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Main-Group Lewis Acids for C−F Bond Activation

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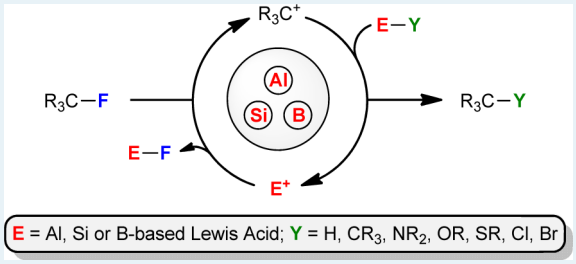
ABSTRACT: The significant benefits of fluorinated compounds have inspired the development of diverse techniques for the activation and subsequent (de)functionalization of rather inert C−F bonds. Although substantial progress has been made in the selective activation of C(sp^2)−F bonds employing transition metal complexes, protocols that address nonactivated C(sp^3)−F bonds are much less established. In this regard, the use of strong main-group Lewis acids has emerged as a powerful tool to selectively activate C(sp^3)−F bonds in saturated fluorocarbons. This Perspective provides a concise overview of various cationic and neutral silicon-, boron-, and aluminum-based Lewis acids that have been identified to facilitate the heterolytic fluoride abstraction from aliphatic fluorides. The potential of these Lewis acids in hydrodefluorination as well as defluorinative C−F bond functionalization reactions is highlighted. Emphasis is placed on the underlying mechanistic principles to provide a systematic classification of the individual reactions. Finally, brief insight into the related C−F bond activation chemistry using carbocations or Brønsted acids is presented.



KEYWORDS: *C−F bond activation, C−F bond functionalization, fluorine, homogeneous catalysis, hydrodefluorination, main-group Lewis acids*

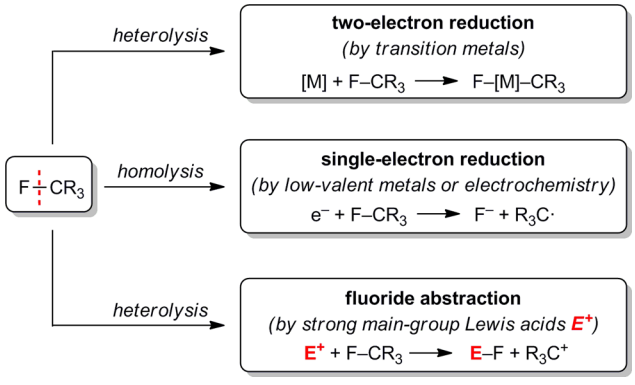
INTRODUCTION

The importance of the C−F bond is reflected in the extensive use of fluorinated building blocks in diverse areas of synthetic chemistry, including materials science, polymer chemistry, crop protection, and drug discovery.[1−4] The high demand for organofluorine compounds is mainly attributed to the unique nature of the C−F bond, which is characterized by the small size (r_W = 1.47 Å) and high electronegativity (χ = 4) of the fluorine atom, resulting in a short, highly polar C−F bond with low polarizibility.[5] These features make the C−F bond the strongest covalent single bond (105 kcal·mol^{-1}) that carbon forms with any element. In addition to the thermodynamic stability, kinetic issues account for the notorious inertness of C−F bonds, with the fluorine being neither a good Lewis base nor a good leaving group.

Although the chemical robustness is among the reasons why fluorinated compounds have found widespread applications, it is the same strong and unreactive C−F bond that makes these molecules extremely long-lived and potentially toxic. The role of fluorinated hydrocarbons as greenhouse gases and, as such, their contribution to global warming is generally accepted.[6] Fluorochlorocarbons have even been found to deplete the ozone layer, and no practical large-scale procedure for their disposal exists.[7] In light of the environmental concerns associated with organofluorine compounds, the development of novel synthetic methods for the activation of C−F bonds is of vital importance. Aside from the simple degradation of fluorinated molecules, protocols for the selective functionalization of C−F bonds would allow for the synthesis of partially fluorinated synthetic intermediates from readily available per- or oligofluorinated starting materials.

Among the various methods known for C−F bond activation (Scheme 1),[8] substantial progress has been made employing

Scheme 1. General Strategies for the Activation of C−F Bonds



transition metals for C−F bond cleavage.[9−17] This approach typically relies on the reductive heterolysis of the C−F bond through oxidative addition of the C−F bond to an electron-rich metal center (Scheme 1, upper). Alternative protocols involve the homolytic splitting of C−F bonds via a single-electron transfer process mediated either by low-valent metals[18] or electrochemically[19−21] (Scheme 1, center). While the latter method is applicable to both C(sp^2)−F and C(sp^3)−F bonds,

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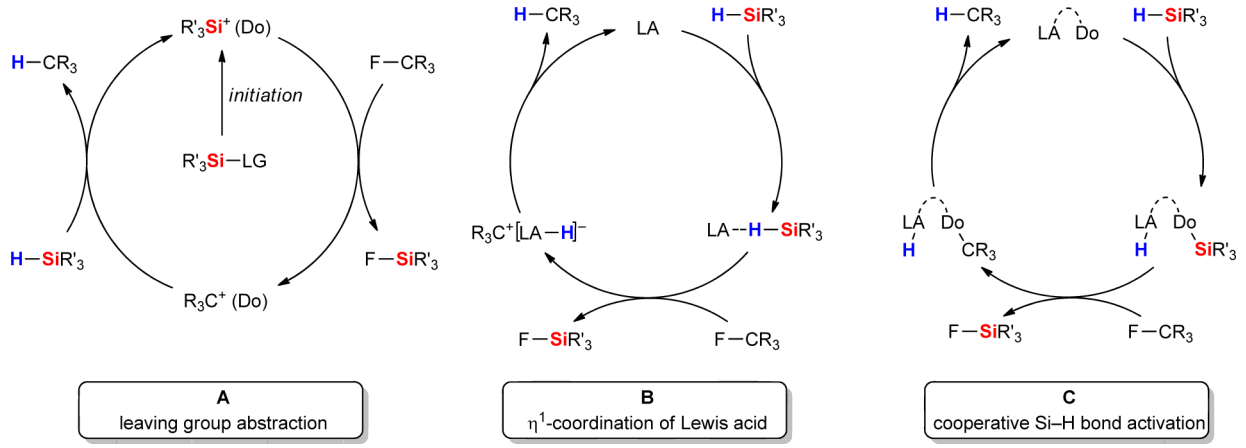
Scheme 2. Different Approaches to the Generation of the Main-Group Lewis Acid for Catalytic C−F Bond Activation



transition metal-mediated C−F bond activation provides a reliable tool for not only chemoselective but also catalytic transformations.[9−17] The substrate scope, however, is mainly limited to the more activated C(sp^2)−F bond of aromatic and vinylic fluorocarbons, and only a few exceptions exist.[22−24] On the other hand, catalytic procedures for the selective activation of aliphatic C(sp^3)−F bonds and, in particular, the functionalization of unreactive perfluorinated alkyl groups such as the aryl trifluoromethyl group had not been known for a long time.[8] In recent years, C−F bond activation using main-group Lewis acids has emerged as a promising, conceptually novel strategy to selectively activate C−F bonds in saturated fluorocarbons (Scheme 1, lower). In this unconventional approach, the C−F bond-breaking event proceeds through heterolytic abstraction of the fluoride anion by a strong Lewis acid rather than by involving a redox process.

