Research Article
doi.org/10.1002/cctc.202200029
Chemistry Europe
European Chemical Societies Publishing

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Chlorodefluorination of Fluoromethanes and Fluoroolefins at a Lewis Acidic Aluminum Fluoride

Xinzi Pan,[a] Maria Talavera,[a] Gudrun Scholz,[a] and Thomas Braun*[a]

Chlorodefluorination reactions of fluoromethanes and fluoroolefins catalysed by the highly Lewis acidic nanoscopic aluminum chlorofluoride (ACF, $AlCl_xF_{3-x}$, $x \approx 0.05–0.3$) in the presence of $ClSiEt_3$ were studied. Both fluoromethanes and fluoroolefins convert under mild reaction conditions by fluorine-chlorine exchange steps into chlorinated fluoro derivatives. MAS NMR studies provided information on the interaction of silanes and hexafluoropropene with the ACF surface.

Introduction

In the past decades, fluorinated compounds have been widely applied in industry, especially in material science, agriculture and pharmacy.[1] C–F bond activation of polyfluorinated compounds is a common methodology to obtain industrially valuable derivatives. Reaction steps can include defluorination pathways such as dehydrofluorination, hydrodefluorination or Friedel-Craft reactions among others.[2]

In order to accomplish a C–F bond activation step, the strength of the C–F bond has to be overcome.[3] To achieve this goal, transition metal based catalysts,[2a–d,f,h,4] homogeneous Lewis acidic compounds like silylium and germylium ions[5] as well as heterogeneous catalysts can be used.[6] For the latter, aluminum chlorofluoride, (ACF, $AlCl_xF_{3-x}$, $x \approx 0.05–0.3$), which is an amorphous, nanoscopic solid Lewis acid, proofed to be suitable in heterogeneous catalytic C–F bond activation reactions.[7] Even though ACF itself shows strong catalytic ability,[7a–c,8] its catalytic performance becomes unique in the presence of main group compounds.[7d–g,9] Thus, ACF catalyzed the C–F bond activation of fluorinated methanes in the presence of $HSiEt_3$, towards both Friedel-Crafts and hydrodefluorination products depending on the solvent used.[7f] More recently, the dehydrofluorination of polyfluoropropanes led to the synthesis of industrially relevant fluoroolefins.[7g] In addition, the activation of 1-fluoropentane at ACF resulted in dehydrofluorination in the presence of $HGeEt_3$, but when $HSiEt_3$ was used instead, Friedel-Craft products were obtained.[7e] Aside from fluoroalkanes, tetrafluoropropenes can also be activated by ACF in the presence of $HSiEt_3$ or $HGeEt_3$ to provide various defluorination products.[7d]

The selective conversion of C–F bonds into C–Cl bonds in polyfluorinated compounds allows for further functionalization processes, which might be more effective with chlorinated substrates in comparison with fluorinated ones.[10] In addition, chlorinated derivatives such as olefins can be used in refrigerants, fluids[11] or as adhesion-promoting additives in coating systems.[12] While the formation of C–F bonds from their halogen congeners is a well-established method for synthesis of different fluorinated compounds,[13] for the reverse reaction, the halodefluorination, some studies for aliphatic systems are reported, and there are some rare examples for a stepwise exchange at aryl moieties.[10,14] Thus, Hilmersson and co-workers demonstrated that YbI_3 can activate alkyl C–F bonds by F/I substitution under mild reaction conditions.[15] Regarding F/Cl exchange reactions, $C(sp^3)$–F bonds could be converted into $C(sp^3)$–Cl bonds using boron trihalides as the chlorine source, including some iron-catalyzed reactions.[16] In addition, chlorodefluorination reactions at fluoroalkanes have been described using Lewis acidic aluminum chloride derivatives as the chlorine source in stoichiometric reactions or as catalyst in presence of chlorosilane.[6a,17]

Herein, we describe the unprecedented chlorodefluorination of fluoroolefins and fluoromethanes under mild conditions by ACF in the presence of chlorinated silanes or germanes. In addition, the derivatives $ACF \cdot ClSiEt_3$ and $ACF \cdot C_3F_6$ have been characterized by MAS-NMR spectroscopy.

