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Selective reduction of a C−Cl bond in halomethanes with Et$_3$GeH at nanoscopic Lewis acidic Aluminium fluoride

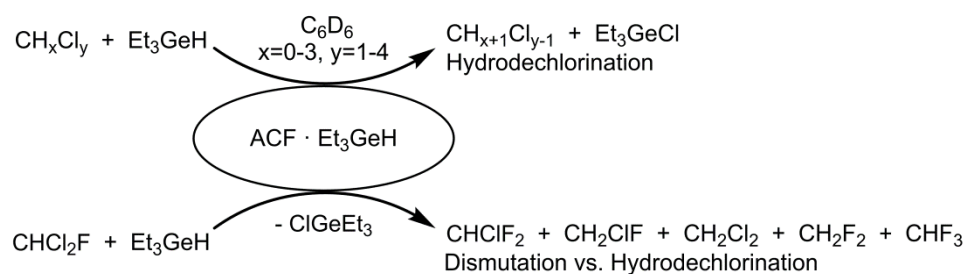Gisa Meißner, Michael Feist, Thomas Braun, Erhard Kemnitz

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Graphical Abstract for:

Selective Reduction of a C–Cl Bond in Halomethanes with Et$_3$GeH at Nanoscopic Lewis Acidic Aluminium Fluoride

G. Meißner, Michael Feist, T. Braun* and E. Kemnitz*

$$CH_xCl_y + Et_3GeH \xrightarrow[\substack{x=0-3,\ y=1-4}]{C_6D_6} CH_{x+1}Cl_{y-1} + Et_3GeCl$$

Hydrodechlorination

ACF · Et$_3$GeH

$$CHCl_2F + Et_3GeH \xrightarrow{-\ ClGeEt_3} CHClF_2 + CH_2ClF + CH_2Cl_2 + CH_2F_2 + CHF_3$$

Dismutation vs. Hydrodechlorination

Catalytic selective C–Cl bond cleavage reactions at moderate reaction conditions at a Lewis-acidic amorphous aluminum chloro fluorid (ACF) in the presence of Et$_3$GeH are presented. Chloromethanes and hydrochlorofluoromethanes as substrates were tested and *Pulse*TA® experiments reflect the interactions between the catalyst and reactants.

Selective Reduction of a C–Cl Bond in Halomethanes with Et$_3$GeH at Nanoscopic Lewis Acidic Aluminium Fluoride

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Dedicated to Prof. J. A. Gladysz on the occasion of his 65th birthday

ARTICLE INFO

ABSTRACT

The selective activation of C–Cl bonds of hydrochlorofluoromethanes and chloromethanes at moderate reaction conditions using ACF in a combination with Et$_3$GeH is presented. The reactions of the chloromethanes (CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4) in the presence of Et$_3$GeH and ACF as catalyst led to the activation of only one C–Cl bond resulting in the hydrodechlorination. Friedel-Crafts reactions with benzene as solvent are suppressed by Et$_3$GeH. A selective hydrodechlorination of hydrochlorofluoromethanes was achieved, because a transformation of a C–F bond into a C–H bond by the combination of ACF with Et$_3$GeH did not occur. Supporting *Pulse*TA® experiments illustrated the interaction between the solid catalyst and Et$_3$GeH, the solvent benzene or CH_2Cl_2.

