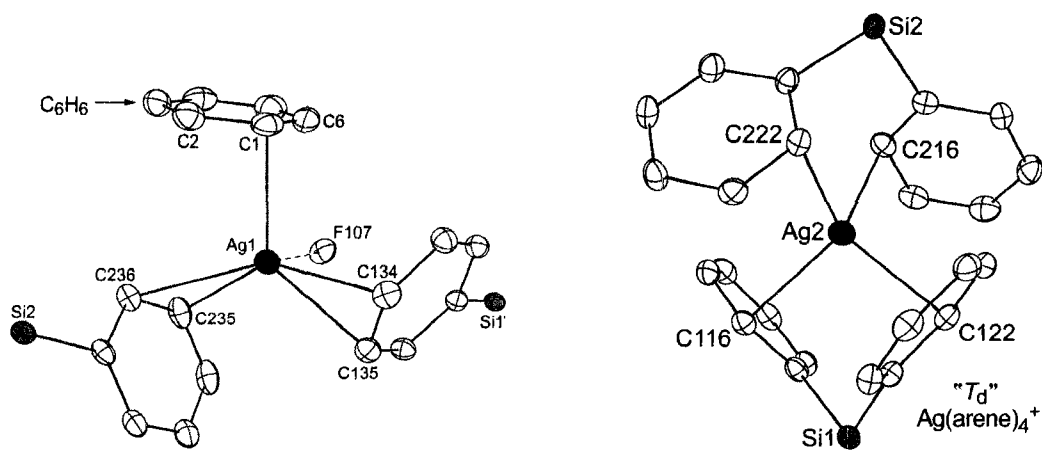


Figure 5.11. Drawings of the Ag1 and Ag2 coordination spheres in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ (50% probability ellipsoids; H atoms omitted for clarity). For the Ag1 coordination sphere: Ag1–C1, 2.484(3) Å; Ag1–C134, 2.631(3) Å; Ag1–C135, 2.482(3) Å; Ag1–C235, 2.442(3) Å; Ag1–C236, 2.666(3) Å; Ag···F107, 2.706(3) Å. For the Ag2 coordination sphere: 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).

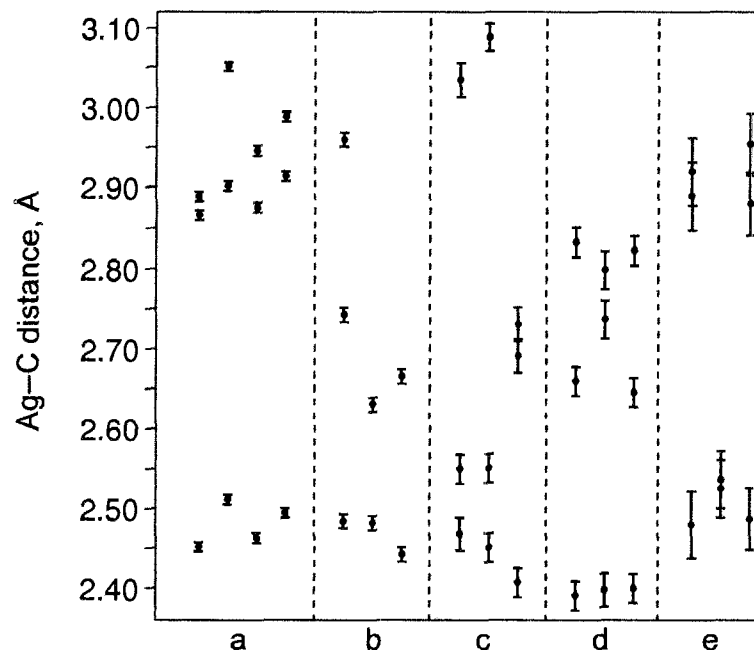


Figure 5.12. Plots of the Ag–C bond distances ($\pm 3\sigma$ error bars) in the structures of the tetrahedral $\text{Ag}_2(\text{arene})_4^+$ and trigonal-planar $\text{Ag}_1(\text{arene})_3^+$ coordination units in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ (**a** and **b**, respectively; this work), the trigonal-planar $\text{Ag}(\text{arene})_3^+$ coordination unit in $\text{Ag}(\text{CHPh}_3)(1\text{-Me-CB}_{11}\text{F}_{11})$ (**c**, ref. 34), the trigonal-planar $\text{Ag}(\text{C}_6\text{H}_6)_3^+$ coordination unit in $\text{Ag}(\text{C}_6\text{H}_6)_3(\text{B}(\text{C}_6\text{F}_5)_4)$ (**d**, ref. 53), and the trigonal-pyramidal $\text{Ag}(\text{C}_6\text{D}_6)_3^+$ coordination unit in $\text{Ag}(\text{C}_6\text{D}_6)_3(\text{BF}_4)$ (**e**, ref. 52).³ The distances with the same x -axis value involve the same arene ligand. Very long Ag–C bond distances are included to emphasize the variable η^x coordination of arenes to Ag^+ ions ($1 \leq x \leq 2$).

The Ag² cation is strongly coordinated to two phenyl groups from each anion, forming the first example of a Ag(arene)₄⁺ complex. The coordination geometry is distorted tetrahedral; the distortion is due to the bis(bidentate) nature of the Ag(arene)₄⁺ unit. The six tetrahedral C–Ag–C angles range from 102.0(1) to 122.2(1)°, and their sum is 655.8(6)° (the sum for an ideal tetrahedron is 657.0°). For comparison, the N–Ag–N angles in Ag(en')₂⁺ complexes range from 76.3 to 138.4°.⁵⁴ There are no contacts between Ag₂ and any F atom shorter than 4.7 Å.

It is well known that Ag⁺ and Cu⁺ coordinate the arenes in such a way that the metal ion is nearly above the plane of the six-membered ring and is bonded (i) to two C atoms with equal Ag–C bond distances (i.e., dihapto, or η², coordination), (iii) to two C atoms with unequal Ag–C distances (i.e., η^x, coordination; (1 ≤ x ≤ 2)), or (iii) to only one C atom (i.e., monohapto, or η², coordination).⁴⁸⁻⁵¹ Most published structures are in the η^x category, and Kitagawa, Komatsu, and co-workers⁵³ have used the following equation (previously developed by Kochi and co-workers for halogen, not metal, complexes of arenes;⁵⁵ d₁ is the shorter of the two Ag–C(arene) distances, d₂ is the longer Ag–C(arene) distance, and the other parameters are defined in the structural diagrams shown below):⁵¹

$$x = 1 + 2(d_1^2 - d^2)^{1/2} / [(d_1^2 - d^2)^{1/2} + (d_2^2 - d^2)^{1/2}]$$



The grab angle α is the complement of the angle between arene planes that are part of the same molecule or molecular ion. This parameter does not appear in the formula but will be discussed later. The d, d₁, d₂, and α structural parameters and the (tentative; see below) derived η^x values for Ag₁ and Ag₂ are listed in Table 5.4.

Table 5.4. Structural and Kitagawa/Komatsu hapticity parameters for $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ ^a

Ag; arene	d_1 , Å	d_2 , Å	d, Å	β , deg	apparent x value	α , deg
Ag1; C1/C6	2.484(3)	2.743(3)	2.463	30.3	1.42	—
Ag1; C135/C134	2.482(3)	2.631(3)	2.413	32.7	1.71	—
Ag1; C235/C236	2.442(3)	2.666(3)	2.405	31.0	1.54	—
Ag2; C116/C111	2.452	2.866	2.412	34.4	1.44	83.6
Ag2; C122/C121	2.511	2.902	2.467	36.2	1.41	83.6
Ag2; C216/C211	2.463	2.875	2.419	35.7	1.46	83.1
Ag2; C222/C221	2.495	2.914	2.452	35.9	1.45	83.1

^a The apparent hapticity parameter x does not describe the true hapticity of the arene ligands in this compound for reasons described in the text.

Kitagawa, Komatsu, and co-workers' use of the Kochi equation leads to the interpretation that the Ag2^+ ions in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$ are $\eta^{1.4}\text{--}\eta^{1.5}$ coordinated to its four arene ligands, a conclusion that is not supported by the drawings of the Ag–arene interactions shown in Figure 5.13. In that figure, it is obvious that Ag2 is not directly over a single arene C atom for any of its four arene ligands. This is a necessary *but not sufficient* condition for $\eta^{1.5}$ or η^2 coordination. However, it is also obvious that Ag2 is virtually equidistant from the two next-closest arene C atoms, which is a necessary *and* sufficient condition for η^1 coordination. Figure 5.14 shows the projection of Ag1, Ag2, and silver(I) ions in several other silver(I)–arene complexes onto the least-squares plane of one of their arene ligands. It can be seen that in most cases the Ag^+ ion does not project onto an arene C–C bond, and the Kochi equation is only valid when the atom that interacts with an arene ligand is directly over one C atom or one C–C bond. In the example shown in Figure 5.14 from the Kitagawa/Komatsu paper, use of the equation to determine the η^x value was justified (and $\eta^x = \eta^{1.36}$ in that case), but its use is not justified for most silver(I)–arene complexes and certainly not for $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$. Otherwise, we would be left with the unreasonable interpretation that the Ag2 interaction with the C116 arene is closer to η^2 coordination than is the Ag1 interaction with the C1 arene in the Kitagawa/Komatsu compound.

Finally, the grab-angles α for Ag2 in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$, at 83.6 and 83.1°, are significantly smaller than those previously reported in the literature. For most bidentate (bis)arene ligands coordinated to tetrahedral Ag^+ ions, the α values are ca. 130°. ⁵¹ The reason for this is that the two arene ligands on each $1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10}^-$ anion are nearly perpendicular (the interplane angles are 96.4° for one anion and 96.9° for the other) to accommodate bidentate coordination to Ag2. In all of the examples cited in ref ⁵¹, the arene substituents were not bonded to a common atom (unlike the phenyl groups in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$, which are bonded to a common Si atom in each of the two anions).

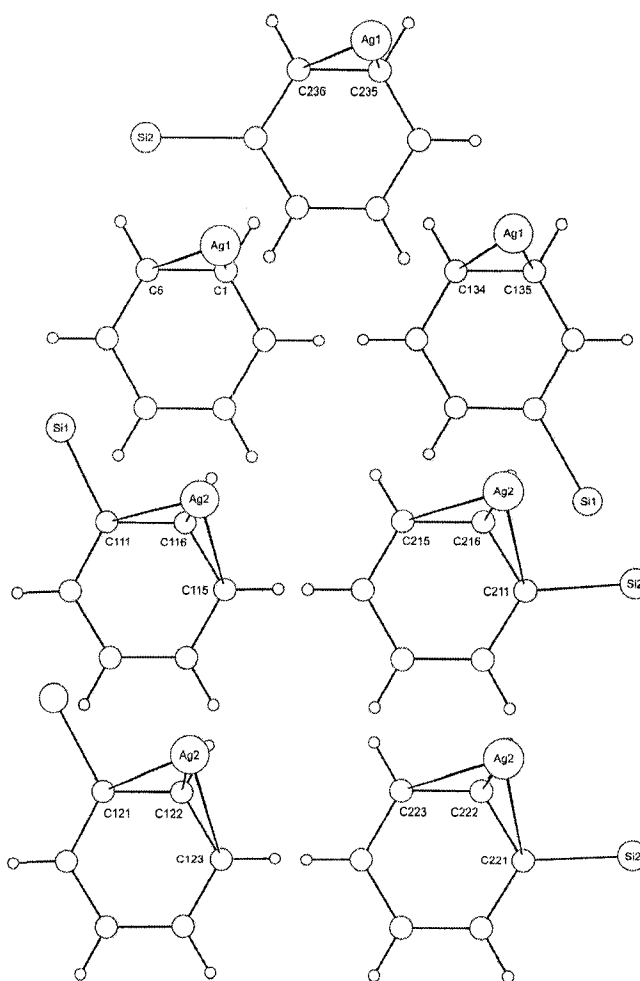


Figure 5.13. Drawings of the Ag1 and Ag2 arene interactions in $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2 \cdot \text{C}_6\text{H}_6$. The Ag–C distances (Å) shown are: Ag1–C1, 2.484(3); Ag–C6, 2.743(3); Ag1–C134, 2.631(3); Ag1–C135, 2.482(3); Ag1–C235, 2.442(3); Ag1–C236, 2.666(3); Ag2–C116, 2.452(2); Ag2–C111, 2.866(2); Ag2–C115, 2.888(2); Ag2–C122, 2.511(2); Ag2–C121, 2.902(2); Ag2–C123, 3.051(2); Ag2–C216, 2.463(2); Ag2–C211, 2.875(2); Ag2–C215, 2.946(2); Ag2–C222, 2.495(2); Ag2–C221, 2.914(2); Ag2–C223, 2.989(2).

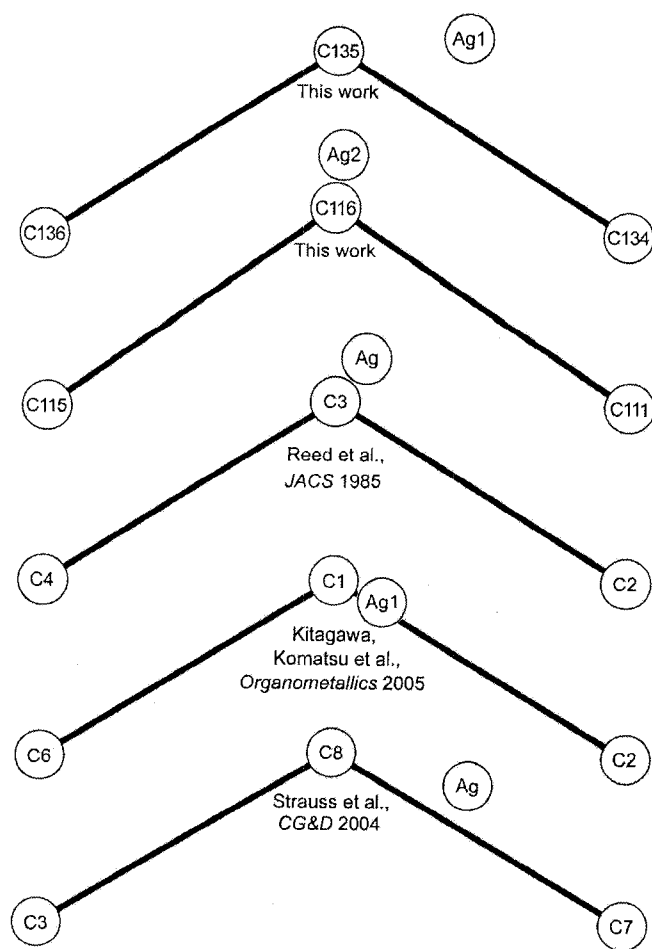


Figure 5.14. Diagrams showing the projection of the Ag^+ ion onto the plane of the arene to which it is bonded for several silver(I)-complexes (the least-squares plane of the arene is the plane of the page). Only three C atoms of each arene ligand is shown. The three examples from the literature are from refs. 56, 53, and 34 (middle diagram, second-lowest diagram, and lowest diagram, respectively).

Cation-anion lattice packing in salts of icosahedral borane and carborane anions. (a) **Introduction.** The structures described above exhibit interesting similarities and differences with respect to how the anions and cations are arranged in three-dimensional space, and this subject will be discussed in the remainder of this chapter. For many (1+)(1-) salts such as CsF, KI, CsI, and NMe₄I, either the NaCl ("rock salt") structure or the CsCl structure is observed.⁴¹ The NaCl structure type is based on a cubic close-packed array of the larger ions with the ions of opposite charge occupying all of the octahedral holes (interstices). The coordination number for both cations and anions is six. The CsCl structure type is not based on a close-packed array of ions. Each ion is surrounded by eight ions of opposite charge at the corners of a cube. Some icosahedral borane and carborane salts with cations of identical charge exhibit one or the other of these structures, at least all of the substituents are similar in size, because in those cases the overall shape of the anions is roughly spherical. Two of the salts discussed above, NMe₄(1,12-Me₂-CB₁₁F₁₀) and Cs(1-Me-12-I-CB₁₁F₁₀), are in this category. The two salts of the 1-Me-12-SiPh₃-CB₁₁F₁₀⁻ anion have very different lattice packings, almost certainly because of the large size of the SiPh₃ substituent. They will be discussed separately. Finally, the salt (N(*n*-Bu)₄)₄B₂₄F₂₂, which is a (1+)(4-) salt, is in a totally different category. The lattice packing in this salt will be discussed first.

(b) **Cation-anion packing in (N(*n*-Bu)₄)₄B₂₄F₂₂.** There are no known simple (1+)(4-) salts with monatomic ions. There are approximately 70 (4+)(1-) salts with monatomic ions that can be considered ionic compounds (as opposed to molecular substances such as TiCl₄).⁴¹ But in these cases, the size of the cation is always much smaller than the anion (the cation is smaller even in the case of UF₄; the ionic radii of U⁴⁺ and F⁻ are 1.05⁵⁷ and 1.33 Å,⁴¹ respectively). The effective radius of the N(*n*-Bu)₄⁺ cation is 4.1 Å.⁵⁸ The short and long radii of the B₂₄F₂₂⁴⁻ anion are 3.8 and 6.4 Å, respectively. The anion radii were estimated by adding 0.7 Å to one-half of the average F...F distances across each icosahedral fragment or one-half of the F12...F12' distance, respectively.

Therefore, the radii of the cation and anion in this salt are about the same. (The addition of 0.7 Å to one-half the F...F distances in icosahedral fluoroborane and carborane anions will be justified in section (c), below.)

The lattice packing in $(N(n\text{-Bu})_4)_4B_{24}F_{22}^{4-}$ was found to be based on an idealized hexagonal close-packed array of $B_{24}F_{22}^{4-}$ anions with a complicated arrangement of cations in the octahedral and tetrahedral holes. A drawing of the anion and cation layers is shown in Figure 5.15. The anion centroids are defined as the midpoint of the B1–B1' bond, and these are displayed as large spheres, representing the anion centroids, attached to two smaller spheres representing the B1 and B1' atoms so that the orientation of the anions can be seen. Figure 5.15 also includes a drawing of the 12 closest anion centroids around each centroid. Both drawings in Figure 5.15 show the ABAB... packing of roughly hexagonal layers of anions. The central centroid is 14.62 Å from two centroids and 18.90 Å from four centroids within the close-packed layer (these layers are the crystallographic *ab* plane; the centroids in each layer are rigorously coplanar). In the layers of centroids above and below the central centroid are three (each) centroid nearest neighbors, one at 12.71 Å and two at 14.1 Å.

Another structure of a salt of the $N(n\text{-Bu})_4^+$ cation and a 4[−] anion is the structure of $N(n\text{-Bu})_4(Ni_{24}Pt_{14}(CO)_{44})^{59}$. In that structure, the anion is much larger than the cation. The roughly spherical metal-carbonyl cluster has O...O distances of ca. 13.4 Å and therefore a radius of ca. 7 Å. The tetraanions in this compound do not form a close-packed array but instead form hexagonal close-packed layers (these layers are in the crystallographic *bc* planes; in this case too the anion centroids are coplanar) that are stacked so that the anion centroids are in register every two layers and the centroids in every other layer are offset by one-half along the crystallographic *b* axis. Two drawings of three successive layers of anion centroids in this structure are shown in Figure 5.16. It is clear that the packing of ions in (1+)(4−) salts is quite complex, and any further analysis of (1+)(4−) lattice packing is beyond the scope of this dissertation.

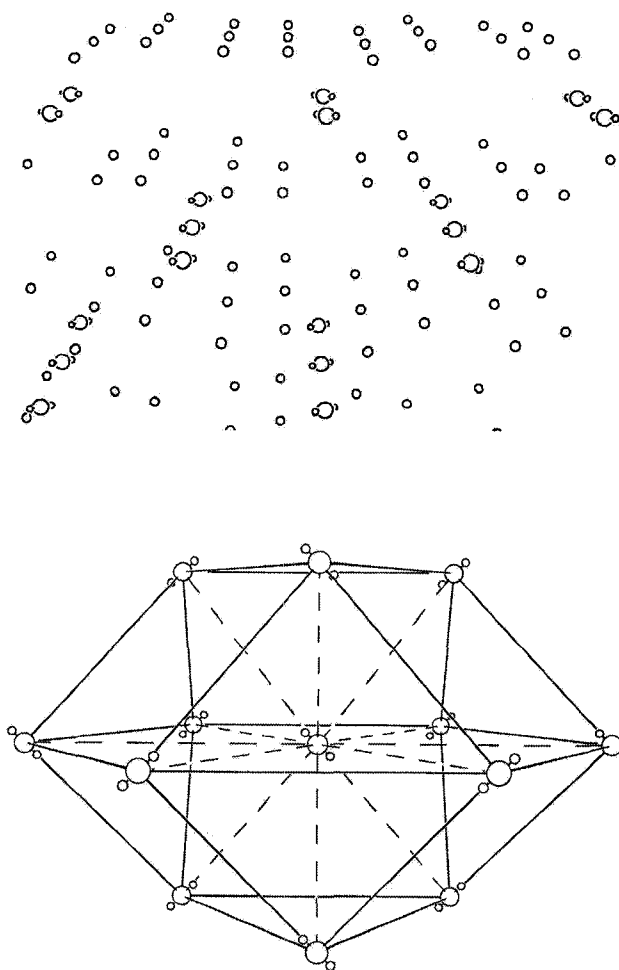


Figure 5.15. Two drawings showing the arrangement of the tetraanion centroids in $(N(n\text{-Bu})_4)_4B_{24}F_{22}$. The centroids are defined as the B1–B1' bond midpoints in the $B_{24}F_{22}^{4-}$ anions, are displayed as large spheres, and are attached to two smaller spheres representing the B1 and B1' atoms. In the upper drawing the intermediate size spheres are N atoms from the $N(n\text{-Bu})_4^+$ cations (i.e., these represent the cation centroids).

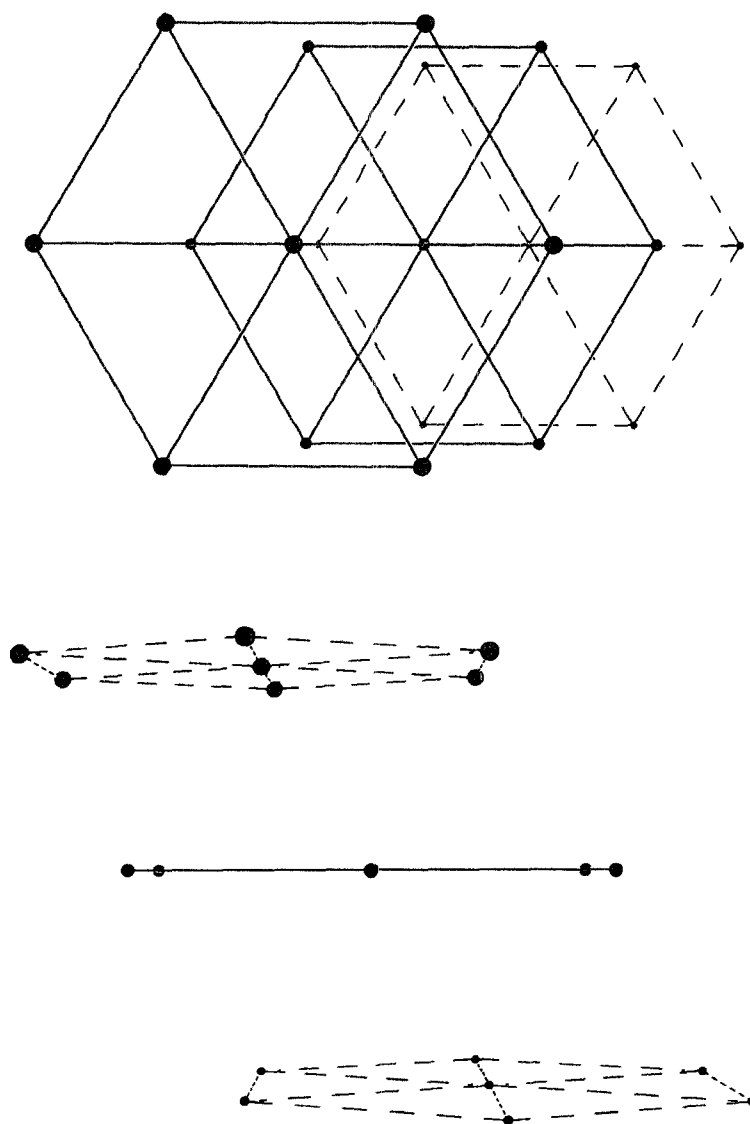


Figure 5.16. Two perpendicular views of the arrangement of the tetraanion centroids in $(\text{N}(n\text{-Bu})_4)_4(\text{Ni}_{24}\text{Pt}_{14}(\text{CO})_{44})$ (coordinates taken from ref. 59). The hexagonal close-packed layers are parallel to the crystallographic bc plane.

(c) **Cation-anion packing in $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ and $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$.** The cations and anions in $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ are arranged in a CsCl-type lattice; the cations and anions in $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$ are arranged in a NaCl-type lattice. In order to analyze these two packing arrangements, it is necessary to define the radii of carborane anions (this will also be of value for future structural studies by other workers in the field). Since the C1–B_{ub} bonds in the $1\text{-Me-12-I-CB}_{11}\text{F}_{10}^-$ anion, at 1.721(3)–1.733(3) Å, are slightly shorter than B12–B_{lb} bonds, at 1.788(3)–1.791(3) Å, it might be expected that the centroid of the twelve atoms that comprise the carborane core (i.e., C1 and B2–B12) would differ significantly from the centroid of the ten atoms B2–B11. However, these two centroids are only 0.008 Å apart, so the former definition of the centroid was chosen for the packing analyses discussed in this dissertation.

The eight N···centroid distances in $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ range from 6.31 to 7.00 Å and average 6.62 Å, as shown in Figure 5.17. The 12 centroid···centroid distances for the (centroid)₈ cube surrounding each cation are 7.78 (× 8) and 7.35 (× 4) Å and average 7.64 Å. The $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ anion is obviously larger than the NMe_4^+ cation, which has an effective ionic radius of 2.79 Å.⁵⁸ The antipodal H₃C···CH₃ distance and a typical antipodal F···F distance in the anion are 3.178(3) and 3.070(2) Å, respectively.

The six Cs···centroid distances in $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$ range from 5.50 to 6.02 Å and average 5.80 Å. The cubic close-packed array of anion centroids is shown in Figure 5.17. The 12 centroid···centroid distances range from 7.66 to 8.90 Å and average 8.18 Å. The six-coordinate ionic radius of Cs⁺ is 1.67 Å.^{41,60} The antipodal H₃C···I distance and a typical antipodal F···F distance in the anion are 3.440(2) and 3.068(2) Å.

Antipodal X···X distances, ionic radii, and interionic distances for $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$, and several other (1+)(1−) salts are listed in Table 5.5.^{41,58,61} Two situations are possible for NaCl- and CsCl-type lattices: (i) the Cl[−] are in van der Waals contact and the M⁺–Cl[−] distance is either *equal to or less than* the

Table 5.5. Structural and lattice packing parameters for selected (1+)(1-) salts^a

compd	$\frac{1}{2}(X \cdots X)$, Å ^b	anion radius, Å ^c	cation radius, Å ^c	radius ratio	lattice type	cation...cent. distances, Å ^d	cent...cent. distances, Å ^d
LiCl		1.81	0.76	0.420	NaCl	2.566	3.63 ^f
NaCl		1.81	1.02	0.564	NaCl	2.814	3.98 ^f
Cs(1-Me-12-I- CB ₁₁ F ₁₀)	3.068(2) (X = F), 3.440(2) (X = I, C) (av. 3.13)	4.13 ^e	1.67	0.404	NaCl	5.50-6.02 (av. 5.80)	7.66-8.90 (av. 8.18)
Cs(1-H-CB ₁₁ Br ₁₁) ^f	3.617(1) (X = Br) 2.82 (X = H, Br) (av. 3.48)	4.78 or 5.09 ^g	1.67	0.349 or 0.328	NaCl	6.75-6.77 (av. 6.76)	9.30 × 6, 9.82 × 6 (av. 9.56)
CsCl		1.81	1.67	0.923	CsCl	3.56	5.04 ^f
NMe ₄ (1,12-Me ₂ - CB ₁₁ F ₁₀)	3.070(2) (X = F), 3.178(3) (X = C) (av. 3.09)	3.83 ^h	2.79 ⁱ	0.728	CsCl	6.31-7.00 (av. 6.62)	7.78 × 8, 7.35 × 4 (av. 7.64)

^a All averages (av.) are weighted averages. ^b This is one-half times the distance between the named substituent atoms bonded to antipodal pairs of icosahedron cage atoms (i.e., C1/B12 or B_{10b}/B₁₆). ^c From ref. 41 unless otherwise indicated. ^d cent. = the CB₁₁ centroid. ^e This work; 4.13 = 5.80 - 1.57. ^f Coordinates for the analysis of this compound were taken from ref. 61; . ^g This work; 4.78 = $\frac{1}{2}$ (9.56); 5.09 = 6.76 - 1.67. ^h This work; 3.83 = 6.62 - 2.79. ⁱ The ionic radius of the NMe₄⁺ cation is taken from ref. 58.

