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Carbon−Carbon Coupling of $C(sp^3)$−F Bonds Using Alumenium Catalysis

Weixing Gu,[†,‡] Mason R. Haneline,[‡,§] Christos Douvris,[‡,||] and Oleg V. Ozerov*,[†,‡]

Departments of Chemistry, Texas A&M University, College Station, Texas 77842, and Brandeis University, 415 South Street, Waltham, Massachusetts 02454

Received May 14, 2009; E-mail: ozerov@mail.chem.tamu.edu

Abstract: Dialkylalumenium cation equivalents coupled with the hexabromocarborane anion function as efficient and long-lived catalysts for alkylation of aliphatic C−F bonds (alkylative defluorination or AlkDF) by alkylaluminum compounds. Only $C(sp^3)$−F bonds undergo AlkDF; $C(sp^2)$−F bonds are unaffected. Examples of compounds undergoing AlkDF include monofluoroalkanes, *gem*-difluorocyclopentane, and compounds containing a CF_3 group attached to either an aryl or an alkyl substituent. Conversion of C−F bonds to C−Me bonds is accomplished with high fidelity using Me_3Al as the stoichiometric reagent. In reactions with Et_3Al, hydrodefluorination of the C−F bonds is competitive with alkylation, indicative presumably of competitive hydride vs alkyl transfer from Et_3Al. In a trialkylaluminum reagent, 1.1−1.4 alkyl groups per Al can be used to replace C−F bonds. Organoaluminum compounds efficiently remove water from the reaction mixture, obviating the need for rigorously dry solvents. Some organoaluminum compounds, especially methylaluminoxane, are capable of AlkDF with more reactive substrates, but catalysis by alumenium offers an advantage over the uncatalyzed C−F activation in terms of both increased rate and, in some cases, a dramatically increased selectivity.

Introduction

Carbon−fluorine bonds are among the most robust functionalities in chemistry.[1] Activation of C−F bonds is thus a fundamental challenge of note.[2] It is also often viewed through the prism of remediation of polyfluoroorganic atmospheric pollutants such as chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs), all of which are very potent greenhouse gases.[3] Reductive removal of fluorine can be accomplished by strong reductants with or without a transition-metal catalyst.[2] Selective replacement of F in a C−F bond with another substituent presents a separate challenge. In particular, catalytic conversion of $C(sp^3)$−F bonds to C−C bonds is especially rare.[4]

Transition-metal catalysis of C−F activation generally relies on the reductive cleavage of the C−F bond, either in an oxidative addition process or by electron transfer.[2] In 2005, we reported on a new approach for hydrodefluorination (HDF) of aliphatic C−F bonds in which the critical C−F cleavage step is a nonredox process of abstraction of fluoride by a highly Lewis acidic silylium cation.[5,6] Reed and co-workers reported on the stoichiometric abstraction of fluoride with silylium reagents paired with the undecaiodocarborane.[7] We recently demonstrated that utilization of halogenated carboranes as companion anions (instead of $[B(C_6F_5)_4]^-$) led to the dramatic improvement of the longevity of the catalytic C−F activation.[8] We conceived of a related "alkylative defluorination" (AlkDF) process mediated by R_2Al^+ equivalents (in place of R_3Si^+) paired with a carborane anion (Scheme 1). Given the greater polarity of Al−C bonds, it seemed reasonable to expect that an alkyl group transfer from Al would be more facile and a catalytic replacement of C−F by an alkyl group can be realized. Trialkylaluminum compounds are readily available and thus are a very reasonable stoichiometric reagent. Here we report on the success of our strategy.

Our work here benefits significantly from the knowledge available through the accomplishments of other groups. The guiding precedent for the use of a Lewis acidic main group

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[†] Texas A&M University.

[‡] Brandeis University.

[§] Current address: Heraeus Metal Processing Inc., Santa Fe Springs, CA 90670.

[||] Current address: University of Colorado, Boulder, CO 80309.

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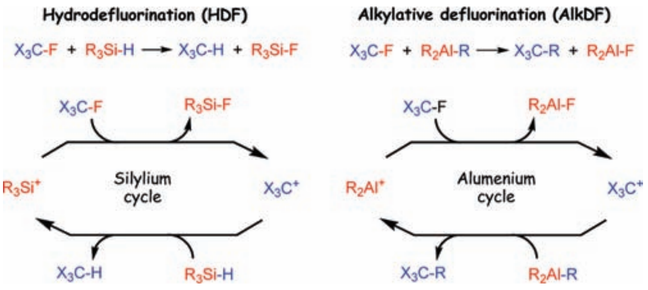
Scheme 1



cation for abstraction of fluoride for a fluoroalkane comes from the work of Krause and Lampe over 30 years ago, who observed Si−H/C−F redistribution by mass spectrometry in the gas phase upon collision of SiH_3^+ with CF_4.[9] In the condensed phase, however, charge balance is an obvious requirement, and the reactivity of highly electrophilic cations such as silylium can be exploited only if paired with robust weakly coordinating anions.[10] So far, halogenated derivatives of carba-*closo*-dodecaborate(−) (often referred to as carborane anions; see Figure 1) have proven to be the best; in fact, they are ostensibly unmatched in this regard. Their development and use as inert partners to highly reactive cations has been pioneered by the Reed group. The chemistry of these remarkable anions, and the utilization of their derivatives in catalysis, has been reviewed, most recently and comprehensively by Körbe, Shreiber, and Michl in 2006.[11]

Several recent reports on the use of aluminum compounds are relevant to C−F activation. Akiyama et al. have recently detailed activation of benzotrifluorides by the mixtures of $NbCl_5$ and $LiAlH_4$; however, it is not clear whether Al plays any role besides reducing Nb to a reactive state.[12] Terao, Kambe, and co-workers demonstrated that triorganoaluminums (without any added catalyst) efficiently convert a C−F bond in a primary alkyl fluoride into a C−C bond.[13] As our investigations demonstrate (vide infra), this reaction is largely limited to monofluoroalkanes. Rosenthal, Krossing and co-workers used $^iBu_2AlH$ as the source of H for HDF catalyzed by addition of a trityl salt of $B(C_6F_5)_4^-$, $Al(C_6F_5)_4^-$, or $Al(OC(CF_3)_3)_4^-$.[14] Just as in the case of Si-based HDF with $B(C_6F_5)_4^-$,[5] these anions failed to sustain the catalysis for more than a few dozen turnovers. Intermediacy of R_2Al^+-like species was postulated. The groups of Sen and Reed reported the preparation of $Et_2Al[HCB_{11}H_5Br_6]$ (**A**), a species with an alumenium (R_2Al^+) cation-like reactivity.[15] Notably, compound **A** was prepared via treatment of $Ph_3C[HCB_{11}H_5Br_6]$ (**B**) with Et_3Al.

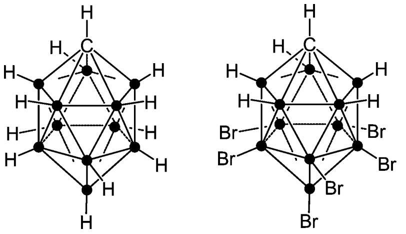


Figure 1. Schematic representations of the parent carborane anion $[HCB_{11}H_{11}]^-$ (left) and of the hexabromocarborane anion $[HCB_{11}Br_6H_5]^-$ (right) used in this work.

