C–F Activation

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Catalytic Hydrodefluorination of Fluoromethanes at Room Temperature by Silylium-ion-like Surface Species**

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Breaking C–F bonds catalytically under moderate reaction conditions can be considered a fundamental challenge in synthetic chemistry.[1] The conversions can provide new reaction pathways to otherwise unaccessible fluorinated compounds and building blocks.[2] From an environmental point of view, the defluorination of (poly)fluorinated compounds is also of considerable interest because of the "supergreenhouse gas" behavior of chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).[3] Although significant progress was made for the intermolecular activation of highly fluorinated aromatics and olefins,[1] C–F bond cleavage reactions of fluorinated alkanes are less developed. Major achievements include the employment of silylium or alumylium ions as homogeneous Lewis-acidic catalysts, which are stabilized by weakly coordinating anions.[4] In the presence of hydrogen sources such as tertiary silanes, the hydrodefluorination of highly fluorinated, but not perfluorinated alkanes, was achieved under exceptionally mild reaction conditions.[4b,c] Carbocationic species are discussed as intermediates, and in the presence of aromatic compounds Friedel–Crafts products were generated. A C–F bond cleavage step or even a hydrodefluorination of fluoromethanes has so far not been reported with these catalytic systems. Note, that for a homolytic cleavage, the C–F bond strengths in poly- and perfluorinated alkanes are less compared to those in polyfluorinated methanes.[5] This bond strength has to be considered as one reason for the C–F bond cleavage of polyfluorinated methanes being considerably more difficult. However, for breaking a C–F bond heterolytically, C_2F_6 would have a higher bond dissociation energy than CF_4.[6] In addition, increasing fluorine content leads to a substantial strengthening of each C–F bond in fluorinated methanes.[1a,7] Remarkably, Goldman et al. reported stoichiometric C–F activation reactions of CH_3F and CHF_3 with an iridium pincer compound.[8] In these cases, an initial C–H activation step is required to achieve a net C–F activation. Stoichiometric C–F activation reactions were also reported by Jones et al., by using $[Cp^*_2ZrH_2]$ under an H_2 atmosphere for the hydrodefluorination of CH_2F_2,[9] and by Mikami et al. for the α-difluoromethylation of lithium enolates when using CHF_3 as the difluoromethylation agent.[10] Some heterogeneous catalysts were developed and are capable of C–F activation of fluoromethanes at elevated temperature in the gas phase. Thus, aluminum, transition-metals, and alkaline-earth-metal oxides,[3a,11] sulfated metal oxides,[3a,11b] or metal phosphates[3a] are able to catalyze the decomposition of fluoromethanes to yield metal fluorides and carbon oxides, or result in the hydrolysis of fluoromethanes at 250–850 °C. Recently, it was shown that CHF_3 can be mineralized by solid alkali hydroxides to give the corresponding fluorides, CO, and H_2O at moderate temperatures. An initial C–H interaction is considered as the crucial reaction step.[12] Mass spectrometric experiments revealed that lanthanide cations can react with CH_3F in the gas phase, whereas no reaction was found for CHF_3 and CF_4.[13]

Herein we report on the heterogeneous C–F activation of fluoromethanes in solution with nanoscopic aluminum chlorofluoride (ACF) in the presence of Et_3SiH. ACF is an amorphous chlorine-containing aluminum fluoride $AlCl_xF_{3-x}$ $(x \approx 0.05–0.3)$ and is considered to be a Lewis acid with an acidity comparable to SbF_5.[14] Catalytic experiments under very mild reaction conditions led either to hydrodefluorination or, in the presence of benzene, Friedel–Crafts-type reactions. The conversions are presumably mediated by a silylium-ion-like surface species which initiates the C–F activation step.

In an initial experiment ACF was treated with Et_3SiH in benzene. A ^{19}F NMR spectrum of the reaction solution revealed the formation of small amounts of Et_3SiF. ^{19}F Hahn spin-echo MAS NMR studies showed that weakly bound surface fluorine species, which were present at the ACF before treatment with Et_3SiH, vanished after the contact with the silane (see Figure S1 in the Supporting Information). Because of the small amounts of the formed Et_3SiF, it was not possible to identify any hydride species on the solid surface by MAS NMR spectroscopy. Nevertheless, the ^1H MAS NMR spectrum revealed broad signals for surface-bound Et_3SiH (Figure 1 a). The immobilized Et_3SiH species were also detected by $^{29}Si\{^1H\}$ CP MAS NMR spectroscopy. We presume that Et_3SiH reacts with the Lewis-acidic sites of ACF to give a surface bound entity $ACF \cdots H{-}SiEt_3$ (Figure 1 b), which has considerable silylium ion character. Note that the resulting particles are not active anymore in the isomerization of 1,2-dibromohexafluoropropane into 2,2-dibromohexafluoropropane, whereas ACF catalyzes this isomerization at room temperature.[15]