Results and Discussion

F/Cl Exchange Reactions at Fluoroalkanes

The reaction of monofluoromethane (**1a**) with $ClSiEt_3$ in the presence of ACF as catalyst was carried out at 70 °C in C_6D_{12} (Scheme 1). After 4 days, monochloromethane (**2a**) was formed with 72% yield (Table 1, entry 1). The F/Cl exchange reaction was only possible when using C_6D_{12} as solvent, in order to avoid Friedel-Craft reactions in the presence of aromatic solvents.[7f,18] When the reaction was performed without addition of chlorosilane, approximately 6% of compound **2a** was observed after

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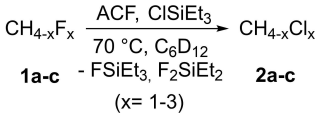
Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202200029



Scheme 1. ACF catalyzed F/Cl exchange reactions at fluoromethanes in the presence of $ClSiEt_3$.

Table 1. ACF catalyzed F/Cl exchange reactions at fluoromethanes in the presence of $ClSiEt_3$.[a]

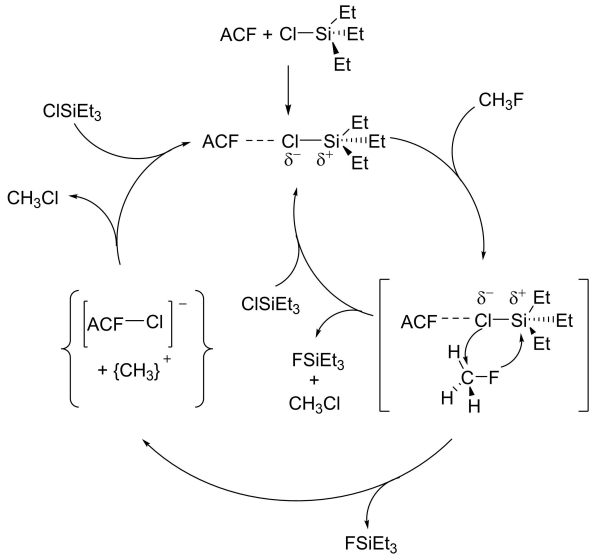
Entry	Substrate	$n_{substrate}$ [mmol]	Time [days]	Yield[b] [%]	Products
1	CH_3F (**1a**)	0.20	4	72	CH_3Cl (**2a**)
2[c]	**1a**	0.23	7	6	**2a**
3[d]	**1a**	0.18	7	0	–
4	CH_2F_2 (**1b**)	0.11	7	90	CH_2Cl_2 (**2b**), CH_2DCl (**2b'**) and CH_3Cl (**2c**) (92:6:2)
5	CHF_3 (**1c**)	0.11	7	60	**2c** and **2b** (traces)

[a] $V[C_6D_{12}] = 0.4$ mL, n(active acid sites) = 25 μmol, $n(ClSiEt_3) = 0.3$ mmol. The number of active acid sites at ACF is calculated by assuming that 1 g ACF contains 1 mmol of active sites.[20b,21] [b] Based on the formation of the products; calculated by integration of signals in the ^1H NMR spectra on using $PhCF_3$ as internal standard. For mixtures, total yield is given. [c] Without addition of $ClSiEt_3$. [d] Without ACF.

7 days as ACF can also be a source of chlorine atoms (Table 1, entry 2).[19] However, when the catalyst ACF was not present, the reaction did not take place (Table 1, entry 3).

Longer reaction times were needed in order to activate CH_2F_2 (**1b**) or CHF_3 (**1c**), and the generation of additional minor products was observed. Thus, difluoromethane (**1b**) transformed with 83% yield into CH_2Cl_2 (**2b**) as well as into small amounts of the H/D exchange product CDH_2Cl (**2b'**) and **2a** in a 92:6:2 ratio (Table 1, entry 4). It has been reported previously that ACF is able to catalyze H/D exchange reactions at alkanes even under mild conditions.[20] Finally, CHF_3 (**1c**) was converted into $CHCl_3$ (**2c**, 51%) and traces of **2b** (Table 1, entry 5). The lower conversion of **1c** can be explained by the stronger C–F bond in comparison to the C–F bonds in **1a** or **1b**.[3]

Mechanistically, it is known that ACF interacts with silanes and germanes.[7f,22] Therefore, ACF might initially interact with $ClSiEt_3$ at the surface and form ACF···Cl–$SiEt_3$ which resembles the interaction in the previously reported molecular $Me_3Si{\cdots}Cl{\cdots}Al(OC(CF_3)_3)_3$ compound.[23] This interaction leads to a polarized silicon-chlorine bond and any silylium-like species might be prone to activate the C–F bond in fluoromethane to form fluorosilane (Scheme 2). This activation leads formally to a surface-bound chloride at ACF as well as a carbenium-like species, which upon reaction with the former, would give chloromethane and recover the catalyst. This can occur stepwise or in a concerted fashion (Scheme 2). The formation of Friedel-Craft products when C_6D_6 is used as solvent supports the presence of intermediate carbenium-like species.[7f18] This proposal resembles mechanisms, which were described for the hydrodehalogenation of halomethanes by ACF.[7e,f] However, we cannot entirely exclude that ACF mediates the F/Cl exchange independently and the chlorosilane only acts as chlorine source