Results and Discussion

A summary of the catalytic AlkDF reactions is provided in Table 1. In the majority of reactions we utilized $Et_2Al[HCB_{11}H_5Br_6]$ (**A**) as a (pre)catalyst; alternatively, $Ph_3C[HCB_{11}H_5Br_6]$ (**B**) or $Ph_3C[B(C_6F_5)_4]$ (**C**) was used. Given that **A** was isolated via reaction of **B** with Et_3Al,[15] it appears sound to assume that **B** and **C** are swiftly converted to the corresponding Et_2Al[Anion] by the excess of Et_3Al in our catalytic reactions.

In the idealized form, we may refer to R_2Al^+ and R_3C^+ cations here. However, it is unlikely that true free cations exist in our catalytic reaction mixtures, especially in the less polar solvents. Except perhaps the more stabilized carbocations, the cations under study undoubtedly exist as adducts with the anion, solvent, or one of the reactants or products. Nonetheless, considering the weakly coordinating nature of the hexabromocarborane anion or of the solvents employed here, it appears reasonable to treat these species in solution as close synthons of the requisite cations.

Reactions with Benzotrifluorides. We first examined the AlkDF reactivity with p-$FC_6H_4CF_3$ (**1**; Scheme 2). This substrate is convenient because of the presence of the aromatic C−F moiety, which allows tracking both the substrate and the products by ^{19}F NMR. As in the Si-mediated HDF chemistry,[5,8] here we saw no evidence of activation of the aromatic C−F bonds. We used C_6F_6 as the internal integration standard for ^{19}F NMR.

Entries 1−4 (Table 1) document C−F activation of **1** using different R_3Al reagents and **A** as the catalyst (0.33% loading) under otherwise the same conditions. With Et_3Al, $^iBu_3Al$, and $^iBu_2AlH$, 90−100% consumption of **1** was observed in 1 h; the reaction with Me_3Al was slower, but led to complete consumption of **1** in 24 h (or less). The catalytic system worked with low catalyst loading as well. In one experiment (entry 5), we observed nearly 10^4 turnovers at 98% conversion in the catalyzed reaction of **1** with Et_3Al. With Me_3Al, a 94% yield of p-$FC_6H_4CMe_3$ was registered by ^{19}F NMR in situ. Reactions with other alkylaluminum compounds, however, resulted in mixtures of products. Reaction with Et_3Al (entry 2) led to three products ($FC_6H_4CH_2CH_2CH_3$, $FC_6H_4CHEt_2$, $FC_6H_4CEt_3$) in 18%, 61%, and 15% yields (by ^{19}F NMR), respectively. Reaction with $^iBu_3Al$ gave two related products ($FC_6H_4CHC_8H_{18}$, $FC_6H_4CC_{12}H_{27}$) in 33% and 62% respective yields. With $^iBu_2AlH$ as a reagent, two products ($FC_6H_4CH_2C_4H_9$, $FC_6H_4CH_3$) were observed in 58% and 32% respective yields. We

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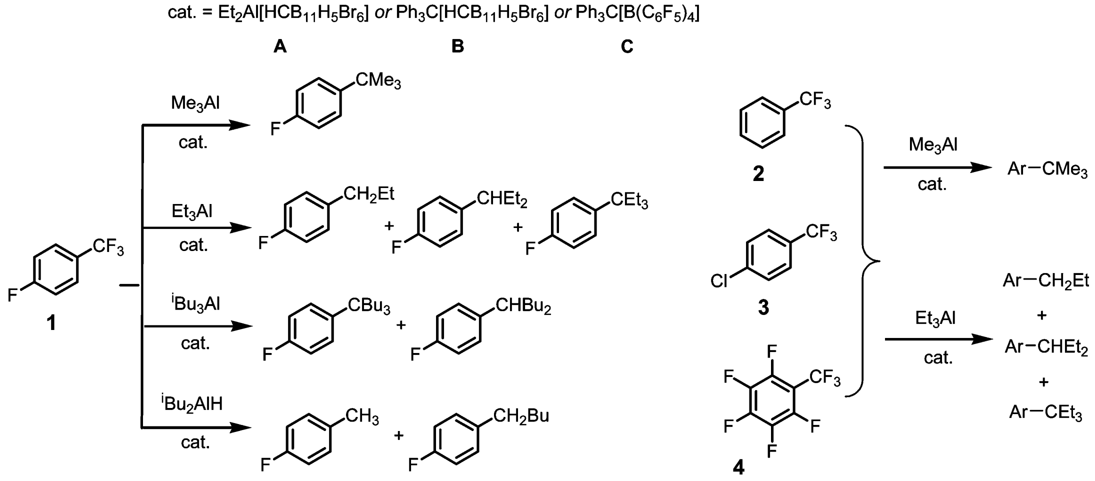
Table 1. Summary of AlkDF Reactions Initiated at Ambient Temperature with an Al/F Ratio of 1

no.	substrate	R_3Al	catalyst	catalyst loading[a] (%)	solvent	C−F conversion[b] (%)	Al−F conversion[b] (%)	TON[c]
1	**1**	Me_3Al	**A**	0.33	hexanes	41 (100)	38 (95)	123
2	**1**	Et_3Al	**A**	0.33	hexanes	93	87	280
3	**1**	$^iBu_3Al$	**A**	0.33	hexanes	100	89	300
4	**1**	$^iBu_2AlH$	**A**	0.33	hexanes	96	72	290
5	**1**[d]	Et_3Al	**A**[e]	0.01	hexanes	98	93	9800
6	**1**	Et_3Al	**A**	0.33	$C_6H_4Cl_2$	100[f]	98	300
7	**1**	Et_3Al	**B**	0.33	hexanes	21 (90)	18 (82)	63
8	**1**	Et_3Al	**C**	0.33	hexanes	16 (50)	13 (45)	48
9	**1**	Et_3Al	**B**	0.33	$C_6H_4Cl_2$	100[f]	88	300
10	**1**	Et_3Al	**C**	0.33	$C_6H_4Cl_2$	100[f]	86	300
11	**2**	Et_3Al	**A**	0.33	hexanes	90	85	270
12	**3**	Et_3Al	**A**	0.33	hexanes	25 (93)	21 (89)	75
13	**1**	Et_3Al	**A**[e]	0.33	hexanes	100[f]	94	300
14	**2**	Et_3Al	**A**[e]	0.33	hexanes	100[f]	98	300
15	**3**	Et_3Al	**A**[e]	0.33	hexanes	100[f]	92	300
16	**2**	Me_3Al	**A**	0.33	hexanes	35 (94)[g]	30 (64)	110
17	**4**[h]	Et_3Al	**A**	2.00	$C_6H_4Cl_2$	23 (100)	NA	13
18	**4**[h]	Me_3Al	**A**[e]	2.00	hexanes	66 (100)	49 (84)	33
19	**4**[h]	Me_3Al	**A**[e]	0.33	hexanes	6 (50)	6 (39)	19
20	**5**[i]	Et_3Al	**A**	0.33	$C_6H_4Cl_2$	51 (92)	50 (90)	150
21	**5**[i]	Me_3Al	**A**[e]	0.33%	hexanes	39 (82)	37 (80)	120
22	**6**	Et_3Al	**A**	0.25	$C_6H_4Cl_2$	100[f]	95	400
23	**1**	Me_3Al/Et_3SiH	**B**	0.33	hexanes	100	90[j]	300

[a] Catalyst loading vs the number of C−F bonds. [b] Conversion after 3 h (after 24 h in parentheses) based on the disappearance of C−F bonds or the appearance of Al−F bonds by ^{19}F NMR. [c] Turnover number after 3 h. [d] Reaction was carried out in a glass vial with stirring. [e] Catalyst introduced as a solution in *o*-$C_6H_4Cl_2$. [f] Reaction complete in <10 min. [g] Conversion of 94% after 36 h. [h] Reactions were carried out at 85 °C. [i] Reactions were carried out at 50 °C. [j] Only Al−F was observed by ^{19}F NMR, no Si−F observed.