Hydrodefluorination. The simplest transformation of C−F bonds is hydrodefluorination (HDF), that is, the replacement of fluoride by hydride. Because of the strength of the C−F bond and the resulting high activation barrier of the C−F bond heterolysis, an exceptionally potent Lewis acid with high fluoride affinity is required. The covalent formation of the more stable main-group element−fluorine bond is considered to be the thermodynamic driving force for the overall transformation. The implementation of catalytic variants therefore implies that the active Lewis acid must be regenerated in a subsequent step to maintain turnover. Conventional main-group element-based compounds are generally not sufficiently reactive to mediate the heterolytic cleavage of the inert C−F bond, and preactivation is required to increase the Lewis acidity.

Contingent on the activation mode, three elementary catalytic cycles might be distinguished, as exemplified by the catalytic HDF using silicon-based electrophiles (Scheme 2). In the first scenario (mechanism A), a highly Lewis acidic silicon cation is generated from a suitable precursor by heterolytic leaving group (LG) abstraction. The cationic silicon intermediate is able to cleave the C−F bond in R_3C−F, forming a carbenium ion and a fluorosilane. Subsequent hydride transfer from a hydrosilane as the stoichiometrically added hydride source to the carbenium ion affords the hydrodefluorinated target molecule and regenerates the silylium ion catalyst. The reactivity of the cationic silicon electrophile is dramatically influenced by the presence of electron donors (denoted as Do), essentially almost any σ and π basic molecule, including solvents or counteranions. As a consequence, strongly coordinating Lewis bases and any irreversible Lewis pair formation must be avoided.

The second scenario (mechanism B) relies on the activation of the fluorophilic electrophile by another Lewis acid (LA). Although the exact coordination mode often remains unclear, η^1-coordination of the silane is expected to be a more potent source of electrophilic silicon than an η^2-based σ-complex. While no positive charge is developed at the silicon atom, the thus-activated silane is now sufficiently electrophilic to abstract fluoride from R_3C−F with release of a carbenium ion and a Lewis acid-stabilized hydride that then acts as the hydride transfer reagent.

In a third scenario (mechanism C), the hydrosilane is cooperatively activated by a Lewis acid and a Lewis base (Do), also referred to as a frustrated Lewis pair (FLP),[25] resulting in a donor-stabilized silicon cation and a Lewis acid-coordinated hydride. Subsequent fluoride abstraction and generation of a donor-stabilized carbenium ion is followed by an intramolecular hydride transfer, thereby closing the catalytic cycle. All three approaches share a catalytically active silicon Lewis acid capable of fluoride abstraction that is regenerated by hydride transfer to an intermediate carbenium ion. The hydrosilane is beneficial in a dual way, serving as the catalyst precursor as well as the hydride source.

In the following section, a survey of various main-group Lewis acids organized by the element (silicon, aluminum, and boron) and its application in the HDF of aliphatic C−F bonds is presented.

Silicon Electrophiles. Silicon electrophiles are particularly attractive for C−F bond activation because these are known to combine both Lewis acidity and fluoride affinity. In this regard, silylium ions, which are tricoordinate silicon cations (R_3Si^+), are extremely strong Lewis acids, reacting with almost any σ and π basic molecule.[26−29] The potential of these electron-deficient compounds to readily abstract fluoride from fluorocarbons was demonstrated by the Ozerov group when these authors disclosed the catalytic HDF of C(sp^3)−F bonds at room temperature (Scheme 3).[30,31] The active silylium ion catalyst $R_3Si^+X^-$ is conveniently prepared in situ by abstraction of a hydride from a hydrosilane with the requisite trityl salt $Ph_3C^+X^-$ (X^- = weakly coordinating anion). The efficiency of the catalysis is highly dependent on the nature of the counteranion. Initially, Ozerov and co-workers employed $[B(C_6F_5)_4]^-$ as the weakly coordinating anion but identified its decomposition by the silicon cation to limit TONs. The

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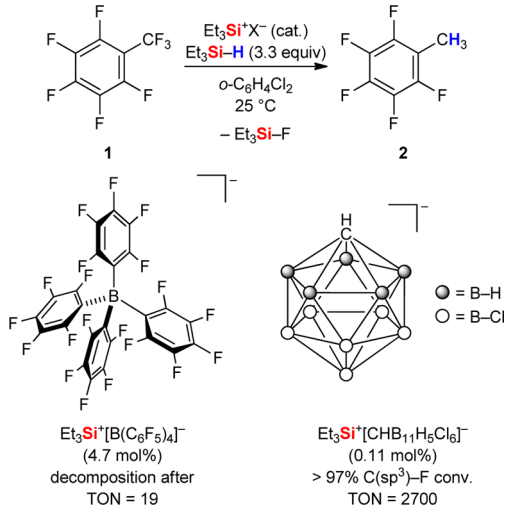
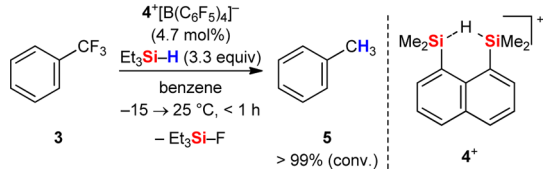
Scheme 3. Pronounced Counteranion Effect in the Silylium Ion-Catalyzed HDF



choice of halogenated carboranes as supporting counteranions then led to a dramatically enhanced protocol for the catalytic HDF of C(sp^3)−F bonds.[32−34] Using silylium−carborane catalyst $Et_3Si^+[CHB_{11}H_5Cl_6]^-$, perfluorinated toluene (**1**) was converted to pentafluorotoluene (**2**) with excellent chemoselectivity and unprecedented TONs of ≤2700! According to mechanism A (Scheme 2), these catalytic HDF reactions proceed via silylium ion-mediated fluoride abstraction followed by hydride transfer to the intermediate carbenium ion from a triorganosilane added as the stoichiometric hydride source. The overall process, a formal Si−H/C−F metathesis, is thermodynamically favorable, as Si−F bonds are stronger than C−F bonds and C−H bonds are stronger than Si−H bonds.