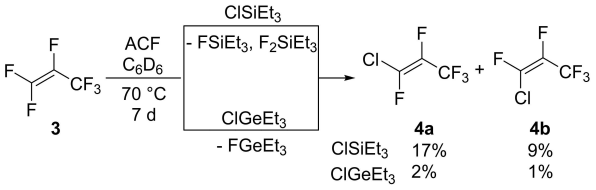


Scheme 2. Conceivable mechanism of the ACF catalyzing the F/Cl exchange at CH_3F (**1a**).

for the regeneration of ACF catalyst, as it was proposed by Young et al. for the chlorodefluorination of benzotrifluorides with $AlCl_3$ and chlorosilanes.[6a] Note that MAS NMR studies indicate that terminal surface bound fluorides are removed in the presence of chlorosilane (see below).

F/Cl Exchange Reactions at Fluoroalkenes

In order to apply the F/Cl exchange reaction further, fluoropropenes were chosen as reaction substrates to activate $C(sp^2)$–F bonds, which is a unique reaction step at ACF. Thus, a reaction of 1,1,2,3,3,3-hexafluoropropene (**3**) with $ClSiEt_3$ catalyzed by ACF at 70 °C in C_6D_6 yielded, after 7 days, *cis*-1-chloro-1,2,3,3,3-pentafluoro-1-propene (**4a**) and *trans*-1-chloro-1,2,3,3,3-pentafluoro-1-propene (**4b**)[24] approximately in a ratio of 2:1 (Scheme 3). $FSiEt_3$ and F_2SiEt_2 were formed as by-products. Note that when silane was not added, only traces of compounds **4a**/**b** were observed. The influence of the chlorine source in the catalytic reaction was also studied by using different main group chlorine sources. Thus, $ClGeEt_3$ and $ClSnPh_3$ were tested with ACF as catalyst. While $ClGeEt_3$ gave the same products



Scheme 3. ACF catalyzed F/Cl exchange reactions at 1,1,2,3,3,3-hexafluoropropene (**3**) in the presence of $ClSiEt_3$ or $ClGeEt_3$.

outcome, but only with a very low conversion, no reaction occurred with $ClSnPh_3$.

The scope on the F/Cl exchange reaction was broadened by testing other polyfluoropropenes. Thus, the reaction of 1,1,3,3,3-pentafluoropropene (**5**) with $ClSiEt_3$ catalyzed by ACF at 70 °C in C_6D_6 gave a mixture of *trans*-1-chloro-1,3,3,3-tetrafluoro-1-propene (**6a**) (27%),[24] *cis*-1-chloro-1,3,3,3-tetrafluoro-1-propene (**6b**)[24] (16%) as well as monodeuterated 1,1,1,3,3,3-hexafluoropropane (**7d**)[25] (13%) and 1,1-dichloro-3,3,3-trifluoro-1-propene (**8**)[24] (4%) (Scheme 4). While compounds **6** and **8** stem from the halogen exchange reaction, compound **7d** seems to be formed by hydrofluorination of **5** with HF followed by H/D exchange.[20a,26]

When C_6D_{12} was used as solvent the monochlorinated products **6a** and **6b** together with compound **7** were obtained in a 1.5:1:0.6 ratio. As a different reactivity was observed in this reaction compared with hexafluoropropene, F/Cl exchange was again attempted with $ClGeEt_3$. Compound **5** transformed in the presence of ACF and $ClGeEt_3$ at 70 °C in C_6D_{12} into to the mixture of **6a** and **6b**, but with lower conversion. This again demonstrates that $ClSiEt_3$ shows a better performance towards F/Cl exchange.