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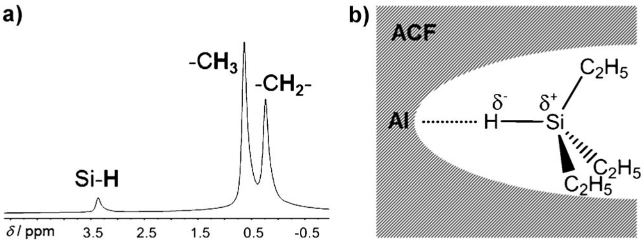


Figure 1. a) ^{1}H MAS NMR spectrum which shows the signals for surface-bound Et_3SiH ($\nu_{rot} = 10$ kHz) with the SiH resonance at $\delta = 3.45$ ppm. For Et_3SiH in C_6D_6 solution the resonance is observed at $\delta = 3.85$ ppm. b) Schematic representation of ACF···H–$SiEt_3$.

The presence of silylium-like species at the surface prompted us to study the reactivity towards fluorinated methanes. On treatment of CH_3F with ACF in C_6D_6 in the presence of Et_3SiH at room temperature at one atmosphere (Table 1, entry 1), a vigorous reaction and the evolution of gaseous products was observed. The ^{1}H (Figure 2), ^{13}C, ^{19}F, and ^{29}Si{^{1}H} NMR spectra (see Figure S3 in the Supporting Information) of the solution revealed the formation of $C_6D_5CH_3$ as well as Et_3SiF and traces of Et_2SiF_2. Small amounts of xylenes and methane were also detected. In addition, H_2 and HD were generated as a result of Friedel–Crafts reactions with C_6D_6 (Scheme 1 a). H_2 formation can be explained by H/D exchange reactions. Note that catalytic H/D exchange between deuterated alkanes and benzene at ACF was described recently.[16]

CH_3F in C_6D_6 was consumed completely after 24 hours at room temperature in the presence of an excess of silane (2 equivalents), thus resulting in a turnover number (TON) of 100 (based on the amount of Lewis-acidic sites at the ACF;

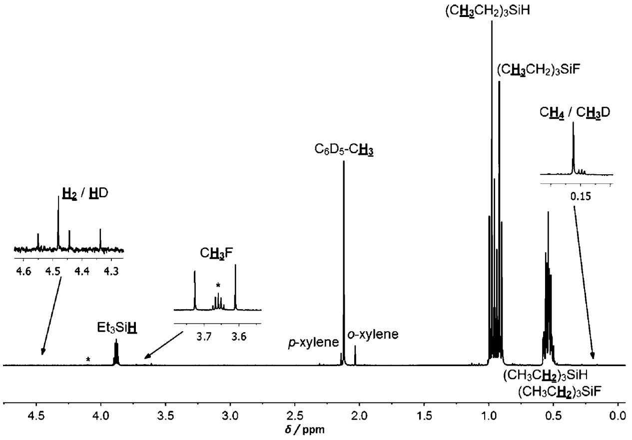
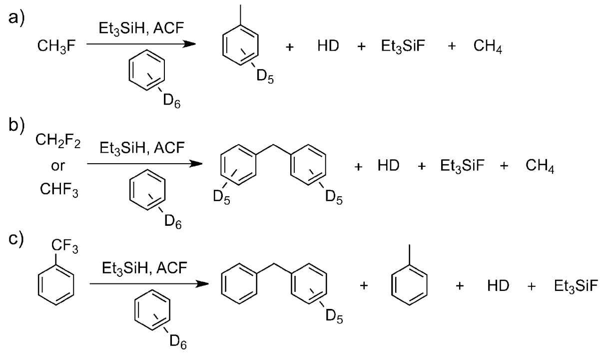


Figure 2. ^{1}H NMR spectrum of the ACF-catalyzed reaction of CH_3F with Et_3SiH in C_6D_6 as the solvent (Table 1, entry 1; * denotes ^{29}Si satellites from the signal for Et_3SiH).



Scheme 1. ACF-catalyzed C–F activation reactions of fluoromethanes and trifluorotoluene.

