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Hydrodefluorination and Other Hydrodehalogenation of Aliphatic Carbon−Halogen Bonds Using Silylium Catalysis

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Abstract: Trialkylsilylium cation equivalents partnered with halogenated carborane anions (such as $Et_3Si[HCB_{11}H_5Cl_6]$) function as efficient and long-lived catalysts for hydrodehalogenation of C−F, C−Cl, and C−Br bonds with trialkylsilanes as stoichiometric reagents. Only $C(sp^3)$−halogen bonds undergo this reaction. The range of C−F bond-containing substrates that participate in this reaction is quite broad and includes simple alkyl fluorides, benzotrifluorides, and compounds with perfluoroalkyl groups attached to an aliphatic chain. However, CF_4 has proven immune to this reaction. Hydrodechlorination was carried out with a series of alkyl chlorides and benzotrichlorides, and hydrodebromination was studied only with primary alkyl bromide substrates. Competitive experiments established a pronounced kinetic preference of the catalytic system for activation of a carbon−halogen bond of a lighter halide in primary alkyl halides. On the contrary, hydrodechlorination of $C_6F_5CCl_3$ proceeded much faster than hydrodefluorination of $C_6F_5CF_3$ in one-pot experiments. A solid-state structure of $Et_3Si[HCB_{11}H_5Cl_6]$ was determined by X-ray diffraction methods.

Introduction

Carbon−fluorine bonds are arguably the most unreactive organic functionality.[1] Activation of C−F bonds attracts interest because of the inherent fundamental challenge. On the other hand, it is also often viewed in the context of environmental concerns over a number of polyfluoroorganic compounds. Chlorofluorocarbons (CFC) or freons are destructive toward the ozone layer.[2] In addition, CFC, their ozone-friendly replacements hydrofluorocarbons (HFC), and perfluorocarbons (PFC) have tremendous global warming potentials and have been called "super-greenhouse gases".[3] Outside of the atmosphere, harmful derivatives of the perfluorooctanesulfonic acid have been found to accumulate in the biota.[4] Dehalogenation of environmental pollutants in general has been viewed through the prism of green chemistry.[5]

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 one-electron reduction.[6] The subject of carbon−fluorine bond activation was recently thoroughly reviewed from an organic vantage point by Amii and Uneyama.[7] The transition metal catalysis has worked better for polyfluoroarenes and fluoroalkenes, which possess π-systems that provide a relatively low energy avenue for attack on the molecule.[8,9] Aliphatic, $C(sp^3)$−F bonds present a greater fundamental challenge,

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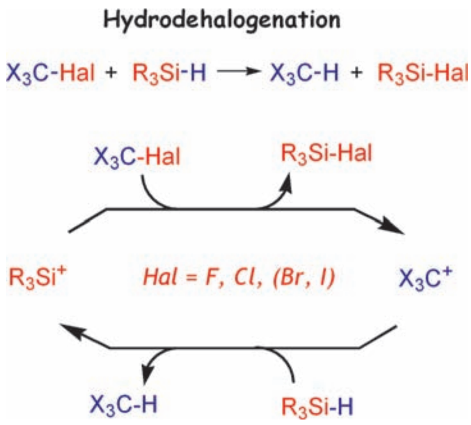
Scheme 1



generally lacking either Lewis basicity or acidity (or electrophilicity or nucleophilicity, respectively, in kinetic terms), with correspondingly less success in evidence.[10,11] Increased fluorination of alkyl chains ostensibly exacerbates the problem. While some catalytic examples of activation of primary alkyl fluorides with transition metals exist,[10] activation of perfluoroalkyl groups has required rather drastic reducing conditions.[6,11] 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 one 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).

Our group became interested in the alternative activation of C−F bonds by means of fluoride abstraction by fluorophilic Lewis acids. Inorganic Lewis acids (e.g., SbF_5, ACF, or $AlCl_xF_{3-x}$) have substantial history in industrial processes involving polyfluoroorganics,[12] but they appear incompatible with the concept of hydrodefluorination. In 2005, we demonstrated that utilization of silylium cation-like compounds as catalysts for HDF in solution is possible when they are partnered with a sufficiently weakly coordinating anion, such as $[B(C_6F_5)_4]^-$.[13] This chemistry was conceived as implementation of the catalytic cycle shown in Scheme 1 (Hal = F).[14] We view the work of Krause and Lampe, who observed Si−H/C−F redistribution by mass spectrometry in the gas phase upon collision of SiH_3^+ with CF_4, as the guiding precedent for our HDF concept.[15] The groups of Müller and of Rosenthal and Krossing have recently described C−F activation using similar approaches.[16] The HDF reactivity in our initial report was limited by the low stability of $[B(C_6F_5)_4]^-$, and we later communicated that halogenated carborane anions (Figure 1) are vastly superior to it in terms of stability and hence substrate scope in HDF reactions.[17] Our finding of the high catalytic competence of carborane-paired silylium cations was presaged by Reed et al., who reported stoichiometric abstraction of fluoride from aliphatic C−F bonds with $Et_3Si[HCB_{11}I_{11}]$ and isolation of stable fluorinated carbocations.[18] We have also explored related R_2Al^+-based catalysis that allows replacement of C−F by C−alkyl, a process we dubbed alkylative defluorination (AlkDF).[19] Our investigations have relied heavily on the prior work of others on the chemistry of carborane anions[20,21] and of silylium cation accessibility in condensed phases;[22,23] the work by the Reed group has been especially influential for us.

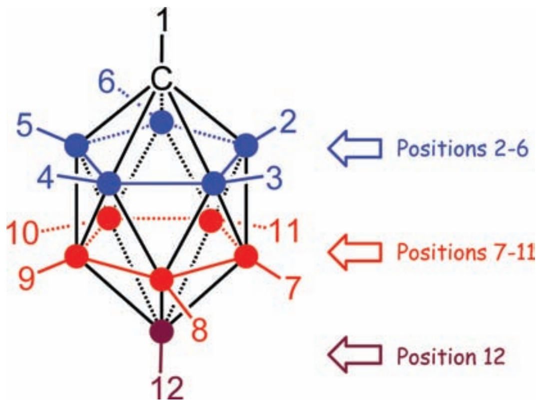


Figure 1. Schematic representation of the parent carborane anion $[HCB_{11}H_{11}]^-$. Dots represent boron atoms. In $[HCB_{11}H_{11}]^-$, each vertex of the icosahedron bears a hydrogen. In $[HCB_{11}H_5Hal_6]^-$, positions 7−12 are halogenated, whereas in $[HCB_{11}Hal_{11}]^-$, boron atoms in all positions 2−12 bear halogens.