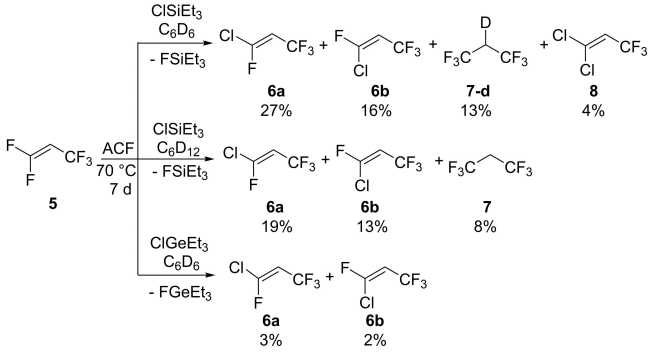
To figure out the influence of the substitution pattern at pentafluoropropene isomers in the F/Cl exchange reaction, *cis*-1,2,3,3,3-pentafluoropropene (**9**) was tested. Thus, compound **9** was treated with $ClSiEt_3$ at 70 °C in presence of ACF as catalyst in C_6D_6 to yield a mixture of *cis*-1-chloro-2,3,3,3-tetrafluoro-1-propene (**10**)[27] and *cis*-1,3,3,3-tetrachloro-2-fluoro-1-propene (**11**) in a ratio of 5.5:1, respectively, together with small amounts of *cis*-1,2,3,3,3-pentachloropropene (**12**)[28] (Scheme 5). Interestingly, although the fluorine atoms at the 1-position of the olefin are always the most reactive ones, the activation of the CF_3 group is preferred over an activation of the C(sp^2)–F bond at the 2-position. Note that activation of allylic CF_3 moieties has been previously found at ACF, but any halogen exchange reaction is unique.[7d,29]

Compound **11** showed, in ^{19}F NMR spectrum, a doublet at $\delta = -108.5$ ppm with F,H coupling constant of 30 Hz. The *trans* arrangement of the olefin is confirmed by the coupling constant[24] and the corresponding olefinic proton at $\delta =$ 5.44 ppm as a doublet in the ^1H NMR spectrum.

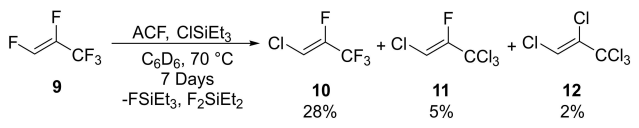
Treatment of 1,3,3,3-tetrafluoropropene (**13**) with $ClSiEt_3$ and ACF as catalyst at 70 °C in C_6D_6 yielded 27% of *trans*-1,1,1,3-tetrachloropropene (**14**)[28] and 21% of *trans*-1-chloro-3,3,3-trifluoropropene (**15**)[24] (Scheme 6). It can be presumed that an initial activation of the C(sp^2)–F bond takes place to form compound **15**, which then reacts further by the activation of the C(sp^3)–F moiety to give compound **14.**

Finally, 3,3,3-trifluoropropene (**16**), which bears only C-(sp^3)–F bonds was studied. The reaction of **16** and $ClSiEt_3$ catalyzed by ACF at 70 °C in C_6D_{12} yielded 11% of 3,3,3-trichloropropene (**17**)[30] as main product together with traces of 3,3-dichloro-3-fluoropropene (**18**) and 3-chloro-3,3-difluoropropene (**19**) (Scheme 7).

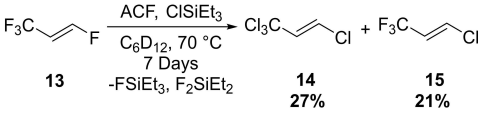
Mechanistically, the activation of the CF_3 moiety of the polyfluoropropenes would follow a comparable pathway as explained above for the fluoromethanes. Any intermediate carbenium-like species will be allylic, which leads to further stabilization.[7d,29,31] This can also include allylic substitution for compound **16** *via* an initial fluoride abstraction.[7d,g,29] However, the unusual C(sp^2)–F bond activation steps presumably proceed *via* a different mechanism based on an ACF mediated addition of chlorosilane at the double bond followed by fluorosilane elimination reaction (Scheme 8). As described above, ACF might interact with $ClSiEt_3$ at the surface and form ACF···Cl–$SiEt_3$. Then, the fluorinated olefin would attack to the silylium-like species to selectively form a β-silylcarbeniumion, which might be stabilized by the β-effect, with the silyl group *geminal* to the CF_3 moiety.[32] Next, the surface-bound chloride of ACF would attack the cationic intermediate species to give a chlorofluorosilylpropane derivative, which in presence of ACF would lead to the F/Cl exchange products by fluorosilane elimination. Alternatively, the addition reaction could take place *via* a direct attack of the coordinated silane at the olefin and not *via* a



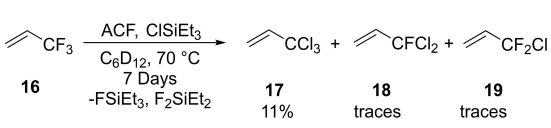
Scheme 4. ACF catalyzed F/Cl exchange reactions at 1,3,3,3-pentafluoropropene (**5**) in the presence of $ClSiEt_3$ or $ClGeEt_3$.