Scheme 2. AlkDF Reactions with Benzotrifluorides



interpret the formation of these mixtures as a result of competition between the transfer of an alkyl group or a β-hydride from R_3Al to a carbocation. Notably, this is not applicable to Me_3Al, for which only methyl transfer products were observed. The preponderance of hydride transfer with $^iBu_2AlH$ is also consistent with our proposal.

We have also tested other benzotrifluorides. The AlkDF reaction with **2** proceeded with 90+% conversion in 3 h, similar to that of **1**, while the reaction with **3** required up to 24 h (Scheme 2 and entries 11 and 12 in Table 1). On the other hand, the much more electron poor **4** reacted much more slowly, requiring a higher temperature and a higher catalyst loading (entries 17−19, Table 1) to reach near-complete conversion. As with **1**, **2**−**4** gave a single product with Me_3Al and a mixture when Et_3Al was used.

It is tempting to analyze why, in which cases, and by how much the transfer of hydride is favored over the transfer of the alkyl. However, the consideration of the system in full is daunting. There are only four possible products (only three observed) (Scheme 3), yet there are consecutively six carbocations, each of which can abstract an alkyl or a hydride from the aluminum compound. Furthermore, trialkylaluminum compounds in solution exist in equilibrium with their dimers. It is conceivable that both dimers and monomers can be donors of alkyl or hydride. As the reaction proceeds, alkyl groups on Al are replaced with fluorides. That introduces even more possibilities for structures of aluminum compounds that may exist in solution: the dimers (or even higher oligomers) may or may not contain fluorides, and fluorides or alkyls may be bridging. Little is known about structures of organoaluminum fluorides in solution; there is evidence in support of tetramers for Me_2AlF and Et_2AlF.[16] Even though it is likely that only some of the

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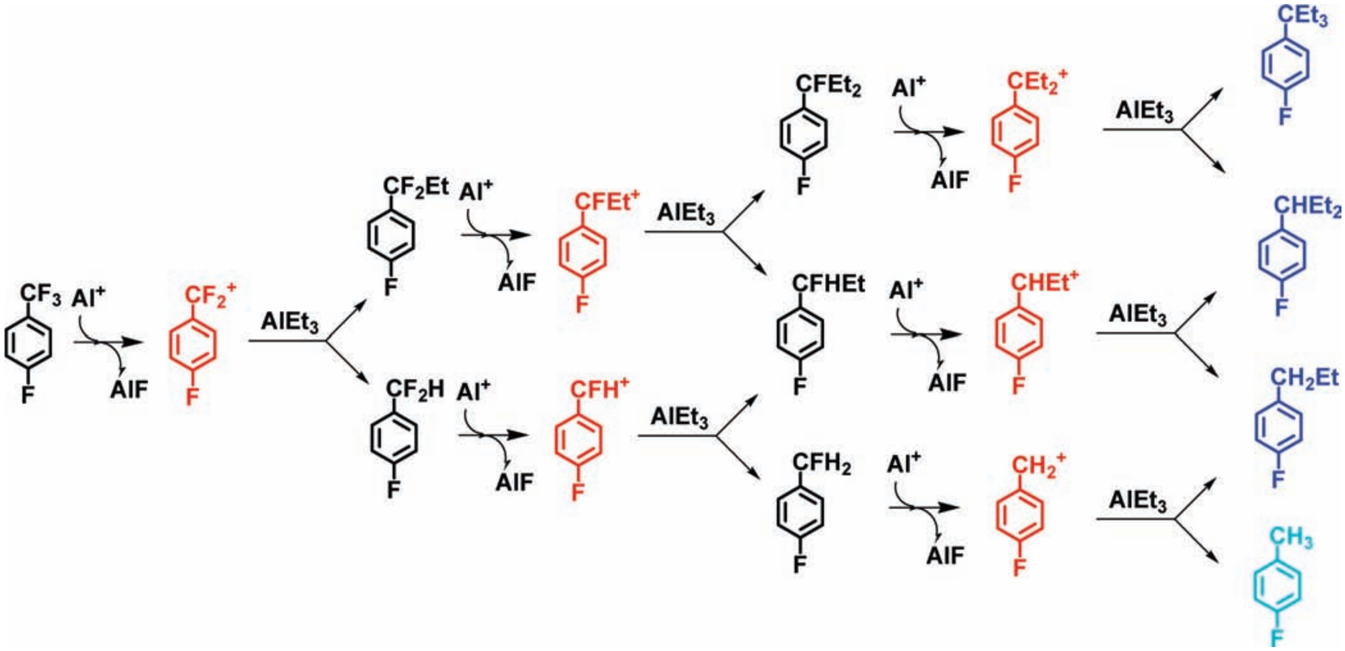
Scheme 3. Possible Routes To Generate Multiple Products in AlkDF Reactions with $AlEt_3$



plausible Al compounds are capable of alkyl/hydride transfer, the number of potential scenarios is difficult to digest. We can only proffer that sterics evidently play a part. The reactions between Et_3Al and benzotrifluorides do not produce $ArCH_3$. This is consistent with the preference for alkyl abstraction being greater for smaller carbocations and vice versa the hydride abstraction being favored for larger carbocations. In the synthesis of the catalyst **A** itself, Ph_3C^+ cation (a very sterically encumbered cation) was reported to react with Et_3Al via abstraction of β-hydride and release of ethylene.[15]

C−F activation appears to proceed faster in more polar solvents. A reaction that gives 93% conversion in 1 h in hexanes is complete in 10 min or less in *o*-dichlorobenzene (entries 2 and 6). We also found that introduction of the catalyst as a solution in $C_6H_4Cl_2$ (instead of a pure solid) to hexanes solutions led to a significant increase in rate. The reasons behind the solvent acceleration may be two-fold: (1) A more polar solvent may simply allow more of the catalyst to be dissolved or at least to be dissolved more rapidly. (2) A more polar solvent may lower the energy of the presumably polar transition state.

We found it possible to use **B** as the (pre)catalyst in place of isolated **A** in reactions with Et_3Al. The apparent rates of conversion were similar (cf. entries 7 and 9). The trityl salt **B** is presumably rapidly converted to **A** in the reaction mixture. The reaction between **B** and Me_3Al was much slower, and we did not use **B** as a (pre)catalyst in reactions with Me_3Al. In our Si-based HDF work, we demonstrated that $[B(C_6F_5)_4]^-$ can support some of the reactive cations involved; however, it is ultimately destroyed during the course of the reaction.[5,8] Rosenthal and Crossing recently reported HDF catalysis of primary alkyl fluorides and of $C_6H_5CF_3$ (**2**) using $^iBu_2AlH$ and **C** as a (pre)catalyst, but their results were limited to 20 turnovers or less.[14] In our hands, **C** gave better results in reactions of **1** with Et_3Al. In $C_6H_4Cl_2$, it supported a 300 TON reaction to completion. The advantage of **C** is that it is a commercially available reagent. However, in contrast to an analogous reaction with **A** (entry 2), in hexanes **C** supported a reaction only to a maximum of 50% conversion (entry 8). It is reasonable to posit that a carborane anion is superior to $[B(C_6F_5)_4]^-$ in the Al-based AlkDF for the same reasons as in the Si-based HDF chemistry, although $[B(C_6F_5)_4]^-$ appears to be more long lived in the Al process.