In a similar manner, Müller and co-workers reported an elegant HDF in which the hydride-bridged disilyl cation 4^+ acts as the catalyst (Scheme 4).[35] Cation 4^+ combines the silicon

Scheme 4. Catalytic HDF with a Hydride-Bridged Disilyl Cation



electrophile and the hydride source in the same molecule. Stabilized in the form of its $[B(C_6F_5)_4]^-$ salt, catalytic amounts of 4^+ facilitate the full conversion of trifluoromethyl benzene (**3** → **5**) and 1-fluorodecane (not shown) into the corresponding defluorinated hydrocarbons under mild reaction conditions, yet with moderate TONs of ≤45.

Not only cationic tricoordinate silicon electrophiles[36] but also neutral tetracoordinate organosilicon compounds have proven to be useful in C−F bond activation. In this case, however, an initial activation to further increase the Lewis acidity of the silicon atom is essential. A remarkable approach for generating potent silicon electrophiles is the electrophilic activation of hydrosilanes by another strong Lewis acid, either a main-group Lewis acid or a cationic transition metal complex (mechanism B, Scheme 2). As demonstrated by the following contributions, these methods lead to highly electro- and fluorophilic silicon intermediates capable of abstracting fluoride from C(sp^3)−F bonds.

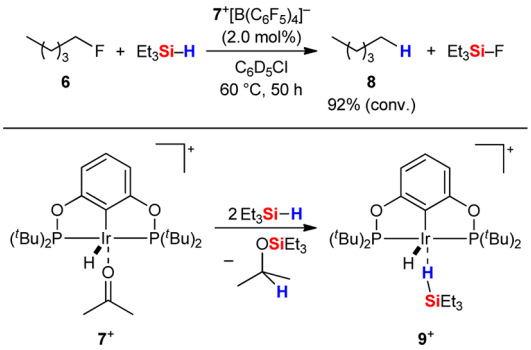
In an early example, Vol'pin and co-workers reported the chemoselective HDF of the trifluoromethyl group in **1** by treatment with triethylsilane in the presence of $AlCl_3$ (Scheme 5).[37] Although an overstoichiometric amount of the aluminum

Scheme 5. Chemoselective HDF of Perfluorinated C(sp^3)−F Bonds

Lewis acid had to be employed,[38] this simple reaction setup led to complete conversion of the C(sp^3)−F bonds already at room temperature, whereas the C(sp^2)−F bonds remained untouched. The mechanism of this HDF is still a matter of debate. It is assumed that $AlCl_3$-mediated F−Cl exchange[39] is followed by the hydrogenolysis of the resulting C−Cl bond. It cannot be ruled out, though, that the hydrosilane is activated by $AlCl_3$, thereby generating the fluorophilic silicon electrophile that is operative in the C−F bond cleavage. Fluoride abstraction and hydride transfer may as well occur by a concerted reaction pathway but, more likely, through a two-step mechanism involving carbenium ion-like intermediates prior to the reduction step (cf. mechanism B, Scheme 2).[40]

A few years ago, the laboratory of Brookhart introduced cationic iridium(III) hydride pincer complex 7^+ as a highly active catalyst for the reduction of a broad range of alkyl halides by triethylsilane (Scheme 6).[41] The substrate scope also

Scheme 6. Si−H Bond Activation with Brookhart's Iridium(III) Pincer Complex



included the catalytic HDF of fluoropentane (**6** → **8**). The catalytically active species 9^+ is stabilized by $[B(C_6F_5)_3]_4^-$ as the weakly coordinating anion and formed in situ by hydrosilylation of acetone-coordinated precursor 7^+ (7^+ → 9^+). Unexpectedly, the catalytic cycle involves a Si−H bond activation according to mechanism B (Scheme 2) rather than a classical oxidative addition pathway as evidenced by the X-ray crystal structure of a previously unprecedented η^1 (end-on) silane σ-complex 9^+.[42] The hydrosilane coordinates trans to the ipso carbon of the pincer ligand with an Ir−H−Si angle of 157°. Compared with more common η^2 (side-on) silane σ-complexes, the η^1-coordination mode accounts for the high electrophilicity

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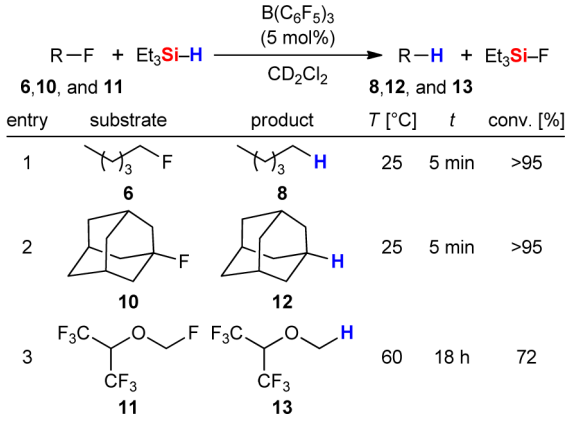
of the silicon atom in 9^+, thereby making it a potent silicon cation transfer reagent. Experimental observations (no major isomerizations in the dehalogenated products observed) and kinetic studies (primary alkyl halides react faster than secondary) revealed that, in contrast to HDF reactions using the $Ph_3C^+X^-/Et_3SiH$ and $AlCl_3/Et_3SiH$ systems (vide supra), the participation of carbenium ion intermediates is unlikely.[43] Instead, it is assumed that silyl transfer from 9^+ to an aliphatic fluoride produces a silyl-substituted fluoronium ion, which is subsequently reduced by the resulting neutral iridium dihydride complex, affording the defluorinated product with regeneration of the catalyst.