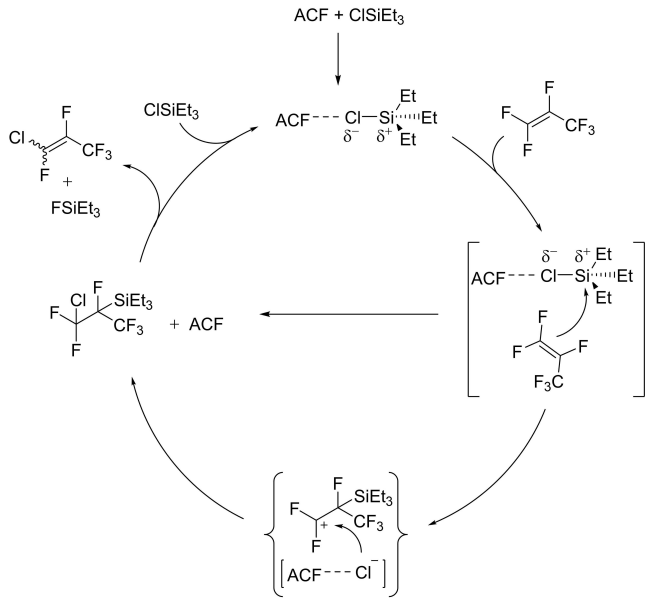
Scheme 5. ACF catalyzed F/Cl exchange reactions at *cis*-1,2,3,3,3-pentafluoropropene (**9**) with $ClSiEt_3$.



Scheme 6. ACF catalyzed F/Cl exchange reactions at *trans*-1,3,3,3-tetrafluoropropene (**13**) in the presence of $ClSiEt_3$.



Scheme 7. ACF catalyzed F/Cl exchange reactions at 3,3,3-trifluoropropene (**16**) in the presence of $ClSiEt_3$.



Scheme 8. Proposed mechanism for the F/Cl exchange reactions at C(sp^2)–F bonds catalyzed by ACF at compound **3**, as an example.

stepwise sequence to form the chlorofluorosilylpropane derivative. The last reaction step resembles the reported formation of 3,3,3-trifluoropropene by the elimination of fluorogermane at $CF_3CH(GeR_3)CH_2F$ or $CF_3CHFCH_2(GeR_3)$ (R = Et, *n*Bu, Ph) when ACF is present in the reaction mixture.[7d] Note also that S_NV mechanisms have been reported for nucleophilic substitutions at olefins.[33] Such reaction steps can involve olefin coordination at the Lewis-acidic surface and a subsequent attack of silane. However, as olefin coordination is not favored (see below), such a pathway is less likely. On the other hand, chloride attack at an olefin after silane coordination at the surface would also result in an S_NV type mechanism,[34] but at least tertiary silanes show typically silylium ion type reactivity.[7e,f,22b]

MAS NMR Studies

The chlorodefluorination of fluoromethanes could in principle also proceed through the initial activation of fluoromethane at ACF to give a carbenium-like ion followed by the reaction with silane. However, differential thermal analysis (DTA) demonstrated that the interaction of silanes with ACF is stronger than the interaction with halomethanes.[18] On the other hand, a possible initial interaction of the Lewis acid sites ACF with the C=C bond of the fluorinated olefins could be plausible as it has been proposed for the hydroarylation of olefins.[29]

In order to get a further insight on the interaction of the key species with ACF and support the mechanisms described above, ACF···$ClSiEt_3$ and ACF···C_3F_6 were prepared by loading $ClSiEt_3$ or $CF_3CF{=}CF_2$ onto ACF (see Supporting Information). The ^{19}F MAS NMR spectrum of ACF···$ClSiEt_3$ showed a signal at $\delta = -168$ ppm, corresponding to the bulk fluorine atoms of ACF (Figure S17), while the ^{19}F spin-echo rotor-synchronized experiment displayed in addition a resonance at $\delta = -202$ ppm (Figure 1, black). The signal corresponds to terminal surface-bound fluorine sites. It exhibits a remarkable reduced intensity compared to the one for ACF (Figure 1, red), which indicates that there are less terminal bound fluorine sites present.