In the present work, we report on the extended scope of substrates for Si-catalyzed HDF chemistry. In addition, we report that the silylium system also efficiently catalyzed hydrodechlorination (HDCl, Scheme 1, Hal = Cl), similarly to HDF. Activation of C−Cl bonds in competition or in concert with C−F bonds is of direct relevance to the remediation of CFCs.[24] In this article, we analyze the relative preferences of the silylium system for hydrodehalogenation[25] of C−F vs C−Cl as well as C−Br and C−I bonds for simple and easily comparable substrates.

Results and Discussion

Hydrodefluorination Reactions. The summary of the HDF reactions is presented in Table 1 and Scheme 2. The reactions

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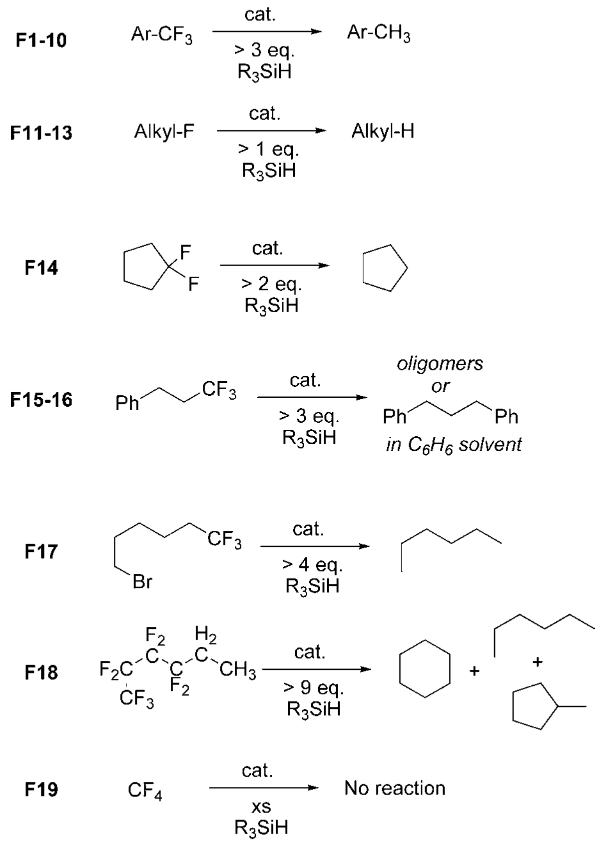
Table 1. Hydrodefluorination Reactions Catalyzed by Ph_3C[anion]

#	substrate	catalyst anion	R_3SiH	temp (°C)[a]	cosolvent	time (h)	cat. %	Si−F yield %[b]	C−F conv %[c]	TON[d]
F1	$C_6H_5CF_3$	$HCB_{11}Cl_{11}$	Et_3SiH	25	o-$C_6H_4Cl_2$	12	0.050	42	>97	2000
F2	p-$FC_6H_4CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	−35	o-$C_6H_4Cl_2$	72	0.072	88	>97	1380
F3	p-$FC_6H_4CF_3$	$HCB_{11}Cl_{11}$	Et_3SiH	−35	o-$C_6H_4Cl_2$	84	0.072	87	>97	1380
F4	p-$FC_6H_4CF_3$	$HCB_{11}H_5Br_6$	Et_3SiH	−35	o-$C_6H_4Cl_2$	96	0.072	72	>97	1380
F5	p-$FC_6H_4CF_3$	$HCB_{11}H_5I_6$	Et_3SiH	45	o-$C_6H_4Cl_2$	24	0.12	78	91	750
F6	p-$FC_6H_4CF_3$	$HCB_{11}H_5Cl_6$	Hex_3SiH	25	hexanes	72	0.10	85	>97	960
F7	p-$FC_6H_4CF_3$	$HCB_{11}Cl_{11}$	Et_3SiH	25	C_6H_6	12	0.21	61	>97	480
F8	$C_6F_5CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	o-$C_6H_4Cl_2$	24	0.080	84	>97	1250
F9	$C_6F_5CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	neat	6	0.080	82	>97	1250
F10	$C_6F_5CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	o-$C_6H_4Cl_2$	72	0.036	76	>97	2,700
F11	n-$C_{10}H_{21}F$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	o-$C_6H_4Cl_2$	24	0.17	97	>97	600
F12	n-$C_{10}H_{21}F$	$HCB_{11}H_5Cl_6$	Hex_3SiH	25	hexanes	50	0.50	79	>97	200
F13	c-$C_6H_{11}F$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	o-$C_6H_4Cl_2$	24	0.11	87	>97	900
F14	c-$(CH_2)_4CF_2$	$HCB_{11}H_5Cl_6$	Hex_3SiH	25	hexanes	24	0.13	87	>97	760
F15	$Ph(CH_2)_2CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	neat	24	0.13	79	>97	780
F16	$Ph(CH_2)_2CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	C_6H_6	48	0.13	75	>97	780
F17	$Br(CH_2)_5CF_3$	$HCB_{11}H_5Cl_6$	Et_3SiH	25	neat	24	0.13	66	>97	750
F18	n-$C_4F_9C_2H_5$	$HCB_{11}H_5Cl_6$	Hex_3SiH	50	neat	120	0.50	92	>97	200[d]
F19	CF_4	$HCB_{11}H_5Cl_6$	Et_3SiH	90	o-$C_6H_4Cl_2$	48	8	0	0	0

[a] Temperature at which the reaction was initiated; the reactions were then allowed to stand at RT. Some developed an initial exotherm. [b] Fraction of F from the original aliphatic C−F bonds, found in the Si−F bond of Et_3SiF and Et_2SiF_2. [c] 100% − fraction of C−F bonds remaining in the starting material; >97% means no starting material observed by ^{19}F NMR. [d] Number of C−F bonds consumed per molecule of catalyst.