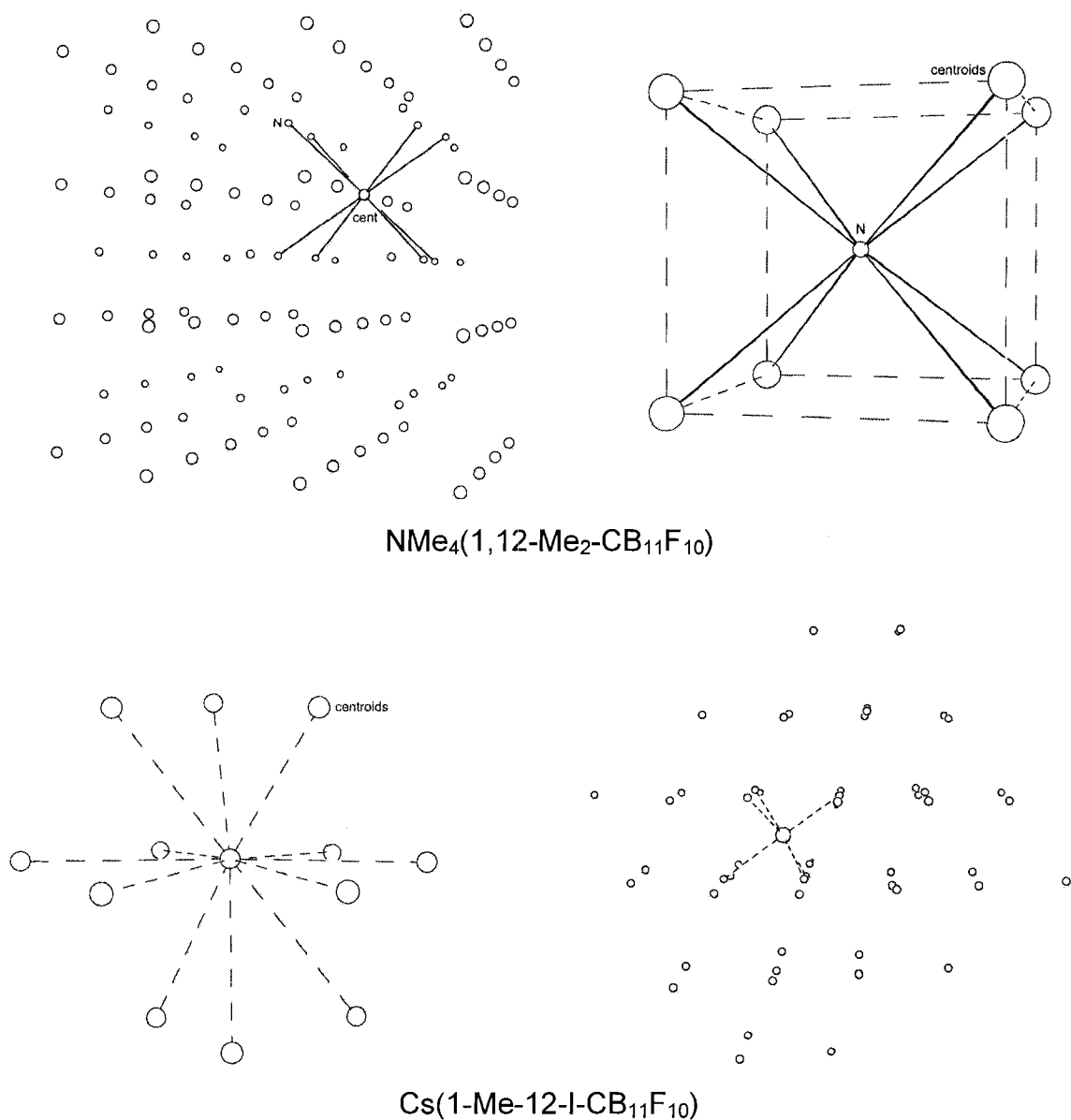


Figure 5.17. The packing of cations and anions in $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ (N atoms and CB_{11} centroids shown as small and large spheres, respectively) and $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$. The bottom left drawing shows the cubic closest-packed ABCABC... arrangement of CB_{11} centroids in $\text{Cs}(1\text{-Me-12-I-CB}_{11}\text{F}_{10})$ (Cs^+ cations are not shown in this drawing). The bottom right drawing shows one Cs^+ cation in a pseudo-octahedral hole of six CB_{11} centroids.

sum of the M^+ and Cl^- radii; or (ii) the Cl^- are *not* in van der Waals contact and the $M^+ - Cl^-$ distance is *equal to* the sum of the M^+ and Cl^- radii. An example of situation (i) is exhibited by LiCl. One-half times the $Cl^- \cdots Cl^-$ distance is 1.81 Å, which is precisely the ionic radius of the Cl^- ion. Furthermore, the sum of the ionic radii of Li^+ and Cl^- , which is 2.57 Å, which is equal to the observed $Li^+ \cdots Cl^-$ distance of 2.566 Å in LiCl. Consider next the parameters for NaCl in Table 3.4. One-half times the $Cl^- \cdots Cl^-$ distance in this salt is 1.98 Å, which is nearly 10% longer than the Cl^- ionic radius of 1.81 Å. This means that the Cl^- ions are not truly close-packed in NaCl but exhibit an "expanded close-packed" array of anions. On the other hand, the $Na^+ \cdots Cl^-$ distance, at 2.81 Å, is within 1% of the sum of the Na^+ and Cl^- ionic radii, which is 2.83 Å. Therefore, NaCl is an example of situation (ii). A more extreme example of situation (ii) is exhibited by CsCl. The distance between ions of the same charge is 5.04 Å, significantly more than twice the Cs^+ or the Cl^- ionic radius.

Although the fluorocarborane anions are conceptually spherical or approximately spherical anions, they are, of course, not truly spherical anions. Therefore, the effective radius of a 1-Me- $CB_{11}F_{11}^-$ anion is *shorter* than the sum of the average centroid $\cdots$ F distance plus the van der Waals radius of an F atom (which is 1.35–1.50 Å),^{62,63} as shown in Figure 5.18. Instead, the data in Table 5.5 were used to estimate the *effective* ionic radii of the carborane anions. Consider the salt $Cs(1-H-CB_{11}Br_{11})$,⁶¹ which has the NaCl-type structure. One-half times the average centroid $\cdots$ centroid distance is 4.78 Å; The difference between the average $Cs^+ \cdots$ centroid distance and the ionic radius of Cs^+ is 5.09 Å. The effective ionic radius of the 1-H- $CB_{11}Br_{11}^-$ anion is between these two values (which only differ by 6.5%). In a similar way, the effective ionic radii of the 1,12-Me₂- $CB_{11}F_{10}^-$ and 1-Me-12-I- $CB_{11}F_{10}^-$ anions were determined to be 3.83 and 4.13 Å, respectively. The ionic radius ratios for $Cs(1-Me-12-I-CB_{11}F_{10})$ and $NMe_4(1,12-Me_2-CB_{11}F_{10})$ are 0.404 and 0.728, so it is sensible that these two salts exhibit the NaCl-type and CsCl-type structures, respectively.⁴¹

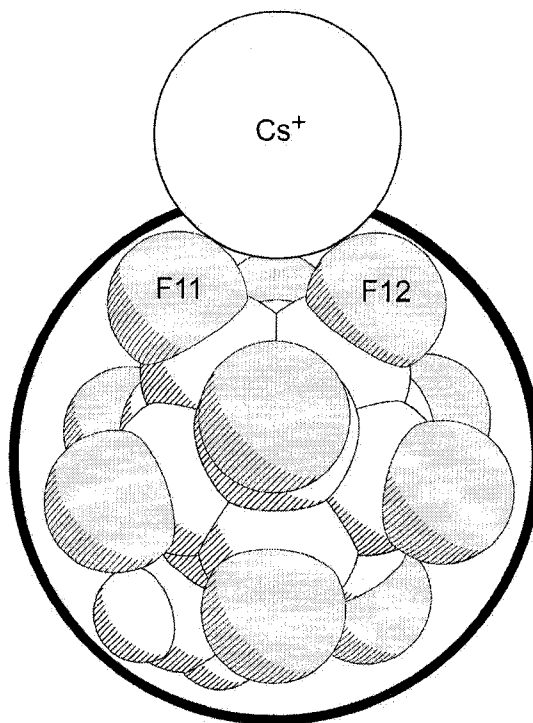


Figure 5.18. Drawing of a space-filling model of the 1-Me-CB₁₁F₁₁ anion enclosed in a sphere with a radius equal to the sum of the centroid...F12 distance plus the van der Waals radius of an F atom. The placement of the Cs⁺ ion, with a radius that is not to scale, demonstrates that the centroid...Cs⁺ distance can be significantly shorter than the sum of the anion van der Waals radius plus the Cs⁺ ionic radius.

(d) Cation-anion packing in Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) and Ag₂(1-Me-12-SiPh₃-CB₁₁F₁₀)₂·C₆H₆. The 1-Me-12-SiPh₃-CB₁₁F₁₀[−] anion is much larger than the 1-R-12-X-CB₁₁Y₁₀[−] anions considered in section (b) (R = CH₃, X = F, CH₃, I, Y = F; R = H, X, Y = Br). Furthermore, the phenyl groups in the 12-SiPh₃ anion interact strongly with both Cs⁺ and Ag⁺. Therefore, it is not surprising that the ion packing in these two salts is entirely different from simple packing arrangements like the NaCl and CsCl structures.

The Cs⁺ ions in Cs(1-Me-12-SiPh₃-CB₁₁F₁₀) have only three CB₁₁ centroids that can be considered to be nearest neighbors, as shown in Figure 5.19. The three Cs⁺⋯centroid distances are 5.279, 5.279, and 5.752 Å, which are similar to the six Cs⁺⋯centroid distances of 5.50–6.02 Å in Cs(1-Me-12-I-CB₁₁F₁₀). The next closest CB₁₁ centroid is 10.9 Å from the Cs⁺ cation. The three-connected arrays form corrugated layers that are stacked in the third dimension (the space between these corrugated layers is the location of the edge-face phenyl-phenyl interactions shown in Figure 3.7).

Surprisingly, Ag⁺ cations in Ag₂(1-Me-12-SiPh₃-CB₁₁F₁₀)₂·C₆H₆ are surrounded by more CB₁₁ centroids, albeit at longer distances, than are the Cs⁺ cations in the corresponding cesium salt. The six (Ag2) or seven (Ag1) Ag⁺⋯centroid distances range from 5.74 to 9.40 Å, as shown in Figure 5.20. The Ag1⋯centroid distances of 5.76, 7.99, 7.73, 7.61, 9.40, 5.74, and 9.21 Å can be compared with the six equidistant Ag⁺⋯centroid distances of 6.19 Å in Ag(CHPh₃)(1-Me-CB₁₁F₁₁), in which the Ag⁺ ions also have a trigonal-planar array of arene ligands. Finally, most of the centroid⋯centroid distances shown in Figure 5.20 range from 10.2 to 11.8 Å (none was shorter than 10.2 Å). These are significantly longer than the centroid⋯centroid distances of 7.66–8.90 Å in Cs(1-Me-12-I-CB₁₁F₁₀).

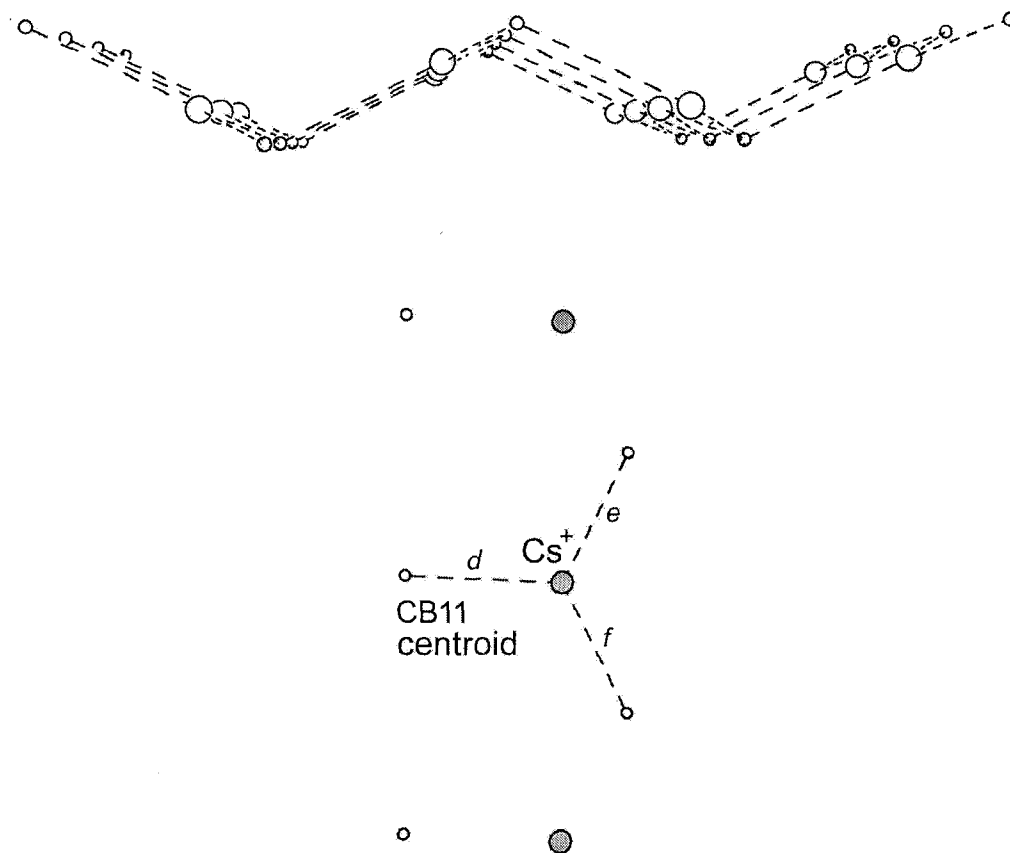


Figure 5.19. Drawings of the Cs⁺ ions and CB₁₁ centroids in the structure of Cs(1-Me-12-SiPh₃-CB₁₁F₁₀). The Cs⁺ ions and the centroids are shown as larger and smaller spheres, respectively. The Cs⁺...centroid distances labelled d–f are 5.752, 5.279, and 5.279 Å, respectively.

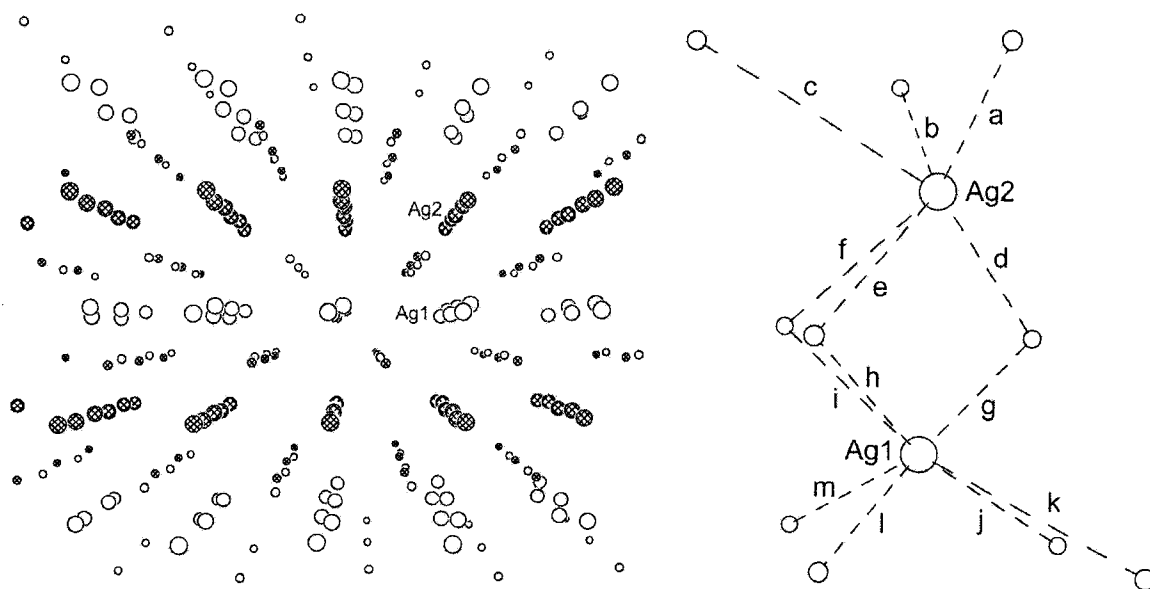


Figure 5.20. Drawings of the Ag^+ ions and CB_{11} centroids in the structure of $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$. The Ag1 and Ag2 cations are shown as the larger spheres that are open and cross-hatched, respectively, and the centroids are shown as smaller spheres that are open for the anion containing Si1 and cross-hatched for the anions containing Si2. The $\text{Ag}^+\cdots\text{centroid}$ distances labelled a–m are 6.53, 7.58, 9.11, 6.54, 7.78, 8.80, 5.76, 7.99, 7.73, 7.61, 9.40, 5.74, and 9.21 Å, respectively.

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Chapter 6

Coordinating and Ion-Pairing Properties of 1-Me-CB₁₁F₁₁⁻,

1,12-Me₂-CB₁₁F₁₀⁻, and 1-Me-12-H-CB₁₁F₁₀⁻

Introduction

The possibility of changing the coordinating ability and/or the ion-pairing ability of 1-Me-12-X-CB₁₁F₁₀⁻ anions by selectively substituting X = F with X = CH₃ or H was discussed in Chapter 1. Linkage isomers of Fe(Cp)(CO)₂(Y) were also discussed in Chapter 1 (Y⁻ = 12-CB₁₁H₁₂⁻ or 7-CB₁₁H₁₂⁻). This chapter consists of (i) an in-depth computational study of the electrostatic potential of the fluorocarborane anions CB₁₁H₁₂⁻, 1-Me-CB₁₁F₁₁⁻, 1,12-Me₂-CB₁₁F₁₀⁻, and 1-Me-12-H-CB₁₁F₁₀⁻ at various distances and angles, (ii) an in-depth computational study of the relative energies of various linkage-isomers of Fe(Cp)(CO)₂⁺ complexes with CB₁₁H₁₂⁻, 1-Me-CB₁₁F₁₁⁻, or 1,12-Me₂-CB₁₁F₁₀⁻, and (iii) some preliminary experimental evidence that suggests that 1,12-Me₂-CB₁₁F₁₀⁻ is more weakly ion-pairing with Li⁺ in DME than 1-Me-CB₁₁F₁₁⁻ and is more weakly coordinating towards Fe(Cp)(CO)₂⁺ than is 1-Me-CB₁₁F₁₁⁻. The DFT calculations (see Chapter 2 for experimental detail) were performed by Dr. Alexey A. Popov at Moscow State University and were analyzed and interpreted by the author of this dissertation.

In the simplest possible model of the electrostatic potential of an anion, it can be considered as a point charge, a dimensionless point in space with a negative charge equal to the electron charge. This approximation is probably a good one at very long distances from the anion. However, real anions, even atomic ions such as F⁻ and I⁻, are not point charges. At the center of an atomic anion (i.e., at the nucleus), the electrostatic potential is positive and very high. The potential will shift from positive to negative at some distance from the center of the anion, and the negative electrostatic potential will probably be highest at a distance close to the ionic radius of the anion.

The same will be true for a polyatomic anion, although the potential will be a more complicated function of the distance from the center of the anion (however that is defined) and will also depend on angular coordinates as well as the distance coordinate. A graphic approximating the situation for 1-Me-CB₁₁F₁₁⁻ and 1,12-Me₂-CB₁₁F₁₀⁻ is shown in Figure 6.1, along with a larger view representing both anions with some of the atoms labeled. The expectation is that the minimum potential energy of an ion pair consisting of 1-Me-CB₁₁F₁₁⁻ and a 1+ point charge will be lower at position 12 than at position 7, lower at position 7 than at position 2, and lower at position 2 than at position 1, which is the the position of the cage C atom. Substitution of F12 for a CH₃ group.

Computational Results

CB₁₁H₁₂⁻ and linkage isomers of Fe(Cp)(CO)₂(CB₁₁H₁₂). In order to validate the DFT methodology that was used for the calculations discussed in this dissertation, the DFT-optimized structure of Fe(Cp)(CO)₂(CB₁₁H₁₂) was determined and compared with the known solid-state structure determined by X-ray crystallography.¹ The results are listed in Table 6.1. The agreement is very good, especially considering that the H atoms were not precisely located in the X-ray crystallographic study. Focusing on distances and angles involving atoms other than H atoms, the Fe–CO distances are 1.788(2)/1.796(2) Å (X-ray) vs. 1.769/1.776 Å (DFT), the Fe–B distances are 2.593(2) Å (X-ray) vs. 2.542 Å (DFT), the Fe–C(Cp) distances are all ca. 2.1 Å for both structures, the OC–Fe–CO angles are 93.7(1)° (X-ray) vs. 92.3° (DFT), and the C1⋯B12–Fe angles are 168.5(1)° (X-ray) and 169.9° (DFT).

The DFT-optimized structures and relative energies of isomers of Fe(Cp)(CO)₂-(CB₁₁H₁₂) with the Fe atom bonded to H7, H2, or H1 were also determined, and these results are also listed in Table 6.1. Interestingly, the structure around the Fe atom does not change significantly for the three B–H–Fe isomers, but their relative energies are 0.0, 12.3, and 43.2 kJ mol⁻¹ for the 12-, 7-, and 2- isomers, respectively. To further explore

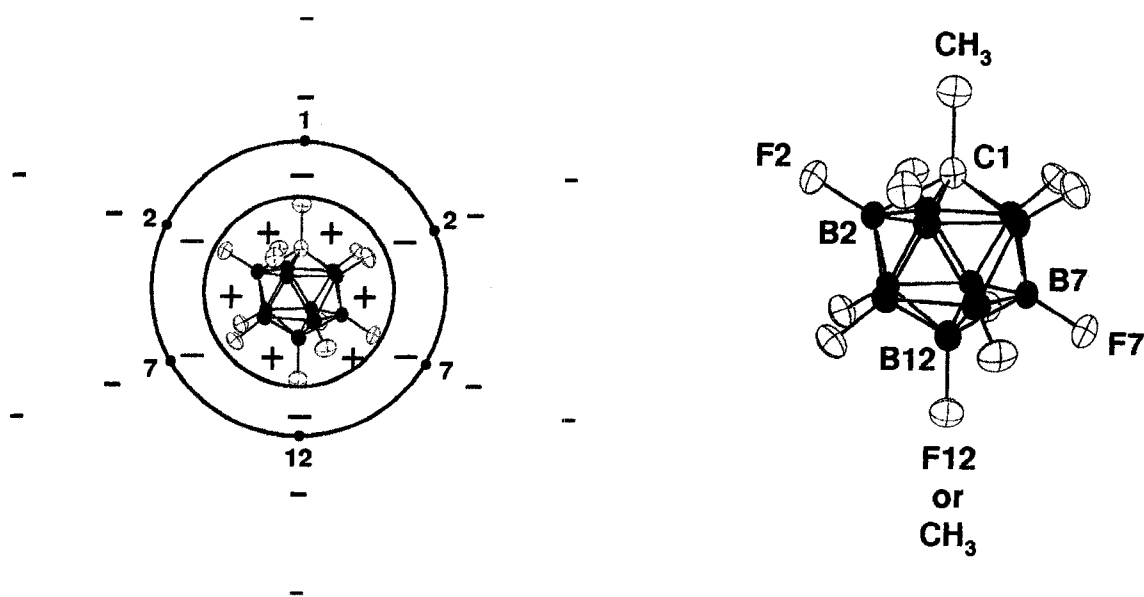


Figure 6.1. (Left) A depiction of the expected electrostatic potential surrounding the $1\text{-Me-CB}_{11}\text{F}_{11}^-$ and $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ anions along the directions of the C-CH₃ bond, an upper- or lower-belt B-F bond (five equivalent directions if H atoms on the CH₃ groups are ignored), and the antipodal B-F or B-CH₃ bond. Note that the potential switches from positive to negative at a certain distance from each vertex, reaches a maximum negative value at some distance, then diminishes to zero at very long distances. (Right) A drawing depicting both the $1\text{-Me-CB}_{11}\text{F}_{11}^-$ and $1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10}^-$ anions, oriented the same way as in the drawing on the left.

Table 6.1. Distances (Å) and angles (deg) for X-ray structure of Fe(Cp)(CO)₂(12-CB₁₁H₁₂) and DFT-predicted distances, angles, and relative ΔH_f° values (kJ mol⁻¹) for isomers of Fe(Cp)(CO)₂(CB₁₁H₁₂)^a

parameter	12-isomer		7-isomer		2-isomer		1-isomer	
	X-ray	DFT	DFT		DFT		DFT	
Fe-CO	1.788(2), 1.796(2)	1.769, 1.776	1.769, 1.778		1.772, 1.779		1.779, 1.789	
Fe-H	1.563(22) ^b	1.600	1.605		1.606		1.747	
Fe-B	2.593(2)	2.542	2.526		2.517		2.681 ^c	
Fe-C(Cp)	2.066(2)–2.094(2)	2.098–2.126	2.099–2.126		2.101–2.125		2.085–2.126	
B-H(Fe)	1.18(2) ^b	1.307	1.305		1.296		1.747 ^d	
B-H-Fe	141(2) ^b	121.6	120.2		119.9		134.3 ^e	
Cl⋯B12-Fe	168.5(2)	169.9						
OC-Fe-CO	93.7(1)	92.3	92.2		92.1		92.5	
rel. ΔH_f°		0.0	11.6		42.6		148.6	
relative minimum electrostatic potential								
energy of free CB ₁₁ H ₁₂ [−] ion and 1+ charge		0.0	12.3		43.2		133.3	

^a The DFT geometry optimization was done at the PBE/TZ2P level and the relative energy and electrostatic potential energy calculations were done at the PBE0/6-311G(2d,p) level. ^b H atoms in the X-ray structure were not precisely located. ^c This is the Fe–C(carborane) distance. ^d This is the C–H(Fe) distance. ^e This is the C–H–Fe angle.

this system, electrostatic potentials at various distances from the four types of vertices of $\text{CB}_{11}\text{H}_{12}^-$ were calculated and converted to electrostatic potential energies for a positive point charge at each distance by multiplying by $2625.5 \text{ kJ mol}^{-1} \text{ a.u.}^{-1}$. The results are shown in Figure 6.2, and the maximum (i.e., most negative) electrostatic potentials, minimum (i.e., most negative) potential energies, and both Mulliken and potential-fit H-atom charges are listed in Table 6.2. Drawings of the three B–H–Fe isomers are shown in Figure 6.3.