In addition, the silicon species immobilized on the surface of ACF are indicated by a ^1H-^{29}Si cross polarization MAS NMR spectrum, which was compared with other ACF derivatives loaded with silanes (Figure 2). Thus, three resonances at around $\delta = 74$, 37and 12 ppm were observed for ACF loaded with

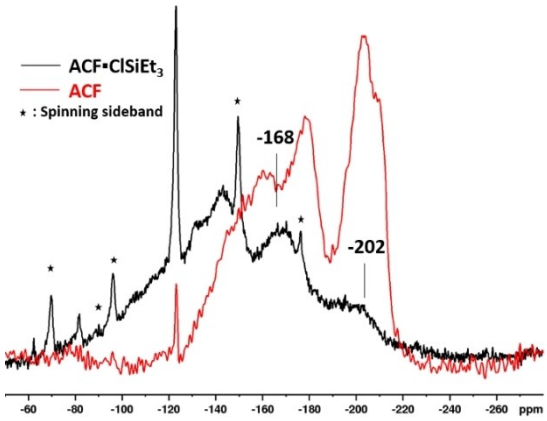


Figure 1. ^{19}F spin-echo rotor-synchronized MAS NMR spectra of $ClSiEt_3$-loaded ACF (black, $\tilde{\nu}_{rot} = 10$ kHz) and ACF (red, $\tilde{\nu}_{rot} = 25$ kHz). $CFCl_3$ and fluorinated grease from the synthesis appear at $\delta = -81$ and -123 ppm, respectively.

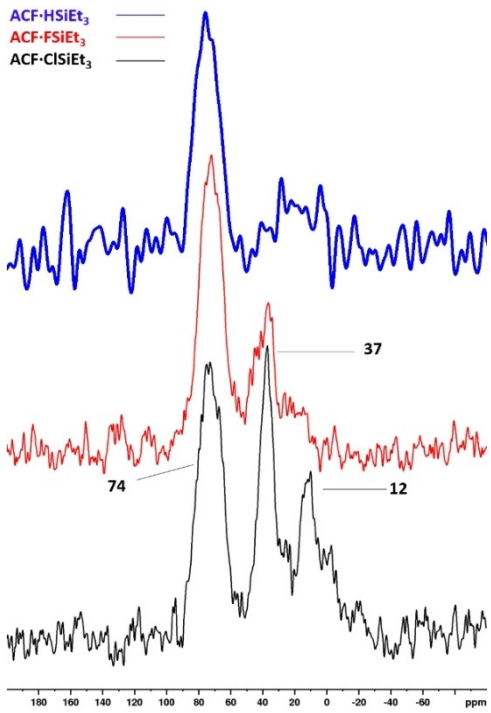


Figure 2. Comparison of ^1H–^{29}Si CP MAS NMR spectra of ACF·$HSiEt_3$ (blue, $\tilde{\nu}_{rot} = 10$ kHz), ACF·$FSiEt_3$ (red, $\tilde{\nu}_{rot} = 10$ kHz) and ACF·$ClSiEt_3$ (black, $\tilde{\nu}_{rot} = 10$ kHz).

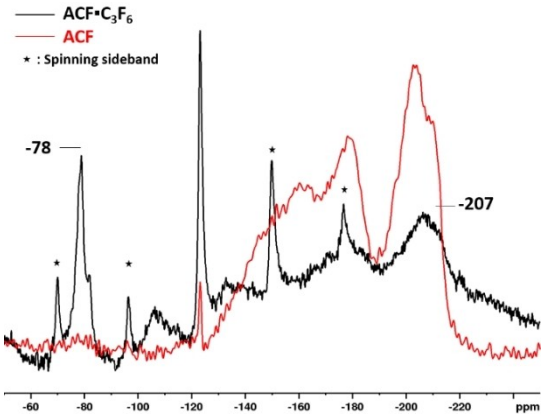


Figure 3. ^{19}F rotor-synchronized spin-echo MAS NMR spectra of C_3F_6-loaded ACF (black, $\tilde{\nu}_{rot} = 10$ kHz) and ACF (red, $\tilde{\nu}_{rot} = 25$ kHz). $CFCl_3$ and fluorinated grease from the synthesis appear at $\delta = -81$ and 123 ppm, respectively.

$ClSiEt_3$ (Figure 2, black line). Resonances at $\delta = 74$ ppm also appear in the MAS NMR spectra for ACF···$HSiEt_3$ (Figure 2, blue line)[7e] and ACF···$FSiEt_3$ (Figure 2, red line) and this might tentatively indicate the presence of silylium-like species on the surface of ACF.[23,35] The signal at 37 ppm, which appears in both spectra of halosilane-loaded ACF, might correspond, by comparison with NMR chemical shifts of solutions, to fluorosilane or chlorosilane species, which do not exhibit a polarized Si-halogen bond.[36] Finally, the resonance at $\delta = 12$ ppm could be assigned to Cl_2SiEt_2.[37] The latter signal indicates that ACF could promote the formation of Cl_2SiEt_2 from $ClSiEt_3$.