Scheme 2. Summary of HDF Reactions Showing the Main HDF Products



R = ethyl or n-hexyl;
cat. = $Ph_3C[HCB_{11}H_5Hal_6]$ or $Ph_3C[HCB_{11}Cl_{11}]$

were carried out with the use of the fluoroorganic compound and Et_3SiH (or trihexylsilane in a few cases) as the stoichiometric reagents. Triphenylmethyl (trityl) salts of halogenated carborane anions were used to generate the trialkylsilylium derivatives in situ via abstraction of hydride from the excess trialkylsilane reagent. Thus, the trityl salts are truly *pre*catalysts, while the trialkylsilylium derivatives R_3Si[Anion] can be viewed as the active catalysts in the reaction mixture. However, for the sake of simplicity, we will refer to trityl salts Ph_3C[anion] as catalysts, as well. A few of the reactions were performed neat; in others, solvent was added. However, it should be noted that the volume of added solvent was typically less than half that of the combined volume of the reactant (hence the designation "cosolvent" in Table 1). The results in entries F8, F9, F11, F16, F17, and F19 were communicated by us in 2008.[17] The expected fluoro-containing product in the HDF reactions is Et_3SiF; however, we have also observed Et_2SiF_2 in several reactions here, as well as previously.[13,17] Et_2SiF_2 is presumably formed via redistribution of the substituents on Si in this highly Lewis acidic medium. Observation of Et_2SiF_2 has been accompanied by observation of Et_4Si (by GC-MS).

The HDF protocol worked very well for the defluorination of benzotrifluorides (reactions F1−11), with complete consumption of C−F bonds and turnover numbers up to 2700. The parent benzotrifluoride was completely consumed in 12 h (reaction F1). However, the yield of the expected HDF product (toluene) was merely 17%. The reaction was accompanied by precipitation of a solid material, which we surmise to be a mixture of oligo- or polymers resulting from repeated Friedel−Crafts attacks by the generated benzylic carbocations on the $PhCF_3$, $PhCH_3$, and the resulting oligomers themselves. In support of this hypothesis, the ^{13}C NMR spectrum of the reaction mixture contained overlapping resonances in the 40−42 ppm region, consistent with the Ar−CH_2−Ar linkages (40.3 ppm for $PhCH_2Ph$[26]). We have previously discussed the Friedel−Crafts reactivity in silylium- and aluminium-catalyzed C−F activation reactions.[17,19] Reed et al. also reported stoichiometric Friedel−Crafts attack by the fluorinated carbocations on aromatic rings.[18]

The Friedel−Crafts self-condensation should be less likely for p-$FC_6H_4CF_3$ as substrate because of the deactivating influence of fluorine on the *ortho*- and *meta*-positions. Indeed, HDF of p-$FC_6H_4CF_3$ in the same o-$C_6H_4Cl_2$ solvent gave generally higher yields of the expected HDF product p-$FC_6H_4CH_3$ and no solid residues (reactions F2−4). However, Friedel−Crafts attack on o-$C_6H_4Cl_2$ accounted for as much as

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Table 2. Hydrodechlorination Results of Reactions Initiated at 25 °C

#	substrate	catalyst	R_3SiH	cosolvent	time, h	cat. %	C−H product yield %[a]	C−C conv %[b]	TON[c]
Cl1[d]	*p*-$FC_6H_4CCl_3$	none	Et_3SiH	*o*-$C_6H_4Cl_2$	12		0	0	0
Cl2[d]	*p*-$FC_6H_4CCl_3$	radical initiator	Et_3SiH	*o*-$C_6H_4Cl_2$	12	8.7	0	0	0
Cl3	*p*-$FC_6H_4CCl_3$	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.080	33(51)	100	1260
Cl4	*p*-$FC_6H_4CCl_3$	$Ph_3C[B(C_6F_5)_4]$	Et_3SiH	*o*-$C_6H_4Cl_2$	12	0.12	60	81	670
Cl5	*p*-$FC_6H_4CCl_3$	$B(C_6F_5)_3$	Et_3SiH	*o*-$C_6H_4Cl_2$	12	0.31	12	52	170
Cl6	$C_6F_5CCl_3$	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.090	82	100	1110
Cl7	$C_6F_5CCl_3$	$Ph_3C[HCB_{11}H_5Cl_6]$	Et_3SiH	*o*-$C_6H_4Cl_2$	1	0.14	46(50)	100	740
Cl8	$C_6F_5CCl_3$	$Ph_3C[HCB_{11}H_5Cl_6]$	Et_3SiH	*o*-$C_6H_4Cl_2$	48	0.020	32(37)	100	4,900
Cl9	*n*-$C_8H_{17}Cl$	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.25	78	100	400
Cl10	*c*-$C_6H_{11}Cl$	$Ph_3C[HCB_{11}H_5Cl_6]$	Et_3SiH	*o*-$C_6H_4Cl_2$	12	0.20	48[e]	100	500
Cl11	*c*-C_5H_9Cl	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.17	46	100	580
Cl12	*p*-$FC_6H_4CH_2Cl$	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.20	43(44)	100	500
Cl13	$C_6F_5CH_2Cl$	$Ph_3C[HCB_{11}H_5Cl_6]$	Hex_3SiH	hexanes	12	0.23	82	100	440

[a] (Moles of main HDCl product divided by moles of substrate) × 100%; the values in parentheses are for the Friedel−Crafts products, where measured. [b] 100% − fraction of C−Cl bonds remaining in the starting material. [c] Number of C−Cl bonds consumed per molecule of catalyst. [d] Heated at 80 °C. [e] 34% cyclohexane and 14% methylcyclopentane.

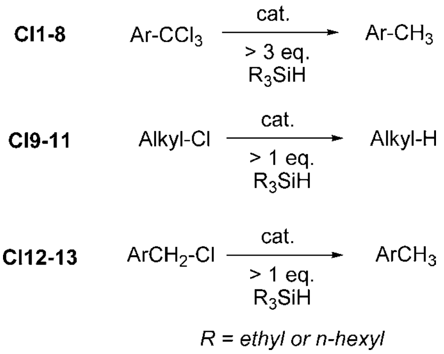
half of the products. When the HDF of *p*-$FC_6H_4CF_3$ was performed in hexanes (reaction F6), the Friedel−Crafts attack on the solvent was obviated, but the yield of *p*-$FC_6H_4CH_3$ rose only to 62%, presumably owing to Friedel−Crafts attack on the product. The various small ^{19}F NMR resonances in the aryl fluoride region are consistent with the self-attack taking place with this substrate. The Friedel−Crafts chemistry can be taken advantage of to divert the reaction to a different dominant product, as illustrated by using benzene as cosolvent (reaction F7). In this case, preferential Friedel−Crafts attack on benzene takes place, and the chief product is *p*-$FC_6H_4CH_2Ph$ in 83% yield.