Table 1: ACF-catalyzed C–F activation reactions;

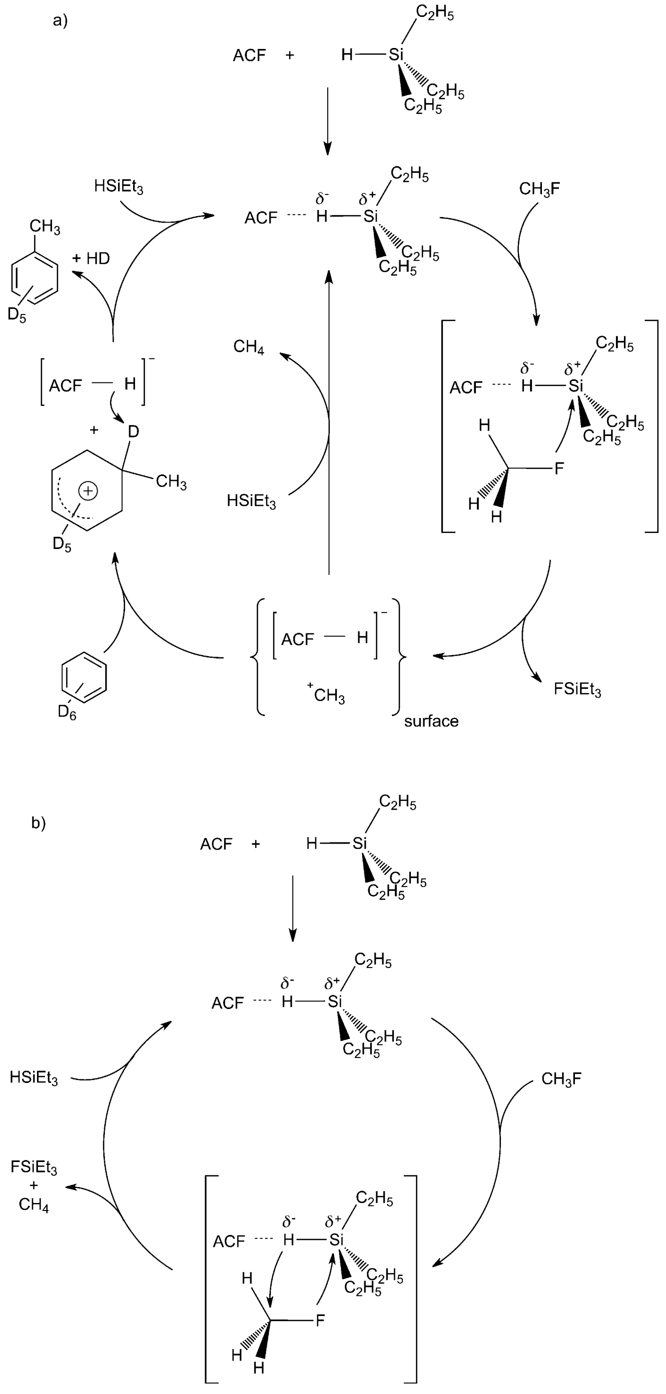
Entry	Substrate	Solvent[a]	$n_{substrate}$ [mmol]	$n_{act. sites}$ [μmol]	n_{Et3SiH} [mmol]	T [°C]	t [d]	Conv. [%][c]	Main product[d]	TON[e]
1	CH_3F	C_6D_6	n.d.[b]	1.5	0.3	25	1	50	$C_6D_5CH_3$	100
2	CH_2F_2	C_6D_6	n.d.[b]	12.5	0.3	25	4	88	$(C_6D_5)_2CH_2$	21.1
3	CHF_3	C_6D_6	n.d.[b]	25.0	0.6	70	4	20	$(C_6D_5)_2CH_2$	4.8
4	$C_6H_5CF_3$	C_6D_6	0.3	25.0	0.9	70	7	70	$(C_6D_5)PhCH_2$	25.2
5	$C_6H_5CH_2F$	C_6D_6	0.15	12.5	0.15	70	1	35	$(C_6D_5)PhCH_2$	n.d.[f]
6	$C_6H_5CF_3$	o-$C_6H_4Cl_2$	0.3	25.0	0.9	70	7	25	$PhCH_3$	9
7	$C_6H_5CF_3$	neat	0.3	25.0	0.9	70	7	42	$PhCH_3$	15
8	CH_3F	C_6D_6	2.55	6.00	1.56	25	2	75	$C_6D_5CH_3$	195
9	CH_3F	o-$C_6H_4Cl_2$	2.64	6.00	1.56	25	2	73	CH_4	190
10	CH_3F	neat	2.62	6.00	2.68	25	2	89	CH_4	400
11	CH_2F_2	C_6D_6	2.73	12.5	1.56	25	4	17	$(C_6D_5)_2CH_2$	21
12	CH_2F_2	o-$C_6H_4Cl_2$	2.58	12.5	1.56	25	4	65	CH_4	82
13	CH_2F_2	neat	2.63	12.5	1.56	25	4	90	CH_4	112
14	CHF_3	C_6D_6	2.57	25.0	0.6	70	4	81	$(C_6D_5)_2CH_2$	20
15	CHF_3	o-$C_6H_4Cl_2$	2.77	25.0	0.6	70	4	17	CH_4	4
16	CHF_3	neat	2.72	25.0	1.2	70	4	13	CH_4	6.3

