# New Horizons in C-F Activation by Main Group Electrophiles

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## I. Introduction.

### I-A. Overview and significance.

Fluoroorganic materials benefit our society through a number of dedicated uses.[1] Fluoropolymers possess many unique and useful properties owing to their inertness, strength and "non-stick" properties.[2] About 30% of agrochemicals and 10% of pharmaceuticals contain carbon-fluorine bonds.[3] Perfluoroalkane liquids have been explored as artificial blood substitutes because of their inertness and high $O_2$ solubility. They have also attracted interest as an alternative, "fluorous" medium for catalytic processes owing to their coincident hydrophobicity and oleophobicity.[4] The main "green" chemistry[5] benefit of a reaction medium that is easily separable from the products is the reduction of solvent waste.

On the other hand, some of the fluoroorganics that brought technological advances into our daily lives were later understood to have deleterious effects on the environment. Perfluoroctanesulfonic and perfluorooctanoic acids and their derivatives, valuable surfactants and additives in fluoropolymer processing, have been recently shown to be toxic, widely spread in the biota, and highly persistent.[6] The most publicly known example of fluoroorganics' effect on the environment is undoubtedly the story of chlorofluorocarbons (CFCs or chlorofluoroalkanes). They revolutionized refrigeration and cooling, but were eventually found to be destructive towards the ozone layer.[7] The 1987 *Montreal Protocol on Substances that Deplete the Ozone Layer*[8] that plotted the course for the phase-out of CFCs stands out as one successful example of international environmental legislation. The use of CFCs has been substantially reduced and the ozone hole expansion curtailed.[9] Under the Montreal protocol, the chief replacements for CFCs have been hydrofluorocarbons (HFCs or partially fluorinated alkanes) that are ozone-safe. Hydrochlorofluorocarbons (HCFCs or partially chlorinated/fluorinated alkanes) served a transitional role and possess diminished ozone-destroying potential.

What is less well-known is that CFCs are very potent greenhouse gases. [10] In a rare example of a positive unintended consequence, the reduction of CFC emissions under the Montreal protocol not only protected the ozone layer, but also mitigated the contribution to global warming.[10] However, this mitigation is diminished by that the replacements for CFCs (HFCs and HCFCs) are themselves only somewhat less potent greenhouse gases. [10,11] Other polyfluoroalkanes besides those used in refrigeration are also on the greenhouse effect "radar". The bromine-containing relatives of CFCs (halons) that find uses in fire extinguishing and other areas possess very high GWPs.[12] Perfluorocarbons (perfluoroalkanes, or PFCs) are an unwanted by-product in aluminum manufacture[13] where electrolysis cells with carbon anodes and fluoride-containing melts generate $CF_4$ and larger PFCs. PFCs are also broadly used in semiconductor industry for etching silicon wafers.[14] The GWP values for PFCs are also very high and they possess atmospheric lifetimes so high (up to 50,000 yrs) as to be considered eternal on the timescale of human civilization.[15] The atmospheric lifetimes of HFCs, CFCs, and HCFCs are not as high, but still count in tens and hundreds of years. Together these fluorinated pollutants have been referred to as "super-greenhouse gases"[16] (we will refer to them as collectively as SGHGs in this proposal). Because of the long lifetimes and of the very high GWPs (thousands of times that of $CO_2$) the emissions of SGHGs contribute very significantly to radiative forcing. By various estimates,[17] SGHG emissions account for 10-20% of the net human activity effects and these numbers grow in models for the future.[10,11] There are virtually no natural sources of SGHGs and long lifetimes mean very slow removal from the atmosphere. The importance of SGHGs in effects on climate is recognized by both international organizations and the US government. SGHGs feature prominently in IPCC reports[18] and in the Kyoto Protocol documentation,[19] while the Environmental Protection Agency's website features a dedicated section on high GWP gases (=SGHGs).[20]

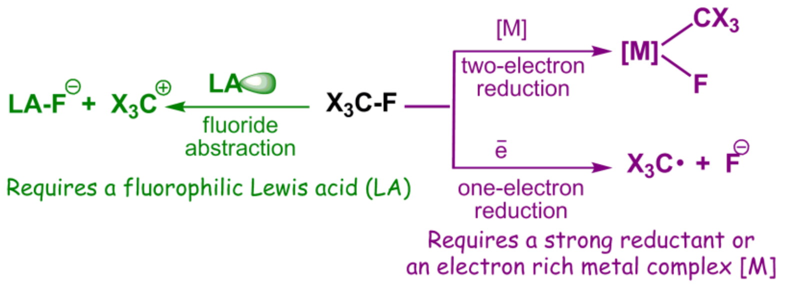
Reductions in the use of SGHGs and supplanting the need for them with new technologies are ultimately the way to curtail their release into the environment. However, this requires innovation and time for implementation. Thus, destruction of the stockpiles and of the generated waste streams is necessary to alleviate the effect.[21] For example, leakage of CFCs into the atmosphere from existing stockpiles alone is expected to contribute 6 billion ton $CO_2$-equiv before 2015.[21] Interestingly, nuclear energy production accounts for a notable fraction of CFC emissions arising from heat exchange equipment in enrichment schemes.[22] One way to think of the benefit of minimizing SGHG emissions is that removing their contribution buys extra years (in terms of the overall global warming results) for solving the ultimately more demanding $CO_2$ problem.[10,11]