In a previous communication,[17] we compared the reactivity of different halogenated carboranes in the HDF reactions (with $C_6F_5CF_3$) and determined that $[HCB_{11}H_5Cl_6]^-$ supported the fastest rate. However, it is important to note that $[HCB_{11}H_5Cl_6]^-$, $[HCB_{11}H_5Br_6]^-$, and $[HCB_{11}Cl_{11}]^-$ all support HDF reactions proceeding to completion with high turnover numbers (e.g., reaction F2−4). In fact, it is possible that the observed small rate differences have to do with relative solubility of the different anions. Here, we also tested $[HCB_{11}H_5I_6]^-$ as the supporting anion, but discovered that the $Ph_3C[HCB_{11}H_5I_6]$ did not initiate the HDF reaction at room temperature and did not appear to dissolve in the reaction mixture at all. The reaction was initiated by gentle heating, but failed to proceed to completion (reaction F5), probably because of the low solubility of the catalytic species.

$C_6F_5CF_3$ as a substrate and its HDF product $C_6F_5CH_3$ offer no opening for a Friedel−Crafts electrophile to attack. Thus, a neat reaction (reaction F9) produced a high 86% yield of $C_6F_5CH_3$, with no other products detected. Nonetheless, the HDF reaction of $C_6F_5CF_3$ with *o*-$C_6H_4Cl_2$ cosolvent (reaction F8) resulted in a comparable fraction of Friedel−Crafts attack on *o*-$C_6H_4Cl_2$.

1-Fluorodecane and fluorocyclohexane also readily underwent HDF (reactions F11−13). In agreement with the benzotrifluoride reactivity, the HDF of 1-fluorodecane proceeded much more selectively in the absence of aromatic Friedel−Crafts targets, producing a 96% yield of *n*-decane in reaction F12. In the case of cyclohexane (reaction F13), GC-MS analysis revealed, besides the expected cyclohexane, an impurity of the apparent gross formula $C_{12}H_{22}$. The formula weight is suggestive of two cyclohexyl units, but at present we do not know its identity. *gem*-Difluorocyclopentane (reaction F14) offers an example of a CF_2-containing substrate. It was defluorinated readily in hexanes. Cyclopentane was detected by GC-MS, but because of its high volatility, we have not obtained the information about the yield.

Scheme 3. Summary of HDCl Reactions Showing Main HDCl Products



Reactions F15−17 offer examples of substrates with CF_3 groups that are not benzylic. We have previously described the reactivity of $Ph(CH_2)_3CF_3$, which is dominated by Friedel−Crafts chemistry either in self-condensation (reaction F15) or by attack on benzene cosolvent (reaction F16). The HDF of $Br(CH_2)_5CF_3$ gave an opportunity to access the reactivity of a non-benzylic CF_3 group in the absence of Friedel−Crafts targets (reaction F17), and this reaction gave *n*-hexane as the major product. This implies that hydride*bromin*ation (HDBr) also took place (other examples later in the text). *n*-$C_4F_9C_2H_5$ was an even more challenging substrate with a perfluorobutyl chain (reaction F18). As we described earlier, it did undergo HDF, albeit slowly even at elevated temperature (50 °C), and gave a mixture of various C_6 hydrocarbons.

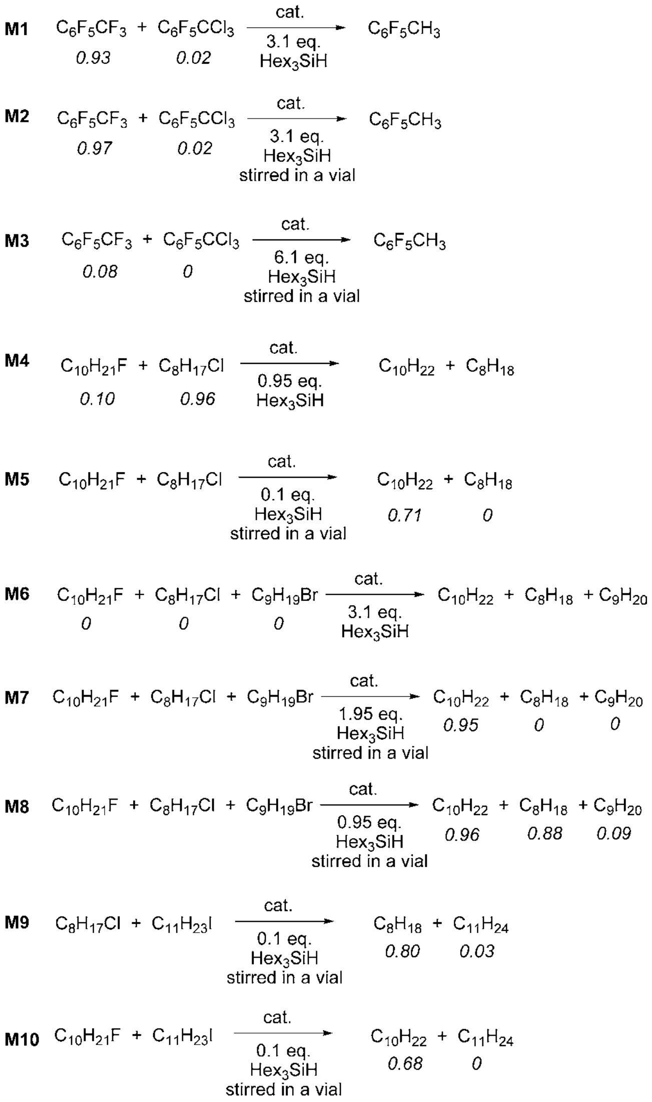
Carbon tetrafluoride is perhaps the ultimate challenge of C−F activation chemistry. Regrettably, our HDF protocol did not lead to consumption of CF_4 even at 90 °C (reaction F19). At ca. 1 atm pressure, the concentration of CF_4 in solution phase is much smaller than of the liquid substrates in other reactions, but the presence of CF_4 in solution was readily evinced by ^{19}F NMR. We may only conclude that CF_4 is much more difficult to activate by our HDF protocols than even its seemingly close relatives in reactions F15−18.