Activation of Nonbenzylic C−F Bonds. Activation of C−F bonds in benzylic positions should be easier to achieve if the rate-limiting step is the abstraction of fluoride and thus generation of a carbocation.[17] To extend the range of reactivity, we tested the potential of AlkDF on C−F bonds where the carbon is attached to an sp^3-hybridized carbon of an alkyl group instead. *gem*-Difluorocyclopentane (**6**) was easily and completely consumed using Et_3Al in $C_6H_4Cl_2$ with **A** as the catalyst (entry 22). Cyclopentane (33%) and ethylcyclopentane (67%) were the only two identified products (vide infra).

Reactions of $PhCH_2CH_2CF_3$ (**5**) led to more complex mixtures. We observed competitive cyclization to indane derivatives. Thus, with Me_3Al (entry 21), two products (**I** and **II**, Scheme 4) in a 68:32 ratio were observed by GC/MS. Scheme 5 depicts a possible Friedel−Crafts mechanism for the formation of **I**. It echoes our proposal for the Friedel−Crafts pathways in the Si-based reactions.[8] The key step is the intramolecular attack of a carbocation on the phenyl ring. Scheme 5, for the sake of argument, depicts this attack involving the RCF_2^+ cation (which would form upon the first fluoride abstraction). However, it is impossible to tell from the data in hand which of the possible carbocations get involved. In fact, the observation of **II** evinces that none of the formed cations *always* attack the phenyl ring. In reactions with Et_3Al (entry 20), in addition to the cyclization to indane, we observed the varied Et/H transfer (vide supra) as well. GC/MS analysis indicated formation of **III**, **IV**, and **V** (Scheme 4).

Reactions with **5** were slower than the analogous reactions with benzotrifluorides **1**−**3**. The lower apparent rate with **5** is consistent with the notion that an electronically average aryl group is a more stabilizing substituent for a carbocation than an alkyl group. The most challenging substrate that was activated

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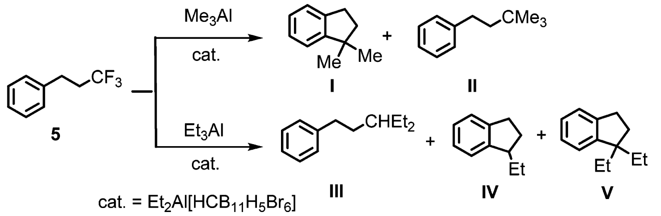
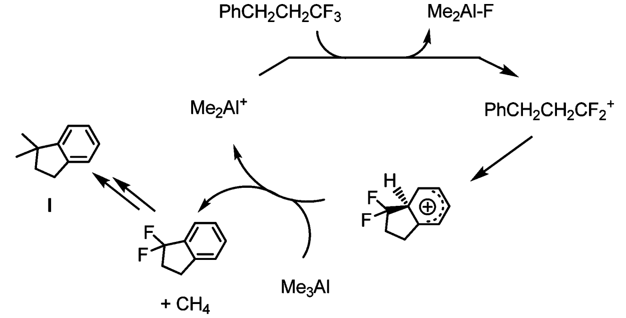
[17] It should be noted that the putative product of abstraction of fluoride from $ArCF_3$ is a *difluoro*benzyl cation, which is presumably less stable than the parent $ArCH_2^+$.

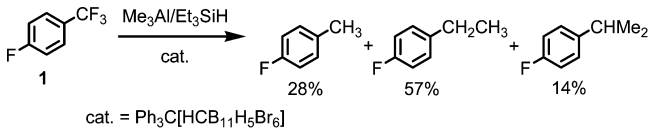
Scheme 4. Reactions of (3,3,3-Trifluoropropyl)benzene



Scheme 5. Possible Friedel−Crafts Mechanism for the Formation of **I**



Scheme 6. Competitive Reactions Involving Me_3Al and Et_3SiH



in the Si-catalyzed HDF,[8] nonafluorohexane ((perfluorobutyl)-ethane), did not react with Et_3Al and catalyst **A** at all.

Competitive Reaction with Et_3SiH and Me_3Al Reagents. We sought to test whether a silane hydride donor is competitive with an aluminum alkyl donor. A reaction of 1 equiv of substrate **1**, 3 equiv of Et_3SiH, 3 equiv of $AlMe_3$, and 0.01 equiv of of catalyst **B** in hexanes (entry 23, Table 1) resulted in complete consumption of **1** in 24 h and generation of a mixture of three products ($FC_6H_4CH_3$, $FC_6H_4CH_2Me$, $FC_6H_4CHMe_2$) in 28%, 57%, 14% yields, respectively (Scheme 6). Thus, 71% of the C−F bonds were converted to C−H bonds, and 29% of the C−F bonds were converted to C−C bonds. Mixing Et_3SiH and Me_3Al with or without catalyst **B** resulted in no change in the ^1H NMR spectrum after 24 h, indicating that there was no alkyl/hydride exchange between the Si and Al starting materials. However, only Al−F bonds (and no Si−F bonds) were observed upon the completion of the reaction, indicating that ligand exchange between Si and Al that involves fluoride can indeed occur. Because of this, although the hydrides transferred to C *ultimately* come from Si, we cannot ascertain whether all hydrides are transferred to C *directly* from Si. It is possible that hydrides are first transferred from Si to Al and only then to C. On the other hand, from the lack of *ethyl* transfer to C we can infer that alkyl transfer from Si to Al is negligible. Although the kinetic details remain obscured, this experiment shows that the hydride from Et_3SiH can be competitive with the Me from Me_3Al in replacing the F in C−F. The selectivity for a specific combination of hydride/alkyl transfer is low.

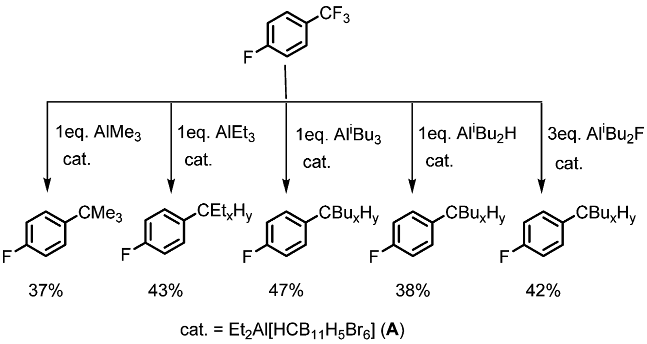
Efficiency of the Utilization of the R_3Al Reagent. The experiments in Table 1 employ the same number of moles of the R_3Al reagent as the number of moles of C−F bonds to be consumed (1:1 Al:F ratio and 3:1 R:F ratio). If only one alkyl (or hydride) group from each R_3Al can be transferred to the carbon of the C−F substrate, this is an equimolar ratio. We set out to test how many R groups can indeed participate. We performed several experiments (Table 2, Scheme 7) in which we used 1 equiv of R_3Al per molecule of **1**, in other words, one-third of the amount in experiments in Table 1 so that the Al:F ratio is 1:3 and the R:F ratio is consequently 1:1. If only one R group from each R_3Al were to be transferred, 33% C−F conversion would be observed. The actual C−F conversions ranged from 37% to 47%, corresponding to ca. 1.1−1.4 R groups from each R_3Al getting transferred (Table 2). Another corroborating data point (entry 5, Table 2) is the reaction with 3 equiv of $^iBu_2AlF$ per molecule of **1**. In this case, the conversion was 42%, or in other words, 0.14 ^iBu group from each $^iBu_2AlF$ was transferred. Since $^iBu_2AlF$ is the product of a transfer of one ^iBu group from $^iBu_3Al$, the results are roughly equivalent.