In a metal-free approach, Stephan and co-workers reported the F−H exchange between alkyl fluorides and Et_3SiH employing tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, as the Lewis acid catalyst (Table 1).[44] Although this contribution

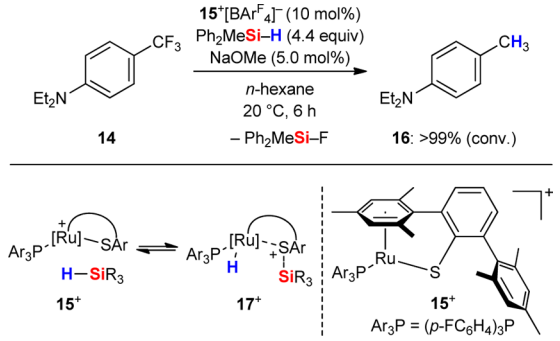
Table 1. $B(C_6F_5)_3$-Catalyzed HDF of Alkyl Fluorides



seems to be completely independent of Brookhart's work at first glance, a closer look at the catalytic cycle reveals the parallels of these, especially with respect to the Si−H bond activation mode.[45,46] The electron-deficient borane has been shown to activate the silane through η^1-coordination in the same manner as Brookhart's iridium(III) pincer complex.[42,47] The overall process of the $B(C_6F_5)_3$-catalyzed HDF is believed to share the general features with mechanism B (Scheme 2). Consequently, 1-fluoropentane (**6**) is transformed into pentane (**8**) with full conversion in 5 min at ambient temperature (**6** → **8**, entry 1, Table 1). 1-Fluoroadamantane (**10**) is also hydrodefluorinated (**10** → **12**, entry 2), supporting a S_N1-type reaction pathway. Remarkably, even dialkyl ether **11** reacted, albeit at elevated temperatures and prolonged reaction times, resulting in the selective HDF of the fluoromethoxy group (**11** → **13**, entry 3). Since C−F bond activation through fluoride abstraction typically requires exceptionally strong electrophiles, heteroatoms often prevent the reaction due to their nucleophilicity and the potential of donor−acceptor interactions, that is Lewis pair formation with the Lewis acid. Both CF_3 groups in fluorocarbon **11** do not react, indicating the expected lower reactivity of the $B(C_6F_5)_3/Et_3SiH$ system compared with silylium ions. In turn, it is exactly this reduced Lewis acidity that allows for the conversion of heteroatom-substituted substrates.

A conceptually new entry into the HDF of C(sp^3)−F bonds was recently disclosed by Oestreich and co-workers.[48] The polar Ru−S bond in tethered cationic ruthenium(II) complex 15^+ was found to serve as a reactive site for the cooperative heterolytic activation of triorganosilanes (15^+ → 17^+, Scheme 7). The reversible splitting of the Si−H bond by a σ-bond

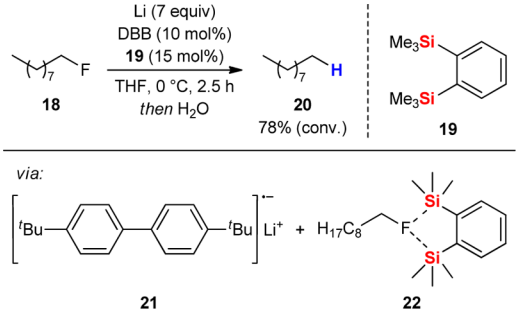
Scheme 7. Catalytic C(sp^3)−F Bond Activation Using Cooperative Si−H Bond Activation by a Polar Ru−S Bond [Ar^F = 3,5-Bis(trifluoromethyl)phenyl]



metathesis results in the formation of a ruthenium(II) hydride and a sulfur-stabilized silicon cation that is sufficiently electrophilic to abstract fluoride from activated C(sp^3)−F bonds. On the basis of this novel strategy to generate silicon electrophiles, a catalytic protocol for the HDF of CF_3-substituted anilines under mild reaction conditions was realized (e.g., **14** → **16**, Scheme 7). The catalytic cycle is likely to proceed through sulfur-stabilized silicon and carbenium ions and basically follows mechanism C with its elementary steps [Scheme 2 with LA = Ru(II) and Do = ArS^-]. Cooperative Si−H bond activation and subsequent fluoride abstraction is followed by an intramolecular hydride transfer from the ruthenium hydride to the intermediate carbenium ion, affording the hydrocarbon along with equimolar amounts of a fluorosilane as the byproduct. Intriguingly, the catalysis is accelerated by an alkoxide or hydroxide additive, generating a Ru−H cocatalyst that facilitates the crucial intramolecular Ru-to-C hydride transfer by formation of a hydride-bridged dimeric Ru−S complex.

It is worthy of mention that the Yus group developed an alternative protocol in which primary, secondary, and tertiary aliphatic monofluorides are reductively defluorinated by lithium metal catalyzed by 4,4′-di-*tert*-butylbiphenyl (DBB) or naphthalene, respectively (Scheme 8).[49] Interestingly, the addition of a catalytic amount of 1,2-bis(trimethylsilyl)benzene (**19**) proved to be crucial to maintaining turnover. A plausible explanation is that disilane **19** acts as a fluorophilic Lewis acid that coordinates to the fluorine atom of fluoroalkane **18**, thereby lowering its LUMO energy. The Lewis acid/Lewis base adduct **22** is now activated to undergo a reductive cleavage of

Scheme 8. Reductive HDF Enabled by a Silicon Lewis Acid



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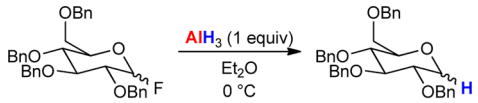
the C−F bond by single-electron transfer from in situ-generated **21**.

Aluminum Electrophiles. In addition to silicon, elements of the third main group are known for their electrophilicity. In an early example, Nicolaou and co-workers utilized an equimolar amount of AlH_3 to readily convert glycosyl fluoride **23** into the defluorinated tetrahydropyran **24** under mild reaction conditions (Scheme 9).[50] The dual role of the alane is remarkable, serving as the hydride source and Lewis acid without the demand for further activation.

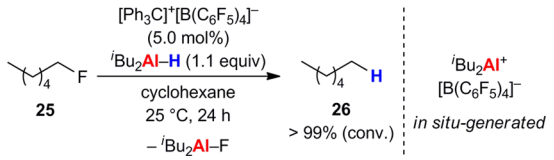
Scheme 9. HDF with Alane as Lewis Acid and Hydride Source



23 **24**: 90%

In analogy to the HDF reactions using silylium ion catalysis (Scheme 3), alumenium ions (R_2Al^+) have also been applied to catalytic C−F bond activation. Rosenthal, Krossing, and co-workers reported the room-temperature HDF of 1-fluorohexane (**25**) and postulated alumenium ion $^iBu_2Al^+$ as the active catalyst, generated in situ from diisobutylaluminum hydride and a trityl salt $Ph_3C^+X^-$ {X = $B(C_6F_5)_4$, $Al(C_6F_5)_4$, and $Al[OC(CF_3)_3]_4$} (Scheme 10).[51] A catalytic cycle according