The differences in electrostatic potentials at a given distance along various B–H vectors persists even at relatively long distances from the vertex. The maximum potentials are at 2.5 Å from B2, B7, and B12. The electrostatic potential along the B12–H12 vector is 14%, 10%, and 7% larger than the potential along the B2–H2 vector at 2.5, 5, and 9 Å, respectively, from the B12 and B2 vertices. As far as a point charge is concerned, the icosahedral $\text{CB}_{11}\text{H}_{12}^-$ anion does not generate a "nearly isotropic" electric field at any chemically reasonable distance. If a Li^+ ion is moved from a position 3.0 Å from C1 along the anion C_5 axis to a position 3.0 Å from B12, the potential energy would decrease by 93.4 kJ mol^{-1} in vacuo and by 13.0 kJ mol^{-1} in DME ($\epsilon = 7.2$).

As stated at the end of Chapter 1, two linkage isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(\text{CB}_{11}\text{H}_{12})$ were observed in dichloromethane solution at 25 °C, the Fe–H12 isomer (relative abundance 2.7) and the Fe–H7 isomer (relative abundance 1.0).² However, the H atoms with the greatest negative charge are the lower-belt H atoms, H7–H11, not H12. This can be interpreted as computational evidence that H12 is *not* the most hydridic H atom in $\text{CB}_{11}\text{H}_{12}^-$, in spite of the conventional wisdom cited in Chapter 1. On the sole basis of virtually equal H-atom *Mulliken* charges for H7–H12, the Fe–H7 isomer should be five times more abundant than the Fe–H12 isomer, not nearly three times less abundant, because there are five equivalent "H7" atoms and only one H12 atom. Therefore, the reason for the "apparently inverted" observed linkage isomer abundances is the

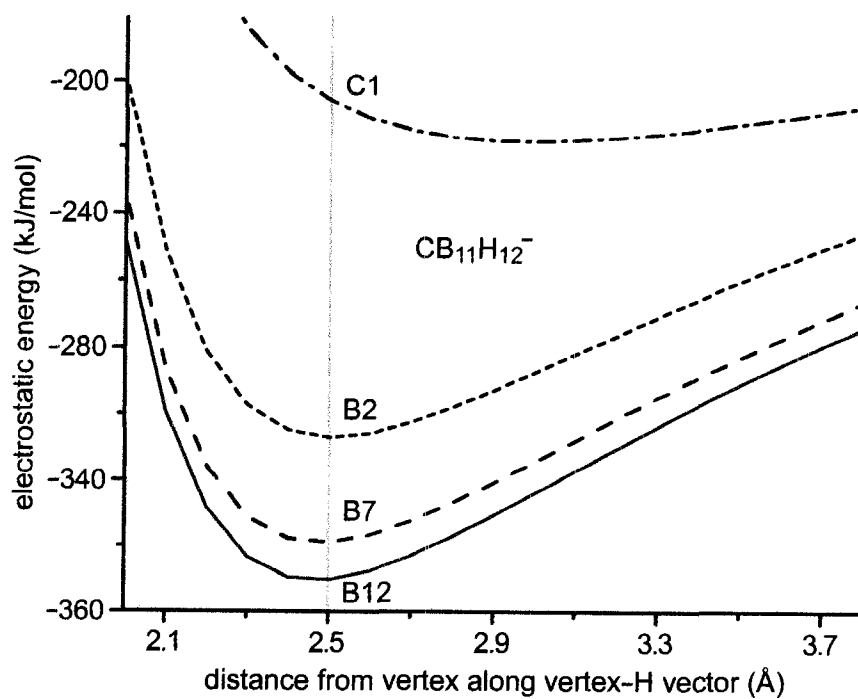


Figure 6.2. The electrostatic potential energy of a positive point charge at various distances from the four types of vertices of the $\text{CB}_{11}\text{H}_{12}^-$ anion. Each curve is labeled with the vertex type.

Table 6.2. DFT predicted distances, maximum electrostatic potentials and potential energies, and H atom charges for $\text{CB}_{11}\text{H}_{12}^-$ ^a

vertex-H (distance, Å)	maximum electro- static potential, a.u. (distance from vertex, Å)	minimum electro- static potential energy, kJ mol^{-1}	H atom Mulliken charge	H atom potential- fit charge
C1-H1 (1.089)	-0.08263 (3.0)	-216.9	+0.043	+0.191
B2-H2 (1.197)	-0.11692 (2.5)	-307.0	-0.135	-0.039
B7-H7 (1.200)	-0.12908 (2.5)	-338.9	-0.165	-0.086
B12-H12 (1.201)	-0.13338 (2.5)	-350.2 ^b	-0.164	-0.065

^a The geometry optimization was done at the PBE/TZ2P level and the potential and atom-charge calculations were performed at the PBE0/6-311G(2d,p) level. The electrostatic static potential energy of a positive point charge 3.0 Å from B12 is $-310.3 \text{ kJ mol}^{-1}$.

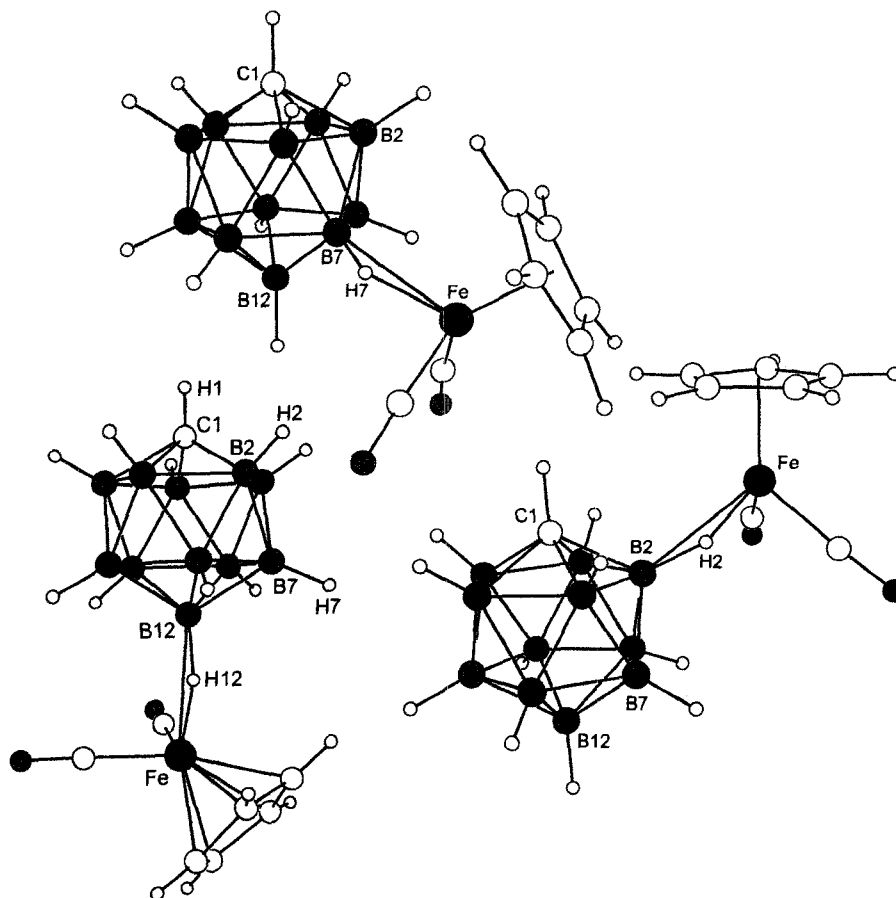


Figure 6.3. Drawings of the three B–H–Fe isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(\text{CB}_{11}\text{H}_{12})$. The 12-isomer is from the X-ray structure (ref 1), and the 7- and 2-isomers are DFT-optimized structures.

aforementioned anisotropic electrostatic potential surrounding $\text{CB}_{11}\text{H}_{12}^-$, which orients the anion so that the B12–H12 bond points at the cation. The electrostatic potential, of course, takes into account the distribution of *all* of the electrons present in $\text{CB}_{11}\text{H}_{12}^-$, not just the H-atom charges.

Note that the DFT-optimized Fe–B12 distance in $\text{Fe}(\text{Cp})(\text{CO})_2(\text{CB}_{11}\text{H}_{12})$ is 2.542 Å, virtually the same distance from B12 at which the electrostatic potential in the free $\text{CB}_{11}\text{H}_{12}^-$ anion is a maximum. Furthermore, the DFT-optimized B12–H12–Fe angle is 121.6° largely because H12 is bent away from the pseudo- C_5 axis of the anion. The C1...B12–Fe angle is 169.9° (168.5(2)° in the X-ray structure). Therefore, the Fe atom lies close to the pseudo- C_5 axis of the anion, ca. 2.5 Å from B12, as shown in Figure 6.4. Remarkably, the relative maximum electrostatic potential energies of the free $\text{CB}_{11}\text{H}_{12}^-$ anion and the relative energies of the three Fe–H(B) isomers are the same to within 1 kJ mol^{–1}. *This suggests that the relative coordinating abilities of different carborane anions towards a 1+ cation (like $\text{Fe}(\text{Cp})(\text{CO})_2^+$) might be estimated by comparing the DFT-predicted electrostatic potential energies of a point positive charge at particular distances from "the most strongly coordinating" anion vertex.*

1-Me- $\text{CB}_{11}\text{F}_{11}^-$, 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$, and 1-Me-12-H- $\text{CB}_{11}\text{F}_{10}^-$. The DFT-predicted electrostatic potentials, electrostatic potential energies, and F-atom charges for these three anions are listed in Table 6.3. Plots of the potential energies as a function of distance of the 1+ point charge from each type of vertex for 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ and 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ are shown in Figure 6.5 and 6.6.

The minimum electrostatic potential energies for a positive point charge and the 1-Me- $\text{CB}_{11}\text{F}_{11}^-$ anion are 2.7 Å from B12 (–367.8 kJ mol^{–1}), B7 (–359.0 kJ mol^{–1}), or B2 (–326.0 kJ mol^{–1}). The substitution of F12 with a CH₃ group significantly raises the minimum potential energy in the B12–CH₃ direction (–277.9 kJ mol^{–1} at 3.3 Å), but it lowers the minimum potential energy in the B7–F7 and B2–F2 directions. In fact, the minimum potential energy in the B7–F7 direction for 1,12-Me₂- $\text{CB}_{11}\text{F}_{10}^-$ is –366.0 kJ

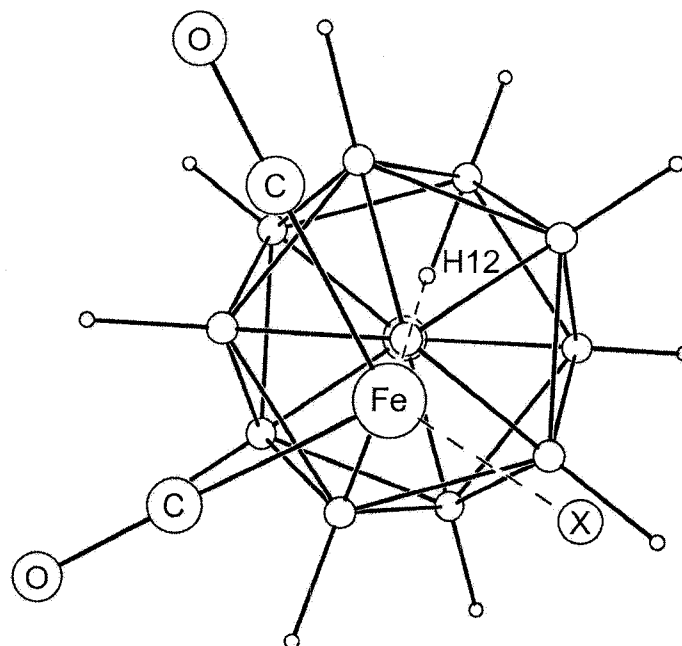


Figure 6.4. Drawing of the DFT-optimized structure of $\text{Fe}(\text{Cp})(\text{CO})_2(12\text{-CB}_{11}\text{H}_{12})$ looking down the $\text{B}_{12}\cdots\text{C}_1$ vector. The cyclopentadienide ligand has been replaced with the centroid (X) of the five-membered ring. The $\text{C}_1\cdots\text{B}_{12}\text{-Fe}$ angle is 169.9° .

Table 6.3. DFT predicted electrostatic potentials, potential energies, and F-atom charges for fluorocarborane anions

anion	vertex	vertex-X distance, Å (X)	maximum electrostatic potential, a.u. (distance from vertex, Å)	minimum electrostatic potential energy, kJ mol ⁻¹	Mulliken charge (atom)	potential fit charge (atom)
1-Me-CB ₁₁ F ₁₁ ⁻	C1	1.522 (CH ₃)	-0.06952 (3.5)	-182.5		
	B2	1.374 (F)	-0.12415 (2.7)	-326.0	-0.475 (F)	-0.252 (F)
	B7	1.380 (F)	-0.13675 (2.7)	-359.0	-0.482 (F)	-0.269 (F)
	B12	1.379 (F)	-0.14008 (2.7)	-367.8	-0.470 (F)	-0.247 (F)
1,12-Me ₂ -CB ₁₁ F ₁₀ ⁻	C1	1.524 (CH ₃)	-0.07343 (3.5)	-189.8		
	B2	1.350 (F)	-0.12818 (2.7)	-336.5	-0.478 (F)	-0.269 (F)
	B7	1.357 (F)	-0.13939 (2.7)	-366.0	-0.488 (F)	-0.284 (F)
	B12	1.594 (CH ₃)	-0.10583 (3.3)	-277.9		
1-Me-12-H-CB ₁₁ F ₁₀ ⁻	C1	1.523 (CH ₃)	-0.07273 (3.6)	-191.0		
	B2	1.374 (F)	-0.12745 (2.7)	-334.6		
	B7	1.382 (F)	-0.13913 (2.7)	-365.3		
	B12	1.198 (H)	-0.10281 (2.7)	-269.9		

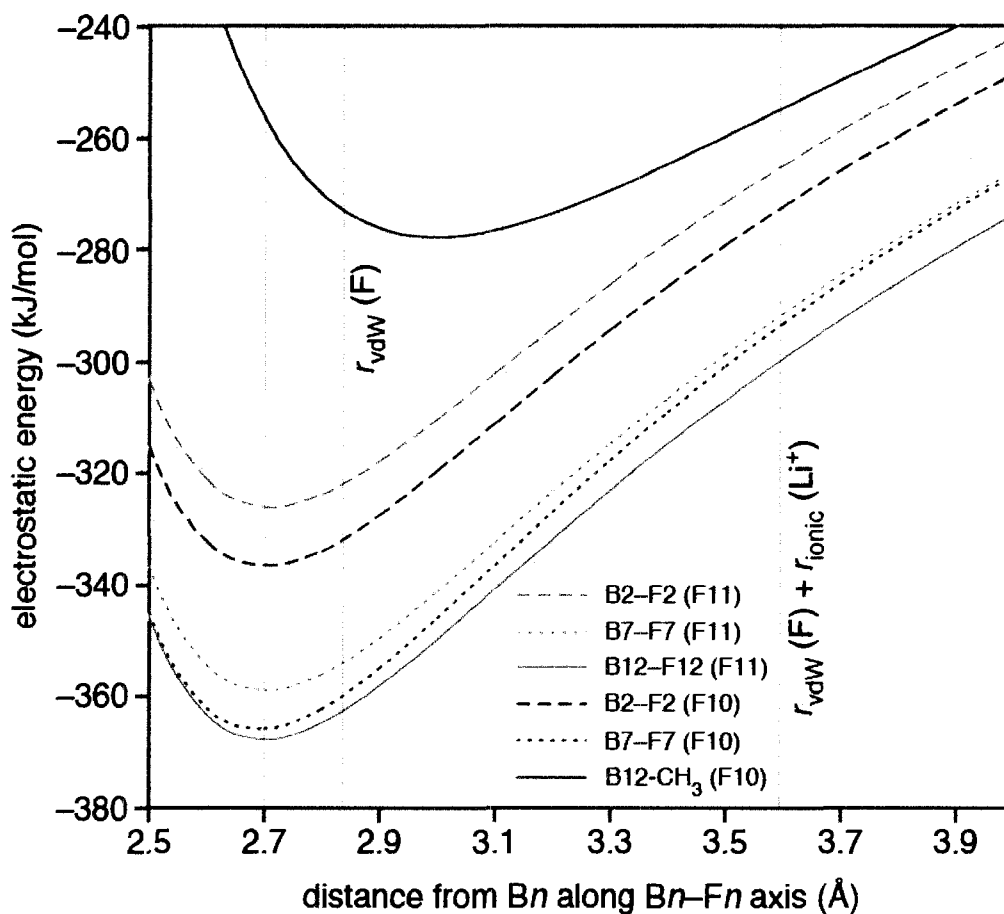


Figure 6.5. DFT-Predicted potential energy as a function of distance for a positive point charge from the three types of boron vertices in 1-Me-CB₁₁F₁₁⁻ (F11) and 1,12-Me₂-CB₁₁F₁₀⁻ (F10).

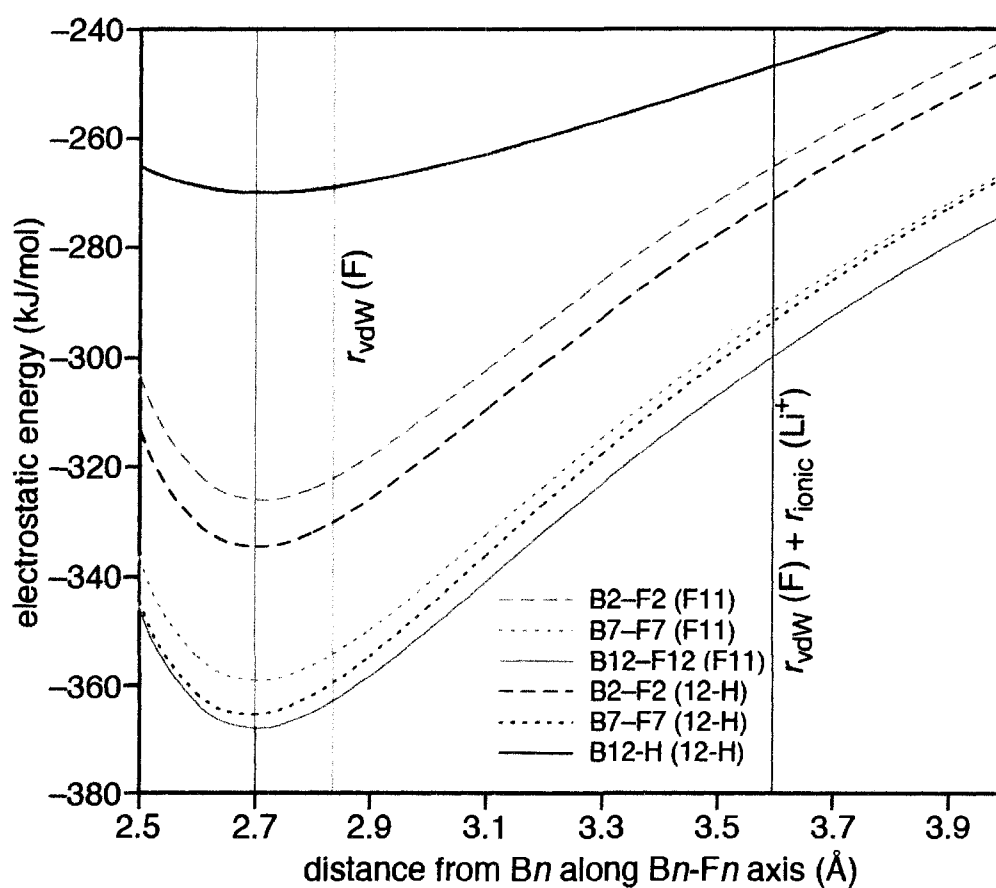


Figure 6.6. DFT-Predicted potential energy as a function of distance for a positive point charge from the three types of boron vertices in 1-Me-CB₁₁F₁₁⁻ (F11) and 1-Me-12-H-CB₁₁F₁₀⁻ (12-H).

mol⁻¹ (at 2.7 Å), virtually the same as in the B12–F12 direction for the 1-Me-CB₁₁F₁₁⁻ anion. A comparison of the potential energies at the boron vertices of 1-Me-CB₁₁F₁₁⁻ and 1-Me-12-H-CB₁₁F₁₀⁻ shows essentially the same result. Substituting the F12 atom in the 1-Me-CB₁₁F₁₁⁻ anion with either a CH₃ group or an H atom resulted in a shift of negative charge density from the pseudo-*C*₅ axis to the lower-belt region. This suggests that the ion-pairing ability of the three anions should be approximately the same, although for the 1-Me-CB₁₁F₁₁⁻ a cation will be aligned along the B12–F12 direction and in the other two anions the cation will be aligned along the B7–F7 direction.

To test this hypothesis, the dc conductivity of 0.010 M DME solutions of NMe₄(1-Me-CB₁₁F₁₁) and NMe₄(1,12-Me₂-CB₁₁F₁₀) were determined. The conductivities (three replicates each for two solutions of each anion) were 158 and 184 μS cm⁻¹, respectively, a difference of only 16%.

The DFT-predicted F-atom charges are greater for both the lower-belt and upper-belt F atoms than for F12 in 1-Me-CB₁₁F₁₁⁻, suggesting once again (i.e., cf. CB₁₁H₁₂⁻) that the electrostatic potential is a more relevant property than atom charges for estimating the relative ion-pairing abilities of different sites on a given anion or of different anions. To extend this conclusion to coordinating abilities, the DFT-optimized structures and relative energies of the three Fe–F(B) linkage isomers of the composition Fe(Cp)(CO)₂(1-Me-CB₁₁F₁₁) were determined. The results are listed in Table 6.4 and drawings of the three structures are shown in Figure 6.7. Unlike the structure of Fe(Cp)(CO)₂(12-CB₁₁H₁₂), the Fe atom in Fe(Cp)(CO)₂(1-Me-CB₁₁F₁₁) is not near the pseudo-*C*₅ axis, as shown in Figure 6.8. The C1···B12–F12 angle is 178.0°, the C1···B12–Fe angle is 155.7°, and the Fe···B12 distance is 3.268 Å, well beyond the sum of van der Waals radii. It is clear that the Fe atom is coordinated to an F12 lone pair, not to the B12–F12 sigma-bond electrons.

The relative energies are similar in magnitude to the electrostatic potential

Table 6.4. DFT-Predicted distances (Å) and angles (deg) for Fe(Cp)(CO)₂(1-Me-CB₁₁F₁₁) and Fe(Cp)(CO)₂(1,12-Me₂-CB₁₁F₁₀) isomers

Fe(Cp)(CO) ₂ (1-Me-CB ₁₁ F ₁₁)			
parameter	12-isomer	7-isomer	2-isomer
Fe–CO	1.785, 1.791	1.784, 1.793	1.784, 1.796
Fe–F; Fe–B	2.078; 3.268	2.083; 3.269	2.106; 3.259
Fe–C(Cp)	2.070–2.153	2.073–2.153	2.073–2.151
B–F(Fe)	1.438	1.437	1.431
B–F–Fe	135.9	135.7	119.9
B–F	1.363–1.386	1.363–1.387	1.364–1.381
OC–Fe–CO	92.8	93.0	93.1
rel. ΔH_f°	0.0	7.1	24.5

Fe(Cp)(CO) ₂ (1,12-Me ₂ -CB ₁₁ F ₁₀)			
parameter	12-isomer	7-isomer	2-isomer
Fe–CO	1.779, 1.782	1.783, 1.795	1.784, 1.787
Fe–H; Fe–C	1.732; 2.468		
Fe–F; Fe–B		2.099; 3.252	2.078; 3.273
Fe–C(Cp)	2.086–2.145	2.074–2.151	2.073–2.152
C–H(Fe)	1.162		
C–H–Fe	115.7		
B–F(Fe)		1.433	1.444
B–F–Fe		133.1	135.9
B–F	1.364–1.392	1.365–1.392	1.364–1.390
OC–Fe–CO	93.5	93.1	92.1
rel. ΔH_f°	1.8	0.0	13.2

Table 6.5. DFT-Predicted distances (Å) and angles (deg) for Fe(Cp)(CO)₂(1-Me-12-H-CB₁₁F₁₀) isomers

parameter	Fe(Cp)(CO) ₂ (1-Me-12-H-CB ₁₁ F ₁₀)		
	12-isomer	7-isomer	2-isomer
Fe–CO	1.778, 1.788	1.784, 1.789	1.783, 1.796
Fe–H; Fe–B	1.621; 2.465		
Fe–F; Fe–B		2.072; 3.255	2.101; 3.254
Fe–C(Cp)	2.089–2.139	2.072–2.153	2.073–2.151
B–H(Fe)	1.284		
B–H–Fe	115.7		
B–F(Fe)		1.443	1.432
B–F–Fe		135.0	133.2
B–F	1.362–1.383	1.363–1.389	1.364–1.390
OC–Fe–CO	91.4	93.0	93.1
rel. ΔH_f°	0	41.3	57.0

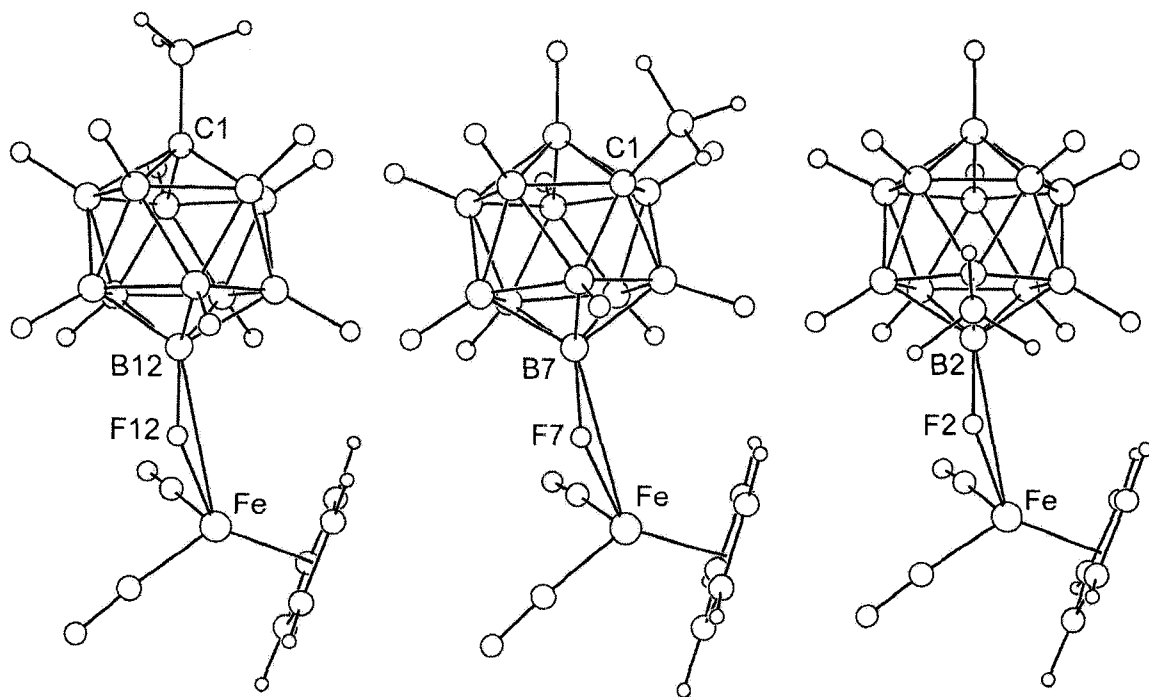


Figure 6.7. The three DFT-optimized Fe–F(B) linkage isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$

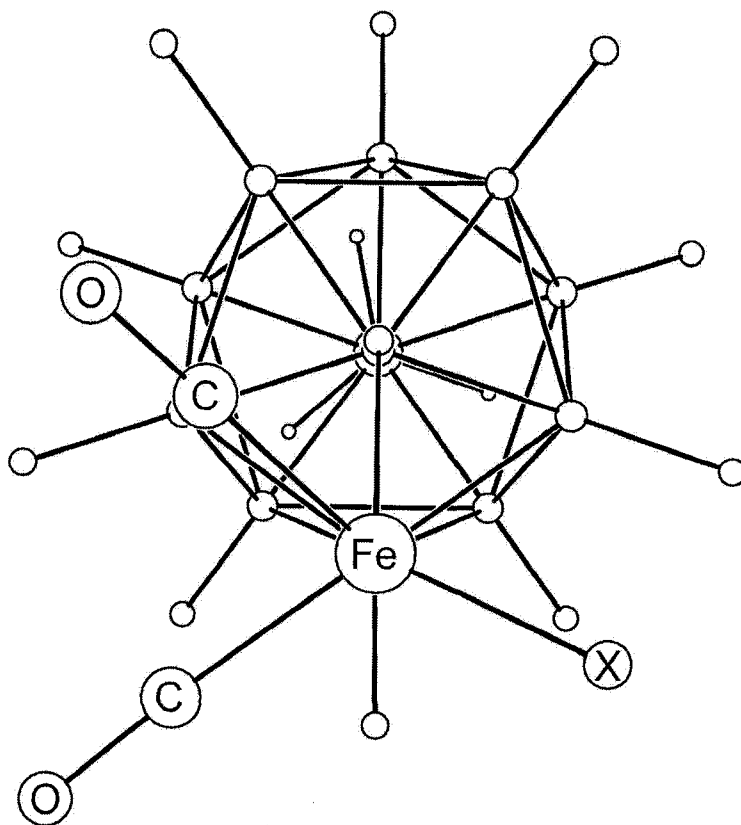


Figure 6.8. Drawing of the DFT-optimized structure of $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$ looking down the $\text{B12}\cdots\text{C1}$ vector. The cyclopentadienide ligand has been replaced with the centroid (X) of the five-membered ring. The $\text{C1}\cdots\text{B12-F12}$ and $\text{C1}\cdots\text{B12-Fe}$ angles are 178.0° and 155.7° , respectively.

energies at 3.25 Å. The most stable isomer is the 12-isomer, and the differences in the relative energies between the 7- and 2-isomers are 7.1 and 24.5 kJ mol⁻¹, respectively.