Hydrodechlorination Reactions. The hydrodechlorination (HDCl) reactions, summarized in Table 2 and Scheme 3, were performed similarly to the HDF reactions. Either Et_3SiH or trihexylsilane were used as stoichiometric sources of H in reactions with benzotrichloride and alkyl monochloride substrates. To begin with, we performed two control experiments for the HDCl of p-$FC_6H_4CCl_3$ where we used either no catalyst at all (reaction C11) or a known radical initiator (reaction C12) to test whether HDCl can proceed without a catalyst or via radical pathways. Radical HDCl with silanes has been studied before.[25] C−Cl bonds are weaker with respect to homolysis than C−F bonds, and so radical HDCl is more plausible with C−Cl bonds. Nonetheless, we saw no NMR-detectable reaction in reactions C11 and C12. Reaction with $Ph_3C[HCB_{11}H_5Cl_6]$ as catalyst (reaction C13) proceeded with complete consumption of the substrate. The expected HDCl product p-$FC_6H_4CH_3$ was formed in 33% yield, with most of the balance probably belonging to Friedel−Crafts products. The same reaction (in o-$C_6H_4Cl_2$) was also catalyzed by $Ph_3C[B(C_6F_5)_4]$ (reaction C14) and $B(C_6F_5)_3$ (reaction C15); however, they did not proceed to completion. We have previously discussed the superiority of carborane anions to $[B(C_6F_5)_4]^-$ in HDF and AlkDF;[17] the same arguments about the anion instability presumably apply for HDCl, as well. $B(C_6F_5)_3$ has been used for reduction of C−O bonds to C−H bonds when partnered with Et_3SiH,[27] where it ostensibly works by reversibly abstracting hydride from Et_3SiH and generating small concentrations of Et_3Si^+.[28] Our brief experimentation with $B(C_6F_5)_3$ in HDF showed that it is a very poor catalyst;[13] its performance here in HDCl is superior.

For the remainder of the experiments in Table 2, we used $Ph_3C[HCB_{11}H_5Cl_6]$ as the catalyst. HDCl of $C_6F_5CCl_3$ (reactions C16−8) was carried out with turnover numbers up to 4900. Friedel−Crafts products were abundant when o-$C_6H_4Cl_2$ was used as cosolvent, but in hexanes, a high yield of $C_6F_5CH_3$ was obtained. HDCl reactions of alkyl and benzyl chlorides (reactions C19−13) proceeded smoothly, again, with a significant amount of byproduct when aromatic Friedel−Crafts targets were present. Interestingly, in the case of cyclohexyl chloride, we observed both cyclohexane and methylcyclopentane products. It is likely that some of the generated cyclohexyl cations rearrange to the more stable methylcyclopentyl cations in the course of the reaction. We have also performed a competition experiment between of p-$FC_6H_4CH_2Cl$ and $C_6F_5CH_2Cl$. When a 1:1 mixture of these substrates was subjected to HDCl conditions with only 1 equiv of trihexylsilane, we found that p-$FC_6H_4CH_2Cl$ was completely consumed and at least 95% of $C_6F_5CH_2Cl$ remained intact. This generally tracks with our previous HDF[13,17] and AlkDF[19] observations that the rate is governed by the relative stabilities of the generated carbocations.

Comparative Hydrodehalogenation Reactions. Having observed efficient HDF, HDCl, and even HDBr with silylium catalysis, it became of interest to compare the relative preference of the catalytic system for these reactions. We decided to explore competition reactions between analogous C−F-, C−Cl-, C−Br-, and C−I-containing substrates. Comparing rates of reactions with different substrates in separate reaction vessels is complicated by the vagaries of the influence of the exact medium polarity on the rate, the self-acceleration of these reactions because of high exothermicity, and other uncertainties. We opted to subject the different substrates obligatorily to the same conditions by performing competition reactions in the same vessel (Scheme 4).

Scheme 4. Hydrodehalogenation Competition Reactions[a]



[a] All substrates are in the amount of 1 equiv each, and the italic numbers underneath compounds show the measured quantities at the last evaluation point in equivalents. Reactions were conducted in NMR tubes unless noted otherwise. Full details are in the Supporting Information.

At first, we selected $C_6F_5CF_3$ and $C_6F_5CCl_3$ for benzotrihalide comparison. These substrates are immune to Friedel−Crafts side reactions and possess convenient intermediate reactivity. In order to obviate Friedel−Crafts reactions with solvent, we used alkane cosolvent (hexanes or cyclohexane). We used trihexylsilane to increase the solubility of the silylium species formed in situ. For the same reason we opted for $Ph_3C[HCB_{11}Cl_{11}]$ as the catalyst. When a 1:1 mixture $C_6F_5CF_3$ and $C_6F_5CCl_3$ was treated with $Ph_3C[HCB_{11}Cl_{11}]$ and only 1 equiv of Hex_3SiH in an NMR tube, it was found that $C_6F_5CCl_3$ was consumed at a notably faster rate (reaction M1), with 93% of $C_6F_5CF_3$ remaining intact after 98% of $C_6F_5CCl_3$ had been consumed. A similar result was obtained in a vial with continuous stirring: 97% unreacted $C_6F_5CF_3$ at the point of 98% consumption of $C_6F_5CCl_3$ (reaction M2). In an experiment with 2 equiv of Hex_3SiH provided, $C_6F_5CF_3$ was consumed after $C_6F_5CCl_3$ was exhausted (reaction M3). Thus, the observed preference for $C_6F_5CCl_3$ is a result of its faster rate of conversion and not a function of suppression of HDF by HDCl products.

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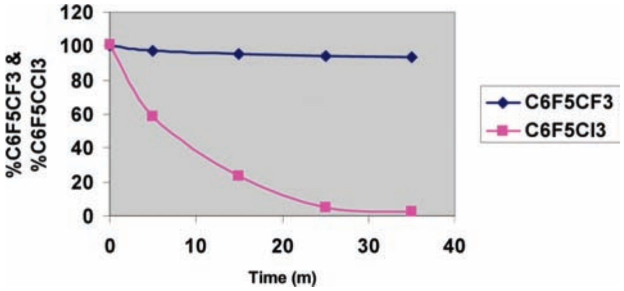

Figure 2. Preferential consumption of $C_6F_5CCl_3$ over $C_6F_5CF_3$ in reaction M1.

We have previously argued that the first fluoride abstraction in $ArCF_3$ is rate-limiting. If the same holds for $ArCCl_3$, then ostensibly the abstraction of chloride from $C_6F_5CCl_3$ is faster than of fluoride from $C_6F_5CF_3$. However, this also means that the comparison is flawed in that we are comparing the rate of abstraction of chloride from the $C_6F_5CCl_2^+$ cation and the rate of abstraction of fluoride from a *different* cation, $C_6F_5CF_2^+$.

Contemplating relative affinity of different Lewis acids for different Lewis bases "on the back of the envelope" is challenging, and so we sought a more straightforward comparison. We selected 1-fluorodecane, 1-chlorooctane, 1-bromononane, and 1-iodoundecane for comparative analysis. It is logical to assume that the reactivity of all the corresponding long-chain alkyl fragments is roughly the same. The C_8-C_{11} range was convenient for reasons of solubility and convenient volatility (not volatile enough to evaporate quickly during transfers and easily observable by GC-MS).