Different methods for the destruction of various SGHGs do exist, however, the high stability especially of PFCs exacts high demands on such processes, leading to consideration of such exotic options as treatment with sodium vapor at 830 ˚C.[23] Plasma methods have been used,[24] as well as decomposition with various element oxides.[25] Temperatures of 400-600 ˚C are referred to as relatively low in PFC abatement.[26] Burdeniuc and Crabtree described a ca. 250 ˚C process for decomposition of CFCs with alkali metal oxalates, but of PFCs, only those that can aromatize[27] (6-membered rings) reacted.[28] Aromatization of cyclic perfluoroalkanes has also been reported with thiolates.[29]

All in all, there is room for improvement in processes for conversion of SGHGs to environmentally benign compounds and this provides one motivation for the study of C-F bond activation. On a more fundamental level, activation of C-F bonds is a noteworthy challenge because C-F is arguably the most inert, unreactive functionality in organic chemistry.[1] The problem of C-F bond activation has historically drawn practitioners of transition metal-based catalysis, in which the cleavage of the C-F bond is typically conceived to proceed reductively, through either oxidative addition of C-F to a metal center or via one-electron reduction.[30] The subject of carbon-fluorine bond activation was recently thoroughly reviewed from an organic vantage point by Amii and Uneyama.[3] The transition metal catalysis has worked better for polyfluoroarenes and fluoroalkenes, which possess $\pi$-systems that provide a relatively low energy avenue for attack on the molecule.[31,32] Aliphatic compounds with only C($sp^3$)-F bonds present a greater fundamental challenge, generally lacking either Lewis basicity or acidity (or electrophilicity or nucleophilicity, respectively, in kinetic terms), with correspondingly less success in evidence.[33,34] Increased fluorination of alkyl chains ostensibly exacerbates the problem. The C-F bonds are stronger in perfluoroalkyl chains and the carbon chain is also more sterically and electronically shielded by the fluorine atoms.[30] As with any strong bond "activation and functionalization", part of the challenge is how to integrate the event of breaking the reticent bond into a catalytic cycle, especially in a process that converts C-F bonds to other C-element bonds. Conceptually, the simplest transformation of a C-F bond is to a C-H bond, which can be termed hydrodefluorination (HDF).

## I-B. Our approach.

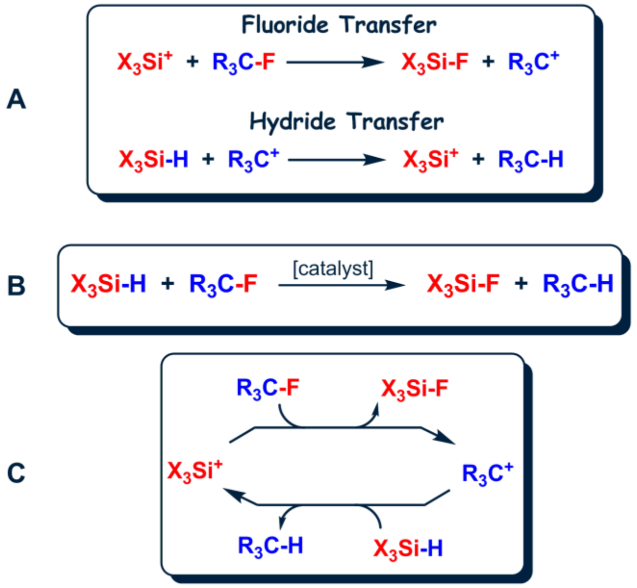
We became interested in developing new methods for HDF and other types of C-F bond conversion in polyfluoroalkanes under mild conditions. Much of the previous effort in C-F activation concentrated on reductive cleavage of the C-F bond (Figure 1), either by strong reducing agents (e.g., reactive metals) or by electron-rich transition metal centers.[30] In the transition metal community the mechanistic allure of C-F oxidative addition (not always *concerted* oxidative addition) has been particularly strong. We were attracted to a conceptually different approach to C-F activation, where the key C-F cleavage proceeds by a Lewis acid abstraction of fluoride rather than a redox event. Conventional acids, such as $SiO_2$, $TiO_2$ or concentrated $H_2SO_4$,[35] require high temperatures for cleavage of C-F bonds in perfluoroalkyl groups. Inorganic Lewis acids (e.g., $SbF_5$, ACF or $AlCl_xF_{3-x}$) have substantial history in industrial processes involving polyfluoroorganics and activation of C-Cl and C-F bonds,[36] but they appear incompatible with the concept of hydrodefluorination and often operate only at high temperature, as well.