Selected bond lengths and angles for the DFT-optimized structures and the relative energies of the isomers of 1,12-Me₂-CB₁₁F₁₀⁻ and 1-Me-12-H-CB₁₁F₁₀⁻ are shown in Table 6.4 and 6.5, respectively. For 1,12-Me₂-CB₁₁F₁₀⁻, the substitution of the F12 resulted in the stronger coordinating ability on the lower-belt, the B7–F7 direction, however, the difference in the relative energies for the 12- and 7-isomers is only 1.8 kJ mol⁻¹. As shown in Figure 6.9, the DFT-optimized structure of the 12-isomer shows the agostic interaction between Fe and the C–H bond. For 1-Me-12-H-CB₁₁F₁₀⁻, the substitution of F12 to H resulted in much stronger coordinating ability on the B12–F12 direction compared to the upper-belt and the lower-belt. The relative energies for 7- and 2-isomers were 41.3, and 57.0 kJ mol⁻¹. As opposed to the ion-pairing ability, even after the substitution of the F12 to CH₃ or H, the B12-vertex was strongly coordinating site of the anions.

To summarize, DFT calculations predicted that the substitution of the F12 atom with a CH₃ group or a H atom increased the electrostatic potential energies in the B12–X direction significantly, indicating that the ion-pairing ability towards this vertex become weaker. The electrostatic potential energies of both the upper-belt and lower-belt decreased for both 1,12-Me₂-CB₁₁F₁₀⁻ and 1-Me-12-H-CB₁₁F₁₀⁻. The minimum energies for both anions were located at the lower-belt. For the 1-Me-CB₁₁F₁₁⁻, the minimum energy was located at the B12–F12 direction. The comparison of the minimum energies for these three anions suggested that the substitution on the B12-vertex weaken the overall ion-pairing ability of the anions, however, the difference was very small. Conductivity measurement of TBA salts of 1,12-Me₂-CB₁₁F₁₀⁻ and 1-Me-CB₁₁F₁₁⁻ also indicated that 1,12-Me₂-CB₁₁F₁₀⁻ is more weakly ion-pairing, however, the difference was only 16%. Change in the coordinating ability upon substitution of the B12-vertex was also predicted by DFT calculations by comparing the relative energies of 2-, 7-, and

12-isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$, $\text{Fe}(\text{Cp})(\text{CO})_2(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, and $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-12-H-CB}_{11}\text{F}_{10})$ individually. The strongest coordinating site for $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-CB}_{11}\text{F}_{11})$ was located along the B12–F12 direction. For $\text{Fe}(\text{Cp})(\text{CO})_2(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$, the substitution of F12 to CH_3 changed the strongest coordinating site to the lower-belt, however, the B12– CH_3 was the second strongest coordinating site, and the difference was only 1.8 kJ mol^{-1} . In $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-12-H-CB}_{11}\text{F}_{10})$, the strongest coordinating site was the B12–H direction. The relative energies for the 7- and 2- isomers increased significantly by substituting the F12 atom to a H atom.

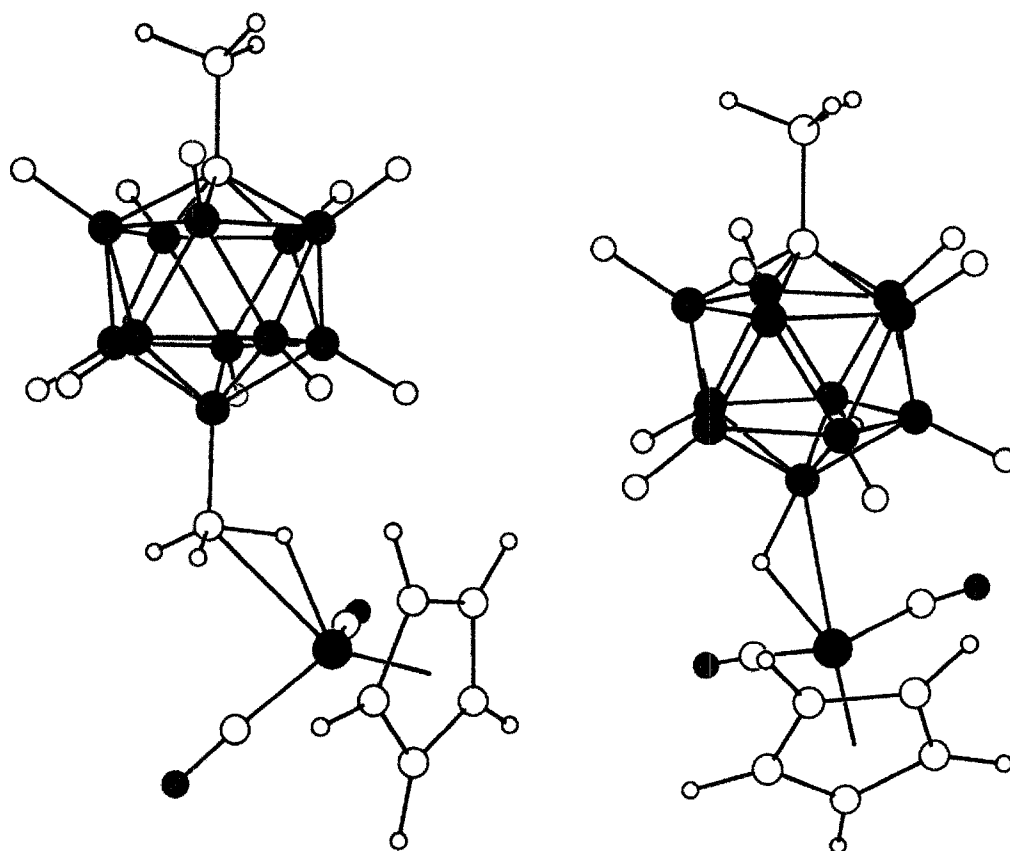


Figure 6.9. Drawings of the DFT-optimized 12-isomers of $\text{Fe}(\text{Cp})(\text{CO})_2(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$ (left) and $\text{Fe}(\text{Cp})(\text{CO})_2(1\text{-Me-12-H-CB}_{11}\text{F}_{10})$ (right). (color coding: green, B; yellow, F; blue, Fe; red, O; large white, C; small white, H)

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- (1) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643-6648.
- (2) Ivanov, S. V.; Rockwell, J. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorganic Chemistry* **1996**, *35*, 7882–7891.

Appendix A

Crystallographic Data

Table A1-1. Crystal data and structure refinement for NMe₄(1,12-Me₂-CB₁₁F₁₀).

Empirical formula	C ₇ H ₁₈ B ₁₁ F ₁₀ N	
Formula weight	425.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 18.240(4)$ Å	$\alpha = 90^\circ$
	$b = 11.086(4)$ Å	$\beta = 126.347(13)^\circ$
	$c = 10.913(3)$ Å	$\gamma = 90^\circ$
Volume	1777.4(8) Å ³	
Z	4	
Density (calculated)	1.589 Mg/m ³	
Absorption coefficient	0.157 mm ⁻¹	
$F(000)$	848	
Crystal size	0.40 × 0.36 × 0.30 mm ³	
Theta range for data collection	2.30 to 28.27°.	
Index ranges	$-24 \leq h \leq 24, -14 \leq k \leq 14, -14 \leq l \leq 14$	
Reflections collected	1481	
Independent reflections	2177 [$R_{\text{int}} = 0.0496$]	
Completeness to $\theta = 28.27^\circ$	98.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2177/0/150	
Goodness-of-fit on F^2	1.356	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0622, wR2 = 0.1743$	
R indices (all data)	$R1 = 0.0750, wR2 = 0.1832$	
Largest diff. peak and hole	0.467 and -0.488 e Å ⁻³	

Table A1-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for NMe₄(1,12-Me₂-CB₁₁F₁₀). U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
N(1)	0	2127(2)	7500	30(1)
F(1)	1373(1)	-890(1)	10598(1)	38(1)
F(2)	2585(1)	-3016(1)	12842(1)	36(1)
F(3)	799(1)	-3746(1)	9357(1)	36(1)
F(4)	666(1)	-1709(1)	7093(1)	37(1)
F(5)	2376(1)	194(1)	9265(1)	36(1)
B(1)	1836(1)	-1623(2)	10278(2)	26(1)
B(2)	2529(1)	-2835(2)	11548(2)	25(1)
B(3)	1548(1)	-3154(2)	9672(2)	24(1)
B(4)	1477(1)	-2028(2)	8416(2)	25(1)
B(5)	2409(1)	-1015(2)	9520(2)	25(1)
C(1)	3544(2)	-642(2)	12732(2)	38(1)
C(2)	3034(1)	-1559(2)	11395(2)	29(1)
C(3)	131(6)	1007(7)	8380(11)	100(3)
C(4)	1043(4)	2370(6)	8554(8)	74(2)
C(5)	383(7)	3128(10)	8609(12)	129(4)
C(6)	349(8)	1995(11)	6615(12)	122(4)

Table A1-3. Bond lengths [Å] and angles [°] for NMe₄(1,12-Me₂-CB₁₁F₁₀).

N(1)-C(6)	1.445(6)	C(3)-C(6)#1	1.404(13)
N(1)-C(6)#1	1.445(6)	C(3)-C(3)#1	1.682(17)
N(1)-C(5)#1	1.477(7)	C(4)-C(5)	1.497(12)
N(1)-C(5)	1.477(8)	C(4)-C(6)	1.755(13)
N(1)-C(3)	1.499(6)	C(5)-C(6)#1	1.742(14)
N(1)-C(3)#1	1.499(6)	C(5)-C(5)#1	1.95(2)
N(1)-C(4)#1	1.555(6)	C(6)-C(3)#1	1.404(13)
N(1)-C(4)	1.555(6)	C(6)-C(5)#1	1.742(14)
F(1)-B(1)	1.359(2)		
F(2)-B(2)	1.370(2)	C(6)-N(1)-C(6)#1	168.4(10)
F(3)-B(3)	1.364(2)	C(6)-N(1)-C(5)#1	73.2(6)
F(4)-B(4)	1.366(2)	C(6)#1-N(1)-C(5)#1	116.2(8)
F(5)-B(5)	1.364(2)	C(6)-N(1)-C(5)	116.2(8)
B(1)-C(2)	1.763(3)	C(6)#1-N(1)-C(5)	73.2(7)
B(1)-B(3)	1.784(3)	C(5)#1-N(1)-C(5)	82.6(11)
B(1)-B(4)	1.784(3)	C(6)-N(1)-C(3)	112.2(5)
B(1)-B(5)	1.805(3)	C(6)#1-N(1)-C(3)	56.9(6)
B(1)-B(2)	1.802(3)	C(5)#1-N(1)-C(3)	164.8(6)
B(2)-C(2)	1.749(3)	C(5)-N(1)-C(3)	106.2(7)
B(2)-B(5)#2	1.775(3)	C(6)-N(1)-C(3)#1	56.9(6)
B(2)-B(3)	1.783(3)	C(6)#1-N(1)-C(3)#1	112.2(5)
B(2)-B(4)#2	1.796(3)	C(5)#1-N(1)-C(3)#1	106.2(7)
B(3)-C(2)#2	1.759(3)	C(5)-N(1)-C(3)#1	164.8(6)
B(3)-B(4)	1.801(3)	C(3)-N(1)-C(3)#1	68.2(8)
B(3)-B(5)#2	1.804(3)	C(6)-N(1)-C(4)#1	110.7(5)
B(4)-C(2)#2	1.753(3)	C(6)#1-N(1)-C(4)#1	71.5(6)
B(4)-B(5)	1.782(3)	C(5)#1-N(1)-C(4)#1	59.1(5)
B(4)-B(2)#2	1.796(3)	C(5)-N(1)-C(4)#1	104.7(6)
B(5)-C(2)	1.757(3)	C(3)-N(1)-C(4)#1	106.1(4)
B(5)-B(2)#2	1.775(3)	C(3)#1-N(1)-C(4)#1	90.5(5)
B(5)-B(3)#2	1.804(3)	C(6)-N(1)-C(4)	71.5(6)
C(1)-C(2)	1.555(3)	C(6)#1-N(1)-C(4)	110.7(5)
C(2)-B(4)#2	1.754(3)	C(5)#1-N(1)-C(4)	104.7(6)
C(2)-B(3)#2	1.759(3)	C(5)-N(1)-C(4)	59.1(5)

C(3)-N(1)-C(4)	90.5(5)	F(3)-B(3)-B(1)	125.63(16)
C(3)#1-N(1)-C(4)	106.1(4)	C(2)#2-B(3)-B(1)	105.63(14)
C(4)#1-N(1)-C(4)	160.0(5)	B(2)-B(3)-B(1)	60.69(12)
F(1)-B(1)-C(2)	120.16(16)	F(3)-B(3)-B(4)	122.20(15)
F(1)-B(1)-B(3)	124.98(16)	C(2)#2-B(3)-B(4)	59.01(11)
C(2)-B(1)-B(3)	105.50(14)	B(2)-B(3)-B(4)	107.87(14)
F(1)-B(1)-B(4)	125.35(16)	B(1)-B(3)-B(4)	59.69(12)
C(2)-B(1)-B(4)	105.42(13)	F(3)-B(3)-B(5)#2	119.10(16)
B(3)-B(1)-B(4)	60.64(11)	C(2)#2-B(3)-B(5)#2	59.06(11)
F(1)-B(1)-B(5)	120.75(16)	B(2)-B(3)-B(5)#2	59.30(11)
C(2)-B(1)-B(5)	58.97(11)	B(1)-B(3)-B(5)#2	108.08(14)
B(3)-B(1)-B(5)	107.98(14)	B(4)-B(3)-B(5)#2	107.76(13)
B(4)-B(1)-B(5)	59.54(11)	F(4)-B(4)-C(2)#2	120.81(16)
F(1)-B(1)-B(2)	120.56(16)	F(4)-B(4)-B(5)	123.60(15)
C(2)-B(1)-B(2)	58.75(11)	C(2)#2-B(4)-B(5)	105.55(14)
B(3)-B(1)-B(2)	59.63(12)	F(4)-B(4)-B(1)	125.14(15)
B(4)-B(1)-B(2)	107.78(14)	C(2)#2-B(4)-B(1)	105.84(13)
B(5)-B(1)-B(2)	107.33(13)	B(5)-B(4)-B(1)	60.81(12)
F(2)-B(2)-C(2)	119.70(16)	F(4)-B(4)-B(2)#2	119.44(15)
F(2)-B(2)-B(5)#2	125.27(16)	C(2)#2-B(4)-B(2)#2	59.02(11)
C(2)-B(2)-B(5)#2	106.05(14)	B(5)-B(4)-B(2)#2	59.47(11)
F(2)-B(2)-B(3)	124.42(16)	B(1)-B(4)-B(2)#2	108.17(14)
C(2)-B(2)-B(3)	106.14(13)	F(4)-B(4)-B(3)	121.87(15)
B(5)#2-B(2)-B(3)	60.95(12)	C(2)#2-B(4)-B(3)	59.29(11)
F(2)-B(2)-B(4)#2	120.57(16)	B(5)-B(4)-B(3)	108.23(14)
C(2)-B(2)-B(4)#2	59.27(11)	B(1)-B(4)-B(3)	59.68(11)
B(5)#2-B(2)-B(4)#2	59.87(11)	B(2)#2-B(4)-B(3)	107.97(13)
B(3)-B(2)-B(4)#2	108.78(14)	F(5)-B(5)-C(2)	119.64(16)
F(2)-B(2)-B(1)	119.43(15)	F(5)-B(5)-B(2)#2	125.77(15)
C(2)-B(2)-B(1)	59.52(11)	C(2)-B(5)-B(2)#2	105.61(14)
B(5)#2-B(2)-B(1)	108.58(14)	F(5)-B(5)-B(4)	124.92(15)
B(3)-B(2)-B(1)	59.68(11)	C(2)-B(5)-B(4)	105.78(14)
B(4)#2-B(2)-B(1)	108.59(13)	B(2)#2-B(5)-B(4)	60.66(12)
F(3)-B(3)-C(2)#2	120.63(16)	F(5)-B(5)-B(1)	119.54(15)
F(3)-B(3)-B(2)	123.99(15)	C(2)-B(5)-B(1)	59.33(11)
C(2)#2-B(3)-B(2)	105.19(13)	B(2)#2-B(5)-B(1)	108.19(14)

B(4)-B(5)-B(1)	59.65(11)	B(3)#2-C(2)-B(1)	112.40(14)
F(5)-B(5)-B(3)#2	120.52(15)	C(6)#1-C(3)-N(1)	59.6(4)
C(2)-B(5)-B(3)#2	59.17(11)	C(6)#1-C(3)-C(3)#1	104.4(7)
B(2)#2-B(5)-B(3)#2	59.75(11)	N(1)-C(3)-C(3)#1	55.9(4)
B(4)-B(5)-B(3)#2	108.45(14)	C(5)-C(4)-N(1)	57.8(4)
B(1)-B(5)-B(3)#2	108.35(13)	C(5)-C(4)-C(6)	99.1(6)
C(1)-C(2)-B(2)	119.69(15)	N(1)-C(4)-C(6)	51.3(3)
C(1)-C(2)-B(4)#2	119.61(15)	N(1)-C(5)-C(4)	63.1(4)
B(2)-C(2)-B(4)#2	61.71(11)	N(1)-C(5)-C(6)#1	52.6(4)
C(1)-C(2)-B(5)	118.88(16)	C(4)-C(5)-C(6)#1	99.0(7)
B(2)-C(2)-B(5)	111.95(14)	N(1)-C(5)-C(5)#1	48.7(5)
B(4)#2-C(2)-B(5)	112.14(14)	C(4)-C(5)-C(5)#1	87.3(8)
C(1)-C(2)-B(3)#2	119.11(15)	C(6)#1-C(5)-C(5)#1	84.3(6)
B(2)-C(2)-B(3)#2	112.10(14)	N(1)-C(6)-C(3)#1	63.5(4)
B(4)#2-C(2)-B(3)#2	61.70(11)	N(1)-C(6)-C(4)	57.2(4)
B(5)-C(2)-B(3)#2	61.77(11)	C(3)#1-C(6)-C(4)	100.7(6)
C(1)-C(2)-B(1)	118.83(15)	N(1)-C(6)-C(5)#1	54.2(4)
B(2)-C(2)-B(1)	61.74(12)	C(3)#1-C(6)-C(5)#1	97.7(7)
B(4)#2-C(2)-B(1)	112.38(14)	C(4)-C(6)-C(5)#1	86.7(6)
B(5)-C(2)-B(1)	61.70(11)		

Symmetry transformations used to generate equivalent atoms:

#1: $-x, y, -z + 3/2$; #2: $-x + 1/2, -y - 1/2, -z + 2$

Table A1-4. Anisotropic displacement parameters ($\text{\AA} \times 10^3$) for $\text{NMe}_4(1,12\text{-Me}_2\text{-CB}_{11}\text{F}_{10})$. The anisotropic displacement factor exponent takes the form:
 $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	31(1)	31(1)	31(1)	0	20(1)	0
F(1)	30(1)	42(1)	48(1)	-7(1)	26(1)	7(1)
F(2)	38(1)	48(1)	27(1)	3(1)	23(1)	-2(1)
F(3)	24(1)	42(1)	41(1)	2(1)	18(1)	-6(1)
F(4)	22(1)	48(1)	28(1)	8(1)	8(1)	6(1)
F(5)	38(1)	24(1)	44(1)	6(1)	24(1)	4(1)
B(1)	23(1)	28(1)	31(1)	1(1)	18(1)	4(1)
B(2)	25(1)	31(1)	24(1)	2(1)	17(1)	1(1)
B(3)	20(1)	29(1)	26(1)	2(1)	15(1)	1(1)
B(4)	21(1)	28(1)	24(1)	4(1)	13(1)	5(1)
B(5)	23(1)	25(1)	27(1)	4(1)	15(1)	5(1)
C(1)	34(1)	43(1)	42(1)	-2(1)	25(1)	3(1)
C(2)	28(1)	33(1)	32(1)	4(1)	20(1)	5(1)
C(3)	115(6)	82(5)	151(8)	81(5)	106(7)	53(5)
C(4)	30(3)	91(5)	76(4)	-13(4)	17(3)	-12(3)
C(5)	105(7)	112(7)	125(8)	-82(6)	43(6)	-31(5)
C(6)	156(9)	169(10)	122(8)	37(6)	127(8)	46(7)

Table A1-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for NMe₄(1,12-Me₂-CB₁₁F₁₀).

	x	y	z	U _{eq}
H(1A)	4201	-712	13246	57
H(1B)	3407	-814	13458	57
H(1C)	3345	179	12335	57

Table A3-1. Crystal data and structure refinement for Ag₂(1-Me-12-SiPh₃-CB₁₁F₁₀)₂·C₆H₆

Empirical formula	C ₂₃ H ₂₁ AgB ₁₁ F ₁₀ Si	
Formula weight	742.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 18.4204(6) Å	$\alpha = 90^\circ$
	<i>b</i> = 19.1497(7) Å	$\beta = 117.838(2)^\circ$
	<i>c</i> = 19.1230(7) Å	$\gamma = 90^\circ$
Volume	5964.9(4) Å ³	
<i>Z</i>	8	
Density (calculated)	1.653 Mg/m ³	
Absorption coefficient	0.796 mm ⁻¹	
<i>F</i> (000)	2920	
Crystal size	0.14 × 0.11 × 0.09 mm ³	
Theta range for data collection	1.64 to 33.24°	
Index ranges	-28 ≤ <i>h</i> ≤ 27, -29 ≤ <i>k</i> ≤ 29, -29 ≤ <i>l</i> ≤ 29	
Reflections collected	149946	
Independent reflections	22872 [<i>R</i> _{int} = 0.1086]	
Completeness to theta = 33.24°	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9340 and 0.8933	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	22872/0/829	
Goodness-of-fit on <i>F</i> ²	0.961	
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0459, <i>wR</i> 2 = 0.0947	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0950, <i>wR</i> 2 = 0.1130	
Largest diff. peak and hole	0.716 and -0.765 e Å ⁻³	

Table A3-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2\cdot\text{C}_6\text{H}_6$. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ag(1)	4803(1)	7935(1)	4660(1)	22(1)
Ag(2)	10065(1)	7568(1)	7564(1)	21(1)
Si(1)	7946(1)	7409(1)	6045(1)	16(1)
Si(2)	12101(1)	7288(1)	9197(1)	16(1)
F(106)	7687(1)	6524(1)	3002(1)	31(1)
F(102)	5876(1)	6806(1)	2710(1)	29(1)
F(103)	5441(1)	5673(1)	3636(1)	31(1)
F(104)	6963(1)	4692(1)	4475(1)	27(1)
F(105)	8341(1)	5218(1)	4091(1)	30(1)
F(110)	8965(1)	6759(1)	4912(1)	26(1)
F(111)	7359(1)	7803(1)	3982(1)	26(1)
F(107)	5929(1)	7247(1)	4387(1)	26(1)
F(108)	6625(1)	5901(1)	5542(1)	26(1)
F(109)	8486(1)	5570(1)	5825(1)	25(1)
F(202)	14341(1)	5284(1)	11448(1)	28(1)
F(203)	12751(1)	4396(1)	10461(1)	28(1)
F(204)	11358(1)	4967(1)	10819(1)	32(1)
F(205)	12092(1)	6172(1)	12035(1)	33(1)
F(206)	13936(1)	6381(1)	12425(1)	35(1)
F(211)	14023(1)	6881(1)	10833(1)	28(1)
F(207)	13263(1)	5632(1)	9563(1)	27(1)
F(208)	11321(1)	5420(1)	9150(1)	26(1)
F(209)	10910(1)	6555(1)	10187(1)	25(1)
F(210)	12553(1)	7490(1)	11179(1)	27(1)
C(101)	6843(2)	5762(1)	3547(2)	23(1)
C(102)	6513(2)	5286(1)	2826(2)	25(1)
C(112)	8987(2)	8268(1)	5591(2)	22(1)
C(113)	9578(2)	8781(1)	5744(2)	24(1)
C(114)	9936(2)	9130(1)	6456(2)	27(1)
C(115)	9674(2)	8992(1)	7019(2)	24(1)
C(116)	9064(1)	8491(1)	6862(2)	20(1)

C(111)	8724(1)	8102(1)	6151(2)	19(1)
C(122)	9192(1)	6489(1)	7117(2)	19(1)
C(123)	9608(2)	6086(1)	7794(2)	20(1)
C(124)	9328(2)	6059(1)	8356(2)	21(1)
C(125)	8646(2)	6440(1)	8244(2)	22(1)
C(126)	8228(2)	6846(1)	7571(2)	19(1)
C(121)	8486(1)	6879(1)	6985(2)	18(1)
C(132)	6970(2)	8612(1)	5932(1)	19(1)
C(133)	6301(1)	8969(1)	5904(2)	20(1)
C(134)	5690(2)	8606(1)	5992(2)	22(1)
C(135)	5753(2)	7884(1)	6100(2)	21(1)
C(136)	6424(1)	7530(1)	6112(2)	19(1)
C(131)	7048(1)	7888(1)	6041(1)	17(1)
C(6)	5257(2)	8735(2)	3738(2)	35(1)
C(5)	5099(2)	8334(2)	3078(2)	35(1)
C(4)	4297(2)	8194(2)	2521(2)	31(1)
C(3)	3650(2)	8451(2)	2630(2)	29(1)
C(2)	3811(2)	8847(2)	3292(2)	30(1)
C(1)	4612(2)	8996(1)	3844(2)	30(1)
C(235)	4143(2)	6817(2)	4117(2)	26(1)
C(234)	4502(2)	6421(2)	4802(2)	29(1)
C(233)	4140(2)	6397(1)	5296(2)	26(1)
C(216)	11384(1)	7482(1)	7536(2)	21(1)
C(215)	11044(2)	7300(2)	6738(2)	25(1)
C(214)	11002(2)	6608(2)	6525(2)	29(1)
C(213)	11308(2)	6094(2)	7104(2)	26(1)
C(212)	11634(2)	6276(1)	7901(2)	20(1)
C(211)	11675(1)	6974(1)	8136(2)	18(1)
C(221)	11289(1)	7908(1)	9173(2)	18(1)
C(226)	11398(2)	8628(1)	9279(2)	22(1)
C(225)	10767(2)	9059(1)	9235(2)	24(1)
C(224)	10005(2)	8782(1)	9069(2)	23(1)
C(223)	9878(2)	8066(1)	8954(2)	21(1)
C(222)	10516(1)	7635(1)	9013(2)	18(1)
C(231)	13056(1)	7811(1)	9432(2)	18(1)
C(232)	13430(2)	8225(1)	10110(2)	22(1)

C(236)	13420(2)	7802(1)	8928(2)	21(1)
C(201)	12912(2)	5411(1)	11475(2)	22(1)
C(202)	13174(2)	4892(2)	12154(2)	29(1)
B(106)	7490(2)	6438(2)	3598(2)	22(1)
B(102)	6465(2)	6600(2)	3431(2)	22(1)
B(103)	6209(2)	5948(2)	3963(2)	23(1)
B(104)	7078(2)	5386(2)	4448(2)	21(1)
B(105)	7867(2)	5688(2)	4225(2)	21(1)
B(110)	8173(2)	6538(2)	4630(2)	20(1)
B(111)	7291(2)	7109(2)	4125(2)	20(1)
B(107)	6499(2)	6802(2)	4354(2)	20(1)
B(108)	6880(2)	6051(2)	4992(2)	21(1)
B(109)	7912(2)	5883(2)	5156(2)	18(1)
B(112)	7558(2)	6770(1)	5096(2)	16(1)
B(202)	13589(2)	5593(2)	11119(2)	21(1)
B(203)	12691(2)	5090(2)	10551(2)	21(1)
B(204)	11899(2)	5413(2)	10754(2)	22(1)
B(205)	12315(2)	6113(2)	11454(2)	24(1)
B(206)	13363(2)	6229(2)	11681(2)	24(1)
B(211)	13394(2)	6472(2)	10797(2)	20(1)
B(207)	12971(2)	5776(2)	10095(2)	19(1)
B(208)	11915(2)	5661(2)	9867(2)	18(1)
B(209)	11682(2)	6292(2)	10432(2)	19(1)
B(210)	12593(2)	6801(2)	11000(2)	20(1)
B(212)	12351(2)	6524(2)	10017(2)	16(1)

Table A3-3. Bond lengths [Å] and angles [°] for Ag₂(1-Me-12-SiPh₃-CB₁₁F₁₀)₂·C₆H₆.