When a 1:1 mixture of 1-fluorodecane and 1-chlorooctane was treated with $Ph_3C[HCB_{11}Cl_{11}]$ in the presence of 0.95 equiv of Hex_3SiH in an NMR tube (reaction M4), we were able to observe gradual consumption of the reagents with a distinct and strong preference for HDF: 96% of 1-chlorooctane remained when 90% of 1-fluorodecane had been consumed. Figure 2 depicts the progress of the reaction. The shape of the lines should not be assigned mechanistic significance in view of the possibly incomplete solubility of the catalyst and/or its slow dissolution in the absence of agitation. We also performed an experiment pitting 1-fluorodecane and 1-chlorooctane against each other with each reagent being in 10-fold excess with respect to Hex_3SiH. In this way, we can count the concentrations of the two reagents as being constant and equal throughout the reaction. In this case, GC-MS analysis detected no *n*-octane (HDCl) at the point where 71% (based on Hex_3SiH) *n*-decane (HDF) was measured (reaction M5).

In another NMR tube experiment (reaction M6, also Figure 3), we subjected a 1:1:1 mixture of 1-fluorodecane, 1-chlorooctane, and 1-bromononane to hydrodehalogenation in the presence of 3.1 equiv of Hex_3SiH. An analogous reaction with 1.95 equiv of Hex_3SiH was performed in a vial with continuous stirring (reaction M7). GC-MS analysis of the products revealed 96% yield of *n*-decane (HDF) before any *n*-octane (HDCl) or *n*-nonane (HDBr) was detected. At the end of the reaction, 88% of *n*-octane (HDCl) and 9% of *n*-nonane (HDBr) were measured. When a 1:1:1 mixture of 1-fluorodecane, 1-chlorooctane, and 1-bromononane was subjected to hydrodehalogenation in the presence of 0.95 equiv of Hex_3SiH (reaction M8), GC-MS analysis detected 0.95 equiv of *n*-decane and no *n*-octane or *n*-nonane among the products. Not surprisingly, hydrodeiodination (HDI) was found to be slower than HDCl of HDF with little or no conversion of 1-iodoundecane in the presence of a sufficient amount of either 1-fluorodecane or 1-chlorooctane (reactions M9 and M10).

The results emerging from the experiments with alkyl halides demonstrated the distinct preference for hydrodehalogenation of lighter halides, with the preference for HDF over HDCl being greater than for HDCl over HDBr. If that halide abstraction is rate-limiting in all of these cases, it appears that the silylium catalyst prefers to abstract a lighter halide. This selectivity can be rationalized on the basis of the hard acid silylium exhibiting preference for harder bases. In fact, such selectivity is not new. Recently, Terao, Kambe, and co-workers observed a strong preference for the attack on alkyl fluorides (vs bromides or iodides) by Et_2AlCl, likewise a hard acid.[29] Nonetheless, this is an intriguing selectivity that is completely opposite the preferences in oxidative addition reactions with transition metal complexes (that much prefer heavier halides). It is also opposite the selectivity displayed by silyl *radicals* in hydrodehalogenation reactions.[30]

Structure of $Et_3Si[HCB_{11}H_5Cl_6]$. An X-ray diffraction study of a suitable single crystal revealed the solid-state structure of $Et_3Si[HCB_{11}H_5Cl_6]$ (Figure 4). $Et_3Si[HCB_{11}H_5Cl_6]$ fortuitously crystallized with two independent molecules in the asymmetric unit, providing us with two sets of metric data. Although the two molecules are crystallographically independent, they possess identical connectivity and similar bond distances and angles. Several other trialkylsilylium adducts of halogenated carboranes have been crystallographically characterized, and the structural features of $Et_3Si[HCB_{11}H_5Cl_6]$ generally parallel those. The Si in $Et_3Si[HCB_{11}H_5Cl_6]$ is attached to a Cl of the "meta" belt. Interestingly, the "meta" belt has been the exclusive point of

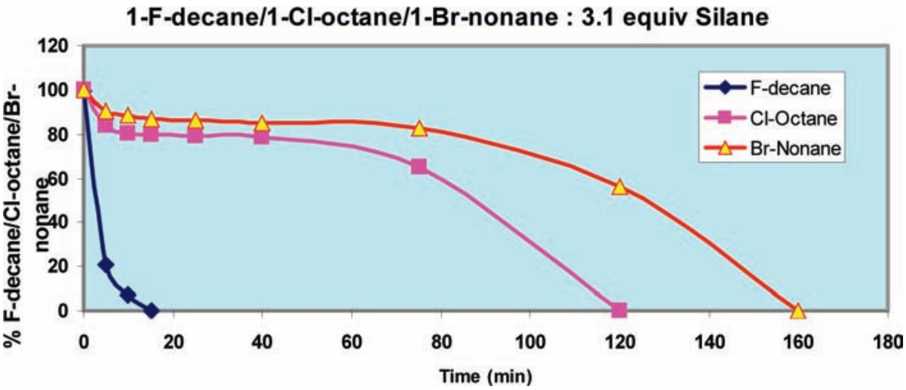

Figure 3. Preferential consumption of the alkyl fluoride over alkyl chloride and over alkyl bromide in reaction M6.

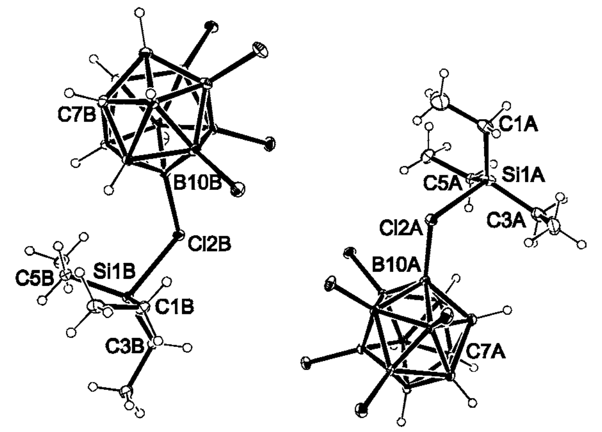

Figure 4. ORTEP drawing (50% probability ellipsoids) of the two independent molecules of $Et_3Si[HCB_{11}H_5Cl_6]$ showing selected atom labeling. The disorder of one of the ethyl groups is not shown. Selected bond distances (Å) and angles (deg): Cl2A−Si1A, 2.3044(13); Cl2A−B10A, 1.862(4); Cl2B−Si1B, 2.2815(11); Cl2B−B10B, 1.860(4); Si1A−Cl2A−B10A, 115.02(12); Si1B−Cl2B−B10B, 114.35(11); C1A−Si1A−C5A, 119.9(2); C3A−Si1A−C5A, 111.3(2); C1A−Si1A−C3A, 114.61(18); C1B−Si1B−C3B, 115.15(16); C1B−Si1B−C5B, 118.06(15); C3B−Si1B−C5B, 114.85(15).

attachment in the solid state for trialkylsilyls with several different alkyls and a variety of hexa- and undecahalogenated carboranes.