Requires a fluorophilic Lewis acid (LA)

Requires a strong reductant or an electron rich metal complex [M]

**Figure 1**. Reductive and heterolytic C-F cleavage strategies



**Scheme 1**. Silylium-catalyzed HDF. **A**: Half-reactions; **B**: Net reaction; **C**: Catalytic cycle.

In 2005, we reported an execution of the non-redox approach under ambient conditions by using a silylium ($R_3Si^+$) Lewis acid.[37] Our silylium-catalyzed process was conceived as an implementation of the two half-reactions shown in Scheme 1-A. These half-reactions can be described in Lewis acid-base terms as transfer of fluoride from a carbenium ion (carbocation) $R_3C^+$ to a silylium cation $X_3Si^+$ complemented by hydride transfer from $X_3Si^+$ to $R_3C^+$. The sum of the two half reactions is the net reaction (Scheme 1-**B**), a C-F/Si-H metathesis. The proposed catalytic cycle (Scheme 1-**C**) is a sequence of the two half-reactions in Scheme 1-**A**. The guiding precedent for our silylium work is the gas-phase studies of Krause and Lampe who studied collisions of $H_3Si^+$ with $CF_4$ and of $CF_3^+$ with $SiH_4$. Their findings indicated that "*the major reaction of positive ions containing fluorine is* $H^-$ *abstraction and the major reaction of positive silicon ions with* $CF_4$ *is* $F^-$ *abstraction*".[38] In the condensed phases, silylium cations and silylium cation-like behavior have proven to be a substantial synthetic challenge, in some ways more so than carbocations.[39] Largely through the efforts of Reed and Lambert, utilization of weakly coordinating anions such as $[B(C_6F_5)_4]^-$ and halogenated carboranes led to the isolation of trialkylsilylium derivatives that approach the free silylium ion character[40,41] as well as a true silylium cation with bulky aryl substituents.[42] Even with the state-of-the-art weakly coordinating anions, silylium cations and many carbocations are likely to form adducts with the anion, the solvent or the reagents/products of our catalytic reactions. We will discuss "cations" with this understanding in mind.

Utilizing $Et_3SiH$, successful HDF was recorded for a series of benzotrifluorides and alkyl fluorides.[37] In general, increased fluorination in the substrate led to slower reactivity, and appeared consistent with the fluoride transfer reaction in Scheme 1-**A** being rate-limiting. Only $C(sp^3)$-F bonds were attacked. Isolation of $Et_3Si[B(C_6F_5)_4]$ proved unnecessary and the more robust $Ph_3C[B(C_6F_5)_4]$ could be conveniently used as a pre-catalyst. In the presence of excess $Et_3SiH$ in the reaction mixture, it was rapidly converted into $Et_3Si[B(C_6F_5)_4]$ in situ. Related work on conversion of C-O bonds to C-H bonds was reported by Gevorgyan and Yamamoto, who used $B(C_6F_5)_3$ to generate small concentrations of $Et_3Si[HB(C_6F_5)_3]$ in situ.[43]

## II. Results.

**General information**. This grant was a continuation of previous DOE award (DE-FG02-06ER15815, "*Catalysis of C-F activation by highly electrophilic Si compounds*") on the same topic. During that previous grant period (08/15/2006 – 12/31/2009), the PI was based at Brandeis University (415 South Street, Waltham, MA 02454). The PI (and most of the PI's research group) relocated to Texas A&M University in January 2009 while retaining an Adjunct Professor appointment at Brandeis for 2009. The grant (DE-FG02-10ER16201) that is the subject of this report was awarded to the PI at Texas A&M.

**Focus during the reporting period**. Our previous results demonstrated the feasibility of silylium and alumenium catalysis using $[B(C_6F_5)_4]^-$ and especially carborane derivatives $[HCB_{11}X_{11}]^-$ as supporting anions. The efforts during the reporting period focused on the improvement in the synthetic routes to the key weakly coordinating anions and on the synthesis of more soluble carborane-based anions for use in weakly coordinating solvents.