Ag(1)-C(235)	2.442(3)	F(208)-B(208)	1.374(3)
Ag(1)-C(135)	2.482(3)	F(209)-B(209)	1.368(3)
Ag(1)-C(1)	2.484(3)	F(210)-B(210)	1.373(3)
Ag(1)-C(134)	2.631(3)	C(101)-C(102)	1.522(4)
Ag(1)-C(236)#1	2.666(2)	C(101)-B(105)	1.724(4)
Ag(2)-C(116)	2.452(2)	C(101)-B(102)	1.723(4)
Ag(2)-C(216)	2.463(2)	C(101)-B(104)	1.724(4)
Ag(2)-C(222)	2.495(2)	C(101)-B(103)	1.729(4)
Ag(2)-C(122)	2.511(2)	C(101)-B(106)	1.732(4)
Si(1)-C(131)	1.889(2)	C(102)-H(13)	0.9800
Si(1)-C(121)	1.892(3)	C(102)-H(12)	0.9800
Si(1)-C(111)	1.895(2)	C(102)-H(11)	0.9800
Si(1)-B(112)	2.021(3)	C(112)-C(113)	1.392(4)
Si(2)-C(231)	1.886(2)	C(112)-C(111)	1.402(3)
Si(2)-C(221)	1.893(2)	C(112)-H(112)	0.9500
Si(2)-C(211)	1.900(3)	C(113)-C(114)	1.376(4)
Si(2)-B(212)	2.034(3)	C(113)-H(113)	0.9500
F(106)-B(106)	1.357(3)	C(114)-C(115)	1.396(4)
F(102)-B(102)	1.355(3)	C(114)-H(114)	0.9500
F(103)-B(103)	1.358(3)	C(115)-C(116)	1.399(3)
F(104)-B(104)	1.350(3)	C(115)-H(115)	0.9500
F(105)-B(105)	1.358(3)	C(116)-C(111)	1.414(4)
F(110)-B(110)	1.366(3)	C(116)-H(116)	0.9500
F(111)-B(111)	1.373(3)	C(122)-C(123)	1.391(4)
F(107)-B(107)	1.376(3)	C(122)-C(121)	1.417(3)
F(108)-B(108)	1.369(3)	C(122)-H(122)	0.9500
F(109)-B(109)	1.360(3)	C(123)-C(124)	1.390(3)
F(202)-B(202)	1.361(3)	C(123)-H(123)	0.9500
F(203)-B(203)	1.353(3)	C(124)-C(125)	1.380(4)
F(204)-B(204)	1.359(3)	C(124)-H(124)	0.9500
F(205)-B(205)	1.359(3)	C(125)-C(126)	1.389(4)
F(206)-B(206)	1.349(3)	C(125)-H(125)	0.9500
F(211)-B(211)	1.373(3)	C(126)-C(121)	1.406(3)
F(207)-B(207)	1.381(3)	C(126)-H(126)	0.9500

C(132)-C(133)	1.389(3)	C(214)-H(214)	0.9500
C(132)-C(131)	1.398(3)	C(213)-C(212)	1.396(4)
C(132)-H(132)	0.9500	C(213)-H(213)	0.9500
C(133)-C(134)	1.397(3)	C(212)-C(211)	1.400(4)
C(133)-H(133)	0.9500	C(212)-H(212)	0.9500
C(134)-C(135)	1.397(4)	C(221)-C(226)	1.395(3)
C(134)-H(134)	0.9500	C(221)-C(222)	1.411(3)
C(135)-C(136)	1.399(3)	C(226)-C(225)	1.395(3)
C(135)-H(135)	0.9500	C(226)-H(226)	0.9500
C(136)-C(131)	1.399(3)	C(225)-C(224)	1.391(4)
C(136)-H(136)	0.9500	C(225)-H(225)	0.9500
C(6)-C(5)	1.388(5)	C(224)-C(223)	1.390(4)
C(6)-C(1)	1.388(4)	C(224)-H(224)	0.9500
C(6)-H(6)	0.9500	C(223)-C(222)	1.397(3)
C(5)-C(4)	1.385(4)	C(223)-H(223)	0.9500
C(5)-H(5)	0.9500	C(222)-H(222)	0.9500
C(4)-C(3)	1.391(4)	C(231)-C(232)	1.397(4)
C(4)-H(4)	0.9500	C(231)-C(236)	1.409(3)
C(3)-C(2)	1.384(4)	C(232)-C(233)#2	1.387(3)
C(3)-H(3)	0.9500	C(232)-H(232)	0.9500
C(2)-C(1)	1.386(4)	C(236)-C(235)#2	1.409(3)
C(2)-H(2)	0.9500	C(236)-Ag(1)#2	2.666(2)
C(1)-H(1)	0.9500	C(236)-H(236)	0.9500
C(235)-C(234)	1.385(4)	C(201)-C(202)	1.524(4)
C(235)-C(236)#1	1.409(3)	C(201)-B(202)	1.713(4)
C(235)-H(235)	0.9500	C(201)-B(205)	1.725(4)
C(234)-C(233)	1.388(4)	C(201)-B(204)	1.726(4)
C(234)-H(234)	0.9500	C(201)-B(206)	1.731(4)
C(233)-C(232)#1	1.387(3)	C(201)-B(203)	1.729(4)
C(233)-H(233)	0.9500	C(202)-H(23)	0.9800
C(216)-C(215)	1.396(4)	C(202)-H(22)	0.9800
C(216)-C(211)	1.406(3)	C(202)-H(21)	0.9800
C(216)-H(216)	0.9500	B(106)-B(111)	1.775(4)
C(215)-C(214)	1.379(4)	B(106)-B(110)	1.788(4)
C(215)-H(215)	0.9500	B(106)-B(102)	1.790(4)
C(214)-C(213)	1.389(4)	B(106)-B(105)	1.790(4)

B(102)-B(111)	1.773(4)	B(211)-B(207)	1.792(4)
B(102)-B(107)	1.780(4)	B(211)-B(212)	1.802(4)
B(102)-B(103)	1.807(4)	B(211)-B(210)	1.805(4)
B(103)-B(107)	1.773(4)	B(207)-B(212)	1.794(4)
B(103)-B(108)	1.779(4)	B(207)-B(208)	1.797(4)
B(103)-B(104)	1.788(4)	B(208)-B(212)	1.801(4)
B(104)-B(109)	1.778(4)	B(208)-B(209)	1.802(4)
B(104)-B(108)	1.786(4)	B(209)-B(210)	1.801(4)
B(104)-B(105)	1.790(4)	B(209)-B(212)	1.805(3)
B(105)-B(110)	1.777(4)	B(210)-B(212)	1.798(4)
B(105)-B(109)	1.782(4)		
B(110)-B(112)	1.794(4)		
B(110)-B(109)	1.807(4)		
B(110)-B(111)	1.817(4)		
B(111)-B(112)	1.805(4)		
B(111)-B(107)	1.807(4)		
B(107)-B(112)	1.798(4)		
B(107)-B(108)	1.802(4)		
B(108)-B(112)	1.806(4)		
B(108)-B(109)	1.806(4)		
B(109)-B(112)	1.805(4)		
B(202)-B(211)	1.770(4)		
B(202)-B(203)	1.779(4)		
B(202)-B(207)	1.781(4)		
B(202)-B(206)	1.797(4)		
B(203)-B(207)	1.781(4)		
B(203)-B(204)	1.786(4)		
B(203)-B(208)	1.789(4)		
B(204)-B(209)	1.774(4)		
B(204)-B(208)	1.777(4)		
B(204)-B(205)	1.793(5)		
B(205)-B(210)	1.779(4)		
B(205)-B(209)	1.780(4)		
B(205)-B(206)	1.783(4)		
B(206)-B(211)	1.779(4)		
B(206)-B(210)	1.784(4)		

C(235)-Ag(1)-C(135)	112.95(9)	B(102)-C(101)-B(103)	63.13(16)
C(235)-Ag(1)-C(1)	123.65(10)	B(104)-C(101)-B(103)	62.35(17)
C(135)-Ag(1)-C(1)	123.29(9)	C(102)-C(101)-B(106)	118.1(2)
C(235)-Ag(1)-C(134)	143.20(9)	B(105)-C(101)-B(106)	62.39(17)
C(135)-Ag(1)-C(134)	31.53(8)	B(102)-C(101)-B(106)	62.39(17)
C(1)-Ag(1)-C(134)	92.86(9)	B(104)-C(101)-B(106)	114.3(2)
C(235)-Ag(1)-C(236)#1	31.64(8)	B(103)-C(101)-B(106)	114.5(2)
C(135)-Ag(1)-C(236)#1	124.56(8)	C(101)-C(102)-H(13)	109.5
C(1)-Ag(1)-C(236)#1	106.48(9)	C(101)-C(102)-H(12)	109.5
C(134)-Ag(1)-C(236)#1	140.88(7)	H(13)-C(102)-H(12)	109.5
C(116)-Ag(2)-C(216)	122.21(8)	C(101)-C(102)-H(11)	109.5
C(116)-Ag(2)-C(222)	110.30(8)	H(13)-C(102)-H(11)	109.5
C(216)-Ag(2)-C(222)	101.99(8)	H(12)-C(102)-H(11)	109.5
C(116)-Ag(2)-C(122)	102.05(8)	C(113)-C(112)-C(111)	120.9(3)
C(216)-Ag(2)-C(122)	114.77(8)	C(113)-C(112)-H(112)	119.6
C(222)-Ag(2)-C(122)	104.39(8)	C(111)-C(112)-H(112)	119.6
C(131)-Si(1)-C(121)	109.56(10)	C(114)-C(113)-C(112)	121.2(2)
C(131)-Si(1)-C(111)	106.09(11)	C(114)-C(113)-H(113)	119.4
C(121)-Si(1)-C(111)	103.80(11)	C(112)-C(113)-H(113)	119.4
C(131)-Si(1)-B(112)	110.38(11)	C(113)-C(114)-C(115)	119.5(2)
C(121)-Si(1)-B(112)	109.75(11)	C(113)-C(114)-H(114)	120.2
C(111)-Si(1)-B(112)	116.91(11)	C(115)-C(114)-H(114)	120.2
C(231)-Si(2)-C(221)	108.14(11)	C(114)-C(115)-C(116)	119.7(3)
C(231)-Si(2)-C(211)	107.26(10)	C(114)-C(115)-H(115)	120.2
C(221)-Si(2)-C(211)	104.20(11)	C(116)-C(115)-H(115)	120.2
C(231)-Si(2)-B(212)	110.34(11)	C(115)-C(116)-C(111)	121.3(2)
C(221)-Si(2)-B(212)	111.24(10)	C(115)-C(116)-Ag(2)	93.12(16)
C(211)-Si(2)-B(212)	115.26(11)	C(111)-C(116)-Ag(2)	91.70(15)
C(102)-C(101)-B(105)	117.8(2)	C(115)-C(116)-H(116)	119.4
C(102)-C(101)-B(102)	118.3(2)	C(111)-C(116)-H(116)	119.4
B(105)-C(101)-B(102)	114.1(2)	Ag(2)-C(116)-H(116)	85.1
C(102)-C(101)-B(104)	117.6(2)	C(112)-C(111)-C(116)	117.3(2)
B(105)-C(101)-B(104)	62.55(16)	C(112)-C(111)-Si(1)	126.2(2)
B(102)-C(101)-B(104)	114.6(2)	C(116)-C(111)-Si(1)	116.43(17)
C(102)-C(101)-B(103)	118.1(2)	C(123)-C(122)-C(121)	121.3(2)
B(105)-C(101)-B(103)	114.1(2)	C(123)-C(122)-Ag(2)	98.79(16)

C(121)-C(122)-Ag(2)	90.86(15)	Ag(1)-C(135)-H(135)	88.5
C(123)-C(122)-H(122)	119.4	C(135)-C(136)-C(131)	121.4(2)
C(121)-C(122)-H(122)	119.4	C(135)-C(136)-H(136)	119.3
Ag(2)-C(122)-H(122)	80.2	C(131)-C(136)-H(136)	119.3
C(124)-C(123)-C(122)	119.9(2)	C(132)-C(131)-C(136)	117.9(2)
C(124)-C(123)-H(123)	120.1	C(132)-C(131)-Si(1)	120.74(16)
C(122)-C(123)-H(123)	120.1	C(136)-C(131)-Si(1)	121.26(18)
C(125)-C(124)-C(123)	119.9(2)	C(5)-C(6)-C(1)	120.1(3)
C(125)-C(124)-H(124)	120.0	C(5)-C(6)-H(6)	119.9
C(123)-C(124)-H(124)	120.0	C(1)-C(6)-H(6)	119.9
C(124)-C(125)-C(126)	120.7(2)	C(4)-C(5)-C(6)	120.1(3)
C(124)-C(125)-H(125)	119.6	C(4)-C(5)-H(5)	119.9
C(126)-C(125)-H(125)	119.6	C(6)-C(5)-H(5)	119.9
C(125)-C(126)-C(121)	121.0(2)	C(5)-C(4)-C(3)	119.8(3)
C(125)-C(126)-H(126)	119.5	C(5)-C(4)-H(4)	120.1
C(121)-C(126)-H(126)	119.5	C(3)-C(4)-H(4)	120.1
C(126)-C(121)-C(122)	117.2(2)	C(2)-C(3)-C(4)	119.9(3)
C(126)-C(121)-Si(1)	123.89(18)	C(2)-C(3)-H(3)	120.1
C(122)-C(121)-Si(1)	118.87(17)	C(4)-C(3)-H(3)	120.1
C(133)-C(132)-C(131)	121.4(2)	C(3)-C(2)-C(1)	120.4(3)
C(133)-C(132)-H(132)	119.3	C(3)-C(2)-H(2)	119.8
C(131)-C(132)-H(132)	119.3	C(1)-C(2)-H(2)	119.8
C(132)-C(133)-C(134)	120.1(2)	C(2)-C(1)-C(6)	119.6(3)
C(132)-C(133)-H(133)	120.0	C(2)-C(1)-Ag(1)	95.57(18)
C(134)-C(133)-H(133)	120.0	C(6)-C(1)-Ag(1)	85.23(18)
C(135)-C(134)-C(133)	119.6(2)	C(2)-C(1)-H(1)	120.2
C(135)-C(134)-Ag(1)	68.32(15)	C(6)-C(1)-H(1)	120.2
C(133)-C(134)-Ag(1)	107.32(16)	Ag(1)-C(1)-H(1)	89.2
C(135)-C(134)-H(134)	120.2	C(234)-C(235)-C(236)#1	120.1(2)
C(133)-C(134)-H(134)	120.2	C(234)-C(235)-Ag(1)	98.90(18)
Ag(1)-C(134)-H(134)	94.1	C(236)#1-C(235)-Ag(1)	82.99(16)
C(134)-C(135)-C(136)	119.6(2)	C(234)-C(235)-H(235)	119.9
C(134)-C(135)-Ag(1)	80.15(16)	C(236)#1-C(235)-H(235)	119.9
C(136)-C(135)-Ag(1)	101.41(16)	Ag(1)-C(235)-H(235)	88.1
C(134)-C(135)-H(135)	120.2	C(235)-C(234)-C(233)	119.5(2)
C(136)-C(135)-H(135)	120.2	C(235)-C(234)-H(234)	120.3

C(233)-C(234)-H(234)	120.3	C(225)-C(224)-H(224)	120.4
C(234)-C(233)-C(232)#1	120.3(3)	C(224)-C(223)-C(222)	119.9(2)
C(234)-C(233)-H(233)	119.9	C(224)-C(223)-H(223)	120.1
C(232)#1-C(233)-H(233)	119.9	C(222)-C(223)-H(223)	120.1
C(215)-C(216)-C(211)	121.7(3)	C(223)-C(222)-C(221)	121.6(2)
C(215)-C(216)-Ag(2)	95.57(16)	C(223)-C(222)-Ag(2)	96.24(16)
C(211)-C(216)-Ag(2)	91.83(14)	C(221)-C(222)-Ag(2)	92.24(15)
C(215)-C(216)-H(216)	119.2	C(223)-C(222)-H(222)	119.2
C(211)-C(216)-H(216)	119.2	C(221)-C(222)-H(222)	119.2
Ag(2)-C(216)-H(216)	82.4	Ag(2)-C(222)-H(222)	81.3
C(214)-C(215)-C(216)	119.8(3)	C(232)-C(231)-C(236)	117.1(2)
C(214)-C(215)-H(215)	120.1	C(232)-C(231)-Si(2)	121.55(17)
C(216)-C(215)-H(215)	120.1	C(236)-C(231)-Si(2)	121.3(2)
C(215)-C(214)-C(213)	119.9(3)	C(233)#2-C(232)-C(231)	122.0(2)
C(215)-C(214)-H(214)	120.0	C(233)#2-C(232)-H(232)	119.0
C(213)-C(214)-H(214)	120.0	C(231)-C(232)-H(232)	119.0
C(214)-C(213)-C(212)	120.1(3)	C(235)#2-C(236)-C(231)	120.9(2)
C(214)-C(213)-H(213)	120.0	C(235)#2-C(236)-Ag(1)#2	65.37(14)
C(212)-C(213)-H(213)	120.0	C(231)-C(236)-Ag(1)#2	106.89(17)
C(213)-C(212)-C(211)	121.3(2)	C(235)#2-C(236)-H(236)	119.5
C(213)-C(212)-H(212)	119.3	C(231)-C(236)-H(236)	119.5
C(211)-C(212)-H(212)	119.3	Ag(1)#2-C(236)-H(236)	97.4
C(212)-C(211)-C(216)	117.1(2)	C(202)-C(201)-B(202)	118.1(2)
C(212)-C(211)-Si(2)	125.38(19)	C(202)-C(201)-B(205)	118.2(2)
C(216)-C(211)-Si(2)	117.55(19)	B(202)-C(201)-B(205)	114.0(2)
C(226)-C(221)-C(222)	117.4(2)	C(202)-C(201)-B(204)	118.4(2)
C(226)-C(221)-Si(2)	123.96(17)	B(202)-C(201)-B(204)	113.5(2)
C(222)-C(221)-Si(2)	118.62(18)	B(205)-C(201)-B(204)	62.64(18)
C(221)-C(226)-C(225)	121.1(2)	C(202)-C(201)-B(206)	117.9(2)
C(221)-C(226)-H(226)	119.4	B(202)-C(201)-B(206)	62.91(17)
C(225)-C(226)-H(226)	119.4	B(205)-C(201)-B(206)	62.13(17)
C(224)-C(225)-C(226)	120.8(2)	B(204)-C(201)-B(206)	113.9(2)
C(224)-C(225)-H(225)	119.6	C(202)-C(201)-B(203)	118.0(2)
C(226)-C(225)-H(225)	119.6	B(202)-C(201)-B(203)	62.25(16)
C(223)-C(224)-C(225)	119.2(2)	B(205)-C(201)-B(203)	114.2(2)
C(223)-C(224)-H(224)	120.4	B(204)-C(201)-B(203)	62.26(16)

B(206)-C(201)-B(203)	114.4(2)	B(106)-B(102)-B(103)	108.1(2)
C(201)-C(202)-H(23)	109.5	F(103)-B(103)-C(101)	119.3(2)
C(201)-C(202)-H(22)	109.5	F(103)-B(103)-B(107)	126.6(2)
H(23)-C(202)-H(22)	109.5	C(101)-B(103)-B(107)	104.43(19)
C(201)-C(202)-H(21)	109.5	F(103)-B(103)-B(108)	126.1(2)
H(23)-C(202)-H(21)	109.5	C(101)-B(103)-B(108)	105.14(19)
H(22)-C(202)-H(21)	109.5	B(107)-B(103)-B(108)	60.98(17)
F(106)-B(106)-C(101)	119.4(2)	F(103)-B(103)-B(104)	119.6(2)
F(106)-B(106)-B(111)	126.6(2)	C(101)-B(103)-B(104)	58.68(16)
C(101)-B(106)-B(111)	104.68(18)	B(107)-B(103)-B(104)	108.5(2)
F(106)-B(106)-B(110)	126.0(2)	B(108)-B(103)-B(104)	60.12(17)
C(101)-B(106)-B(110)	104.60(19)	F(103)-B(103)-B(102)	119.9(2)
B(111)-B(106)-B(110)	61.33(16)	C(101)-B(103)-B(102)	58.27(15)
F(106)-B(106)-B(102)	120.2(2)	B(107)-B(103)-B(102)	59.61(16)
C(101)-B(106)-B(102)	58.56(16)	B(108)-B(103)-B(102)	108.5(2)
B(111)-B(106)-B(102)	59.63(16)	B(104)-B(103)-B(102)	107.60(19)
B(110)-B(106)-B(102)	108.52(18)	F(104)-B(104)-C(101)	118.6(2)
F(106)-B(106)-B(105)	119.2(2)	F(104)-B(104)-B(109)	126.4(2)
C(101)-B(106)-B(105)	58.59(16)	C(101)-B(104)-B(109)	105.2(2)
B(111)-B(106)-B(105)	108.6(2)	F(104)-B(104)-B(108)	126.9(2)
B(110)-B(106)-B(105)	59.55(17)	C(101)-B(104)-B(108)	105.0(2)
B(102)-B(106)-B(105)	107.79(19)	B(109)-B(104)-B(108)	60.88(16)
F(102)-B(102)-C(101)	119.1(2)	F(104)-B(104)-B(103)	119.6(2)
F(102)-B(102)-B(111)	127.0(2)	C(101)-B(104)-B(103)	58.97(16)
C(101)-B(102)-B(111)	105.2(2)	B(109)-B(104)-B(103)	108.6(2)
F(102)-B(102)-B(107)	125.9(2)	B(108)-B(104)-B(103)	59.70(16)
C(101)-B(102)-B(107)	104.4(2)	F(104)-B(104)-B(105)	119.1(2)
B(111)-B(102)-B(107)	61.13(16)	C(101)-B(104)-B(105)	58.73(16)
F(102)-B(102)-B(106)	120.6(2)	B(109)-B(104)-B(105)	59.92(16)
C(101)-B(102)-B(106)	59.05(16)	B(108)-B(104)-B(105)	108.5(2)
B(111)-B(102)-B(106)	59.78(16)	B(103)-B(104)-B(105)	108.2(2)
B(107)-B(102)-B(106)	108.4(2)	F(105)-B(105)-C(101)	119.1(2)
F(102)-B(102)-B(103)	118.6(2)	F(105)-B(105)-B(110)	126.0(2)
C(101)-B(102)-B(103)	58.60(16)	C(101)-B(105)-B(110)	105.4(2)
B(111)-B(102)-B(103)	108.4(2)	F(105)-B(105)-B(109)	126.3(2)
B(107)-B(102)-B(103)	59.23(16)	C(101)-B(105)-B(109)	104.99(18)

B(110)-B(105)-B(109)	61.03(16)	B(102)-B(111)-B(110)	108.0(2)
F(105)-B(105)-B(104)	119.7(2)	B(106)-B(111)-B(110)	59.68(16)
C(101)-B(105)-B(104)	58.72(16)	B(112)-B(111)-B(110)	59.38(15)
B(110)-B(105)-B(104)	108.66(19)	B(107)-B(111)-B(110)	107.30(19)
B(109)-B(105)-B(104)	59.69(16)	F(107)-B(107)-B(103)	120.3(2)
F(105)-B(105)-B(106)	119.1(2)	F(107)-B(107)-B(102)	120.4(2)
C(101)-B(105)-B(106)	59.02(16)	B(103)-B(107)-B(102)	61.16(17)
B(110)-B(105)-B(106)	60.16(17)	F(107)-B(107)-B(112)	123.6(2)
B(109)-B(105)-B(106)	108.94(19)	B(103)-B(107)-B(112)	107.7(2)
B(104)-B(105)-B(106)	108.37(19)	B(102)-B(107)-B(112)	107.36(18)
F(110)-B(110)-B(105)	121.2(2)	F(107)-B(107)-B(108)	121.8(2)
F(110)-B(110)-B(106)	122.7(2)	B(103)-B(107)-B(108)	59.67(17)
B(105)-B(110)-B(106)	60.29(17)	B(102)-B(107)-B(108)	108.7(2)
F(110)-B(110)-B(112)	122.2(2)	B(112)-B(107)-B(108)	60.22(15)
B(105)-B(110)-B(112)	107.36(18)	F(107)-B(107)-B(111)	121.9(2)
B(106)-B(110)-B(112)	107.07(19)	B(103)-B(107)-B(111)	108.47(19)
F(110)-B(110)-B(109)	120.5(2)	B(102)-B(107)-B(111)	59.24(16)
B(105)-B(110)-B(109)	59.62(16)	B(112)-B(107)-B(111)	60.09(15)
B(106)-B(110)-B(109)	107.9(2)	B(108)-B(107)-B(111)	108.69(19)
B(112)-B(110)-B(109)	60.17(15)	F(108)-B(108)-B(103)	121.1(2)
F(110)-B(110)-B(111)	123.3(2)	F(108)-B(108)-B(104)	122.4(2)
B(105)-B(110)-B(111)	107.3(2)	B(103)-B(108)-B(104)	60.18(17)
B(106)-B(110)-B(111)	59.00(16)	F(108)-B(108)-B(107)	121.5(2)
B(112)-B(110)-B(111)	59.96(15)	B(103)-B(108)-B(107)	59.34(17)
B(109)-B(110)-B(111)	108.08(18)	B(104)-B(108)-B(107)	107.2(2)
F(111)-B(111)-B(102)	120.5(2)	F(108)-B(108)-B(112)	122.9(2)
F(111)-B(111)-B(106)	121.7(2)	B(103)-B(108)-B(112)	107.1(2)
B(102)-B(111)-B(106)	60.59(16)	B(104)-B(108)-B(112)	106.85(18)
F(111)-B(111)-B(112)	123.1(2)	B(107)-B(108)-B(112)	59.78(16)
B(102)-B(111)-B(112)	107.39(19)	F(108)-B(108)-B(109)	122.8(2)
B(106)-B(111)-B(112)	107.1(2)	B(103)-B(108)-B(109)	107.73(19)
F(111)-B(111)-B(107)	121.5(2)	B(104)-B(108)-B(109)	59.32(16)
B(102)-B(111)-B(107)	59.63(16)	B(107)-B(108)-B(109)	107.81(18)
B(106)-B(111)-B(107)	107.8(2)	B(112)-B(108)-B(109)	59.98(15)
B(112)-B(111)-B(107)	59.73(15)	F(109)-B(109)-B(104)	119.8(2)
F(111)-B(111)-B(110)	123.1(2)	F(109)-B(109)-B(105)	120.0(2)