Loading of hexafluoropropene at ACF was confirmed by the characterization of ACF·C_3F_6 by MAS NMR spectroscopy. Thus, the ^{19}F MAS NMR spectrum exhibited the main signal due to the fluorine atoms at the bulk of ACF·C_3F_6 at $\delta = -171$ ppm (Figure S21). As observed for ACF·$ClSiEt_3$, a slight shift compared with pure ACF was observed. The ^{19}F spin-echo rotor-synchronized experiment revealed, in addition to the previous fluorine signal, a broad signal at $\delta = -207$ ppm indicating the presence of terminal fluorine sites of ACF, which only partially disappeared after loading with C_3F_6 (Figure 3). In addition, a resonance at -78 ppm for the CF_3 moiety of hexafluoropropene is present, suggesting the immobilization of a small amount of **3** on ACF surface.

ACF·$ClSiEt_3$ was also characterized by thermogravimetric analysis (TGA). While heating up, there was around 8.6% weight loss from 91.1 °C until 185 °C suggesting desorption of silylated species from ACF·$ClSiEt_3$ (see Figure S23). Thus, TGA data confirm that $ClSiEt_3$ was absorbed on ACF, which also supports the initial interaction between both species to induce the F/Cl exchange reactions. However, the TGA experiment of ACF···C_3F_6 showed a weight loss of only around 1.5% while heating up from 85 °C until 200 °C (see Figure S24). In addition, DSC data indicate that C_3F_6 was absorbed on ACF by physisorption. The low content of loaded gas on the surface of ACF as revealed by MAS NMR and TG analysis supports that the first step of F/Cl exchange reaction at fluoroolefins is the loading of $ClSiEt_3$ on the surface of ACF, instead of the gaseous substrate.

Conclusion

In conclusion, F/Cl exchange reactions of fluoromethanes and fluorinated olefins can be achieved when catalyzed by ACF in the presence of $ClSiEt_3$. Although the chlorodefluorination of fluorinated alkanes has been observed before at Lewis acidic systems, the activation of fluoromethanes has not been established. Conceivable silylium-like species in the reaction process might play a certain role in the mechanism, but the chlorination pathway mediated by ACF seems also to be active. In addition, the catalytic system was able to perform the unprecedented chlorodefluorination of $C(sp^2)$–F bonds. Therefore, the ACF/$ClSiEt_3$ system provides a useful methodology for chlorodefluorination of both fluoroalkyl and fluoroalkenyl compounds.

Experimental Section

General Procedures, Methods and Materials

All reactions were performed in JYoung NMR tubes using typical Schlenk techniques and a MBraun glovebox. C_6D_6 was dried with K-Solvona® and, prior to use, distilled under argon. C_6D_{12} was dried and stored over molecular sieves 3 Å. Reagents were obtained from commercial sources, stored in a glovebox and used as received. Aluminum chlorofluoride (ACF, $AlCl_xF_{3-x}$, $x = 0.05$–0.3) was synthesized according to the literature.[38]

NMR spectra in solution (^1H, ^{19}F) were measured at room temperature on a Bruker DPX 300 machine. ^1H–^1H COSY NMR spectra were acquired on Bruker AVANCE II 500 spectrometer with tetramethylsilane as external standard. ^1H NMR chemical shifts (δ in ppm) were referenced to residual C_6D_5H ($\delta = 7.16$ ppm) or, $C_6D_{11}H$ ($\delta = 1.38$ ppm). ^{19}F NMR spectra were externally calibrated to $CFCl_3$ ($\delta^{19}F = 0$ ppm) and $PhCF_3$ ($\delta^{19}F = -63.7$ ppm) was used as reference and internal standard for quantification. 1H NMR signal assignment was supported by ^1H–^1H COSY NMR experiments. ^{19}F and ^{27}Al solid-state MAS (magic angle spinning) nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 400 spectrometer at room temperature. The samples were filled in 4 mm rotors in a glovebox to avoid contact with moisture. ^{27}Al MAS NMR ($I = 5/2$) spectra were measured at a rotation frequency of 10 kHz, a recycle delay of 5 s, and accumulation numbers of 1024 as well as an excitation pulse duration of 1.3 μs. ^{19}F MAS NMR spectra were registered using a $\pi/2$ pulse length of 4.4 μs, a rotation frequency of 10 kHz, a spectrum width of 400 kHz, a recycle delay of 5 s and an accumulation number of 32. Background signals were suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey.[39] The rotor-synchronized ^{19}F spin-echo experiments were recorded with a rotation frequency of 8 or 10 kHz, a recycle delay of 5 s, an accumulation number of 512, and a dipolar evolution time of 0.1 ms. ^{19}F chemical shifts are referenced to $\delta = 0$ ppm of $CFCl_3$, ^{27}Al chemical shifts are given with respect to $\delta = 0$ ppm of 1 M $AlCl_3$ solution. For both nuclei, α-AlF_3 was used as a secondary standard for calibration. ^1H, ^1H–^{13}C cross-polarization (CP MAS) solid state NMR spectroscopic experiments were recorded on a Bruker AVANCE 400 spectrometer at room temperature. The samples were filled in 4 mm rotors in a glovebox to avoid contact with moisture. ^1H MAS studies were made with a $\pi/2$ pulse length of 2.6 μs, a rotation frequency of 10 kHz, a spectrum width of 400 kHz, a recycle delay of 5 s and an accumulation number of 32. However, both ^{13}C MAS NMR and ^1H–^{13}C CP MAS NMR were measured only for ACF·$ClSiEt_3$ and