Scheme 10. Catalytic HDF with Alumenium Ions



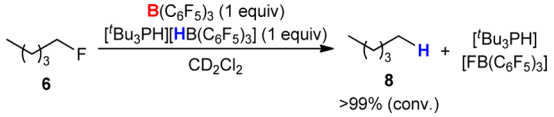
25 **26** > 99% (conv.)

to mechanism A (Scheme 2) seems plausible, but Terao, Kambe, and co-workers demonstrated that organoaluminum reagents (e.g., $^iBu_2AlH$) alone are able to convert C(sp^3)−F bonds of alkyl fluorides into C(sp^3)−H bonds without the need of a catalyst.[52] Both catalyses, however, are less efficient than the silylium ion-based protocols (vide supra) and are largely limited to monofluorinated hydrocarbons. The use of Reed's halogenated carborane $[CHB_{11}H_5Br_6]^-$ as supporting counteranion for the alumenium catalyst then enabled the Ozerov group to develop an improved procedure that even allowed for the HDF of trifluoromethyl groups.[53] Although all these reactions were again completely selective for aliphatic C(sp^3)−F bonds and tolerant of aromatic C(sp^2)−F bonds, HDF was now accompanied by defluorinative alkylation as a result of competitive alkyl or hydride transfer from $^iBu_2AlH$ (vide infra).

The commonly used reductant $LiAlH_4$ was also shown to efficiently activate the C(sp^3)−F bond in fluorocarbons in the absence of a metal catalyst.[54−56] It remains unclear, though, whether the fluoride is substituted in a S_N2-type fashion or abstracted by in situ-formed AlH_3, following a mechanism related to Nicolaou's work (Scheme 9).

Boron Electrophiles. Another important class of main-group Lewis acids is represented by boron-based electrophiles. In particular, the unique feature of $B(C_6F_5)_3$ to be capable of activating small molecules as the Lewis acid component in FLPs has attracted considerable attention.[25,57,58] The laboratories of Alcarazo[59] and Stephan[44] recently showed that the same concept can also be applied to the activation of C(sp^3)−F bonds in alkyl monofluorides. For example, treatment of fluoropentane (**6**) with equimolar amounts of $B(C_6F_5)_3$ and the phosphonium hydridoborate salt $[^tBu_3PH]^+[HB(C_6F_5)_3]^-$ as the hydride source results in the formation of pentane (**8**), along with the generation of $[^tBu_3PH]^+[FB(C_6F_5)_3]^-$ (Scheme 11).[44] In the absence of $B(C_6F_5)_3$, no reaction is observed,

Scheme 11. C(sp^3)−F Bond Activation by $B(C_6F_5)_3$



6 **8** >99% (conv.)

indicating that Lewis acid activation of the C−F bond by the electron-deficient borane is critical for the nucleophilic attack of the hydridoborate.

C−F Bond Functionalization. The beautiful examples discussed above showcase the extraordinary potential of main-group Lewis acids for the HDF of C(sp^3)−F bonds. From a synthetic point of view, it would have even a higher impact to transform the C−F bond directly into another functional group rather than simple replacement by a C−H bond, thus allowing for the synthesis of (partially fluorinated) complex molecules starting from readily available (per)fluorinated building blocks. In contrast with transition metal-mediated protocols in which developments beyond HDF and C−C bond-forming reactions (i.e., cross-couplings) are challenging,[9] main-group Lewis acid-assisted C−F bond activation paves the way for more complex C−F bond functionalizations. The formation of carbenium ion-type intermediates in these reactions (Scheme 2) serves as a versatile linchpin for further manipulations, given the possibility to trap these species by various nucleophiles.

In the following section, the recent promising applications of main-group Lewis acids in the defluorinative functionalization of C−F bonds through heterolytic fluoride abstraction and subsequent C−C or C−Nu (Nu = NR_2, OR, SR, Cl, and Br) bond-forming reactions are highlighted.

Defluorinative C−C Bond Formation. The laboratories of Ozerov[32] and Müller[60] already noticed in their contributions (vide supra) that the silylium ion-catalyzed HDF of some substrates is accompanied by isomerizations or Friedel−Crafts-type reactions. When primary or secondary alkyl fluorides, such as cyclohexylfluoride (**27**), were treated with silylium ion catalyst $\mathbf{4}^+$ and Et_3SiH in the presence of benzene as solvent, no HDF was observed (Scheme 12, upper).[60] Instead, cyclohexylbenzene (**28**) was obtained as the major product along with the evolution of dihydrogen. This result supports the presence of carbenium ions or their synthetic equivalents as intermediates that preferentially react with the aromatic solvent via S_EAr rather than undergoing reduction by Et_3SiH (Scheme 12, lower). Deprotonation of the resulting Wheland complex by the triorganosilane affords alkylated arene **28** with release of dihydrogen and the regenerated silylium ion catalyst. Although this and related intermolecular reactions do not stop at the monoalkylation (di- and trialkylated arenes were also observed), it is an example of the activation of a C(sp^3)−F bond combined with the desirable formation of a new C(sp^3)−C(sp^2) bond. A well-conceived approach of Müller and co-workers to circumvent the selectivity issue through the use of

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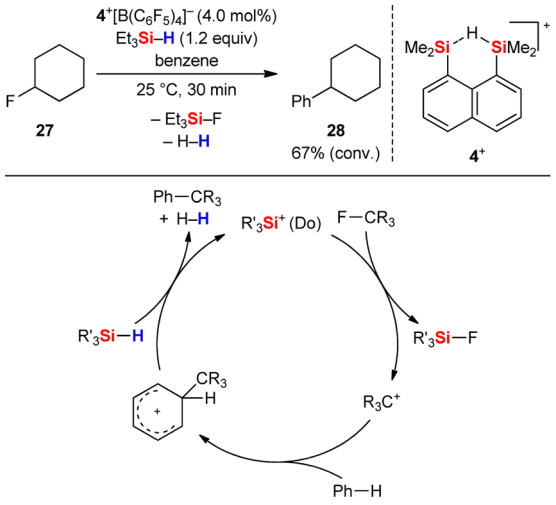
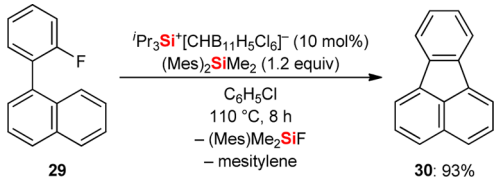
Scheme 12. Defluorinative Friedel–Crafts Alkylation



aryl silanes as coupling partners in ipso-directed substitutions had only limited success.[60]