B(104)-B(109)-B(105)	60.39(16)	B(211)-B(202)-B(207)	60.60(17)
F(109)-B(109)-B(112)	125.1(2)	B(203)-B(202)-B(207)	60.02(16)
B(104)-B(109)-B(112)	107.27(19)	F(202)-B(202)-B(206)	119.2(2)
B(105)-B(109)-B(112)	106.66(19)	C(201)-B(202)-B(206)	59.03(16)
F(109)-B(109)-B(108)	122.4(2)	B(211)-B(202)-B(206)	59.81(16)
B(104)-B(109)-B(108)	59.80(16)	B(203)-B(202)-B(206)	108.79(19)
B(105)-B(109)-B(108)	108.0(2)	B(207)-B(202)-B(206)	108.5(2)
B(112)-B(109)-B(108)	60.03(15)	F(203)-B(203)-C(201)	119.0(2)
F(109)-B(109)-B(110)	122.5(2)	F(203)-B(203)-B(202)	120.0(2)
B(104)-B(109)-B(110)	107.9(2)	C(201)-B(203)-B(202)	58.44(16)
B(105)-B(109)-B(110)	59.35(16)	F(203)-B(203)-B(207)	127.0(2)
B(112)-B(109)-B(110)	59.56(15)	C(201)-B(203)-B(207)	104.8(2)
B(108)-B(109)-B(110)	108.12(19)	B(202)-B(203)-B(207)	60.04(16)
B(110)-B(112)-B(107)	108.7(2)	F(203)-B(203)-B(204)	119.5(2)
B(110)-B(112)-B(111)	60.65(15)	C(201)-B(203)-B(204)	58.78(16)
B(107)-B(112)-B(111)	60.18(15)	B(202)-B(203)-B(204)	107.6(2)
B(110)-B(112)-B(109)	60.26(15)	B(207)-B(203)-B(204)	107.8(2)
B(107)-B(112)-B(109)	107.99(19)	F(203)-B(203)-B(208)	126.3(2)
B(111)-B(112)-B(109)	108.70(19)	C(201)-B(203)-B(208)	104.91(19)
B(110)-B(112)-B(108)	108.65(19)	B(202)-B(203)-B(208)	108.3(2)
B(107)-B(112)-B(108)	60.00(16)	B(207)-B(203)-B(208)	60.43(15)
B(111)-B(112)-B(108)	108.6(2)	B(204)-B(203)-B(208)	59.60(16)
B(109)-B(112)-B(108)	59.99(15)	F(204)-B(204)-C(201)	119.4(2)
B(110)-B(112)-Si(1)	123.71(17)	F(204)-B(204)-B(209)	124.9(2)
B(107)-B(112)-Si(1)	119.13(16)	C(201)-B(204)-B(209)	105.3(2)
B(111)-B(112)-Si(1)	121.21(17)	F(204)-B(204)-B(208)	126.5(2)
B(109)-B(112)-Si(1)	123.10(18)	C(201)-B(204)-B(208)	105.58(18)
B(108)-B(112)-Si(1)	119.79(16)	B(209)-B(204)-B(208)	60.99(16)
F(202)-B(202)-C(201)	120.0(2)	F(204)-B(204)-B(203)	120.7(2)
F(202)-B(202)-B(211)	124.9(2)	C(201)-B(204)-B(203)	58.96(16)
C(201)-B(202)-B(211)	105.31(18)	B(209)-B(204)-B(203)	109.04(18)
F(202)-B(202)-B(203)	120.2(2)	B(208)-B(204)-B(203)	60.29(16)
C(201)-B(202)-B(203)	59.30(16)	F(204)-B(204)-B(205)	118.6(2)
B(211)-B(202)-B(203)	108.8(2)	C(201)-B(204)-B(205)	58.65(16)
F(202)-B(202)-B(207)	125.8(2)	B(209)-B(204)-B(205)	59.85(17)
C(201)-B(202)-B(207)	105.43(19)	B(208)-B(204)-B(205)	108.7(2)

B(203)-B(204)-B(205)	108.2(2)	B(206)-B(211)-B(207)	108.8(2)
F(205)-B(205)-C(201)	118.6(2)	F(211)-B(211)-B(212)	123.9(2)
F(205)-B(205)-B(210)	127.2(2)	B(202)-B(211)-B(212)	107.8(2)
C(201)-B(205)-B(210)	105.31(19)	B(206)-B(211)-B(212)	107.88(18)
F(205)-B(205)-B(209)	126.1(2)	B(207)-B(211)-B(212)	59.89(15)
C(201)-B(205)-B(209)	105.1(2)	F(211)-B(211)-B(210)	123.0(2)
B(210)-B(205)-B(209)	60.79(16)	B(202)-B(211)-B(210)	108.17(19)
F(205)-B(205)-B(206)	119.8(2)	B(206)-B(211)-B(210)	59.70(16)
C(201)-B(205)-B(206)	59.12(16)	B(207)-B(211)-B(210)	107.96(18)
B(210)-B(205)-B(206)	60.10(17)	B(212)-B(211)-B(210)	59.80(15)
B(209)-B(205)-B(206)	108.86(19)	F(207)-B(207)-B(203)	121.1(2)
F(205)-B(205)-B(204)	118.9(2)	F(207)-B(207)-B(202)	120.1(2)
C(201)-B(205)-B(204)	58.71(16)	B(203)-B(207)-B(202)	59.94(16)
B(210)-B(205)-B(204)	108.1(2)	F(207)-B(207)-B(211)	121.1(2)
B(209)-B(205)-B(204)	59.55(17)	B(203)-B(207)-B(211)	107.7(2)
B(206)-B(205)-B(204)	108.2(2)	B(202)-B(207)-B(211)	59.39(17)
F(206)-B(206)-C(201)	119.4(2)	F(207)-B(207)-B(212)	123.3(2)
F(206)-B(206)-B(211)	126.1(2)	B(203)-B(207)-B(212)	108.10(18)
C(201)-B(206)-B(211)	104.2(2)	B(202)-B(207)-B(212)	107.67(19)
F(206)-B(206)-B(205)	120.6(2)	B(211)-B(207)-B(212)	60.34(15)
C(201)-B(206)-B(205)	58.75(17)	F(207)-B(207)-B(208)	123.1(2)
B(211)-B(206)-B(205)	108.2(2)	B(203)-B(207)-B(208)	60.02(16)
F(206)-B(206)-B(210)	127.0(2)	B(202)-B(207)-B(208)	107.87(18)
C(201)-B(206)-B(210)	104.8(2)	B(211)-B(207)-B(208)	108.38(18)
B(211)-B(206)-B(210)	60.89(16)	B(212)-B(207)-B(208)	60.21(15)
B(205)-B(206)-B(210)	59.85(17)	F(208)-B(208)-B(204)	120.2(2)
F(206)-B(206)-B(202)	119.4(2)	F(208)-B(208)-B(203)	121.1(2)
C(201)-B(206)-B(202)	58.06(16)	B(204)-B(208)-B(203)	60.11(16)
B(211)-B(206)-B(202)	59.32(16)	F(208)-B(208)-B(207)	123.4(2)
B(205)-B(206)-B(202)	107.2(2)	B(204)-B(208)-B(207)	107.5(2)
B(210)-B(206)-B(202)	107.9(2)	B(203)-B(208)-B(207)	59.55(15)
F(211)-B(211)-B(202)	119.7(2)	F(208)-B(208)-B(212)	123.7(2)
F(211)-B(211)-B(206)	120.1(2)	B(204)-B(208)-B(212)	107.4(2)
B(202)-B(211)-B(206)	60.86(17)	B(203)-B(208)-B(212)	107.42(19)
F(211)-B(211)-B(207)	121.6(2)	B(207)-B(208)-B(212)	59.82(15)
B(202)-B(211)-B(207)	60.01(17)	F(208)-B(208)-B(209)	121.4(2)

B(204)-B(208)-B(209)	59.44(16)	F(210)-B(210)-B(209)	121.8(2)
B(203)-B(208)-B(209)	107.7(2)	B(205)-B(210)-B(209)	59.62(16)
B(207)-B(208)-B(209)	107.84(19)	B(206)-B(210)-B(209)	107.9(2)
B(212)-B(208)-B(209)	60.15(15)	B(212)-B(210)-B(209)	60.21(15)
F(209)-B(209)-B(204)	119.8(2)	F(210)-B(210)-B(211)	122.3(2)
F(209)-B(209)-B(205)	119.3(2)	B(205)-B(210)-B(211)	107.2(2)
B(204)-B(209)-B(205)	60.60(17)	B(206)-B(210)-B(211)	59.41(16)
F(209)-B(209)-B(210)	122.3(2)	B(212)-B(210)-B(211)	60.01(15)
B(204)-B(209)-B(210)	108.0(2)	B(209)-B(210)-B(211)	107.79(19)
B(205)-B(209)-B(210)	59.60(17)	B(207)-B(212)-B(210)	108.2(2)
F(209)-B(209)-B(208)	122.8(2)	B(207)-B(212)-B(208)	59.97(15)
B(204)-B(209)-B(208)	59.57(16)	B(210)-B(212)-B(208)	108.18(19)
B(205)-B(209)-B(208)	108.1(2)	B(207)-B(212)-B(211)	59.76(16)
B(210)-B(209)-B(208)	108.01(17)	B(210)-B(212)-B(211)	60.19(15)
F(209)-B(209)-B(212)	125.0(2)	B(208)-B(212)-B(211)	107.7(2)
B(204)-B(209)-B(212)	107.28(18)	B(207)-B(212)-B(209)	107.81(19)
B(205)-B(209)-B(212)	107.34(19)	B(210)-B(212)-B(209)	59.96(15)
B(210)-B(209)-B(212)	59.82(15)	B(208)-B(212)-B(209)	59.96(15)
B(208)-B(209)-B(212)	59.89(15)	B(211)-B(212)-B(209)	107.73(19)
F(210)-B(210)-B(205)	121.9(2)	B(207)-B(212)-Si(2)	123.05(16)
F(210)-B(210)-B(206)	121.6(2)	B(210)-B(212)-Si(2)	116.69(17)
B(205)-B(210)-B(206)	60.05(17)	B(208)-B(212)-Si(2)	127.88(18)
F(210)-B(210)-B(212)	121.9(2)	B(211)-B(212)-Si(2)	116.64(16)
B(205)-B(210)-B(212)	107.7(2)	B(209)-B(212)-Si(2)	124.04(17)
B(206)-B(210)-B(212)	107.8(2)		

Symmetry transformations used to generate equivalent atoms:

#1: $x-1, -y + 3/2, z - 1/2$; #2: $x + 1, -y + 3/2, z + 1/2$

Table A3-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2 \cdot \text{C}_6\text{H}_6$. The anisotropic displacement factor exponent takes the form:
 $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	22(1)	21(1)	22(1)	2(1)	11(1)	-1(1)
Ag(2)	18(1)	22(1)	23(1)	1(1)	9(1)	0(1)
Si(1)	16(1)	16(1)	18(1)	2(1)	10(1)	1(1)
Si(2)	17(1)	14(1)	20(1)	-1(1)	11(1)	-1(1)
F(106)	47(1)	28(1)	28(1)	-1(1)	27(1)	1(1)
F(102)	35(1)	29(1)	19(1)	4(1)	9(1)	8(1)
F(103)	23(1)	35(1)	33(1)	-3(1)	10(1)	-6(1)
F(104)	33(1)	15(1)	31(1)	2(1)	14(1)	-3(1)
F(105)	35(1)	24(1)	34(1)	-4(1)	20(1)	8(1)
F(110)	22(1)	27(1)	36(1)	-6(1)	19(1)	-2(1)
F(111)	40(1)	16(1)	28(1)	4(1)	21(1)	1(1)
F(107)	23(1)	32(1)	26(1)	4(1)	13(1)	9(1)
F(108)	29(1)	26(1)	28(1)	5(1)	19(1)	0(1)
F(109)	26(1)	19(1)	23(1)	2(1)	6(1)	7(1)
F(202)	22(1)	24(1)	36(1)	3(1)	12(1)	6(1)
F(203)	36(1)	17(1)	31(1)	1(1)	16(1)	0(1)
F(204)	30(1)	33(1)	37(1)	10(1)	19(1)	-6(1)
F(205)	44(1)	39(1)	25(1)	7(1)	24(1)	13(1)
F(206)	35(1)	34(1)	22(1)	-5(1)	2(1)	3(1)
F(211)	15(1)	22(1)	42(1)	1(1)	9(1)	-2(1)
F(207)	38(1)	24(1)	31(1)	1(1)	26(1)	6(1)
F(208)	29(1)	23(1)	21(1)	-2(1)	6(1)	-11(1)
F(209)	19(1)	31(1)	30(1)	8(1)	16(1)	4(1)
F(210)	30(1)	22(1)	28(1)	-8(1)	13(1)	2(1)
C(101)	26(1)	20(1)	22(1)	1(1)	11(1)	1(1)
C(102)	33(1)	20(1)	19(1)	-4(1)	9(1)	1(1)
C(112)	22(1)	20(1)	27(1)	2(1)	15(1)	2(1)
C(113)	23(1)	22(1)	34(2)	8(1)	20(1)	3(1)
C(114)	20(1)	20(1)	44(2)	6(1)	16(1)	-1(1)
C(115)	22(1)	17(1)	31(1)	0(1)	10(1)	0(1)

C(116)	19(1)	19(1)	24(1)	2(1)	12(1)	1(1)
C(111)	17(1)	18(1)	24(1)	4(1)	12(1)	2(1)
C(122)	20(1)	19(1)	19(1)	-4(1)	10(1)	-4(1)
C(123)	19(1)	15(1)	23(1)	0(1)	7(1)	-2(1)
C(124)	22(1)	18(1)	20(1)	2(1)	7(1)	-3(1)
C(125)	27(1)	21(1)	19(1)	-1(1)	13(1)	-6(1)
C(126)	24(1)	17(1)	22(1)	-1(1)	15(1)	-2(1)
C(121)	19(1)	15(1)	19(1)	-1(1)	9(1)	-2(1)
C(132)	21(1)	19(1)	18(1)	0(1)	10(1)	-2(1)
C(133)	20(1)	17(1)	24(1)	2(1)	10(1)	1(1)
C(134)	20(1)	23(1)	24(1)	1(1)	12(1)	6(1)
C(135)	19(1)	26(1)	21(1)	1(1)	13(1)	1(1)
C(136)	21(1)	18(1)	21(1)	2(1)	12(1)	2(1)
C(131)	17(1)	19(1)	16(1)	-1(1)	9(1)	0(1)
C(6)	34(2)	20(1)	35(2)	8(1)	3(1)	-5(1)
C(5)	36(2)	28(2)	45(2)	11(1)	21(2)	6(1)
C(4)	49(2)	24(2)	25(1)	1(1)	20(1)	-1(1)
C(3)	32(1)	30(2)	23(1)	-2(1)	11(1)	-9(1)
C(2)	37(2)	29(2)	26(1)	-1(1)	16(1)	-5(1)
C(1)	43(2)	17(1)	23(1)	1(1)	11(1)	-6(1)
C(235)	20(1)	28(2)	33(2)	-10(1)	16(1)	-3(1)
C(234)	17(1)	22(1)	45(2)	-7(1)	13(1)	3(1)
C(233)	20(1)	17(1)	38(2)	5(1)	12(1)	1(1)
C(216)	18(1)	22(1)	24(1)	3(1)	11(1)	1(1)
C(215)	22(1)	34(2)	22(1)	4(1)	11(1)	2(1)
C(214)	26(1)	41(2)	19(1)	-2(1)	11(1)	1(1)
C(213)	29(1)	25(1)	27(1)	-6(1)	15(1)	0(1)
C(212)	22(1)	18(1)	23(1)	0(1)	12(1)	2(1)
C(211)	16(1)	22(1)	19(1)	2(1)	11(1)	-1(1)
C(221)	18(1)	16(1)	21(1)	-2(1)	11(1)	-3(1)
C(226)	21(1)	20(1)	30(1)	-4(1)	14(1)	-4(1)
C(225)	29(1)	16(1)	31(1)	-3(1)	17(1)	-1(1)
C(224)	23(1)	21(1)	29(1)	-1(1)	16(1)	4(1)
C(223)	16(1)	26(1)	24(1)	-3(1)	11(1)	-3(1)
C(222)	20(1)	16(1)	19(1)	-2(1)	10(1)	-2(1)
C(231)	18(1)	13(1)	26(1)	2(1)	14(1)	2(1)

C(232)	18(1)	21(1)	30(1)	-1(1)	13(1)	2(1)
C(236)	20(1)	18(1)	26(1)	4(1)	13(1)	2(1)
C(201)	25(1)	22(1)	18(1)	3(1)	10(1)	1(1)
C(202)	33(2)	31(2)	23(1)	9(1)	12(1)	6(1)
B(106)	31(2)	19(1)	21(1)	-1(1)	16(1)	1(1)
B(102)	28(1)	18(1)	21(1)	4(1)	12(1)	4(1)
B(103)	23(1)	24(2)	20(1)	1(1)	9(1)	-1(1)
B(104)	25(1)	14(1)	23(1)	2(1)	10(1)	-1(1)
B(105)	24(1)	16(1)	23(1)	0(1)	12(1)	3(1)
B(110)	21(1)	18(1)	26(2)	-2(1)	15(1)	1(1)
B(111)	26(1)	16(1)	20(1)	1(1)	14(1)	1(1)
B(107)	20(1)	20(1)	22(1)	4(1)	11(1)	3(1)
B(108)	21(1)	20(1)	22(1)	2(1)	11(1)	-1(1)
B(109)	19(1)	15(1)	22(1)	1(1)	10(1)	3(1)
B(112)	18(1)	12(1)	21(1)	1(1)	11(1)	2(1)
B(202)	20(1)	18(1)	24(1)	-1(1)	11(1)	3(1)
B(203)	25(1)	15(1)	24(2)	1(1)	12(1)	-2(1)
B(204)	22(1)	25(2)	21(1)	4(1)	12(1)	-2(1)
B(205)	27(1)	28(2)	18(1)	2(1)	13(1)	4(1)
B(206)	24(1)	24(2)	19(1)	-2(1)	7(1)	2(1)
B(211)	14(1)	18(1)	26(1)	-2(1)	9(1)	-1(1)
B(207)	21(1)	18(1)	22(1)	1(1)	14(1)	1(1)
B(208)	18(1)	17(1)	18(1)	-2(1)	8(1)	-4(1)
B(209)	17(1)	21(1)	20(1)	2(1)	10(1)	0(1)
B(210)	20(1)	20(1)	21(1)	-3(1)	10(1)	0(1)
B(212)	18(1)	17(1)	18(1)	-2(1)	11(1)	-1(1)

Table A3-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ag}_2(1\text{-Me-12-SiPh}_3\text{-CB}_{11}\text{F}_{10})_2 \cdot \text{C}_6\text{H}_6$.

	x	y	z	U_{eq}
H(13)	6158	4929	2875	38
H(12)	6973	5061	2792	38
H(11)	6196	5564	2348	38
H(112)	8758	8027	5100	26
H(113)	9738	8892	5351	29
H(114)	10359	9462	6562	33
H(115)	9909	9238	7507	29
H(116)	8875	8410	7240	24
H(122)	9385	6503	6735	22
H(123)	10081	5829	7874	24
H(124)	9607	5780	8816	25
H(125)	8461	6423	8631	26
H(126)	7761	7106	7505	23
H(132)	7384	8864	5877	23
H(133)	6258	9460	5826	24
H(134)	5234	8850	5977	26
H(135)	5344	7633	6165	25
H(136)	6456	7037	6171	23
H(6)	5808	8831	4119	42
H(5)	5541	8154	3008	42
H(4)	4189	7924	2066	38
H(3)	3099	8355	2250	35
H(2)	3369	9017	3369	36
H(1)	4720	9276	4292	36
H(235)	4385	6832	3774	31
H(234)	4993	6168	4933	34
H(233)	4378	6120	5762	31
H(216)	11420	7961	7676	25
H(215)	10842	7653	6343	30
H(214)	10765	6482	5982	35
H(213)	11294	5618	6959	32

H(212)	11833	5920	8292	25
H(226)	11910	8829	9383	27
H(225)	10858	9547	9319	29
H(224)	9576	9078	9034	28
H(223)	9359	7871	8835	25
H(222)	10426	7145	8943	22
H(232)	13191	8249	10456	27
H(236)	13176	7536	8454	25
H(23)	12872	4454	11957	44
H(22)	13054	5086	12563	44
H(21)	13765	4803	12379	44

Table A4-1. Crystal data and structure refinement for Cs(1-Me-12-SiPh₃-CB₁₁F₁₀).

Empirical formula	C ₂₀ H ₁₈ B ₁₁ CsF ₁₀ Si	
Formula weight	728.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 9.4773(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 20.3255(7) Å	$\beta = 92.127(2)^\circ$
	<i>c</i> = 14.7167(5) Å	$\gamma = 90^\circ$
Volume	2832.94(16) Å ³	
<i>Z</i>	4	
Density (calculated)	1.707 Mg/m ³	
Absorption coefficient	1.429 mm ⁻¹	
<i>F</i> (000)	1408	
Crystal size	0.22 × 0.07 × 0.05 mm ³	
Theta range for data collection	1.71 to 33.14°.	
Index ranges	-14 ≤ <i>h</i> ≤ 14, -30 ≤ <i>k</i> ≤ 30, -22 ≤ <i>l</i> ≤ 22	
Reflections collected	70755	
Independent reflections	10763 [<i>R</i> _{int} = 0.0854]	
Completeness to theta = 33.14°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9268 and 0.7440	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	10763/0/388	
Goodness-of-fit on <i>F</i> ²	1.006	
Final <i>R</i> indices [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0452, <i>wR</i> 2 = 0.0748	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0922, <i>wR</i> 2 = 0.0872	
Largest diff. peak and hole	0.749 and -0.863 e Å ⁻³	

Table A4-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Cs(1-Me-12-SiPh₃-CB₁₁F₁₀). U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(36)	11907(3)	3308(1)	4693(2)	19(1)
C(35)	13347(3)	3417(1)	4839(2)	27(1)
C(34)	13844(3)	3726(1)	5627(2)	31(1)
C(33)	12900(3)	3923(1)	6267(2)	29(1)
C(32)	11458(3)	3816(1)	6123(2)	22(1)
C(31)	10926(3)	3508(1)	5330(2)	16(1)
Si(1)	8970(1)	3415(1)	5087(1)	12(1)
C(1)	7549(3)	871(1)	5136(2)	17(1)
C(2)	7160(3)	151(1)	5159(2)	18(1)
C(11)	8040(3)	3895(1)	5978(2)	14(1)
C(12)	7913(3)	3657(1)	6864(2)	17(1)
C(13)	7241(3)	4020(1)	7523(2)	22(1)
C(14)	6682(3)	4633(1)	7311(2)	23(1)
C(15)	6829(3)	4889(1)	6442(2)	21(1)
C(16)	7498(3)	4526(1)	5784(2)	17(1)
C(21)	8508(3)	3825(1)	3961(2)	13(1)
C(22)	9487(3)	4165(1)	3447(2)	19(1)
C(23)	9055(3)	4518(1)	2674(2)	23(1)
C(24)	7644(3)	4544(1)	2402(2)	22(1)
C(25)	6658(3)	4210(1)	2900(2)	20(1)
C(26)	7085(3)	3857(1)	3668(2)	17(1)
B(2)	6230(3)	1444(2)	5220(2)	19(1)
B(3)	7069(3)	1319(2)	4174(2)	17(1)
B(4)	8868(3)	1119(1)	4432(2)	14(1)
B(5)	9124(3)	1124(1)	5642(2)	14(1)
B(6)	7492(3)	1329(2)	6141(2)	17(1)
B(7)	6752(3)	2134(2)	4565(2)	18(1)
B(8)	8408(3)	1934(2)	4084(2)	16(1)
B(9)	9671(3)	1804(2)	4990(2)	13(1)
B(10)	8828(3)	1935(1)	6049(2)	13(1)

B(11)	6996(3)	2137(2)	5782(2)	17(1)
B(12)	8373(3)	2448(1)	5079(2)	13(1)
F(2)	4869(2)	1239(1)	5316(1)	27(1)
F(3)	6363(2)	1009(1)	3471(1)	29(1)
F(4)	9541(2)	666(1)	3931(1)	22(1)
F(5)	10011(2)	673(1)	6037(1)	22(1)
F(6)	7096(2)	1028(1)	6913(1)	27(1)
F(7)	5755(2)	2505(1)	4107(1)	28(1)
F(8)	8786(2)	2166(1)	3245(1)	25(1)
F(9)	11105(2)	1911(1)	4912(1)	18(1)
F(10)	9601(2)	2163(1)	6794(1)	19(1)
F(11)	6156(2)	2509(1)	6322(1)	23(1)
Cs(1)	7990(1)	2865(1)	1590(1)	19(1)

Table A4-3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for Cs(1-Me-12-SiPh₃-CB₁₁F₁₀).