ACF·$FSiEt_3$. The ^1H–^{29}Si CP MAS spectrum was taken with a contact time of 5 ms, a recycle delay of 5 s and 38825 accumulations, resulting in a total measurement time of nearly 54 h. Values of isotropic chemical shifts of ^1H, ^{13}C and ^{29}Si are given with respect to TMS.

GC-MS spectrometry was measured at a Shimadzu GCMS-QP2010 SE gas-phase chromatograph at 70 eV.

Formation of ACF·$ClSiEt_3$

ACF (300 mg) was suspended in an excess of $ClSiEt_3$ (300 μL, 1.78 mmol) in a Schlenk flask. The reaction mixture was stirred at room temperature for 2 h. The excess of $ClSiEt_3$ was then removed under reduced pressure. The resulting powder was stored in a glovebox, characterized by MAS NMR spectroscopy and used for TG studies.

Formation of ACF·C_3F_6

In a JYoung NMR tube, ACF (200 mg) was suspended in C_6D_6 and an excess of hexafluoropropene (0.4 mmol) was condensed. The reaction mixture was kept at room temperature for 2 h. All the volatiles were then removed under reduced pressure. The resulting powder was stored in a glovebox and characterized by MAS NMR spectroscopy and used for TG studies.

Formation of ACF·$FSiEt_3$

$FSiEt_3$ was synthesized based on literature.[40] 1 g ACF was suspended in an excess of $FSiEt_3$ in a Schlenk tube. The reaction mixture was kept at 70 °C for 24 h. The excess of $FSiEt_3$ was then removed under reduced pressure at room temperature. The resulting powder was stored in a glovebox and characterized by MAS NMR spectroscopy.

General Methodology for the ACF Catalyzed F/Cl Exchange Reactions at Fluorinated Substrates

In a JYoung NMR tube ACF (25 mg) was suspended in C_6D_6 or C_6D_{12} (0.4 mL) and 50 μL $ClSiEt_3$ or 49 μL $ClGeEt_3$ (0.3 mmol) were added. Then, the reaction mixture was frozen to 77 K, the NMR tube was degassed in vacuo and pressurized with the corresponding amount of gaseous substrate. Then, the reaction mixture was heated at 70 °C for 7 days. ^1H and ^{19}F NMR spectroscopy was used for monitoring the reaction progress. After the respective reaction time, the NMR data revealed the conversion of the chlorinated substrate and the formation of fluorosilane and sometimes difluorodiethylsilane or the formation of fluorogermane as well as the olefinic products. The initial amount of dissolved gaseous substrate was determined by ^{19}F NMR spectroscopy in the reaction mixture after 5 minutes at room temperature by comparing the integral ratio of the fluorinated compound to $PhCF_3$ (0.2 mmol) as an internal standard. The same procedure was used to determine the yields. It is assumed that ACF contains approximately 1 mmol g^{-1} acidic sites.[20b,21]

Acknowledgements

We gratefully acknowledge financial support from the CRC 1349 funded by the Deutsche Forschungsgemeinschaft (DFG), German Research Foundation (Gefördert durch die Deutsche Forschungsgemeinschaft – Projektnummer 387284271 – SFB 1349). We also would like to acknowledge Dr. Mike Ahrens for fruitful discussions and the Chinese Scholarship Council for financial support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aluminum · C–F activation · chlorodefluorination · fluorine · Lewis acids

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Manuscript received: January 10, 2022
Revised manuscript received: February 28, 2022
Accepted manuscript online: March 1, 2022
Version of record online: March 19, 2022

Correction added on 09.05.2022, after first online publication: Reference 10 was corrected.