In intramolecular reactions, however, the potential of such reactions appears even more promising, as recently shown by an impressive contribution of Siegel and co-workers. On the basis of the discovery that selected silicon cations are even capable of activating the C(sp^2)–F bond in fluorobenzene,[61] this group disclosed an C(aryl)–C(aryl) coupling of fluorinated arenes leading to a range of polycyclic aromatic hydrocarbons and graphene frameworks (e.g., **29** → **30**, Scheme 13).[62] The

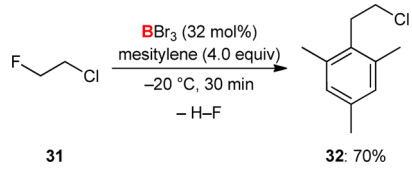
Scheme 13. Intramolecular Friedel–Crafts Coupling of Fluoroarenes by Silylium Ion-Mediated C(sp^2)–F Bond Activation



key step of the catalytic cycle involves the initial activation of the C(sp^2)–F bond by the silylium ion catalyst, followed by an intramolecular S_EAr reaction. The choice of carborane $[CHB_{11}H_5Cl_6]^-$ as the weakly coordinating counteranion and elevated temperatures (>100 °C) are essential for securing high TONs. Remarkably, the proton generated in the final rearomatization step is not simply scavenged by a Brønsted base but transferred from the Wheland intermediate to the electron-rich mesityl ring of the added dimethyldimesitylsilane, thereby regenerating a reactive silyl cation through proto-desilylation.

Although the recent successes of silylium ion catalysis are closely connected to the advent of weakly coordinating anions, the related boron Lewis acid-based reactions have been known for over half a century. In a seminal report, Olah and co-workers reported the BF_3-catalyzed Friedel–Crafts-type alkylation of arenes with alkyl fluorides.[63] Other boron halides also proved to be catalytically active.[64] In agreement with the relative Lewis acid strengths of the boron halides, the order of catalyst activity is BI_3 > BBr_3 > $BC1_3$ > BF_3. It is notable that among the various alkyl halides, alkyl fluorides react preferentially, allowing for haloalkylations of arenes with fluorohaloalkanes by selective substitution of the fluoride (e.g., **31** → **32**, Scheme 14). However, boron halides other

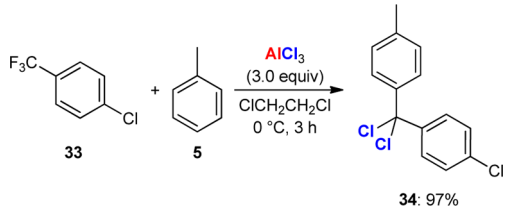
Scheme 14. BBr_3-Catalyzed Defluorinative Chloroalkylation of Mesitylene



than BF_3 were also found to effect halogen exchange of fluoroalkanes.[65] As a result, complete bromodefluorination of C(sp^3)–F bonds can be achieved using overstoichiometric amounts of BBr_3 (not shown).[66,67]

In analogy, aluminum halides have been shown to induce the fluorine–halogen exchange of aliphatic fluorocarbons to afford the corresponding halides.[39,68,69] Even prior to the work of Olah, Henne and Newman discovered that benzotrifluoride is converted to benzotrichloride in the presence of an equimolar amount of $AlCl_3$.[39] The same reaction employing over-stoichiometric amounts of $AlCl_3$ in the presence of an arene results in Friedel–Crafts-type alkylations.[70−72] As an example, clean formation of dichlorodiarylmethane **34** from trifluor-omethyl benzene **33** is observed (Scheme 15).[71] The

Scheme 15. $AlCl_3$-Mediated Defluorinative Chlorination–Arylation Sequence



mechanism of this reaction is assumed to proceed via initial F–Cl exchange, followed by $AlCl_3$-mediated regioselective Friedel–Crafts alkylation of toluene with the resulting benzotrichloride.

While main-group Lewis acid-catalyzed Friedel–Crafts reactions emerged as a reliable tool to couple fluorinated compounds with aromatic rings, C(sp^3)–C(sp^3) bonds are formed in the alkylation reaction of silicon enolates with *tert*-alkyl or allylic fluorides (Scheme 16).[73,74] The activated C(sp^3)–F bonds in these substrates readily split heterolytically in the presence of catalytic amounts of $AlMe_3$[73] or BF_3·OEt_2,[74] respectively. Nucleophilic attack of the silicon enolate at the intermediate carbenium ion affords the corresponding alkylation product and regenerates the Lewis acid catalyst under formation of a Si–F bond. This method provides facile access to the construction of quaternary carbon centers, as demonstrated by the reaction of tertiary fluoride **35** with silyl ketene acetal **36** (Scheme 16, upper). It is noteworthy that ether and ester functionalities are tolerated under the reaction conditions. Moreover, allylic silanes instead of silyl enol ethers also serve as the carbon nucleophile (Scheme 16, lower).

Interestingly, in the absence of external nucleophiles, the use of trialkylaluminum as a stoichiometric reagent results in alkylation of tertiary alkyl fluorides by direct transfer of the alkyl

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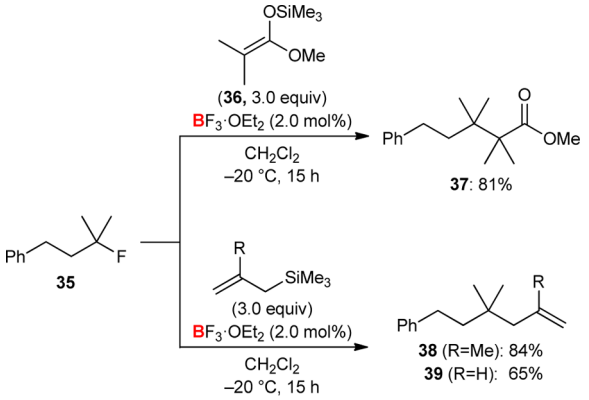
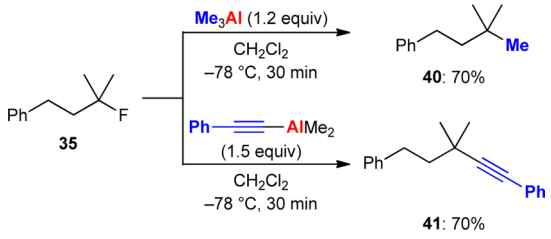
Scheme 16. $BF_3{\cdot}OEt_2$-Catalyzed Defluorinative Alkylation and Allylation of Tertiary Alkyl Fluorides



group from the trialkylaluminum compound, as reported by Maruoka and co-workers (e.g., **35** → **40**, Scheme 17).[73] When