### Results from published work

Ramírez-Contreras, R.; Ozerov, O.V. "**Convenient C-Alkylation of the $[HCB_{11}Cl_{11}]^-$ Carborane Anion**", *Dalton Trans*. **2012**, *41*, 7842-7844.

Our pivotal task was the identification of weakly coordinating anions[44] that are similar to $[B(C_6F_5)_4]^-$ in terms of weak basicity but are superior in terms of stability. As we had proposed, halogenated derivatives of the $[HCB_{11}H_{11}]^-$ carborane anion (Figure 2) proved equal to the task. Our study benefited from the sophistication in the chemistry of carboranes brought to the fore by groups of Michl, Strauss, Reed, Xie and others (reviewed by Korbe et al.)[45]; studies by the Reed group are particularly relevant.[46,47] Carborane anions have been shown to be compatible with the highest levels of Brønsted and Lewis (e.g., silylium and carbocations) acidity in the condensed phase even under harsh conditions. For instance, $H[HCB_{11}Cl_{11}]$, the strongest known Brønsted acid, can be sublimed at 200 °C without decomposition.[48] In contrast, $[B(C_6F_5)_4]^-$ is not compatible with very high levels of Brønsted acidity.[49] It is probably also incompatible with reactive carbocations. Notably, the other common fluorinated tetraarylborate, $[B(C_6H_3(CF_3)_2)_4]^-$, possesses benzylic $CF_3$ groups and is not tolerant of even silylium cations.[50]

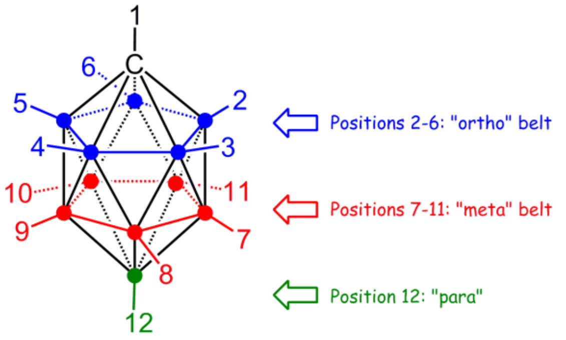
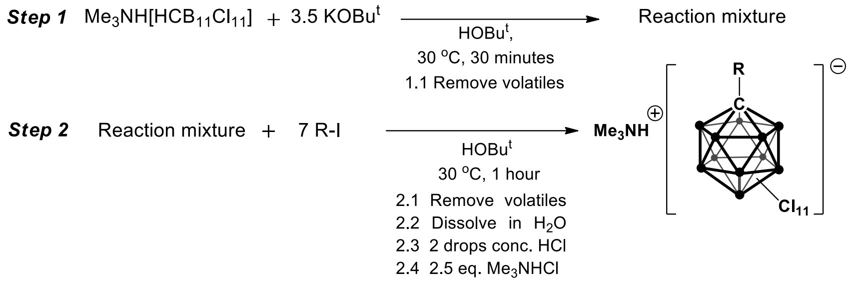


**Figure 2.** Representation of the monocarba-*closo*-dodecaborate(-) $[HCB_{11}H_{11}]^-$ anion, or carborane (dots at vertices 2-12 represent boron atoms; each vertex is capped with an H atom).

However, halogenated carborane anions, and $[HCB_{11}Cl_{11}]^-$ in particular, possessed the disadvantage of relatively low solubility of their salts in weakly coordinating, weakly polar solvents that were necessary to sustain reactivity of silylium cations. To this end, we endeavored to improve the solubility of carborane anions, while preserving their overall stability and weakly coordinating properties. One of the simplest ways we found this could be accomplished is by alkylation of the CH vertex of $[HCB_{11}Cl_{11}]^-$. We were inspired by a previous report on the C-methylation and C-ethylation of $[HCB_{11}F_{11}]^-$ performed with aqueous $NaOH/R_2SO_4$,[51, 52] which suggested acidity of the CH group on the order of water or alcohols. Aqueous conditions are poorly compatible with longer chain alkyl groups, but we manage to adapt the procedure to use tert-butoxide as the non-nucleophilic base in *tert*-butanol to effect alkylation of $[HCB_{11}Cl_{11}]^-$ to the various $[RCB_{11}Cl_{11}]^-$ anions in excellent yield (Scheme 2). We have since demonstrated that $[RCB_{11}Cl_{11}]^-$ are quite comparable to $[HCB_{11}Cl_{11}]^-$ in their electronic properties, but are indeed more solubilizing and also possess the benefit of being slightly less sterically approachable.