Experiments corresponding to entries 8–16 were performed in flame-sealed glass ampoules. Please see the Supporting Information for experimental details. [a] $V[C_6D_6] = 0.6$ mL (entries 1–5), 0.9 mL (entries 8,11,14); $V[o\text{-}C_6H_4Cl_2] = 0.3$ mL (entry 6), 0.7 mL (entries 9, 12, 15). [b] Substrates bubbled into the solvent for 3 min. [c] Based on the conversion of Et_3SiH into Et_3SiF (determined by ^{1}H NMR spectroscopy). [d] In addition to Et_3SiF.
[e] Calculated based on the amount of Et_3SiF formed per number of active acidic sites at the ACF (assuming that 1 g ACF contains 1 mmol of active sites).[16,17] [f] Not determined; see the Supporting Information for further details.

estimated to be 0.978 mmol g^{-1} ACF by NH_3-TPD).[16,17] Condensation of excess CH_3F (1.6 equiv) with a mixture of Et_3SiH and ACF in C_6D_6 as the solvent in a glass ampoule led to an increase of the TON to 195 after leaving the reaction mixture for two days in the sealed ampoule at room temperature (Table 1, entry 8).

With CH_2F_2 or CHF_3 as fluorinated substrates (Scheme 1 b), the formation of the Friedel–Crafts product [D_{10}]diphenylmethane was observed in the C_6D_6 solution. In addition, minor amounts of CH_4 were generated. For CHF_3 the [D_{10}]diphenylmethane formation involves two Friedel–Crafts reaction steps and a subsequent hydrodefluorination reaction. In general, the TONs [21 for CH_2F_2 at room temperature (Table 1, entry 2) and 4.8 for CHF_3 at 70 °C (Table 1, entry 3)] decrease with increasing fluorine content on the fluorinated methane, but the reactions remain clearly catalytic. When the conversion of CHF_3 into [D_{10}]diphenylmethane was performed in a glass ampoule at 70 °C the TON increased to 20 (Table 1, entry 14). However, using this strategy for CH_2F_2 (Table 1, entry 11) did not lead to an increase of the TON, possibly because of the formation of larger (insoluble) Friedel–Crafts products by reaction of CH_2F_2 with [D_{10}]diphenylmethane, and thus deactivation of the catalyst. Note that for all substrates a complete defluorination was observed. A comparable observation was found by Ozerov et al. for fluorinated alkyl groups and it was concluded that in polyfluorinated substrates the first fluoride abstraction is the rate-limiting step.[6] However, for the C–F activation reactions with ACF, the reason for the absence of partly defluorinated products could also be that the substrates stay at the active site until the defluorination is complete. It is also worth mentioning that ^{19}F MAS NMR measurements of the ACF···H–$SiEt_3$ catalyst before and after the catalytic reactions reveal no changes in the spectra, thus suggesting that the identity of the catalytic material remains unchanged (see Figure S2 in the Supporting Information).