C(36)-C(35)	1.391(4)	C(13)-C(14)	1.385(4)
C(36)-C(31)	1.404(4)	C(13)-H(13A)	0.9500
C(36)-Cs(1)#1	3.782(3)	C(14)-C(15)	1.392(4)
C(36)-H(36A)	0.9500	C(14)-H(14A)	0.9500
C(35)-C(34)	1.385(5)	C(15)-C(16)	1.389(4)
C(35)-Cs(1)#1	3.688(3)	C(15)-H(15A)	0.9500
C(35)-H(35A)	0.9500	C(16)-H(16A)	0.9500
C(34)-C(33)	1.383(4)	C(21)-C(22)	1.401(4)
C(34)-Cs(1)#1	3.634(3)	C(21)-C(26)	1.402(4)
C(34)-H(34A)	0.9500	C(22)-C(23)	1.394(4)
C(33)-C(32)	1.392(4)	C(22)-H(22A)	0.9500
C(33)-Cs(1)#1	3.666(3)	C(23)-C(24)	1.383(4)
C(33)-H(33A)	0.9500	C(23)-Cs(1)	3.839(3)
C(32)-C(31)	1.402(4)	C(23)-H(23A)	0.9500
C(32)-Cs(1)#1	3.765(3)	C(24)-C(25)	1.385(4)
C(32)-H(32A)	0.9500	C(24)-Cs(1)	3.635(3)
C(31)-Si(1)	1.885(3)	C(24)-H(24A)	0.9500
C(31)-Cs(1)#1	3.844(3)	C(25)-C(26)	1.388(4)
Si(1)-C(11)	1.880(3)	C(25)-Cs(1)	3.602(3)
Si(1)-C(21)	1.892(3)	C(25)-H(25A)	0.9500
Si(1)-B(12)	2.044(3)	C(26)-Cs(1)	3.789(3)
C(1)-C(2)	1.509(4)	C(26)-H(26A)	0.9500
C(1)-B(2)	1.715(4)	B(2)-F(2)	1.367(3)
C(1)-B(5)	1.722(4)	B(2)-B(11)	1.776(4)
C(1)-B(4)	1.729(4)	B(2)-B(3)	1.777(4)
C(1)-B(3)	1.730(4)	B(2)-B(7)	1.784(5)
C(1)-B(6)	1.749(4)	B(2)-B(6)	1.789(5)
C(2)-H(2A)	0.9800	B(3)-F(3)	1.365(3)
C(2)-H(2B)	0.9800	B(3)-B(4)	1.779(4)
C(2)-H(2C)	0.9800	B(3)-B(7)	1.783(4)
C(11)-C(12)	1.400(4)	B(3)-B(8)	1.790(4)
C(11)-C(16)	1.405(4)	B(4)-F(4)	1.354(3)
C(12)-C(13)	1.391(4)	B(4)-B(9)	1.774(4)
C(12)-H(12A)	0.9500	B(4)-B(8)	1.784(4)

B(4)-B(5)	1.789(4)	Cs(1)-C(32)#3	3.765(3)
B(5)-F(5)	1.358(3)	Cs(1)-C(36)#3	3.782(3)
B(5)-B(9)	1.771(4)	C(35)-C(36)-C(31)	121.4(3)
B(5)-B(10)	1.781(4)	C(35)-C(36)-Cs(1)#1	75.47(16)
B(5)-B(6)	1.786(4)	C(31)-C(36)-Cs(1)#1	81.88(15)
B(6)-F(6)	1.355(3)	C(35)-C(36)-H(36A)	119.3
B(6)-B(10)	1.776(4)	C(31)-C(36)-H(36A)	119.3
B(6)-B(11)	1.783(4)	Cs(1)#1-C(36)-H(36A)	113.6
B(7)-F(7)	1.366(3)	C(34)-C(35)-C(36)	120.2(3)
B(7)-B(8)	1.792(4)	C(34)-C(35)-Cs(1)#1	76.90(18)
B(7)-B(11)	1.798(4)	C(36)-C(35)-Cs(1)#1	83.11(16)
B(7)-B(12)	1.804(4)	C(34)-C(35)-H(35A)	119.9
B(8)-F(8)	1.380(3)	C(36)-C(35)-H(35A)	119.9
B(8)-B(9)	1.779(4)	Cs(1)#1-C(35)-H(35A)	110.3
B(8)-B(12)	1.801(4)	C(33)-C(34)-C(35)	119.5(3)
B(9)-F(9)	1.385(3)	C(33)-C(34)-Cs(1)#1	80.39(18)
B(9)-B(10)	1.797(4)	C(35)-C(34)-Cs(1)#1	81.31(17)
B(9)-B(12)	1.805(4)	C(33)-C(34)-H(34A)	120.2
B(9)-Cs(1)#1	3.916(3)	C(35)-C(34)-H(34A)	120.2
B(10)-F(10)	1.377(3)	Cs(1)#1-C(34)-H(34A)	108.4
B(10)-B(12)	1.806(4)	C(34)-C(33)-C(32)	120.5(3)
B(10)-B(11)	1.812(4)	C(34)-C(33)-Cs(1)#1	77.77(17)
B(11)-F(11)	1.373(3)	C(32)-C(33)-Cs(1)#1	83.26(17)
B(11)-B(12)	1.809(4)	C(34)-C(33)-H(33A)	119.8
F(2)-Cs(1)#2	3.2016(16)	C(32)-C(33)-H(33A)	119.8
F(8)-Cs(1)	2.8963(15)	Cs(1)#1-C(33)-H(33A)	109.4
F(9)-Cs(1)#1	3.0278(15)	C(33)-C(32)-C(31)	121.2(3)
F(10)-Cs(1)#1	3.2378(15)	C(33)-C(32)-Cs(1)#1	75.20(17)
F(11)-Cs(1)#2	3.1342(15)	C(31)-C(32)-Cs(1)#1	82.56(15)
Cs(1)-F(9)#3	3.0278(15)	C(33)-C(32)-H(32A)	119.4
Cs(1)-F(11)#4	3.1342(15)	C(31)-C(32)-H(32A)	119.4
Cs(1)-F(2)#4	3.2016(16)	Cs(1)#1-C(32)-H(32A)	113.1
Cs(1)-F(10)#3	3.2377(15)	C(32)-C(31)-C(36)	117.3(2)
Cs(1)-C(34)#3	3.634(3)	C(32)-C(31)-Si(1)	121.6(2)
Cs(1)-C(33)#3	3.666(3)	C(36)-C(31)-Si(1)	121.1(2)
Cs(1)-C(35)#3	3.688(3)	C(32)-C(31)-Cs(1)#1	76.23(15)

C(36)-C(31)-Cs(1)#1	76.92(15)	C(14)-C(13)-H(13A)	120.0
Si(1)-C(31)-Cs(1)#1	119.85(10)	C(12)-C(13)-H(13A)	120.0
C(11)-Si(1)-C(31)	107.41(12)	C(13)-C(14)-C(15)	119.5(3)
C(11)-Si(1)-C(21)	106.40(11)	C(13)-C(14)-H(14A)	120.2
C(31)-Si(1)-C(21)	108.38(12)	C(15)-C(14)-H(14A)	120.2
C(11)-Si(1)-B(12)	111.51(11)	C(16)-C(15)-C(14)	120.4(3)
C(31)-Si(1)-B(12)	111.56(12)	C(16)-C(15)-H(15A)	119.8
C(21)-Si(1)-B(12)	111.35(12)	C(14)-C(15)-H(15A)	119.8
C(2)-C(1)-B(2)	118.5(2)	C(15)-C(16)-C(11)	121.1(2)
C(2)-C(1)-B(5)	119.2(2)	C(15)-C(16)-H(16A)	119.5
B(2)-C(1)-B(5)	112.9(2)	C(11)-C(16)-H(16A)	119.5
C(2)-C(1)-B(4)	118.6(2)	C(22)-C(21)-C(26)	117.4(2)
B(2)-C(1)-B(4)	113.0(2)	C(22)-C(21)-Si(1)	123.7(2)
B(5)-C(1)-B(4)	62.48(17)	C(26)-C(21)-Si(1)	118.55(19)
C(2)-C(1)-B(3)	118.1(2)	C(23)-C(22)-C(21)	121.0(3)
B(2)-C(1)-B(3)	62.10(18)	C(23)-C(22)-H(22A)	119.5
B(5)-C(1)-B(3)	113.2(2)	C(21)-C(22)-H(22A)	119.5
B(4)-C(1)-B(3)	61.92(17)	C(24)-C(23)-C(22)	120.5(3)
C(2)-C(1)-B(6)	118.8(2)	C(24)-C(23)-Cs(1)	71.10(16)
B(2)-C(1)-B(6)	62.17(18)	C(22)-C(23)-Cs(1)	87.30(17)
B(5)-C(1)-B(6)	61.92(17)	C(24)-C(23)-H(23A)	119.8
B(4)-C(1)-B(6)	113.4(2)	C(22)-C(23)-H(23A)	119.8
B(3)-C(1)-B(6)	113.4(2)	Cs(1)-C(23)-H(23A)	111.9
C(1)-C(2)-H(2A)	109.5	C(23)-C(24)-C(25)	119.5(3)
C(1)-C(2)-H(2B)	109.5	C(23)-C(24)-Cs(1)	87.80(17)
H(2A)-C(2)-H(2B)	109.5	C(25)-C(24)-Cs(1)	77.62(16)
C(1)-C(2)-H(2C)	109.5	C(23)-C(24)-H(24A)	120.2
H(2A)-C(2)-H(2C)	109.5	C(25)-C(24)-H(24A)	120.2
H(2B)-C(2)-H(2C)	109.5	Cs(1)-C(24)-H(24A)	104.5
C(12)-C(11)-C(16)	117.4(2)	C(24)-C(25)-C(26)	120.1(3)
C(12)-C(11)-Si(1)	121.88(19)	C(24)-C(25)-Cs(1)	80.32(16)
C(16)-C(11)-Si(1)	120.66(19)	C(26)-C(25)-Cs(1)	86.88(16)
C(13)-C(12)-C(11)	121.6(2)	C(24)-C(25)-H(25A)	119.9
C(13)-C(12)-H(12A)	119.2	C(26)-C(25)-H(25A)	119.9
C(11)-C(12)-H(12A)	119.2	Cs(1)-C(25)-H(25A)	102.9
C(14)-C(13)-C(12)	120.0(3)	C(25)-C(26)-C(21)	121.5(2)

C(25)-C(26)-Cs(1)	71.66(15)	F(4)-B(4)-B(9)	125.7(2)
C(21)-C(26)-Cs(1)	88.87(15)	C(1)-B(4)-B(9)	105.0(2)
C(25)-C(26)-H(26A)	119.2	F(4)-B(4)-B(3)	120.5(2)
C(21)-C(26)-H(26A)	119.2	C(1)-B(4)-B(3)	59.07(17)
Cs(1)-C(26)-H(26A)	110.0	B(9)-B(4)-B(3)	108.1(2)
F(2)-B(2)-C(1)	119.6(2)	F(4)-B(4)-B(8)	126.2(2)
F(2)-B(2)-B(11)	124.3(2)	C(1)-B(4)-B(8)	105.6(2)
C(1)-B(2)-B(11)	106.6(2)	B(9)-B(4)-B(8)	60.03(16)
F(2)-B(2)-B(3)	120.0(2)	B(3)-B(4)-B(8)	60.32(17)
C(1)-B(2)-B(3)	59.35(17)	F(4)-B(4)-B(5)	119.7(2)
B(11)-B(2)-B(3)	109.2(2)	C(1)-B(4)-B(5)	58.57(16)
F(2)-B(2)-B(7)	125.2(3)	B(9)-B(4)-B(5)	59.61(16)
C(1)-B(2)-B(7)	106.1(2)	B(3)-B(4)-B(5)	107.7(2)
B(11)-B(2)-B(7)	60.69(17)	B(8)-B(4)-B(5)	107.7(2)
B(3)-B(2)-B(7)	60.10(18)	F(5)-B(5)-C(1)	119.8(2)
F(2)-B(2)-B(6)	119.3(2)	F(5)-B(5)-B(9)	124.6(2)
C(1)-B(2)-B(6)	59.84(17)	C(1)-B(5)-B(9)	105.4(2)
B(11)-B(2)-B(6)	60.03(18)	F(5)-B(5)-B(10)	125.7(2)
B(3)-B(2)-B(6)	109.2(2)	C(1)-B(5)-B(10)	106.0(2)
B(7)-B(2)-B(6)	108.7(2)	B(9)-B(5)-B(10)	60.78(16)
F(3)-B(3)-C(1)	118.9(2)	F(5)-B(5)-B(6)	120.9(2)
F(3)-B(3)-B(2)	120.0(2)	C(1)-B(5)-B(6)	59.80(16)
C(1)-B(3)-B(2)	58.55(17)	B(9)-B(5)-B(6)	108.4(2)
F(3)-B(3)-B(4)	119.7(2)	B(10)-B(5)-B(6)	59.73(16)
C(1)-B(3)-B(4)	59.01(16)	F(5)-B(5)-B(4)	118.8(2)
B(2)-B(3)-B(4)	107.7(2)	C(1)-B(5)-B(4)	58.95(16)
F(3)-B(3)-B(7)	126.1(2)	B(9)-B(5)-B(4)	59.76(16)
C(1)-B(3)-B(7)	105.5(2)	B(10)-B(5)-B(4)	108.8(2)
B(2)-B(3)-B(7)	60.14(17)	B(6)-B(5)-B(4)	108.8(2)
B(4)-B(3)-B(7)	108.4(2)	F(6)-B(6)-C(1)	119.1(2)
F(3)-B(3)-B(8)	126.5(2)	F(6)-B(6)-B(10)	126.7(2)
C(1)-B(3)-B(8)	105.3(2)	C(1)-B(6)-B(10)	105.1(2)
B(2)-B(3)-B(8)	107.8(2)	F(6)-B(6)-B(11)	125.8(2)
B(4)-B(3)-B(8)	59.97(17)	C(1)-B(6)-B(11)	104.8(2)
B(7)-B(3)-B(8)	60.20(17)	B(10)-B(6)-B(11)	61.19(17)
F(4)-B(4)-C(1)	119.6(2)	F(6)-B(6)-B(5)	120.7(2)

C(1)-B(6)-B(5)	58.28(16)	B(3)-B(8)-B(12)	108.1(2)
B(10)-B(6)-B(5)	60.00(16)	B(7)-B(8)-B(12)	60.28(17)
B(11)-B(6)-B(5)	108.4(2)	F(9)-B(9)-B(5)	118.4(2)
F(6)-B(6)-B(2)	119.7(2)	F(9)-B(9)-B(4)	119.4(2)
C(1)-B(6)-B(2)	57.99(17)	B(5)-B(9)-B(4)	60.64(16)
B(10)-B(6)-B(2)	108.0(2)	F(9)-B(9)-B(8)	123.3(2)
B(11)-B(6)-B(2)	59.62(17)	B(5)-B(9)-B(8)	108.7(2)
B(5)-B(6)-B(2)	106.5(2)	B(4)-B(9)-B(8)	60.26(16)
F(7)-B(7)-B(3)	118.4(2)	F(9)-B(9)-B(10)	121.2(2)
F(7)-B(7)-B(2)	120.0(2)	B(5)-B(9)-B(10)	59.88(16)
B(3)-B(7)-B(2)	59.76(18)	B(4)-B(9)-B(10)	108.8(2)
F(7)-B(7)-B(8)	122.0(2)	B(8)-B(9)-B(10)	108.6(2)
B(3)-B(7)-B(8)	60.10(17)	F(9)-B(9)-B(12)	124.4(2)
B(2)-B(7)-B(8)	107.5(2)	B(5)-B(9)-B(12)	108.2(2)
F(7)-B(7)-B(11)	123.4(2)	B(4)-B(9)-B(12)	108.7(2)
B(3)-B(7)-B(11)	107.9(2)	B(8)-B(9)-B(12)	60.31(16)
B(2)-B(7)-B(11)	59.43(18)	B(10)-B(9)-B(12)	60.18(16)
B(8)-B(7)-B(11)	108.2(2)	F(9)-B(9)-Cs(1)#1	41.81(11)
F(7)-B(7)-B(12)	125.1(2)	B(5)-B(9)-Cs(1)#1	93.08(14)
B(3)-B(7)-B(12)	108.2(2)	B(4)-B(9)-Cs(1)#1	137.32(16)
B(2)-B(7)-B(12)	107.5(2)	B(8)-B(9)-Cs(1)#1	158.12(17)
B(8)-B(7)-B(12)	60.10(16)	B(10)-B(9)-Cs(1)#1	80.03(13)
B(11)-B(7)-B(12)	60.30(16)	B(12)-B(9)-Cs(1)#1	111.45(15)
F(8)-B(8)-B(9)	122.1(2)	F(10)-B(10)-B(6)	122.1(2)
F(8)-B(8)-B(4)	120.3(2)	F(10)-B(10)-B(5)	119.5(2)
B(9)-B(8)-B(4)	59.71(16)	B(6)-B(10)-B(5)	60.26(17)
F(8)-B(8)-B(3)	120.8(2)	F(10)-B(10)-B(9)	120.0(2)
B(9)-B(8)-B(3)	107.4(2)	B(6)-B(10)-B(9)	107.7(2)
B(4)-B(8)-B(3)	59.71(17)	B(5)-B(10)-B(9)	59.34(16)
F(8)-B(8)-B(7)	122.4(2)	F(10)-B(10)-B(12)	122.7(2)
B(9)-B(8)-B(7)	108.2(2)	B(6)-B(10)-B(12)	108.2(2)
B(4)-B(8)-B(7)	107.8(2)	B(5)-B(10)-B(12)	107.8(2)
B(3)-B(8)-B(7)	59.70(17)	B(9)-B(10)-B(12)	60.14(16)
F(8)-B(8)-B(12)	122.9(2)	F(10)-B(10)-B(11)	125.0(2)
B(9)-B(8)-B(12)	60.56(16)	B(6)-B(10)-B(11)	59.60(17)
B(4)-B(8)-B(12)	108.5(2)	B(5)-B(10)-B(11)	107.4(2)

B(9)-B(10)-B(11)	107.4(2)	B(11)-F(11)-Cs(1)#2	121.22(15)
B(12)-B(10)-B(11)	60.02(16)	F(8)-Cs(1)-F(9)#3	152.55(4)
F(11)-B(11)-B(2)	118.1(2)	F(8)-Cs(1)-F(11)#4	76.49(5)
F(11)-B(11)-B(6)	119.3(2)	F(9)#3-Cs(1)-F(11)#4	118.19(4)
B(2)-B(11)-B(6)	60.35(18)	F(8)-Cs(1)-F(2)#4	129.67(5)
F(11)-B(11)-B(7)	121.5(2)	F(9)#3-Cs(1)-F(2)#4	76.17(4)
B(2)-B(11)-B(7)	59.88(18)	F(11)#4-Cs(1)-F(2)#4	60.54(4)
B(6)-B(11)-B(7)	108.3(2)	F(8)-Cs(1)-F(10)#3	98.14(4)
F(11)-B(11)-B(12)	125.8(2)	F(9)#3-Cs(1)-F(10)#3	61.40(4)
B(2)-B(11)-B(12)	107.6(2)	F(11)#4-Cs(1)-F(10)#3	164.84(4)
B(6)-B(11)-B(12)	107.7(2)	F(2)#4-Cs(1)-F(10)#3	129.77(4)
B(7)-B(11)-B(12)	60.00(17)	F(8)-Cs(1)-C(25)	90.45(5)
F(11)-B(11)-B(10)	124.9(2)	F(9)#3-Cs(1)-C(25)	96.55(5)
B(2)-B(11)-B(10)	107.0(2)	F(11)#4-Cs(1)-C(25)	127.42(6)
B(6)-B(11)-B(10)	59.21(17)	F(2)#4-Cs(1)-C(25)	95.45(5)
B(7)-B(11)-B(10)	107.6(2)	F(10)#3-Cs(1)-C(25)	66.09(5)
B(12)-B(11)-B(10)	59.83(16)	F(8)-Cs(1)-C(34)#3	80.61(6)
B(8)-B(12)-B(7)	59.62(17)	F(9)#3-Cs(1)-C(34)#3	87.10(6)
B(8)-B(12)-B(9)	59.14(16)	F(11)#4-Cs(1)-C(34)#3	60.46(6)
B(7)-B(12)-B(9)	106.5(2)	F(2)#4-Cs(1)-C(34)#3	98.11(6)
B(8)-B(12)-B(10)	107.3(2)	F(10)#3-Cs(1)-C(34)#3	104.90(5)
B(7)-B(12)-B(10)	107.6(2)	C(25)-Cs(1)-C(34)#3	166.44(7)
B(9)-B(12)-B(10)	59.68(16)	F(8)-Cs(1)-C(24)	101.99(5)
B(8)-B(12)-B(11)	107.3(2)	F(9)#3-Cs(1)-C(24)	93.95(5)
B(7)-B(12)-B(11)	59.70(17)	F(11)#4-Cs(1)-C(24)	111.56(6)
B(9)-B(12)-B(11)	107.2(2)	F(2)#4-Cs(1)-C(24)	73.58(5)
B(10)-B(12)-B(11)	60.15(16)	F(10)#3-Cs(1)-C(24)	83.32(5)
B(8)-B(12)-Si(1)	123.27(18)	C(25)-Cs(1)-C(24)	22.07(6)
B(7)-B(12)-Si(1)	124.98(18)	C(34)#3-Cs(1)-C(24)	171.05(7)
B(9)-B(12)-Si(1)	120.59(18)	F(8)-Cs(1)-C(33)#3	68.08(6)
B(10)-B(12)-Si(1)	119.50(18)	F(9)#3-Cs(1)-C(33)#3	91.93(6)
B(11)-B(12)-Si(1)	122.54(18)	F(11)#4-Cs(1)-C(33)#3	76.18(6)
B(2)-F(2)-Cs(1)#2	115.79(16)	F(2)#4-Cs(1)-C(33)#3	119.93(6)
B(8)-F(8)-Cs(1)	148.34(17)	F(10)#3-Cs(1)-C(33)#3	88.66(5)
B(9)-F(9)-Cs(1)#1	120.43(14)	C(25)-Cs(1)-C(33)#3	144.62(7)
B(10)-F(10)-Cs(1)#1	114.87(14)	C(34)#3-Cs(1)-C(33)#3	21.84(7)

C(24)-Cs(1)-C(33)#3	166.28(7)	C(34)#3-Cs(1)-C(32)#3	37.95(6)
F(8)-Cs(1)-C(35)#3	102.31(6)	C(24)-Cs(1)-C(32)#3	150.81(7)
F(9)#3-Cs(1)-C(35)#3	66.65(6)	C(33)#3-Cs(1)-C(32)#3	21.54(6)
F(11)#4-Cs(1)-C(35)#3	68.14(5)	C(35)#3-Cs(1)-C(32)#3	43.65(7)
F(2)#4-Cs(1)-C(35)#3	85.73(6)	F(8)-Cs(1)-C(36)#3	111.51(5)
F(10)#3-Cs(1)-C(35)#3	99.79(5)	F(9)#3-Cs(1)-C(36)#3	50.03(5)
C(25)-Cs(1)-C(35)#3	162.44(7)	F(11)#4-Cs(1)-C(36)#3	89.37(5)
C(34)#3-Cs(1)-C(35)#3	21.79(7)	F(2)#4-Cs(1)-C(36)#3	93.90(5)
C(24)-Cs(1)-C(35)#3	154.78(7)	F(10)#3-Cs(1)-C(36)#3	79.34(5)
C(33)#3-Cs(1)-C(35)#3	37.95(7)	C(25)-Cs(1)-C(36)#3	141.49(6)
F(8)-Cs(1)-C(32)#3	78.17(5)	C(34)#3-Cs(1)-C(36)#3	37.80(7)
F(9)#3-Cs(1)-C(32)#3	77.07(5)	C(24)-Cs(1)-C(36)#3	143.98(6)
F(11)#4-Cs(1)-C(32)#3	96.98(5)	C(33)#3-Cs(1)-C(36)#3	43.57(7)
F(2)#4-Cs(1)-C(32)#3	128.94(6)	C(35)#3-Cs(1)-C(36)#3	21.42(6)
F(10)#3-Cs(1)-C(32)#3	67.93(5)	C(32)#3-Cs(1)-C(36)#3	37.02(6)
C(25)-Cs(1)-C(32)#3	130.26(7)		

Symmetry transformations used to generate equivalent atoms:

#1: $x + 1/2, -y + 1/2, z + 1/2$; #2: $x - 1/2, -y + 1/2, z + 1/2$;

#3: $x - 1/2, -y + 1/2, z - 1/2$; #4: $x + 1/2, -y + 1/2, z - 1/2$

Table A4-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Cs(1-Me-12-SiPh₃-CB₁₁F₁₀). The anisotropic displacement factor exponent takes the form:
 $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(36)	16(1)	16(1)	25(1)	4(1)	3(1)	1(1)
C(35)	15(1)	18(1)	49(2)	7(1)	10(1)	3(1)
C(34)	10(1)	19(2)	63(2)	4(2)	-2(1)	-3(1)
C(33)	22(2)	18(2)	45(2)	-7(1)	-11(1)	-2(1)
C(32)	18(1)	18(1)	30(2)	-3(1)	-3(1)	0(1)
C(31)	12(1)	12(1)	22(1)	3(1)	2(1)	1(1)
Si(1)	11(1)	11(1)	14(1)	0(1)	2(1)	1(1)
C(1)	19(1)	13(1)	19(1)	-2(1)	4(1)	0(1)
C(2)	21(1)	9(1)	24(1)	-4(1)	5(1)	-1(1)
C(11)	11(1)	14(1)	18(1)	-3(1)	2(1)	-2(1)
C(12)	22(1)	13(1)	17(1)	-1(1)	2(1)	3(1)
C(13)	30(2)	23(2)	15(1)	0(1)	6(1)	-1(1)
C(14)	26(2)	20(2)	24(1)	-7(1)	11(1)	0(1)
C(15)	24(2)	13(1)	26(1)	-4(1)	6(1)	1(1)
C(16)	17(1)	14(1)	20(1)	0(1)	4(1)	-2(1)
C(21)	14(1)	11(1)	14(1)	-2(1)	1(1)	2(1)
C(22)	18(1)	18(1)	23(1)	2(1)	2(1)	0(1)
C(23)	24(2)	20(2)	26(2)	8(1)	5(1)	-2(1)
C(24)	30(2)	16(1)	21(1)	4(1)	-1(1)	2(1)
C(25)	19(1)	21(1)	21(1)	-1(1)	-4(1)	5(1)
C(26)	17(1)	18(1)	17(1)	3(1)	5(1)	1(1)
B(2)	13(1)	15(2)	30(2)	-4(1)	3(1)	-1(1)
B(3)	14(1)	14(2)	23(2)	-3(1)	-4(1)	0(1)
B(4)	18(2)	10(1)	15(1)	-1(1)	2(1)	1(1)
B(5)	16(1)	11(1)	15(1)	0(1)	1(1)	1(1)
B(6)	19(2)	15(2)	18(1)	-1(1)	6(1)	-2(1)
B(7)	16(1)	13(1)	26(2)	-2(1)	-3(1)	2(1)
B(8)	20(2)	14(1)	14(1)	-1(1)	-2(1)	2(1)
B(9)	13(1)	14(1)	13(1)	-1(1)	2(1)	2(1)
B(10)	14(1)	12(1)	14(1)	-1(1)	2(1)	-2(1)

B(11)	14(1)	15(1)	22(1)	-5(1)	3(1)	-2(1)
B(12)	11(1)	12(1)	16(1)	-1(1)	2(1)	2(1)
F(2)	14(1)	24(1)	44(1)	-11(1)	6(1)	-5(1)
F(3)	31(1)	25(1)	29(1)	-8(1)	-12(1)	-1(1)
F(4)	27(1)	17(1)	22(1)	-6(1)	7(1)	2(1)
F(5)	28(1)	16(1)	20(1)	3(1)	-4(1)	6(1)
F(6)	37(1)	20(1)	24(1)	2(1)	15(1)	-5(1)
F(7)	22(1)	19(1)	42(1)	-4(1)	-15(1)	7(1)
F(8)	42(1)	20(1)	12(1)	2(1)	1(1)	2(1)
F(9)	13(1)	16(1)	24(1)	-2(1)	5(1)	0(1)
F(10)	22(1)	18(1)	16(1)	-2(1)	-3(1)	0(1)
F(11)	17(1)	18(1)	33(1)	-9(1)	11(1)	-1(1)
Cs(1)	16(1)	21(1)	19(1)	4(1)	-1(1)	2(1)

Table A4-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for Cs(1-Me-12-SiPh₃-CB₁₁F₁₀).

	x	y	z	U _{eq}
H(36A)	11581	3093	4152	23
H(35A)	13991	3280	4398	32
H(34A)	14827	3802	5726	37
H(33A)	13238	4134	6809	35
H(32A)	10824	3955	6570	26
H(2A)	7240	-38	4550	27
H(2B)	6187	105	5353	27
H(2C)	7802	-80	5588	27
H(12A)	8296	3238	7019	21
H(13A)	7164	3847	8119	27
H(14A)	6202	4877	7755	28
H(15A)	6471	5314	6298	25
H(16A)	7590	4706	5194	20
H(22A)	10460	4154	3627	23
H(23A)	9735	4743	2331	28
H(24A)	7352	4788	1878	27
H(25A)	5687	4224	2714	24
H(26A)	6398	3631	4004	20

Table A5-1. Crystal data and structure refinement for (N(*n*-Bu)₄)₄B₂₄F₂₂.