R = Methyl (Me, 83%); Ethyl (Et, 94%); Butyl (Bu, 84%); Hexyl (Hex, 93%)

**Scheme 2**. Synthesis of C-alkylated carborane anions $[RCB_{11}Cl_{11}]^-$.

Another of the desirable properties of carborane-based anions is their propensity (anecdotally much greater than for tetraarylborates) to form crystalline solids, including quality single crystals for structural X-ray analysis. We were gratified to find that the introduction of the flexible alkyl groups did not weaken this propensity and that $[RCB_{11}Cl_{11}]^-$ anions do form crystals quite readily. Figure 3 illustrates it with a silver salt of $[CH_3CH_2CH_2CH_2CB_{11}Cl_{11}]^-$.

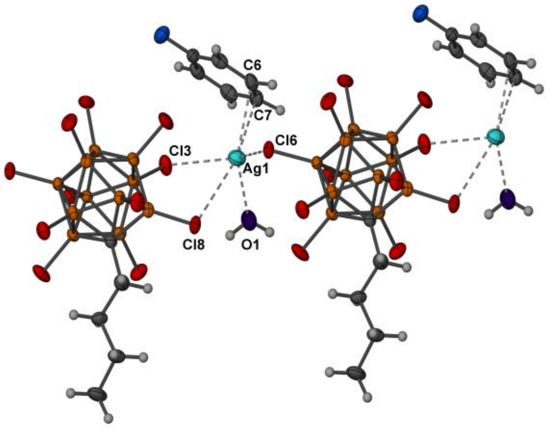


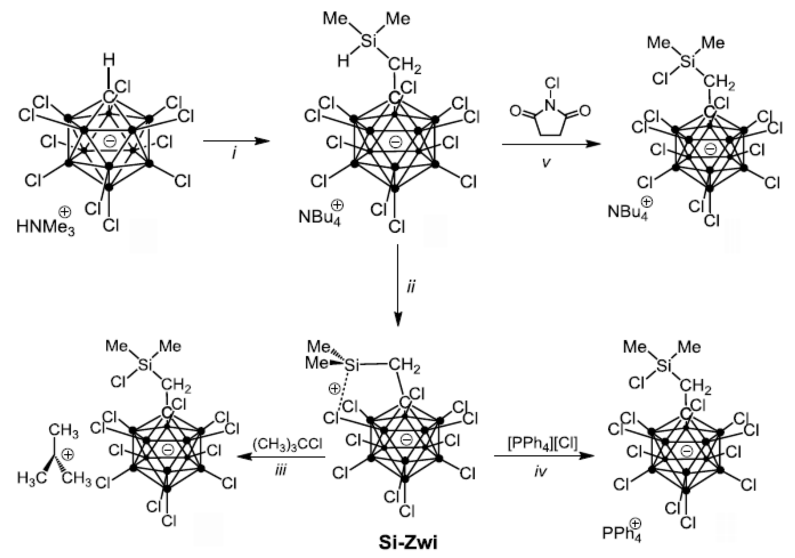
**Figure 3**. ORTEP plot of an X-ray structure of $Ag[^nBuCB_{11}Cl_{11}]\times C_6H_5F\times H_2O$

Ramírez-Contreras, R.; Bhuvanesh, N.; Zhou, J.; Ozerov, O. V. "**Synthesis of a Silylium Zwitterion**", *Angew. Chem., Int. Ed.* **2013**, *52*, 10313-10315..

One of the goals of our proposal was the synthesis of a neutral, zwitterionic silylium-type Lewis acid. We had surmised that a zwitterionic silylium could be prepared, it may be one of the most potent neutral Lewis acids. Furthermore, we had hoped that a neutral, zwitterionic silylium may possess improved solubility in weakly coordinating solvents.

Our approach here relied on the covalent attachment of the silicon functionality to the carborane core using the methodology we established for C-alkylation (vide supra). In the synthesis depicted in Scheme 3, $[HCB_{11}Cl_{11}]^-$ was alkylated with $I\text{-}CH_2SiMe_2H$ to give an intermediate anion $[Me_2HSiCH_2CB_{11}Cl_{11}]^-$, from which the hydride could be abstracted using the standard reaction with $Ph_3C^+$. This resulted in the formation of a silylium zwitterion (**Si-Zwi**, Scheme 3). Based on structural and spectroscopic data, the nature of the silylium center is very similar to silylium adducts with discrete carborane anions, meaning that Si-Zwi possesses a silylium center that is not quenched by the covalent connection to the formal location of the negative charge (in the carborane core). **Si-Zwi** proved to be a powerful Lewis acid indeed, for example, abstracting chloride from $Me_3CCl$ to give solutions of the $Me_3C^+$ cation.