Table 2. AlkDF Reactions of **1** with a Deficiency of R_3Al in Hexanes

no.	catalyst loading[a] (%)	Al reagent	C−F conversion[b] (%)
A1	0.33	1 equiv of Me_3Al	37
A2	0.33	1 equiv of Et_3Al	43
A3	0.33	1 equiv of $^iBu_3Al$	47
A4	0.33	1 equiv of $^iBu_2AlH$	38
A5	0.33	3 equiv of $^iBu_2AlF$	42

[a] $Et_2Al[HCB_{11}H_5Br_6]$ (**A**) was used as the catalyst; the catalyst loading was calculated vs the number of C−F bonds. [b] Terminal conversion.

Scheme 7. AlkDF Reactions of **1** with a Deficiency of R_3Al in Hexanes



Tolerance of Water and Reactions with MAO. Unlike trialkylsilanes, trialkylaluminums can serve as “cleanup” agents in the reaction mixture. In an illustrative experiment (Scheme 8), a mixture containing Et_3Al and **1** (4:1 Al:F ratio) was first treated with water (0.2 equiv per F). Despite this, subsequent addition of catalyst **A** (0.01 equiv per F, 1/20 the amount of water) initiated a 300-turnover reaction that proceeded with 100% conversion. In the presence of an excess of Et_3Al water is converted to aluminoxanes, which are ostensibly not detrimental to the C−F activation. This observation caused us to consider methylaluminoxane (MAO or $(MeAlO)_n$). We found that commercial MAO (10 wt % in toluene) can effect C−F activation of **1**, even without a catalyst (Table 3, Scheme 8). Multiple equivalents of Al per **1** are required for complete conversion, presumably because of the “Me-poor” nature of MAO compared to Me_3Al.[18] MAO is an ill-defined mixture of oligomers that possesses high Lewis acidity. It is often used in

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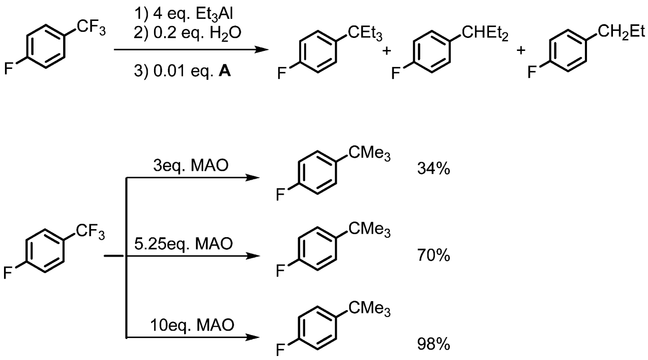
(18) Commercial MAO, however, has a higher than unity ratio of methyl groups to oxygens.

Table 3. AlkDF Reactions of **1** with MAO without Catalyst in Toluene

no.	aluminum reagent	C−F conversion[a] (%)
B1	3 equiv of MAO	34
B2	5.25 equiv of MAO	70
B3	10 equiv of MAO	98

[a] Terminal conversion, reached after 3 h.

Scheme 8. AlkDF Reactions of **1** with Addition of Water and AlkDF Reactions of **1** with MAO



olefin polymerization catalysis as an activator that alkylates the metal halide precursor and abstracts an anionic ligand.[19] The resultant highly electrophilic cationic olefin polymerization catalyst[20] is not unlike a silylium cation in its requirements toward a compatible anion. Since the "[MAO + X]$^-$" anion is adequate to support electrophilic olefin polymerization catalysts, the reactivity observed with MAO here is not surprising. The cleanup role of organoaluminum compounds is also acknowledged in the olefin polymerization chemistry.[19]

Uncatalyzed Reactions with Et_3Al. Terao et al. previously demonstrated that trialkylaluminum reagents can alkylate C−F bonds in primary alkyl fluorides without catalyst.[13] We tested 1-fluorodecane (**7**) and **1** in uncatalyzed AlkDF reactions with Et_3Al (Table 4, Scheme 9). The reactions are much slower than with an alumenium catalyst, and the reaction with **1** in hexanes at room temperature essentially does not proceed. Both substrates undergo defluorination faster in *o*-$C_6H_4Cl_2$. We also carried out an uncatalyzed reaction with **6**. It not only is much slower, but also results in a qualitatively different outcome, producing 24% 1-fluorocyclopentene as one of the products. The latter is an apparent product of formal HF loss[21] and is *not* observed in the defluorination of **6** with a catalyst. Notably, the C(sp^2)−F moiety in 1-fluorocyclopentene does not undergo further defluorination.

Conclusion

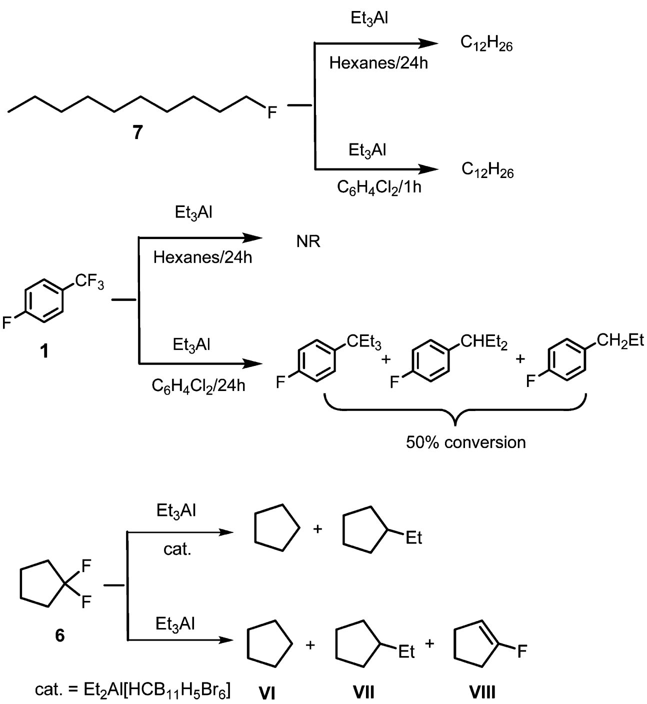
In summary, we have established that alumenium cation equivalent $Et_2Al[HCB_{11}H_5Br_6]$ (**A**) functions as an efficient and long-lived catalyst for Lewis acid C−F activation with trialkylaluminums as stoichiometric reagents. The reaction is very longevous, and turnover numbers of up to 10^4 have been achieved. The catalysis is specific for C(sp^3)−F bonds. Utilization of Me_3Al as the stoichiometric reagent results in the conversion of C−F bonds only to C−Me bonds. Utilization of Et_3Al, $^iBu_3Al$, or $^iBu_2AlH$ results in the competitive replacement of C−F bonds either with C−alkyl or with C−H. Although trialkylaluminum compounds can perform C−F activation without a catalyst for the more reactive substrates, the catalytic protocol results in much faster reactions, as well as improved selectivity. Conveniently, the process is tolerant of small quantities of water because trialkylaluminum compounds can act as cleanup agents in situ.

Table 4. AlkDF Reactions with Et_3Al Carried out without Catalyst

no.	substrate	solvent	C−F conversion[a] (%)	Al−F conversion[b] (%)
C1	**7**	hexanes	41 (100)	35 (93)
C2	**7**	$C_6H_4Cl_2$	100	92
C3	**1**	hexanes	0 (1)	0 (0)
C4	**1**	$C_6H_4Cl_2$	2 (55)	0 (44)

[a] Conversion after 3 h (after 24 h in parentheses) based on the disappearance of substrate C−F by ^{19}F NMR. [b] Conversion after 3 h (after 24 h in parentheses) based on the appearance of Al−F by ^{19}F NMR.