The Si−Cl distances in $Et_3Si[HCB_{11}H_5Cl_6]$ (2.3044(13) and 2.2815(11) Å) are slightly shorter than the analogous distances of 2.323(3) Å in $^iPr_3Si[HCB_{11}H_5Cl_6]$[31] and 2.334(3) Å in $Et_3Si[HCB_{11}Cl_{11}]$.[32] The B−Cl distance involving the chlorine atoms attached to Si in $Et_3Si[HCB_{11}H_5Cl_6]$ (1.862(4) and 1.860(4) Å) are notably longer than the other B−Cl distances that range from 1.782(4) to 1.798(4) Å; elongation of the B−Hal(Si) bond has been observed in other trialkylsilyl carboranes.[31] The sum of angles about Si in the trialkylsilyl fragment has been used to gauge the extent of the approach toward an sp^2-hybridized Si in a true trialkylsilylium cation. In $Et_3Si[HCB_{11}H_5Cl_6]$, this $\sum$CSiC parameter is 345.8(3)° and 348.1(2)° and falls in between the values expected for the sp^2- and the sp^3-hybridization. These values in $Et_3Si[HCB_{11}H_5Cl_6]$ fall within the lower end of the range of values of $\sum_{CSiC}$ in trialkylsilyl adducts with polyhalocarboranes. A series of $R_3Si[HCB_{11}H_5Br_6]$ displayed $\sum_{CSiC}$ of 345−351°.[33] $\sum_{CSiC}$ for $^iPr_3Si[HCB_{11}H_5Hal_6]$[31] where Hal = Cl, Br, or I fell within 347−351°, while for $Et_3Si[HCB_{11}Cl_{11}]$,[32] it was ca. 349.5°. Similar values were recorded for adducts with SO_2 and *o*-$C_6H_4Cl_2$.[32] Trimethylsilyl derivatives of undecafluorinated carboranes displayed slightly more flattened Si, with $\sum_{CSiC}$ of ca. 354.4°.[34] However, given the ca. 2.3° difference between the values of $\sum_{CSiC}$ in the two chemically equivalent but crystallographically independent molecules of $Et_3Si[HCB_{11}H_5Cl_6]$, assigning interpretative significance to such small differences may not be justified.

Conclusion

In summary, we have demonstrated that the silylium carborane catalysts are capable not only of effecting hydrodefluorination of a variety of substrates containing $C(sp^3)$−F bonds but also of analogous reactivity in hydrodechlorination and hydrodebromination. Hydrodechlorination of benzotrichlorides and of a series of alkyl chlorides was efficiently carried out. Competitive studies among various hydrodehalogenations demonstrated that a strong preference for a particular halide may exist and depends on the substrate structure. For primary alkyl halides, a pronounced preference for activation of the lighter halide in a carbon−halogen bond was recorded, with alkyl fluoride reacting by far the fastest. In contrast, in the case of benzotrihalides, the selectivity was reversed and a benzotrichloride underwent hydrodehalogenation much faster than an analogous benzotrifluoride. Our results indicate that hydrodehalogenation of aliphatic carbon−halogen bonds with silanes is readily catalyzed by silylium carborane catalysts with high turnover numbers.

Experimental Methods

General Considerations. Unless specified otherwise, all reactions were carried out under an argon atmosphere using a glovebox in which the only volatile materials were silanes, hydrocarbons, and halogenated hydrocarbons. Hexanes and benzene were dried over NaK/Ph_2CO/18-crown-6, distilled, and stored over molecular sieves in the glovebox. All the substrates and all the haloarenes were dried with CaH_2 and distilled under Ar or vacuum transferred and stored over molecular sieves in the glovebox. $Ph_3C[B(C_6F_5)_4]$ was donated by Albemarle Corp. It was recrystallized and dried under high vacuum before use. $Cs[HCB_{11}H_{11}]$ was purchased by Katchem Czech Republic, and the trityl salts of the carborane anions, as well as $Et_3Si[HCB_{11}H_5Cl_6]$, were synthesized following methods reported by Reed et al.[31,35,36] $B(C_6F_5)_3$ was purchased from Aldrich and used as received. NMR spectra were recorded either on a Varian Inova 400 spectrometer or on a Varian Inova 500 (^1H NMR, 399.755 MHz, ^{19}F NMR, 376.104 MHz, ^{11}B NMR, 160.323 MHz). GC-MS spectra were recorded on a Hewlett-Packard GCD System (EI mode) employing HP-5MS from Agilent Technologies (30 m × 0.25 mm) and 1227032 from J&W Scientific (30 m × 0.25 mm). Helium was used as a carrier gas.

CAUTION: Most of the reactions described here are highly exothermic. For the more active substrates, especially for reactions run neat or with polar cosolvents, the reactions were found to proceed very rapidly, autoaccelerate, and release significant amounts of heat. Some of the reactions (particularly those with Friedel−Crafts side chemistry) produced H_2 as one identified gaseous byproduct. In addition, the pressure could rise in closed reaction vessels owing to the increase in temperature and generation of low-boiling-point byproduct (e.g., Et_2SiF_2). Thus, thorough care must be taken to avoid dangerous pressure buildup in a closed vessel.

Yields/Conversions by NMR and GC-MS. All of the reactions that relied on ^{19}F NMR integrations for calculation of concentrations of reagents and substrates contained an internal integration standard. This standard was C_6F_6, C_6F_5Cl, or C_6F_5Br, none of which participate in hydrodehalogenation reactions. The choice of the particular standard was arbitrary and primarily guided by the convenience of avoiding overlap of ^{19}F NMR resonances. Within the error of integration, there was one-to-one correspondence of the intensity of ^{19}F NMR resonances and concentration among the standards and substrates/reagents. Several experiments in the competitive hydrodehalogenation section relied on ^1H NMR

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integration to judge the consumption of primary alkyl halides. The CH_2-Hal resonance was used for this purpose and integrated against the $C_6F_5CH_3$ standard. The correspondence of integral values and concentration was separately calibrated using mixtures of known concentration of $C_6F_5CH_3$ and the requisite alkyl halides. In most experiments, authentic samples of the main products of the reaction were available. Where GC-MS was used to calculate the yields of products, GC-MS integration was separately calibrated by using mixtures of known concentrations of authentic samples of products and of standards. The standards were typically C_6F_5H or C_6F_5Cl. We estimate a range of 5−15% error in the determinations of yields/conversions, depending on the particulars of the experiment.