On the other hand, our expectations of improved solubility proved to be completely faulty. **Si-Zwi** was essentially insoluble in halogenated arene solvents we typically use for carborane anion salts. Analysis of the single-crystal X-ray structure and DFT calculations allowed us to explain the poor solubility. The solid-state structure showed the Si-Zwi to be disordered (Figure 4A/B). We were able to shed light on the low solubility and on the observed disorder in the solid-state through density functional theory (DFT) calculations on an isolated gas-phase molecule of **Si-Zwi**. The calculated structure matched the XRD structure closely, lending extra credence to the model of the crystallographic disorder, and revealed a nearly $C_{2v}$-symmetric distribution of charge density in **Si-Zwi** (Figure 4C). We posited that it was the origin of the crystallographic disorder: **Si-Zwi** packs in the crystal as though it were a $C_{2v}$-symmetric molecule. The dipole moment of **Si-Zwi** is very high (15.2 D, by DFT) and the "head-to-tail" packing with alternating stacking of layers (Figure 4D) presumably results in a high lattice energy that disfavors dissolution.



**Scheme 3**. Synthesis and reactivity of a silylium zwitterion **Si-Zwi**.

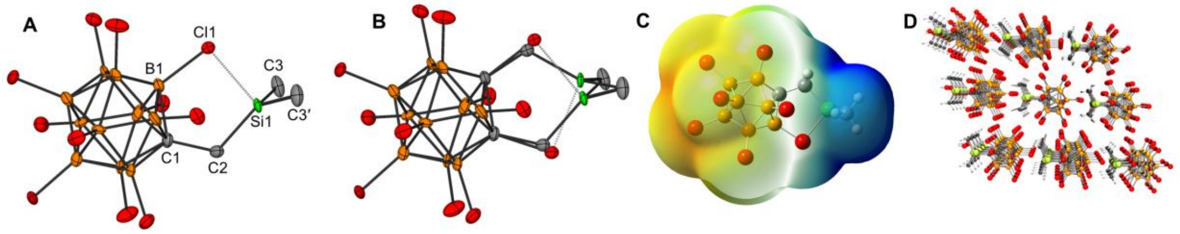
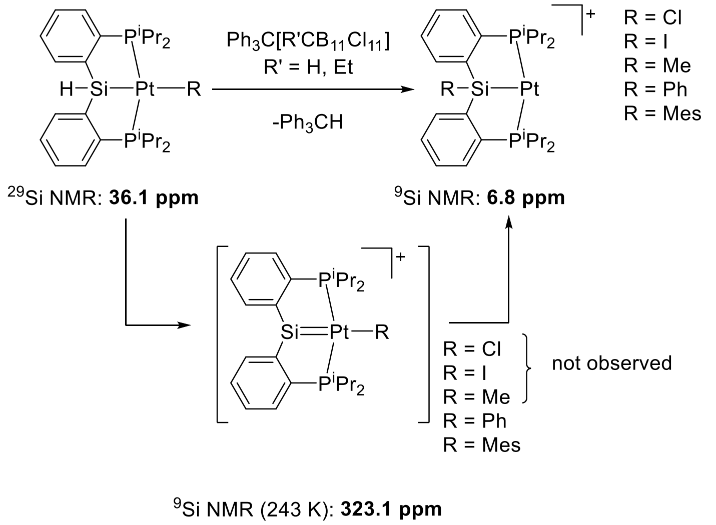


**Figure 4**. (A) ORTEP diagram of the structure of **Si-Zwi** in the solid state. (B) ORTEP diagram of the observed disorder in the crystal. (C) Charge density plot for **Si-Zwi**. (D) Three-dimensional packing diagram of **Si-Zwi** in the crystal.

DFT calculations on the gas phase **Si-Zwi** also accurately predicted its $^{29}$Si NMR chemical shift. **Si-Zwi** resonated at 137.4 ppm in the solid-state $^{29}$Si NMR spectrum; DFT calculation yielded 140.7 ppm. The degree of the downfield $^{29}$Si NMR chemical shift has been used to characterize the degree of silylium character. The **Si-Zwi** value is farther downfield than the values for adducts of $R_3Si^+$ with chlorocarboranes and is comparable to $[Me_3Si][EtCB_{11}F_{11}]$ (138 ppm), for which ionicity was demonstrated in the melt.[52]

DeMott, J. C.; Gu, W.; McCulloch, B. J.; Herbert, D. E.; Goshert, M. D.; Walensky, J. R.; Zhou, J.; Ozerov, O. V. "**Silyl-Silylene Interplay in Cationic PSiP Pincer Complexes of Platinum**", *Organometallics* **2015**, *34*, 3930-3933.