Scheme 9. AlkDF Reactions with Et_3Al without a Catalyst



Experimental Methods

Chemicals and Materials. Unless specified otherwise, all reactions were carried out under an argon atmosphere using glovebox or Schlenk line techniques. Hexanes and benzene were dried over NaK/Ph_2CO/18-crown-6, distilled, and stored over molecular sieves in a glovebox. C_6F_6, all the substrates, and all the haloarene solvents were purchased from Oakwood Products Inc. or Synquest Lab Inc., dried with CaH_2, and distilled under Ar or vacuum transferred and stored over molecular sieves in a glovebox. $Cs[HCB_{11}H_{11}]$ was purchased from Katchem (Czech Republic), and $Ph_3C[HCB_{11}H_5Br_6]$ and $Et_2Al[HCB_{11}H_5Br_6]$ were prepared from it via literature procedures.[15,22,23]

Physical Methods. NMR spectra were recorded on a Varian iNova 400 spectrometer (^{1}H NMR, 399.755 MHz; ^{19}F NMR,

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376.104 MHz) or a Varian iNova 500 spectrometer (^{11}B NMR, 160.5 MHz) in the noted solvents. Chemical shift are given in δ (ppm). ^{19}F NMR spectra were referenced externally with CCl_3F in $CDCl_3$ at δ −2.3. ^{11}B NMR spectra were referenced externally with BF_3 etherate at δ 0. GC/MS spectra were recorded on a Hewlett-Packard G 1800C GCD system (GCD plus gas chromatograph electron ionization detector) employing HP-5MS from Agilent Technologies (30 m (column length) × 0.25 mm (i.d.)) and 1227032 from J&W Scientific (30 m × 0.250 mm). Helium was used as a carrier gas. The following was a typical program for analyzing the products using the HP-5MS column: initial temperature 60 °C, increase the temperature at a rate of 20 °C/min until a final temperature of 240 °C, hold the temperature for 2 min at 240 °C. The solvent delay was 1.80 min.

Determination of the Al−F Products. The reactions described herein produce Al byproducts. These are primarily of the stoichiometry R_2AlF. It is likely that the mixture contains a mixture of various dimers and possibly oligomers $R_{3-x}AlF_x$. These mixtures give rise to one or more broad resonances in the ^{19}F NMR spectra in the −145 to −160 ppm range. The spectra obtained in our reactions bear close resemblance to the ^{19}F NMR spectrum of commercial $^{i}Bu_2AlF$ (Aldrich) (see the details in the Supporting Information (SI)).

Calibration of ^{19}F NMR. The disappearance of the C−F bonds and the appearance of Al−F bonds was measured vs the C_6F_6 internal standard. In each experiment, the initial (0% conversion or 100% starting material) intensity of the signal of the starting material vs the intensity of the C_6F_6 signal was recorded *before* the addition of the catalyst. As with any NMR integration-based method, errors on the order of 5−10% should be assumed. The relationship between the intensity of the C−F bonds in substrates and in C_6F_6 appears to be essentially the same within errors of measurement. To quantify the relationship between the integration values and concentrations involving Al−F bonds, we performed a calibration using commercial $^{i}Bu_2AlF$ and C_6F_6 (see the details in the SI). It demonstrated that the ^{19}F NMR intensity of 1 mol of C_6F_6 is equal to the ^{19}F NMR intensity of 4.2 mol of Al−F bonds under the parameters of our ^{19}F NMR experiments.

Entry 1. A 40 μL (315 μmol) volume of substrate **1** was mixed with 475 μL (950 μmol) of trimethylaluminum (2 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): p-$FC_6H_4CMe_3$, 94%.

Entry 2. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 18%; $FC_6H_4CHEt_2$, 61%; $FC_6H_4CEt_3$, 15%.

Identification and Quantification of Products in the Reaction of Et_3Al and p-$FC_6H_4CF_3$ (1) by ^{1}H NMR (Analogous to Entry 2). A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of Et_3Al, 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in 0.5 mL of C_6D_{12} in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixture was allowed to stay at room temperature for 24 h. The reaction was monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). After hydrolyzation of the organoaluminum compounds, the mixture was dissolved in $CDCl_3$ for further analysis. Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 18%; $FC_6H_4CHEt_2$, 62%; $FC_6H_4CEt_3$, 13%.

Entry 3. A 40 μL (315 μmol) volume of substrate **1** was mixed with 950 μL (950 μmol) of $^{i}Bu_3Al$ (1 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). The ratio of products in GC/MS is 55:45 $FC_6H_4CHC_8H_{18}$:F−C_6H_4−$CC_{12}H_{27}$.

Entry 4. A 40 μL (315 μmol) volume of substrate **1** was mixed with 820 μL (950 μmol) of $^{i}Bu_2AlH$ (1.16 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_3$, 58%; $FC_6H_4CH_2C_4H_9$, 32%.

Entry 5. A 120 μL (945 μmol) volume of p-$C_6H_4CF_3$ was mixed with 390 μL (2852 μmol) of triethylaluminum, 15.0 μL (129 μmol) of C_6F_6, and 21 μL of a $Et_2Al[HCB_{11}H_5Br_6]$ stock solution which was made by dissolving 10 mg of $Et_2Al[HCB_{11}H_5Br_6]$ in 1 mL of o-dichlorobenzene (0.21 mg, 0.29 μmol) in 1.5 mL of hexanes in a 10 mL glass vial. A clear solution was formed. The mixture was stirred at room temperature for 24 h. The reaction was monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 19%; $FC_6H_4CHEt_2$, 66%; $FC_6H_4CEt_3$, 13%.

Entry 6. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed. A dramatic elevation of temperature was observed at the beginning of the reaction. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2C_6H_3Cl_2$, 10%; $FC_6H_4CH_2CH_2CH_3$, 8%; $FC_6H_4CHEt_2$, 46%; $FC_6H_4CEt_3$, 30%.

Entry 7. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of C_6F_6, and 2.7 mg (3.2 μmol) of $Ph_3C[HCB_{11}H_5Br_6]$ in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 15%; $FC_6H_4CHEt_2$, 52%; $FC_6H_4CEt_3$, 11%.

Entry 8. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of C_6F_6, and 2.9 mg (3.2 μmol) of $Ph_3C[B(C_6F_5)_4]$ in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$\mathrm{FC_6H_4C}F_3$), −110.1 (p-$F\mathrm{C_6H_4CF_3}$)). Yield (based on ^{19}F NMR, after 24 h): $\mathrm{FC_6H_4CH_2CH_2CH_3}$, 8%; $\mathrm{FC_6H_4CHEt_2}$, 28%; $\mathrm{FC_6H_4CEt_3}$, 6%.

Entry 9. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 2.7 mg (3.2 μmol) of $\mathrm{Ph_3C[HCB_{11}H_5Br_6]}$ in a J. Young tube. A colorless solution was formed. A dramatic elevation of temperature was observed at the beginning of the reaction. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$\mathrm{FC_6H_4C}F_3$), −110.1 (p-$F\mathrm{C_6H_4CF_3}$)). Yield (based on ^{19}F NMR, after 24 h): $F\mathrm{C_6H_4CH_2CH_2CH_3}$, 8%; $F\mathrm{C_6H_4CHEt_2}$, 51%; $F\mathrm{C_6H_4CEt_3}$, 32%.

Entry 10. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 2.9 mg (3.2 μmol) of $\mathrm{Ph_3C[B(C_6F_5)_4]}$ in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$\mathrm{FC_6H_4C}F_3$), −110.1 (p-$F\mathrm{C_6H_4CF_3}$)). Yield (based on ^{19}F NMR, after 24 h): $F\mathrm{C_6H_4CH_2CH_2CH_3}$, 8%; $F\mathrm{C_6H_4CHEt_2}$, 48%; $F\mathrm{C_6H_4CEt_3}$, 29%.