Full experimental details on all reactions can be found in the Supporting Information. Here, only representative examples are provided. Reactions F8, F9, F10, F15, F16, and F18 have been reported previously.[17]

Reactions F2, F3, and F4. A J. Young tube was loaded with $Ph_3C[HCB_{11}H_5Cl_6]$ or $Ph_3C[HCB_{11}Cl_{11}]$ or $Ph_3C[HCB_{11}H_5Br_6]$ (5 μmol), C_6F_6 (15 μL, 0.13 mmol), *o*-dichlorobenzene (0.2 mL), and *p*-$FC_6H_4CF_3$ (0.30 mL, 2.3 mmol) and cooled using a precooled (glovebox refrigerator set at −35 °C) copper shot bath. Then, Et_3SiH (1.1 mL, 6.9 mmol) was added slowly, and the tube was allowed to stand for 1 h; then the tube was closed. The ^{19}F NMR spectrum of one of the reactions (F4) was checked after 1 h, to show formation of Et_3SiF (−178.1 ppm) and Et_2SiF_2 (−146.2 ppm), for which 50% Si−F conversion was calculated. After 72, 84, and 96 h for F2, F3, and F4, respectively, all *p*-$FC_6H_4CF_3$ had been consumed and *p*-$FC_6H_4CH_3$ (−121.1 ppm) was present in the spectrum. The ^{19}F NMR measured yield for *p*-$FC_6H_4CH_3$ vs the C_6F_6 standard was 48% for F2, 13% for F3, and 34% for F4. In addition to *p*-$FC_6H_4CH_3$ (m/z^+ 110), Et_3SiF m/z^+ 134 (M), Et_4Si m/z^+ 144 (M), and Et_2SiF_2 (m/z^+ 124), GC-MS analysis indicated formation of the Friedel−Crafts products *p*-$FC_6H_4CH_2C_6H_3Cl_2$ (two isomers, m/z^+ 254 (M) in all of F2, F3, and F4 (^{19}F NMR overlapping near −119.9 ppm)). GC-MS yields of the Friedel-Craft products (calculated vs Et_3SiF) were 36% (F2), 51% (F3), and 42% (F4).

Reaction Cl3. A 10 mL glass vial equipped with a stir bar was charged with $Ph_3C[HCB_{11}H_5Cl_6]$ (3 mg, 5 μmol), *p*-$FC_6H_4CCl_3$ (0.30 mL, 2.1 mmol), and hexanes (0.2 mL) and stirred for 1 min. Hex_3SiH (2.2 mL, 6.4 mmol) was then added, the vial was closed, and the contents were stirred for 12 h. After this time, the mixture was checked by ^{19}F NMR spectroscopy, which showed that the resonance at −112.1 ppm (*p*-$FC_6H_4CCl_3$) had disappeared. *p*-$FC_6H_4CH_3$ (−120.3 ppm) accounted for 33% yield, with various other resonances, likely Friedel−Crafts products (−118.8, −119.1, −124.6, −125.5 ppm), accounting for 51%. GC-MS analysis also detected *p*-$FC_6H_4CH_3$ m/z^+ 109 (M).

Reaction M2. A 10 mL glass vial equipped with a stir bar was charged with $Ph_3C[HCB_{11}Cl_{11}]$ (1.5 mg, 1.9 μmol), $C_6F_5CF_3$ (100 μL, 0.70 mmol), $C_6F_5CCl_3$ (115 μL, 0.70 mmol), C_6F_6 (20 μL, 0.17 mmol), and hexanes (0.8 mL), closed, and stirred for 2 min. An aliquot of the mixture was taken and transferred into an NMR tube, and the ^{19}F NMR spectrum was recorded. Then, 3.1 equiv of Hex_3SiH (780 μL, 2.18 mmol) was added, and the contents were stirred continuously. An aliquot of the reaction mixture was taken after 8 min into an NMR tube, $NBu_4[BH_4]$ was added to quench the reaction, and the ^{19}F NMR spectrum was recorded. Similarly, an aliquot of the reaction mixture was taken at 15 and 20 min into NMR tubes with $NBu_4[BH_4]$, and the ^{19}F NMR spectra were recorded. The NMR spectrum recorded at the end of 20 min revealed 97% of $C_6F_5CF_3$ and only 2% of $C_6F_5CCl_3$ remaining. The resonances at −146.7, −162.1, and −165.6 ppm corresponded to $C_6F_5CH_3$.

X-ray Data Collection, Solution, and Refinement for $Et_3Si[HCB_{11}H_5Cl_6]$. A suitable crystal was obtained by cooling a solution of $Et_3Si[HCB_{11}H_5Cl_6]$ in a mixture of fluorobenzene and hexanes to −35 °C. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo Kα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.[37] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 25 s and a detector distance of 60 mm. The optimized strategy used for data collection consisted of two phi and three omega scan sets, with 0.5° steps in phi or omega; completeness was 92.8%. A total of 2065 frames were collected. Final cell constants were obtained from the *xyz* centroids of 5046 reflections after integration. The lower than expected completeness arises from a faulty version of the program COSMO, which generates run sets and strives to attain sets with the highest combination of completeness and redundancy.[37] The predicted completeness was 99.7%, which was not realized. Later versions produced satisfactory results with other crystals, but additional crystals of this material were not available at that time. Nonetheless, the data are quite satisfactory, and the results of the structure analysis are unequivocal. The error led to a CheckCIF Alert B error; accordingly, a validation reply form section has been added to the CIF to explain the Alert B.

From the lack of systematic absences, the observed metric constants, and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92[38] and refined (full-matrix least-squares) using the Oxford University Crystals for Windows program.[39] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms.

Compound $Et_3Si[HCB_{11}H_5Cl_6]$ contained significant disorder, which was resolved successfully. The two-component disorder was described with a constraint that the occupancies of the major and minor components sum to 1.0. The major component atoms were refined by using anisotropic displacement parameters, and the minor component atoms were refined by using isotropic displacement parameters. The atoms C(5) and C(6) were disordered, with the occupancy of the major component at 0.727(9). The final least-squares refinement converged to $R_1 = 0.0398$ ($I > 2\sigma(I)$, 5550 data) and $wR_2 = 0.0882$ (F^2, 8140 data, 460 parameters).

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Supporting Information Available: Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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