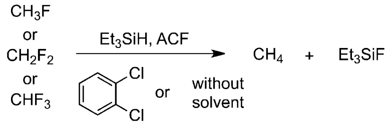
Mechanistically, we presume that Et_3SiH initially binds at the Lewis-acidic sites of ACF, thus resulting in the surface-bound Et_3SiH entities ACF···H–$SiEt_3$. A polarization of the Si–H bond might lead to species which have a silylium ion character. The latter are able to cleave a C–F bond to yield Et_3SiF and carbenium-like species, which in turn attack the solvent (C_6D_6) to form the corresponding Wheland intermediates. These intermediates subsequently react with the remaining hydrogen atom on the ACF, which has hydride character, to release the Friedel–Crafts product as well as HD. The Lewis-acidic ACF site is thereby regenerated (Scheme 2 a). However, in an alternative process ACF···H-$SiEt_3$ converts the C–F bonds into C–H bonds to yield the hydrodefluorination product methane and Et_3SiF. This might occur by a concerted reaction pathway (Scheme 2 b) or again by a two-step mechanism which also involves the carbenium-like species and the ACF-bound hydrogen (Scheme 2 a). Hence, the latter entity could be regarded as a weakly coordinating anion (WCA) which stabilizes the carbenium-like species. Note, that the stabilization of fluorinated carbocations by weakly coordinating anions and the resulting Friedel–Crafts reactivity has also been described for Et_3Si(carborane) in homogeneous phase.[4i]



Scheme 2. Proposed mechanisms for a) the ACF catalyzed C–F activation reaction including a Friedel–Crafts reaction with the solvent C_6D_6 via a carbenium-like intermediate and b) the ACF-catalyzed hydrodefluorination by a concerted mechanism. Both mechanisms are shown for the substrate CH_3F.

To evaluate the scope of the reactions we also tested the reactivity of benzyl fluoride, which should be an intermediate in the Friedel–Crafts reactions of CH_2F_2 or CHF_3, to yield diphenylmethane. Full conversion was obtained at 70 °C in C_6D_6 to give $C_6D_5PhCH_2$ (Table 1, entry 5). Compatible results were found on using trifluorotoluene in C_6D_6 (Scheme 1c), and $C_6D_5PhCH_2$ and toluene were furnished with a TON of 25 (Table 1, entry 4). The values are comparable to those found for CH_2F_2 or CHF_3 in C_6D_6. No activation of CHF_2CHF_2 or C_2F_6 was observed at 70 °C, possibly because activation at the active site at the surface is hampered by their dissimilar steric demand in comparison to that of the other fluorinated substrates.

To achieve a selective hydrodefluorination of the fluorinated methanes, ACF was treated with Et_3SiH and fluorinated substrates in glass ampoules with 1,2-dichlorobenzene as the solvent (Scheme 3). Indeed, a reaction of CH_3F with ACF/Et_3SiH at room temperature (Table 1, entry 9) led, with a high selectivity, to the formation of the hydrodefluorination product CH_4 (TON = 190), and C–C coupling products were only found in traces. Moreover, CH_4 was furnished with a TON of 82 on using CH_2F_2 as the fluorinated substrate (Table 1, entry 12). Note the substantial improvement in activity compared to the reaction in C_6D_6 (TON = 21) leading to the Friedel–Crafts product. Reactions of CHF_3 or trifluorotoluene (Table 1, entries 15 and 6) also gave the hydrodefluorination products CH_4 or toluene, but no increase of the TONs was observed compared to the reactions in C_6D_6 (Table 1, entries 14 and 4).



Scheme 3. ACF-catalyzed C–F activation reaction of fluoromethanes in absence of C_6D_6.

Remarkably, the reaction of CH_3F with Et_3SiH in a glass ampule, without any additional solvent (Table 1, entry 10), yielded Et_3SiF and CH_4 with a TON of 400. Using the same set-up for CH_2F_2, the TON can be increased up to 112 (Table 1, entry 13). A hydrodefluorination of CHF_3 was also achieved. However, for CHF_3 as well as for trifluorotoluene (Table 1, entries 16 and 7), no improvement was found compared to the reactions in C_6D_6.

This work shows that the Lewis acid aluminum chlorofluoride can be used in an unprecedented heterogeneous catalytic process for the C–F activation of fluoromethanes in the presence of Et_3SiH. The C–F bonds are either converted into C–H bonds by hydrodefluorination or into C–C bonds by a Friedel–Crafts-type reaction. A surface-bound silylium-ion-like species is considered to be a crucial intermediate to achieve the C–F bond cleavage step. The established strategy for the hydrodefluorination of fluorinated alkyl groups by WCA-stabilized silylium ions was realized for a heterogeneous system, thus bridging a gap between homogeneous and heterogeneous catalysis. Moreover, the protocol paves a way for the activation of fluorinated methanes. Notably, ACF costs approximately 25 $\$\,g^{-1}$ and is considerably less expensive than the catalysts that are characterized by common weakly coordinating anions. Note that the activation of C–F bonds with silylium-ion-like surface species is complementary to other silyl-group-induced C–F activations, including transformations with transition-metal complexes, which formally bear an anionic silyl ligand.[2b,c,e,18]

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