In another direction, we set out to explore the accessibility of silylium-like species with a transition-metal substituent. Our initial attempt aimed to accomplish that by abstracting a hydride from a Pt-bound silyl carrying a hydrogen substituent. The resulting species may be viewed as a silylene, however, overall analysis of experimental and computational data does not point to strong $\pi$-bonding.[53] The silylene species were not very stable and isomerized into the silyl-Pt cations by net transfer of the anionic substituent R on Pt to Si (Scheme 4). However, when R = mesityl (Scheme 4), the silylene had a half-life of several hours at RT and could be characterized in solution.



**Scheme 4**. Synthesis and isomerization of Pt silylene species.

The $^{29}$Si NMR chemical shift for the Pt silylene species (including a $[HCB_{11}Cl_{11}]^-$ anion in the gas phase), was calculated to be 303 ppm (cf. 323 ppm from the experiment) The calculated Pt-Si distances in the silylene complexes are only marginally (0.02-0.08 Å) shorter than in their silyl isomers. Calculations indicate that the LUMO of silylene (Figure 5) is primarily based on the Si p-orbital, with some delocalization into the aromatic rings and only a modest contribution from a d-orbital of Pt. The Wiberg bond indices for Si-Pt were calculated to be 0.68 in **6b** and 0.74 in **7a**. Thus, although the Si center in the silylene is planar (i.e., sp$^2$-hybridized), the modest extent of $\pi$-bonding between Pt and Si suggests that it may be better analyzed as a platinyl-substituted silylium cation.[53]

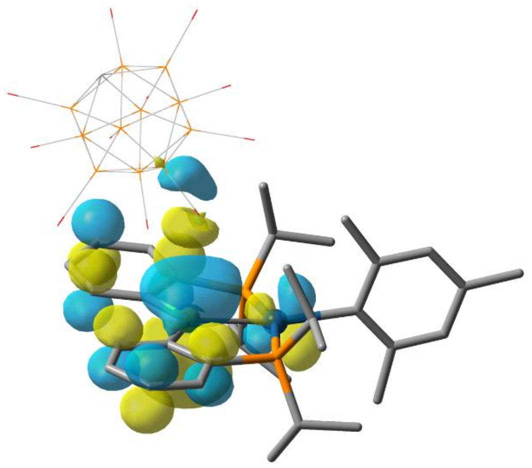
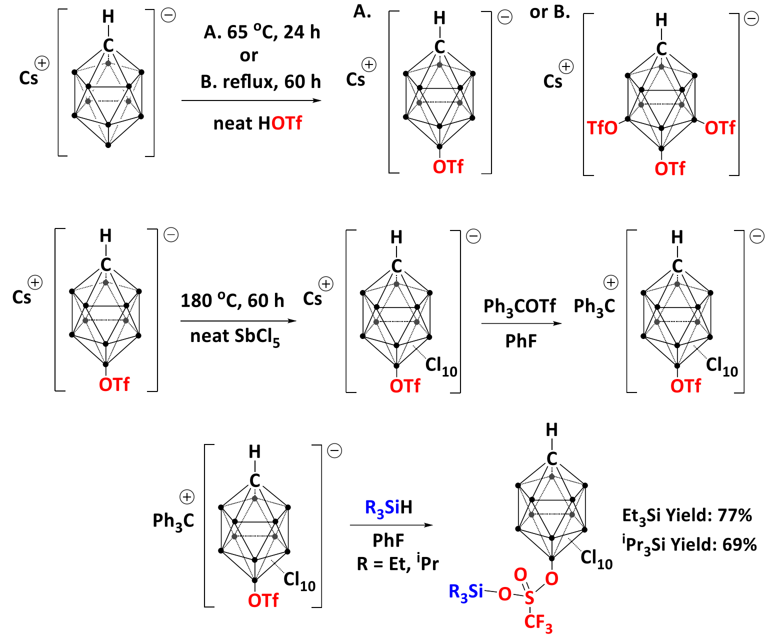


**Figure 5**. Depiction of the LUMO (isovalue = 0.03) of the Pt silylene with $[HCB_{11}Cl_{11}]^-$ counterion. Hydrogen atoms are omitted for clarity.

Press, L. P.; McCulloch, B. J.; Gu, W.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. "**Triflyloxy-Substituted Carboranes as Useful Weakly Coordinating Anions**", *Chem. Commun*. **2015**, *51*, 14034-14037.