Scheme 17. Alkylative Defluorination with Triorganoaluminum Compounds

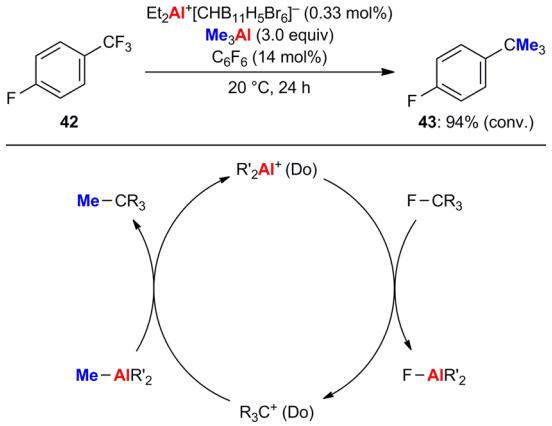


dimethyl(phenylethynyl)aluminum was used, alkyne **41** was obtained in 70% yield (**35** → **41**, Scheme 17). This result indicates the selective transfer of the alkynyl group over the alkyl groups at the aluminum atom. It is important to note that alkylchlorides do not react under the same reaction conditions.

Although trialkylaluminum compounds can perform C-(sp^3)–F activation without a catalyst, these reactions are limited to mainly alkyl monofluorides or activated C(sp^3)–F bonds. A more efficient protocol was developed by Ozerov and co-workers employing alumenium ion $Et_2Al^+[CHB_{11}H_5Br_6]^-$ as a catalyst.[53] Thus, trifluoromethyl benzene **42** undergoes complete defluorinative methylation with Me_3Al as the stoichiometric alkylation reagent (Scheme 18, upper). While the reaction proceeds smoothly at ambient temperature with catalyst loadings as low as 0.33 mol %, almost no conversion occurs in the absence of an alumenium catalyst. The assumed catalytic cycle of this transformation is related to the corresponding catalytic HDF process (cf. mechanism A, Scheme 2). The alumenium ion (R'_2Al^+) acts as the catalytically active species that abstracts a fluoride from the fluorocarbon, thereby forming a carbenium ion and $R'_2Al{-}F$ (Scheme 17, lower). The greater polarity of the Al–Me bond then facilitates an alkyl group transfer from the aluminum reagent to the carbenium ion, yielding alkylation with regeneration of the alumenium ion catalyst.

Defluorinative C–Nu Bond Formation (Nu = NR_2, OR, and SR). The demand for new glycosylation methods stimulated the development of innovative C–F functionalization protocols.[75−79] Several silicon-,[75,76] boron-,[77] and aluminum-based[78,79] main-group Lewis acids were shown to activate the C(sp^3)–F bond at the anomeric position of glycosyl

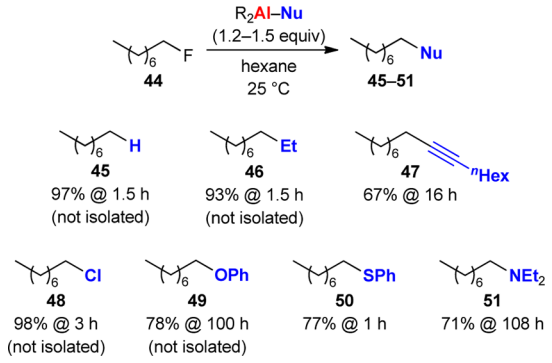
Scheme 18. Alkylative Defluorination Using Alumenium Ion Catalysis



fluorides, thereby allowing for the coupling with various carbon, nitrogen, and oxygen nucleophiles (not shown).

The group of Terao and Kambe demonstrated that triorganoaluminum compounds not only serve as alkylation reagents but also allow for the efficient conversion of nonactivated C(sp^3)–F bonds of alkyl fluorides to C(sp^3)–Nu (Nu = H, C, Cl, O, S, N, Se, and Te) bonds (Scheme 19).[52] The protocol is remarkably general, and only alkyl fluorides react chemoselectively in the presence of other alkyl halides, as verified in a competition experiment.

Scheme 19. Organoalumium Reagents in Defluorinative C(sp^3)–F Bond Functionalization (R = Et or ^{i}Bu)



In an inspiring contribution, Haufe, Shibata, and co-workers recently reported the synthesis of biologically relevant oxazolidinones through desymmetrization of aliphatic difluorides.[80] In the presence of BSA and catalytic amounts of CsF, phenylcarbamate **52** is transformed into oxazolidinone **53** in excellent yield under mild reaction conditions (Scheme 20). As proposed by the authors, this desymmetrizing cyclization is initiated by CsF-induced monodesilylation of BSA (BSA → **54**) which, in turn, deprotonates carbamate **52** (**54** → **55**). One of the C(sp^3)–F bonds in the resulting carbamate anion **55** is then activated by the silicon atom of BSA to induce cyclization through nucleophilic attack of the nitrogen atom, thereby releasing product **53**. The formation of fluorosilane as byproduct is regarded to be the driving force of this reaction. This example showcases the potential of main-group Lewis acid-induced C(sp^3)–F bond activation to build up partially fluorinated complex molecules.

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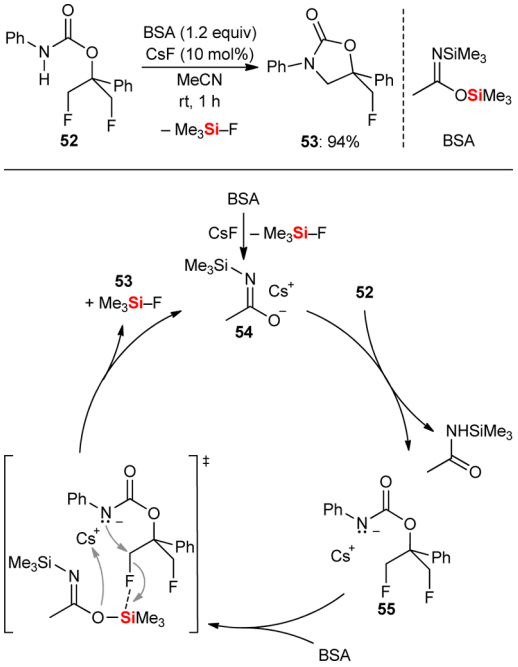
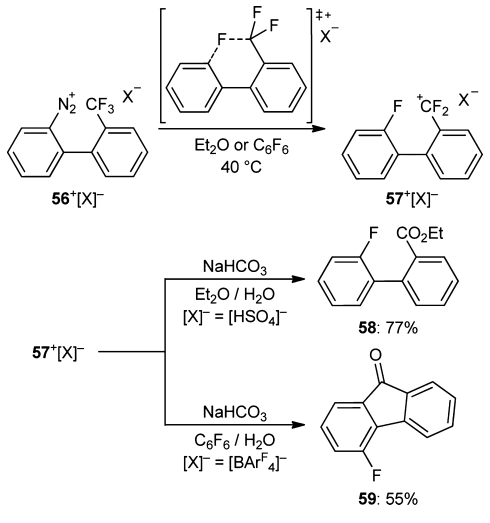
Scheme 20. BSA-Mediated Desymmetrization of Aliphatic Difluorides