Entry 11. A 40 μL (326 μmol) volume of substrate **2** was mixed with 135 μL (987 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 2.3 mg (3.3 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ in 0.5 mL of hexanes in a J. Young tube. A colorless solution with a small amount of precipitate was formed. An elevation of temperature was observed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −66.1 ($\mathrm{C_6H_5C}F_3$)). The ratio of products in GC/MS is 16:66:18 $\mathrm{C_6H_5CH_2CH_2CH_3}$:$\mathrm{C_6H_5CHEt_2}$:$\mathrm{C_6H_5{-}CEt_3}$.

Entry 12. A 40 μL (300 μmol) volume of substrate **3** was mixed with 125 μL (914 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 2.1 mg (3.0 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ in 0.5 mL of hexanes in a J. Young tube. A colorless solution with a small amount of precipitate was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −66.0 ($\mathrm{ClC_6H_4C}F_3$). The ratio of products in GC/MS is 7:71:21 $\mathrm{ClC_6H_4CH_2CH_2CH_3}$:$\mathrm{ClC_6H_4CHEt_2}$:$\mathrm{ClC_6H_4CEt_3}$.

Entry 13. A 40 μL (315 μmol) volume of substrate **1** was mixed with 130 μL (950 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 66 μL of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (predissolved in o-dichlorobenzene, 1 mg/30 μL, 3.2 μmol) in a J. Young tube. A colorless solution was formed. A dramatic elevation of temperature was observed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$\mathrm{FC_6H_4C}F_3$), −110.1 (p-$F\mathrm{C_6H_4CF_3}$). Yield (based on ^{19}F NMR, after 24 h): $\mathrm{FC_6H_4CH_2CH_2CH_3}$, 13%; $\mathrm{FC_6H_4CHEt_2}$, 77%; $\mathrm{FC_6H_4CEt_3}$, 7%.

Entry 14. A 40 μL (326 μmol) volume of substrate **2** was mixed with 135 μL (987 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 70 μL of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (predissolved in o-dichlorobenzene, 1 mg/30 μL, 3.3 μmol) in a J. Young tube. A colorless solution was formed. A dramatic elevation of temperature was observed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −66.1 ($\mathrm{C_6H_5C}F_3$)). The ratio of products in GC/MS is 14:71:15 $\mathrm{C_6H_5CH_2CH_2CH_3}$:$\mathrm{C_6H_5CHEt_2}$:$\mathrm{C_6H_5CEt_3}$.

Entry 15. A 40 μL (300 μmol) volume of substrate **3** was mixed with 125 μL (914 μmol) of triethylaluminum, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 62 μL of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (predissolved in o-dichlorobenzene, 1 mg/30 μL, 3 μmol) in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −66.0 ($\mathrm{ClC_6H_4C}F_3$)). The ratio of products in GC/MS is 13:68:19 $\mathrm{ClC_6H_4CH_2CH_2CH_3}$:$\mathrm{ClC_6H_4CHEt_2}$:$\mathrm{ClC_6H_4CEt_3}$.

Entry 16. Five solutions containing $\mathrm{C_6H_5CMe_3}$ and $\mathrm{C_6H_5Br}$ in different ratios were prepared and analyzed by GC/MS. Integration of the corresponding peaks in the resulting chromatogram gave the coefficient as 1.029 (see the details in the SI). The reaction (entry 17) was set up using 40 μL (326 μmol) of substrate **2** with 2.3 mg (3.3 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 490 μL of $\mathrm{AlMe_3}$ (980 μmol, 2 M in hexanes) in 0.5 mL of hexanes. After 36 h, ^{19}F NMR indicated that 94% of C−F was converted. A 60 μL (572 μmol) volume of bromobenzene was added to the reaction mixture, and the mixture was filtered through Celite, diluted by hexanes, and analyzed by GC/MS. Integration of the resulting chromatogram gave a ratio of 0.48:1.00 corresponding to the formation of 283 (0.48 × 1.029 × 572) μmol of $\mathrm{C_6H_5CMe_3}$. Yield: 87%.

Entry 17. A 40 μL (280 μmol) volume of substrate **4** was mixed with 115 μL (840 μmol) of $\mathrm{AlEt_3}$, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 11.8 mg (16.8 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ in a J. Young tube. A clear solution was formed. The mixture was heated at 85 °C for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −58.9 ($\mathrm{C_6F_5CC}F_3$), −142.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −149.8 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −162.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$)). The ratio of products in GC/MS is 31:61:8 $\mathrm{C_6F_5CH_2CH_2CH_3}$:$\mathrm{C_6F_5CHEt_2}$:$\mathrm{C_6F_5CEt_3}$.

Entry 18. A 40 μL (280 μmol) volume of substrate **4** was mixed with 420 μL (840 μmol) of $\mathrm{AlMe_3}$ (2 M in hexanes), 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 360 μL (16.8 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (1 mg/30 μL of o-dichlorobenzene) in a J. Young tube. A clear solution was formed. The mixture was heated at 85 °C for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −58.9 ($\mathrm{C_6F_5CC}F_3$), −142.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −149.8 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −162.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$)). Yield (based on ^{19}F NMR, after 24 h): $\mathrm{C_6}F_5\mathrm{CMe_3}$, 84%.

Entry 19. A 40 μL (280 μmol) volume of substrate **4** was mixed with 420 μL (840 μmol) of $\mathrm{AlMe_3}$ (2 M in hexanes), 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 60 μL (2.8 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (1 mg/30 μL of o-dichlorobenzene) in a J. Young tube. A clear solution was formed. The mixture was heated at 85 °C for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −58.9 ($\mathrm{C_6F_5CC}F_3$), −142.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −149.8 ($\mathrm{C_6}F_5\mathrm{CCF_3}$), −162.4 ($\mathrm{C_6}F_5\mathrm{CCF_3}$)). Yield (based on ^{19}F NMR, after 24 h): $\mathrm{C_6}F_5\mathrm{CMe_3}$, 38%.

Entry 20. A 40 μL (260 μmol) volume of substrate **5** was mixed with 110 μL (804 μmol) of $\mathrm{AlEt_3}$, 5.0 μL (43 μmol) of $\mathrm{C_6F_6}$, and 1.8 mg (2.6 μmol) of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ in a J. Young tube. A clear solution was formed. The mixture was heated at 50 °C for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −70.2 ($\mathrm{C_6H_5CH_2CH_2C}F_3$). The ratio of products in GC/MS is 34:30:36 $\mathrm{C_6H_4C_5H_{10}}$:$\mathrm{C_6H_4C_7H_{14}}$:$\mathrm{C_6H_5C_7H_{15}}$.

Entry 21. A 40 μL (260 μmol) volume of substrate **5** was mixed with 390 μL (780 μmol) of $\mathrm{AlMe_3}$ (2 M in hexanes), 5.0 μL (43 μmol) of $\mathrm{C_{6}F_{6,\ and}}$ 54 μL of $\mathrm{Et_2Al[HCB_{11}H_5Br_6]}$ solution (predissolved in o-dichlorobenzene, 1 mg/30 μL, 2.6 μmol) in a J. Young tube. A clear solution was formed. The mixture was heated at 50 °C for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −70.2 ($C_6H_5CH_2CH_2CF_3$). The ratio of products in GC/MS is 68:32 $C_6H_4C_5H_{10}$:$C_6H_5C_6H_{13}$.