Another approach to the synthesis of carborane anions with improved solubility was realized in this publication. We noted that formation of B-OTf groups from reactions involving triflic acid with $[HCB_{11}H_{11}]^-$ was obliquely mentioned in the literature, but rather as a nuisance.[54] For example, methylation of $[HCB_{11}H_{11}]^-$ requires a non-nucleophilic base to consume the HOTf by-product lest it react with the B-H bonds of the carborane. We became interested in exploiting OTf as a desirable substituent on the carborane cage and in investigating the behavior of the resultant anions as WCAs in silylium-catalyzed hydrodefluorination and towards highly unsaturated transition metal cations. We surmised that a B-OTf moiety would still be weakly coordinating and may bring advantages of $^{19}$F NMR spectroscopy and altered solubility.



**Scheme 5**. Synthesis of triflate-substituted carborane anions and their derivatives.

We were able to prepare triflate-substituted carboranes via direct reaction of $Cs[HCB_{11}H_{11}]$ with triflic acid (Scheme 5). Stirring $Cs[HCB_{11}H_{11}]$ in neat triflic acid at 65 °C for 24 h resulted in the formation of $Cs[HCB_{11}H_{10}(OTf)]$. We were not able to optimize the conditions for selective bis-triflyloxylation. However, tris-triflyloxylation could be performed effectively via extended reflux of $Cs[HCB_{11}H_{11}]$ in triflic acid.

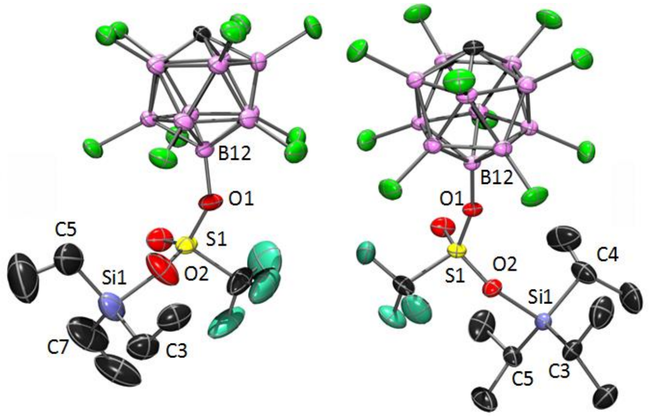


**Figure 6**. ORTEP plot of the X-ray structures of $Et_3Si[HCB_{11}Cl_{10}(OTf)]$ (left) and $^iPr_3Si[HCB_{11}Cl_{10}(OTf)]$ (right).

Fortuitously, the mono-OTf substituted carborane anion $[HCB_{11}H_{10}OTf]^-$ could undergo exhaustive chlorination while preserving the triflate substituent in the product $[HCB_{11}Cl_{10}OTf]^-$. We were then able to synthesize (Scheme 5) trialkylsilylium adducts of this anion. As might be expected, the $R_3Si^+$ moiety is attached to one of the triflate oxygens (Figure 6). Our investigations of the reactivity of these silylium species in hydrodefluorination showed that while they possessed reduced activity compared to

$R_3Si[HCB_{11}Cl_{11}]$, they nonetheless were just as long-lived. We interpret these results as showing that triflate-substituted carborane anions are somewhat more strongly coordinating, yet maintain the enviable robustness of simple halogenated carboranes.

## III. Other outcomes.

**Indirect impacts of the DOE funding on our group's research.** Our work on C-F activation and preparation of new weakly coordinating anions has attracted some industrial attention. During the reporting period, we had a research contract with Entegris Inc. ($50,000 during 09/01/12 – 02/28/13). Also during the reporting period, we have initiated interaction with Dow Chemical Co., which have now resulted in a substantial research award ($300,000 for period of 10/27/15 – 10/26/18). We view this as one of the most important outcomes of our DOE-sponsored work and look forward to finding industrial applications for our know-how.

**Recognitions received by the PI during the previous period**. In 2012, the PI received the Pure Chemistry Award from the American Chemical Society and the Norman Hackerman Award from the Welch Foundation.

**Complete list of publications during the grant period (09/15/2010-08/31/2015)**. The complete list of the Ozerov group publications, with links, is online at http://www.chem.tamu.edu/rgroup/ozerov/

a) Sole funding by DOE-BES and this grant – none. *NB: The PI is fortunate to have had a few relatively unrestricted grants from private agencies. They are used to augment support of a variety of projects in the PI's group, including this one. Therefore, all work is partly supported by multiple sources and is listed below, under (b).*

b) Joint funding by DOE and other federal or non-federal sources. Publications with DOE as the sole federal source a marked with a **. Other publications acknowledge DOE for reasons of either support of personnel during the writing of the manuscripts or because of use of crucial shared laboratory equipment (e.g., glovebox) purchased in part or in full with DOE funds.

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