C–F Bond Functionalization by Carbocations and Protons. Aside from cationic or neutral boron-, silicon-, and aluminum-based main-group Lewis acids, carbocations are potentially suitable electrophiles for C(sp^3)–F bond activation. Carbenium ions generated by C(sp^3)–X bond heterolysis are generally not sufficiently electrophilic to abstract fluoride. In turn, vinyl and aryl carbocations emerging from heterolytic C(sp^2)–X bond splitting are able to react with C(sp^3)–F bonds. In a unique example, the group of Lectka reported that aryl carbocations are able to abstract fluoride from aryl trifluoromethyl groups (Scheme 21).[81] By mild thermolysis of aryl diazonium salt **56**$^+$, an intramolecular fluoride shift from the neighboring CF_3 group to the transient phenyl cation occurs, generating benzylic carbenium ion **57**$^+$. The reaction conditions have a strong influence on the further reaction

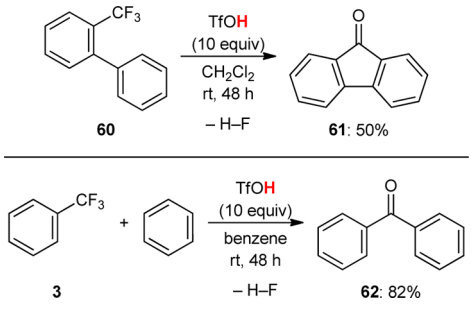
Scheme 21. Intramolecular Fluoride Abstraction by a Phenyl Cation



outcome. Using $[HSO_4]^-$ as counteranion and Et_2O as solvent, biaryl **58** is obtained, whereas the choice of borate anion $[BAr^F{}_4]^-$ in combination with C_6F_6 as solvent results in formation of fluorenone **59**.

Although it is beyond the scope of this Perspective, it is important to note that protons (H^+) do also effect the heterolytic cleavage of C(sp^3)–F bonds. This is related to the silylium ion-assisted C–F bond activation chemistry because silylium ions might be viewed as "fat" protons. Le Fave already reported over 60 years ago that trifluoromethyl aryl derivatives are hydrolyzed to the corresponding carboxylic acids by heating with concentrated sulfuric acid.[82] In contrast, 2-trifluoromethyldiphenyl (**60**) is converted to 9*H*-fluoren-9-one (**61**) under the same reaction conditions, as shown by Pettit and Tatlow a few years later.[83] Wang and Hu recently extended this methodology not only to intra- but also to intermolecular arylations of trifluoromethylated arenes (Scheme 22).[84] In the

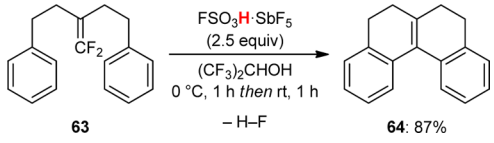
Scheme 22. Intra- and Intermolecular Arylation of Trifluoromethylated Arenes by Brønsted Acid-Mediated C(sp^3)–F Bond Functionalization



presence of trifluoromethanesulfonic acid (triflic acid, TfOH) as a strong Brønsted acid, the C(sp^3)–F bond cleavage/Friedel–Crafts-type process already proceeds at room temperature, affording the corresponding diaryl ketones in moderate to good yields.

Ichikawa and co-workers employed magic acid ($FSO_3H{\cdot}SbF_5$) for the efficient synthesis of substituted [4]- to [6]helicenes starting from 1,1-difluoro-1-alkenes bearing two pendant aryl groups (Scheme 23).[85,86] Initial protonation of the

Scheme 23. Brønsted Acid-Mediated Defluorinative Friedel–Crafts-Type Cyclization of 1,1-Difluoro-1-alkenes



fluorinated alkene results in the formation of an α,α-difluorocarbenium ion that induces a domino Friedel–Crafts-type cyclization. Strong CF···H^+ interactions or hydrogen bonding are believed to play a key role in the Brønsted acid-mediated C–F bond activation chemistry.

CONCLUSION

The latest advancements in the chemoselective activation and functionalization of unreactive C(sp^3)–F bonds are mainly attributed to the application of main-group Lewis acids that combine both Lewis acidity and fluoride affinity. Since the early discovery of the action of aluminum chloride on fluorinated

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compounds by Henne and Newman,[39] several neutral boron- and aluminum-based Lewis acids have been shown to potentially effect C(sp^3)−F bond activation. Whereas the use of conventional aluminum and boron halides often leads to competitive halogen-exchange reactions, readily available organoaluminum reagents allow for the efficient conversion of C(sp^3)−F bonds into various C(sp^3)−Nu bonds by direct transfer of a nucleophilic substituent from the aluminum compound. The development of weakly coordinating anions then paved the way for the recent development of more advanced protocols using exceptionally potent cationic Lewis acids, such as silylium or alumenium ions. Now, even the HDF of perfluoroalkyl groups in polyfluoroalkanes is possible. In addition to electron-deficient cationic silicon electrophiles, neutral triorganosilanes have also proven to be useful for fluoride abstraction if the Si−H bond is initially activated by another strong Lewis acid or cooperatively splitted by an FLP.

The efficiency of these reactions is remarkable, and the high preference for C(sp^3)−F bonds is complementary to the transition metal-mediated activation of, predominantly, C-(sp^2)−F bonds. In terms of both economic and environmental aspects, main-group-based systems are possibly superior, considering main-group elements to be generally cheaper and less toxic than transition metals. Thus, the recent progress in C−F bond activation by main-group Lewis acids holds promise for further developments toward potentially greener and more sustainable processes. Enantioselective variants, however, have not been reported yet, but the recent work by Haufe and Shibata might be promising in this regard.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Ar^F, 3,5-bis(trifluoromethyl)phenyl; BSA, bis(trimethylsilyl)-acetamide; DBB, 4,4′-di-*tert*-butylbiphenyl; FLP, frustrated Lewis pair; HDF, hydrodefluorination; S_EAr, electrophilic aromatic substitution; TON, turnover number

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