Empirical formula	C ₃₂ H ₇₂ B ₁₂ F ₁₁ N ₂	
Formula weight	823.64	
Temperature	373(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pbcn</i>	
Unit cell dimensions	<i>a</i> = 14.6217(12) Å	α = 90°
	<i>b</i> = 34.858(3) Å	β = 90°
	<i>c</i> = 17.5935(14) Å	γ = 90°
Volume	8967.0(13) Å ³	
<i>Z</i>	8	
Density (calculated)	1.220 Mg/m ³	
Absorption coefficient	0.098 mm ⁻¹	
<i>F</i> (000)	3496	
Crystal size	0.43 × 0.33 × 0.11 mm ³	
Theta range for data collection	1.17 to 28.41°.	
Index ranges	-19 ≤ <i>h</i> ≤ 19, -46 ≤ <i>k</i> ≤ 46, -23 ≤ <i>l</i> ≤ 23	
Reflections collected	83067	
Independent reflections	11225 [<i>R</i> _{int} = 0.0853]	
Completeness to theta = 28.41°	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9893 and 0.9591	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	11225/0/515	
Goodness-of-fit on <i>F</i> ²	1.029	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0514, <i>wR</i> 2 = 0.1224	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0870, <i>wR</i> 2 = 0.1418	
Extinction coefficient	0.0046(3)	
Largest diff. peak and hole	0.762 and -0.349 e Å ⁻³	

Table A5-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{N}(n\text{-Bu})_4)_4\text{B}_{24}\text{F}_{22}$. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
B(1)	9573(1)	1316(1)	2162(1)	14(1)
B(2)	9628(1)	1042(1)	1294(1)	16(1)
B(3)	8791(1)	927(1)	1991(1)	16(1)
B(4)	8372(1)	1363(1)	2386(1)	16(1)
B(5)	8951(1)	1749(1)	1931(1)	16(1)
B(6)	9730(1)	1548(1)	1260(1)	15(1)
B(7)	9076(1)	1302(1)	543(1)	18(1)
B(8)	8485(1)	919(1)	1003(1)	19(1)
B(9)	7708(1)	1119(1)	1675(1)	19(1)
B(10)	7815(1)	1629(1)	1635(1)	18(1)
B(11)	8666(1)	1741(1)	941(1)	17(1)
B(12)	7888(1)	1352(1)	780(1)	18(1)
F(2)	10346(1)	800(1)	1112(1)	22(1)
F(3)	8800(1)	585(1)	2394(1)	20(1)
F(4)	8031(1)	1380(1)	3116(1)	21(1)
F(5)	9090(1)	2101(1)	2278(1)	22(1)
F(6)	10531(1)	1730(1)	1048(1)	20(1)
F(7)	9358(1)	1280(1)	-208(1)	25(1)
F(8)	8277(1)	576(1)	638(1)	27(1)
F(9)	6889(1)	938(1)	1854(1)	26(1)
F(10)	7087(1)	1874(1)	1781(1)	25(1)
F(11)	8656(1)	2078(1)	516(1)	23(1)
F(12)	7213(1)	1364(1)	223(1)	25(1)
N(1)	7494(1)	66(1)	3916(1)	19(1)
N(2)	8097(1)	2627(1)	4064(1)	18(1)
C(1)	7627(1)	498(1)	3997(1)	19(1)
C(2)	7915(1)	634(1)	4783(1)	21(1)
C(3)	7842(1)	1071(1)	4840(1)	24(1)
C(4)	8207(1)	1217(1)	5594(1)	29(1)
C(5)	7306(1)	-28(1)	3090(1)	21(1)

C(6)	6417(1)	124(1)	2760(1)	26(1)
C(7)	6355(1)	20(1)	1916(1)	32(1)
C(8)	6273(2)	-406(1)	1756(1)	42(1)
C(9)	6705(1)	-55(1)	4422(1)	24(1)
C(10)	6374(1)	-466(1)	4356(1)	24(1)
C(11)	5582(2)	-529(1)	4899(1)	39(1)
C(12)	5178(1)	-928(1)	4857(2)	39(1)
C(13)	8342(1)	-154(1)	4167(1)	21(1)
C(14)	9191(1)	-96(1)	3690(1)	28(1)
C(15)	9989(2)	-312(1)	3999(1)	41(1)
C(16)	10833(1)	-286(1)	3522(1)	35(1)
C(17)	7645(1)	2263(1)	3752(1)	20(1)
C(18)	6708(1)	2172(1)	4070(1)	32(1)
C(19)	6204(1)	1884(1)	3587(1)	39(1)
C(20)	5271(2)	1782(1)	3849(2)	46(1)
C(21)	7523(1)	2980(1)	3894(1)	20(1)
C(22)	7326(1)	3053(1)	3057(1)	26(1)
C(23)	6810(1)	3431(1)	2949(1)	28(1)
C(24)	7345(2)	3785(1)	3171(1)	41(1)
C(25)	9029(1)	2652(1)	3685(1)	20(1)
C(26)	9577(1)	3011(1)	3872(1)	23(1)
C(27)	10560(1)	2964(1)	3599(1)	29(1)
C(28)	11125(1)	3323(1)	3702(1)	35(1)
C(29)	8187(1)	2607(1)	4926(1)	20(1)
C(30)	8885(1)	2323(1)	5224(1)	21(1)
C(31)	8790(1)	2282(1)	6084(1)	22(1)
C(32)	9584(1)	2057(1)	6419(1)	29(1)

Table A5-3. Bond lengths [Å] and angles [°] for (N(*n*-Bu)₄)₄B₂₄F₂₂.

B(1)-B(1)#1	1.725(4)	B(9)-B(10)	1.785(3)
B(1)-B(6)	1.796(3)	B(9)-B(12)	1.791(3)
B(1)-B(3)	1.800(3)	B(10)-F(10)	1.388(2)
B(1)-B(2)	1.802(3)	B(10)-B(11)	1.787(3)
B(1)-B(5)	1.808(3)	B(10)-B(12)	1.790(3)
B(1)-B(4)	1.808(3)	B(11)-F(11)	1.393(2)
B(2)-F(2)	1.385(2)	B(11)-B(12)	1.792(3)
B(2)-B(6)	1.771(3)	B(12)-F(12)	1.392(2)
B(2)-B(3)	1.778(3)	N(1)-C(5)	1.515(2)
B(2)-B(7)	1.795(3)	N(1)-C(9)	1.517(2)
B(2)-B(8)	1.800(3)	N(1)-C(13)	1.522(2)
B(3)-F(3)	1.389(2)	N(1)-C(1)	1.528(2)
B(3)-B(4)	1.781(3)	N(2)-C(21)	1.519(2)
B(3)-B(8)	1.795(3)	N(2)-C(25)	1.519(2)
B(3)-B(9)	1.806(3)	N(2)-C(29)	1.524(2)
B(4)-F(4)	1.378(2)	N(2)-C(17)	1.531(2)
B(4)-B(5)	1.779(3)	C(1)-C(2)	1.521(2)
B(4)-B(9)	1.797(3)	C(2)-C(3)	1.529(3)
B(4)-B(10)	1.807(3)	C(3)-C(4)	1.517(3)
B(5)-F(5)	1.383(2)	C(5)-C(6)	1.518(3)
B(5)-B(6)	1.784(3)	C(6)-C(7)	1.531(3)
B(5)-B(10)	1.790(3)	C(7)-C(8)	1.518(3)
B(5)-B(11)	1.792(3)	C(9)-C(10)	1.516(3)
B(6)-F(6)	1.384(2)	C(10)-C(11)	1.518(3)
B(6)-B(11)	1.784(3)	C(11)-C(12)	1.511(3)
B(6)-B(7)	1.801(3)	C(13)-C(14)	1.512(3)
B(7)-F(7)	1.386(2)	C(14)-C(15)	1.490(3)
B(7)-B(11)	1.786(3)	C(15)-C(16)	1.496(3)
B(7)-B(8)	1.786(3)	C(17)-C(18)	1.513(3)
B(7)-B(12)	1.794(3)	C(18)-C(19)	1.507(3)
B(8)-F(8)	1.390(2)	C(19)-C(20)	1.483(3)
B(8)-B(9)	1.783(3)	C(21)-C(22)	1.522(2)
B(8)-B(12)	1.788(3)	C(22)-C(23)	1.531(3)
B(9)-F(9)	1.391(2)	C(23)-C(24)	1.512(3)

C(25)-C(26)	1.521(2)	C(29)-C(30)	1.517(2)
C(26)-C(27)	1.524(3)	C(30)-C(31)	1.525(2)
C(27)-C(28)	1.512(3)	C(31)-C(32)	1.521(3)
B(1)#1-B(1)-B(6)	121.18(15)	B(2)-B(3)-B(4)	108.26(13)
B(1)#1-B(1)-B(3)	125.12(10)	F(3)-B(3)-B(8)	118.86(14)
B(6)-B(1)-B(3)	105.82(12)	B(2)-B(3)-B(8)	60.53(11)
B(1)#1-B(1)-B(2)	123.52(14)	B(4)-B(3)-B(8)	107.86(13)
B(6)-B(1)-B(2)	58.99(10)	F(3)-B(3)-B(1)	123.82(14)
B(3)-B(1)-B(2)	59.15(10)	B(2)-B(3)-B(1)	60.49(11)
B(1)#1-B(1)-B(5)	121.27(9)	B(4)-B(3)-B(1)	60.66(10)
B(6)-B(1)-B(5)	59.34(10)	B(8)-B(3)-B(1)	109.44(13)
B(3)-B(1)-B(5)	105.76(13)	F(3)-B(3)-B(9)	118.92(14)
B(2)-B(1)-B(5)	105.95(13)	B(2)-B(3)-B(9)	107.95(13)
B(1)#1-B(1)-B(4)	123.53(17)	B(4)-B(3)-B(9)	60.13(11)
B(6)-B(1)-B(4)	106.01(13)	B(8)-B(3)-B(9)	59.36(11)
B(3)-B(1)-B(4)	59.17(10)	B(1)-B(3)-B(9)	109.22(13)
B(2)-B(1)-B(4)	106.04(13)	F(4)-B(4)-B(5)	123.95(14)
B(5)-B(1)-B(4)	58.94(10)	F(4)-B(4)-B(3)	121.66(14)
F(2)-B(2)-B(6)	122.40(15)	B(5)-B(4)-B(3)	107.80(13)
F(2)-B(2)-B(3)	122.95(15)	F(4)-B(4)-B(9)	118.27(14)
B(6)-B(2)-B(3)	107.83(13)	B(5)-B(4)-B(9)	107.58(13)
F(2)-B(2)-B(7)	118.56(14)	B(3)-B(4)-B(9)	60.62(11)
B(6)-B(2)-B(7)	60.66(11)	F(4)-B(4)-B(10)	119.77(14)
B(3)-B(2)-B(7)	108.17(13)	B(5)-B(4)-B(10)	59.91(11)
F(2)-B(2)-B(8)	119.43(14)	B(3)-B(4)-B(10)	107.85(13)
B(6)-B(2)-B(8)	107.86(13)	B(9)-B(4)-B(10)	59.37(11)
B(3)-B(2)-B(8)	60.21(11)	F(4)-B(4)-B(1)	123.94(14)
B(7)-B(2)-B(8)	59.56(11)	B(5)-B(4)-B(1)	60.52(10)
F(2)-B(2)-B(1)	123.58(14)	B(3)-B(4)-B(1)	60.17(10)
B(6)-B(2)-B(1)	60.32(10)	B(9)-B(4)-B(1)	109.23(13)
B(3)-B(2)-B(1)	60.36(10)	B(10)-B(4)-B(1)	108.94(13)
B(7)-B(2)-B(1)	109.66(13)	F(5)-B(5)-B(4)	122.78(15)
B(8)-B(2)-B(1)	109.09(13)	F(5)-B(5)-B(6)	123.03(15)
F(3)-B(3)-B(2)	122.67(15)	B(4)-B(5)-B(6)	107.77(13)
F(3)-B(3)-B(4)	122.52(14)	F(5)-B(5)-B(10)	118.20(14)

B(4)-B(5)-B(10)	60.81(11)	F(7)-B(7)-B(6)	122.44(15)
B(6)-B(5)-B(10)	107.90(13)	B(11)-B(7)-B(6)	59.67(11)
F(5)-B(5)-B(11)	118.47(14)	B(8)-B(7)-B(6)	107.22(13)
B(4)-B(5)-B(11)	108.35(13)	B(2)-B(7)-B(6)	59.03(10)
B(6)-B(5)-B(11)	59.86(11)	B(12)-B(7)-B(6)	107.72(13)
B(10)-B(5)-B(11)	59.85(11)	F(8)-B(8)-B(9)	120.26(15)
F(5)-B(5)-B(1)	124.48(14)	F(8)-B(8)-B(7)	122.70(15)
B(4)-B(5)-B(1)	60.54(10)	B(9)-B(8)-B(7)	108.37(14)
B(6)-B(5)-B(1)	59.98(10)	F(8)-B(8)-B(12)	121.22(15)
B(10)-B(5)-B(1)	109.67(13)	B(9)-B(8)-B(12)	60.19(11)
B(11)-B(5)-B(1)	108.76(13)	B(7)-B(8)-B(12)	60.27(11)
F(6)-B(6)-B(2)	122.43(14)	F(8)-B(8)-B(3)	121.07(15)
F(6)-B(6)-B(5)	122.66(15)	B(9)-B(8)-B(3)	60.64(11)
B(2)-B(6)-B(5)	108.34(13)	B(7)-B(8)-B(3)	107.82(13)
F(6)-B(6)-B(11)	118.75(14)	B(12)-B(8)-B(3)	108.63(14)
B(2)-B(6)-B(11)	108.21(13)	F(8)-B(8)-B(2)	122.74(15)
B(5)-B(6)-B(11)	60.29(11)	B(9)-B(8)-B(2)	107.96(13)
F(6)-B(6)-B(1)	123.54(14)	B(7)-B(8)-B(2)	60.06(11)
B(2)-B(6)-B(1)	60.69(10)	B(12)-B(8)-B(2)	108.23(13)
B(5)-B(6)-B(1)	60.68(10)	B(3)-B(8)-B(2)	59.26(10)
B(11)-B(6)-B(1)	109.67(13)	F(9)-B(9)-B(8)	121.37(15)
F(6)-B(6)-B(7)	118.63(14)	F(9)-B(9)-B(10)	122.49(15)
B(2)-B(6)-B(7)	60.32(11)	B(8)-B(9)-B(10)	107.96(13)
B(5)-B(6)-B(7)	108.18(13)	F(9)-B(9)-B(12)	122.14(15)
B(11)-B(6)-B(7)	59.75(11)	B(8)-B(9)-B(12)	60.05(11)
B(1)-B(6)-B(7)	109.68(13)	B(10)-B(9)-B(12)	60.08(11)
F(7)-B(7)-B(11)	121.45(15)	F(9)-B(9)-B(4)	121.51(15)
F(7)-B(7)-B(8)	122.26(15)	B(8)-B(9)-B(4)	107.68(13)
B(11)-B(7)-B(8)	107.55(14)	B(10)-B(9)-B(4)	60.57(11)
F(7)-B(7)-B(2)	122.66(15)	B(12)-B(9)-B(4)	108.52(13)
B(11)-B(7)-B(2)	107.11(13)	F(9)-B(9)-B(3)	121.11(15)
B(8)-B(7)-B(2)	60.38(11)	B(8)-B(9)-B(3)	60.01(11)
F(7)-B(7)-B(12)	121.03(15)	B(10)-B(9)-B(3)	107.72(13)
B(11)-B(7)-B(12)	60.08(11)	B(12)-B(9)-B(3)	108.01(13)
B(8)-B(7)-B(12)	59.94(11)	B(4)-B(9)-B(3)	59.26(10)
B(2)-B(7)-B(12)	108.22(13)	F(10)-B(10)-B(9)	122.53(15)

F(10)-B(10)-B(11)	121.71(15)	B(8)-B(12)-B(11)	107.16(13)
B(9)-B(10)-B(11)	107.80(14)	B(10)-B(12)-B(11)	59.86(11)
F(10)-B(10)-B(12)	122.18(15)	B(9)-B(12)-B(11)	107.33(13)
B(9)-B(10)-B(12)	60.13(11)	F(12)-B(12)-B(7)	121.69(15)
B(11)-B(10)-B(12)	60.13(11)	B(8)-B(12)-B(7)	59.79(11)
F(10)-B(10)-B(5)	120.87(15)	B(10)-B(12)-B(7)	107.82(13)
B(9)-B(10)-B(5)	107.63(13)	B(9)-B(12)-B(7)	107.64(13)
B(11)-B(10)-B(5)	60.11(11)	B(11)-B(12)-B(7)	59.73(11)
B(12)-B(10)-B(5)	108.38(13)	C(5)-N(1)-C(9)	111.47(14)
F(10)-B(10)-B(4)	121.66(15)	C(5)-N(1)-C(13)	108.52(13)
B(9)-B(10)-B(4)	60.06(11)	C(9)-N(1)-C(13)	108.03(13)
B(11)-B(10)-B(4)	107.35(13)	C(5)-N(1)-C(1)	108.93(13)
B(12)-B(10)-B(4)	108.16(13)	C(9)-N(1)-C(1)	108.49(13)
B(5)-B(10)-B(4)	59.29(10)	C(13)-N(1)-C(1)	111.43(13)
F(11)-B(11)-B(6)	119.73(14)	C(21)-N(2)-C(25)	111.28(13)
F(11)-B(11)-B(7)	121.07(15)	C(21)-N(2)-C(29)	106.26(12)
B(6)-B(11)-B(7)	60.58(11)	C(25)-N(2)-C(29)	111.18(13)
F(11)-B(11)-B(10)	122.94(15)	C(21)-N(2)-C(17)	111.19(13)
B(6)-B(11)-B(10)	108.03(13)	C(25)-N(2)-C(17)	106.15(12)
B(7)-B(11)-B(10)	108.30(13)	C(29)-N(2)-C(17)	110.86(13)
F(11)-B(11)-B(5)	120.72(15)	C(2)-C(1)-N(1)	115.28(14)
B(6)-B(11)-B(5)	59.84(10)	C(1)-C(2)-C(3)	110.48(15)
B(7)-B(11)-B(5)	108.49(13)	C(4)-C(3)-C(2)	111.48(16)
B(10)-B(11)-B(5)	60.03(11)	N(1)-C(5)-C(6)	116.54(15)
F(11)-B(11)-B(12)	123.16(14)	C(5)-C(6)-C(7)	109.88(16)
B(6)-B(11)-B(12)	108.54(13)	C(8)-C(7)-C(6)	114.56(17)
B(7)-B(11)-B(12)	60.20(11)	C(10)-C(9)-N(1)	117.35(15)
B(10)-B(11)-B(12)	60.01(11)	C(9)-C(10)-C(11)	109.34(16)
B(5)-B(11)-B(12)	108.22(13)	C(12)-C(11)-C(10)	113.62(18)
F(12)-B(12)-B(8)	121.76(15)	C(14)-C(13)-N(1)	116.15(14)
F(12)-B(12)-B(10)	122.18(15)	C(15)-C(14)-C(13)	111.94(16)
B(8)-B(12)-B(10)	107.51(13)	C(14)-C(15)-C(16)	114.33(18)
F(12)-B(12)-B(9)	121.92(15)	C(18)-C(17)-N(2)	115.69(14)
B(8)-B(12)-B(9)	59.76(11)	C(19)-C(18)-C(17)	112.01(17)
B(10)-B(12)-B(9)	59.79(11)	C(20)-C(19)-C(18)	115.68(19)
F(12)-B(12)-B(11)	122.53(15)	N(2)-C(21)-C(22)	115.51(14)

C(21)-C(22)-C(23)	110.96(15)	C(28)-C(27)-C(26)	112.92(16)
C(24)-C(23)-C(22)	114.50(17)	C(30)-C(29)-N(2)	115.64(14)
N(2)-C(25)-C(26)	115.15(14)	C(29)-C(30)-C(31)	110.04(14)
C(25)-C(26)-C(27)	109.92(15)	C(32)-C(31)-C(30)	111.20(15)

Symmetry transformations used to generate equivalent atoms:

#1: $-x + 2, y, -z + 1/2$

Table A5-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{N}(n\text{-Bu})_4)_4\text{B}_{24}\text{F}_{22}$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	16(1)	13(1)	12(1)	0(1)	1(1)	0(1)
B(2)	18(1)	17(1)	13(1)	-2(1)	0(1)	1(1)
B(3)	19(1)	17(1)	13(1)	0(1)	-1(1)	-1(1)
B(4)	17(1)	16(1)	13(1)	0(1)	0(1)	1(1)
B(5)	19(1)	16(1)	15(1)	2(1)	-2(1)	1(1)
B(6)	17(1)	17(1)	12(1)	3(1)	0(1)	-1(1)
B(7)	20(1)	22(1)	13(1)	1(1)	-1(1)	-3(1)
B(8)	22(1)	19(1)	15(1)	-2(1)	-3(1)	-4(1)
B(9)	18(1)	21(1)	17(1)	2(1)	-1(1)	-4(1)
B(10)	17(1)	19(1)	18(1)	2(1)	-1(1)	2(1)
B(11)	18(1)	19(1)	15(1)	3(1)	-2(1)	-2(1)
B(12)	18(1)	22(1)	15(1)	3(1)	-3(1)	-3(1)
F(2)	23(1)	24(1)	20(1)	-4(1)	2(1)	6(1)
F(3)	26(1)	16(1)	19(1)	4(1)	0(1)	-2(1)
F(4)	21(1)	27(1)	14(1)	0(1)	4(1)	3(1)
F(5)	29(1)	15(1)	22(1)	-3(1)	-4(1)	1(1)
F(6)	18(1)	24(1)	19(1)	6(1)	0(1)	-5(1)
F(7)	28(1)	35(1)	12(1)	1(1)	1(1)	-1(1)
F(8)	34(1)	23(1)	23(1)	-7(1)	-5(1)	-5(1)
F(9)	19(1)	31(1)	27(1)	7(1)	-1(1)	-8(1)
F(10)	20(1)	29(1)	27(1)	4(1)	0(1)	8(1)
F(11)	25(1)	22(1)	23(1)	9(1)	-5(1)	0(1)
F(12)	22(1)	33(1)	19(1)	5(1)	-8(1)	-4(1)
N(1)	21(1)	20(1)	15(1)	1(1)	1(1)	-3(1)
N(2)	21(1)	18(1)	16(1)	-2(1)	2(1)	3(1)
C(1)	22(1)	17(1)	19(1)	1(1)	1(1)	-2(1)
C(2)	24(1)	21(1)	18(1)	-1(1)	2(1)	-2(1)
C(3)	25(1)	21(1)	26(1)	-1(1)	4(1)	-1(1)
C(4)	34(1)	23(1)	30(1)	-5(1)	2(1)	-2(1)
C(5)	23(1)	23(1)	17(1)	-1(1)	0(1)	-3(1)

C(6)	26(1)	30(1)	23(1)	2(1)	-3(1)	0(1)
C(7)	28(1)	45(1)	22(1)	4(1)	-5(1)	-5(1)
C(8)	41(1)	55(2)	30(1)	-11(1)	-4(1)	-7(1)
C(9)	27(1)	25(1)	20(1)	-1(1)	6(1)	-5(1)
C(10)	24(1)	22(1)	25(1)	2(1)	0(1)	-5(1)
C(11)	39(1)	36(1)	41(1)	-5(1)	14(1)	-16(1)
C(12)	26(1)	29(1)	63(2)	12(1)	1(1)	-7(1)
C(13)	28(1)	18(1)	17(1)	1(1)	-3(1)	1(1)
C(14)	25(1)	28(1)	32(1)	12(1)	-1(1)	0(1)
C(15)	37(1)	56(2)	32(1)	17(1)	5(1)	20(1)
C(16)	26(1)	40(1)	39(1)	13(1)	-1(1)	3(1)
C(17)	22(1)	18(1)	20(1)	-4(1)	1(1)	1(1)
C(18)	32(1)	24(1)	41(1)	-6(1)	13(1)	-4(1)
C(19)	25(1)	52(1)	39(1)	-16(1)	5(1)	-7(1)
C(20)	35(1)	32(1)	70(2)	-3(1)	14(1)	-5(1)
C(21)	23(1)	18(1)	19(1)	-2(1)	1(1)	4(1)
C(22)	35(1)	23(1)	19(1)	-1(1)	-4(1)	3(1)
C(23)	32(1)	24(1)	28(1)	4(1)	-5(1)	2(1)
C(24)	58(2)	24(1)	43(1)	4(1)	-13(1)	-3(1)
C(25)	20(1)	21(1)	17(1)	-3(1)	4(1)	2(1)
C(26)	25(1)	22(1)	22(1)	-5(1)	2(1)	1(1)
C(27)	22(1)	32(1)	34(1)	-13(1)	3(1)	-1(1)
C(28)	27(1)	38(1)	41(1)	-14(1)	5(1)	-4(1)
C(29)	24(1)	22(1)	15(1)	-2(1)	2(1)	4(1)
C(30)	22(1)	22(1)	18(1)	0(1)	2(1)	5(1)
C(31)	25(1)	22(1)	18(1)	-1(1)	1(1)	1(1)
C(32)	31(1)	32(1)	23(1)	5(1)	-4(1)	0(1)

Table A5-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{N}(n\text{-Bu})_4)_4\text{B}_{24}\text{F}_{22}$.

	x	y	z	U_{eq}
H(1A)	8086	580	3633	23
H(1B)	7058	625	3863	23
H(2A)	8541	556	4881	25
H(2B)	7526	517	5164	25
H(3A)	8186	1187	4428	29
H(3B)	7207	1147	4785	29
H(4A)	8147	1491	5613	44
H(4B)	8840	1148	5643	44
H(4C)	7864	1104	6002	44
H(5A)	7310	-304	3033	25
H(5B)	7807	73	2788	25
H(6A)	6391	400	2820	31
H(6B)	5903	13	3031	31
H(7A)	5828	150	1699	38
H(7B)	6895	117	1660	38
H(8A)	6240	-447	1217	63
H(8B)	5729	-504	1992	63
H(8C)	6798	-537	1957	63
H(9A)	6884	-11	4946	29
H(9B)	6191	113	4316	29
H(10A)	6869	-641	4477	29
H(10B)	6178	-517	3839	29
H(11A)	5792	-483	5414	46
H(11B)	5107	-344	4788	46
H(12A)	4681	-948	5211	59
H(12B)	5639	-1113	4982	59
H(12C)	4957	-975	4352	59
H(13A)	8482	-80	4686	25
H(13B)	8196	-425	4171	25
H(14A)	9070	-181	3175	34

H(14B)	9338	175	3672	34
H(15A)	9820	-579	4050	50
H(15B)	10126	-215	4503	50
H(16A)	11314	-432	3755	52
H(16B)	11019	-22	3480	52
H(16C)	10710	-386	3025	52
H(17A)	7593	2288	3205	24
H(17B)	8046	2047	3854	24
H(18A)	6774	2070	4581	39
H(18B)	6352	2406	4101	39
H(19A)	6160	1985	3074	46
H(19B)	6566	1651	3562	46
H(20A)	5006	1599	3505	68
H(20B)	4898	2009	3863	68
H(20C)	5305	1672	4349	68
H(21A)	7834	3202	4100	24
H(21B)	6944	2955	4159	24
H(22A)	6963	2844	2854	31
H(22B)	7897	3062	2778	31
H(23A)	6634	3454	2420	33
H(23B)	6253	3423	3249	33
H(24A)	6977	4009	3087	62
H(24B)	7890	3801	2869	62
H(24C)	7508	3770	3699	62
H(25A)	8944	2640	3139	23
H(25B)	9385	2429	3833	23
H(26A)	9571	3054	4417	28
H(26B)	9300	3231	3627	28
H(27A)	10844	2755	3876	35
H(27B)	10555	2895	3064	35
H(28A)	11736	3278	3522	53
H(28B)	11144	3390	4231	53
H(28C)	10856	3530	3419	53
H(29A)	8348	2860	5111	25
H(29B)	7594	2542	5137	25
H(30A)	9497	2410	5100	25

H(30B)	8792	2075	4984	25
H(31A)	8769	2535	6314	26
H(31B)	8220	2152	6201	26
H(32A)	9508	2036	6959	43
H(32B)	10147	2187	6309	43
H(32C)	9598	1805	6199	43