Entry 22. A 40 μL (450 μmol) volume of substrate **6** was mixed with 125 μL (914 μmol) of $AlEt_3$, 5.0 μL (43 μmol) of C_6F_6, and 1.6 mg (2.3 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in *o*-$C_6H_4Cl_2$ in a J. Young tube. An orange-colored solution formed. A dramatic elevation of temperature was observed. The mixture was allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −94.8 ($CF_2C_4H_8$). The ratio of products in GC/MS is 33:67 cyclopentane:ethylcyclopentane.

Entry 23. A 40 μL (315 μmol) volume of **1** was mixed with 90 μL (940 μmol) of Me_3Al, 150 μL (940 μmol) of Et_3SiH, 5.0 μL (43 μmol) of C_6F_6, and 2.7 mg (3.2 μmol) of $Ph_3C[HCB_{11}H_5Br_6]$ in 0.4 mL of hexanes in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). The ratio of products in GC/MS is 28:57:14 $FC_6H_4CH_3$:$FC_6H_4CH_2Me$:$FC_6H_4CHMe_2$.

Reaction of 6 with AlEt$_3$ without Catalyst. A 40 μL (450 μmol) volume of substrate **6** was mixed with 155 μL (900 μmol) of $AlEt_3$ and 5.0 μL (43 μmol) of C_6F_6 in 0.3 mL of C_6D_{12} in a J. Young tube. An orange-colored solution formed. The mixture was allowed to stay at room temperature for 24 h. The reaction was monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −94.8 ($CF_2C_4H_8$). Yield (based on ^{19}F NMR, after 24 h): 1-fluorocyclopentene, 24%.

Entry A1. A 40 μL (315 μmol) volume of substrate **1** was mixed with 160 μL (320 μmol) of Me_3Al (2 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in hexanes in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixtures were allowed to stay at room temperature for 5 d. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). Maximum conversion of C−F bond was reached after 3 d. Yield (based on ^{19}F NMR, after 3 d): *p*-$FC_6H_4CMe_3$, 30%.

Entry A2. A 40 μL (315 μmol) volume of substrate **1** was mixed with 45 μL (329 μmol) of Et_3Al, 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in hexanes in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixtures were allowed to stay at room temperature for 5 d. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). Maximum conversion of C−F bond was reached after 3 d. Yield (based on ^{19}F NMR, after 3 d): $FC_6H_4CH_2CH_2CH_3$, 4%; $FC_6H_4CHEt_2$, 18%; $FC_6H_4CEt_3$, 6%.

Entry A3. A 40 μL (315 μmol) volume of substrate **1** was mixed with 315 μL (315 μmol) of $^iBu_3Al$ (1 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in hexanes in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixtures were allowed to stay at room temperature for 5 d. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). Maximum conversion of C−F bonds was reached after 3 d. The ratio of products in GC/MS is 54:25:20 $FC_6H_4CF_3$:$FC_6H_4CHC_8H_{18}$:$FC_6H_4CC_{12}H_{27}$.

Entry A4. A 40 μL (315 μmol) volume of substrate **1** was mixed with 275 μL (319 μmol) of $^iBu_2AlH$ (1.16 M in hexanes), 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.2 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in hexanes in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixtures were allowed to stay at room temperature for 5 d. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). Maximum conversion of C−F bond was reached after 3 d. Yield (based on ^{19}F NMR, after 3 d): $FC_6H_4CH_3$, 20%; $FC_6H_4CH_2C_4H_9$, 13%.

Entry A5. A 40 μL (315 μmol) volume of substrate **1** was mixed with 950 μL (950 μmol, 1 M in hexanes) of $^iBu_2AlF$, 5.0 μL (43 μmol) of C_6F_6, and 2.2 mg (3.15 μmol) of $Et_2Al[HCB_{11}H_5Br_6]$ in hexanes in a J. Young tube. A colorless solution was formed. A small amount of precipitate was observed. The mixture was allowed to stay at room temperature for 5 d. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)). Maximum conversion of C−F bond was reached after 3 d. The ratio of products in GC/MS is 57:15:14:14 $FC_6H_4CF_3$:$FC_6H_4CH_2C_4H_9$:$FC_6H_4CH_2C_4H_9$ (isomer):$FC_6H_4CHC_8H_{18}$.

Entry B1. A 20 μL (157 μmol) volume of substrate **1** was mixed with 470 μL (470 μmol) of methylaluminoxane (1 M in toluene) and 5.0 μL (43 μmol) of C_6F_6 in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 3 d or until no changes could be observed by ^{19}F NMR. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)).

Entry B2. A 20 μL (157 μmol) volume of substrate **1** was mixed with 820 μL (820 μmol) of methylaluminoxane (1 M in toluene) and 5.0 μL (43 μmol) of C_6F_6 in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 3 d or until no changes could be observed by ^{19}F NMR. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)).

Entry B3. A 20 μL (157 μmol) volume of substrate **1** was mixed with 1570 μL (1570 μmol) of methylaluminoxane (1 M in toluene) and 5.0 μL (43 μmol) of C_6F_6 in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 3 d or until no changes could be observed by ^{19}F NMR. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (*p*-$FC_6H_4CF_3$), −110.1 (*p*-$FC_6H_4CF_3$)).

Entry C1. A 40 μL volume of $^nC_{10}H_{21}F$ (200 μmol) was mixed with 28 μL (200 μmol) of triethylaluminum and 5.0 μL (43 μmol) of C_6F_6 in hexanes in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −220.6 ($F(CH_2)_9CH_3$)).

Entry C2. A 40 μL volume of **7** (200 μmol) was mixed with 28 μL (200 μmol) of triethylaluminum and 5.0 μL (43 μmol) of C_6F_6 in $C_6H_4Cl_2$ in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −220.6 ($F(CH_2)_9CH_3$)).

Entry C3. A 40 μL volume of **1** (200 μmol) was mixed with 130 μL (950 μmol) of triethylaluminum and 5.0 μL (43 μmol) of C_6F_6 in hexanes in a J. Young tube. A colorless solution was formed with a small amount of precipitate. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). No product was detected by ^{19}F NMR or GC/MS.

Entry C4. A 40 μL volume of **1** (200 μmol) was mixed with 130 μL (950 μmol) of triethylaluminum and 5.0 μL (43 μmol) of C_6F_6 in $C_6H_4Cl_2$ in a J. Young tube. A colorless solution was formed. The mixtures were allowed to stay at room temperature for 24 h. The reactions were monitored by detecting the increase in the intensity of the ^{19}F NMR resonance of Al−F and decrease in the intensity of the ^{19}F NMR resonance of F substrates (δ −65.3 (p-$FC_6H_4CF_3$), −110.1 (p-$FC_6H_4CF_3$)). Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 3%; $FC_6H_4CHEt_2$, 12%; $FC_6H_4CEt_3$, 30%.

Reaction in "Wet" Solvent. A 1 μL volume of H_2O (56 μmol) was added to 40 μL of 4-fluorobenzotrifluoride (315 μmol), 170 μL of triethylaluminum (1243 μmol), and hexafluorobenzene (5.0 μL, 43 μmol) in 0.5 mL of hexanes in a Schlenk flask under a flow of argon. $Et_2Al[HCB_{11}H_5Br_6]$ (2.2 mg, 3.2 μmol) was added to the mixture, after it was stirred at room temperature for 6 h. ^{19}F NMR spectra were recorded every hour to monitor the reaction. A 100% conversion of C−F was reached in 6 h. Yield (based on ^{19}F NMR, after 24 h): $FC_6H_4CH_2CH_2CH_3$, 20%; $FC_6H_4CHEt_2$, 58%; $FC_6H_4CEt_3$, 15%.

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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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