1. Introduction

Selective monohydrodechlorination[1] reactions which involve the activation of only one C–Cl bond are of high interest because of the environmental relevance of hydrochloromethanes, CCl_4 and hydrochlorofluoromethanes. Although the latter were used as first generation of cooling agents, nowadays their selective degradation is of interest due to their "supergreenhouse gas" behavior and ozone depletion potential.[2-4] The selective cleavage of only one C–Cl bond of per- or polychlorinated substrates is generally difficult to achieve; usually a full dehalogenation of e.g. CCl_4 or $CHClF_2$ at highly reactive materials like metal fluorides occurs,[5,6] or no bond cleavage is observed. Alternative methods include depletion such as catalytic oxidation or hydrolysis.[7-15] Thus, there is some demand for the development of more sophisticated catalysts, which show a unique reactivity and a high selectivity. Useful strategies for hydrodechlorination might also benefit from the generation of thermodynamically favorable bonds such as Si–Cl, Ge–Cl or Al–Cl bonds.[16]
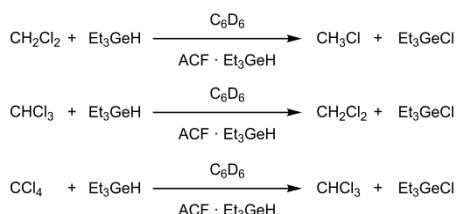
There are several C–Cl bond activation reactions of chlorinated organic substrates described in the literature.[17-24] The simplest derivatization consists of the transformation of a C–Cl bond into a C–H bond, i.e. a hydrodechlorination reaction. In addition to transition metal-mediated conversions by homogeneous catalysis[25-31], a wide range of heterogeneous catalytic reactions were developed.[32-42] Carbon immobilized platinum or palladium catalysts[43-48] as well as palladium and platinum particles supported at alumina are useful for $C(sp^3)$–Cl bond cleavage reactions.[49-53] However, these reactions often require harsh reaction conditions including fairly high temperatures. Recently, we reported the C–Cl bond activation of chloromethanes[54] at nanoscopic ACF ($AlCl_xF_{3−x}$, $x = 0.05$-0.3)[55,56] in combination with Et$_3$SiH, which led to the formation of Friedel-Crafts products when benzene is used as solvent. If the reaction is performed in silane, a complete hydrodechlorination of the chloromethanes was observed.[54] Furthermore, dismutation reactions of halofluoroalkanes are known at ACF.[57] Note that ACF was investigated first by Krespan and Petrov,[55,58,59] and is a very strong Lewis acid with a comparable Lewis acidity to that one of SbF_5.[57,60,61] However, heterogeneous catalytic conversions concerning the activating of only one C–Cl bond of halomethanes at moderate conditions are less developed.[54]

In this paper, the selective activation reactios of one C–Cl bond of hydrochlorofluoromethanes and chloromethanes at moderate reaction conditions at ACF in the presence of Et$_3$GeH are presented.

2. Results and Discussion

Treatment of CH_2Cl_2 with Et_3GeH in the presence of $ACF \cdot Et_3GeH$ as catalyst, which was generated by the immobilization of Et_3GeH at the ACF surface, led to the activation of only one C–Cl bond as a result of a hydrodechlorination reaction. Notably, both in the presence and absence of C_6D_6 as solvent, $ClGeEt_3$ and CH_3Cl as main products were observed (Scheme 1; Table 1, entries 4, 6 and 8).

$$CH_2Cl_2 + Et_3GeH \xrightarrow[ACF \cdot Et_3GeH]{C_6D_6} CH_3Cl + Et_3GeCl$$

$$CHCl_3 + Et_3GeH \xrightarrow[ACF \cdot Et_3GeH]{C_6D_6} CH_2Cl_2 + Et_3GeCl$$

$$CCl_4 + Et_3GeH \xrightarrow[ACF \cdot Et_3GeH]{C_6D_6} CHCl_3 + Et_3GeCl$$

Scheme 1. ACF catalysed C–Cl bond activation with Et_3GeH as hydrogen source in C_6D_6.

The formation of methane as the product of a complete hydrodechlorination or toluene and diphenylmethane as Friedel-Crafts-products were observed only in traces. As mentioned above, this is in contrast to the activation of hydrochloromethanes[54] and hydrofluoro-methanes[62] at ACF and Et_3SiH as hydrogen source, for which diphenylmethane and toluene as products of Friedel-Crafts-like reactions were generated in benzene. Additionally, in both cases a full dehalogenation of the hydrochloromethanes[54] and hydrofluoro-methanes[62] was observed when the reaction was performed in the presence silane.

Furthermore, various chloromethanes were tested as substrates in the presence of $ACF \cdot Et_3GeH$ and Et_3GeH in C_6D_6 or Et_3GeH itself as solvent (Table 1). Accordingly, in all cases the poly- and perchlorinated substrates CH_xCl_y gave selectively $CH_{x+1}Cl_{y-1}$ as main products of monohydrodechlorination as well as Et_3GeCl. The monohydrodechlorination of a higher chlorinated substrate might be preferred, possibly because a higher chlorinated carbenium-like ion is more stable compared to a non-chlorinated cation on the surface.[63-66]

However, with an increasing number of bound chlorine atoms at the substrate, a higher reaction temperature is beneficial. Thus, the activation of CH_3Cl and CH_2Cl_2 gave good conversions at 25 °C, whereas the reactions of $CHCl_3$ and CCl_4 were run at 70 °C. Note that the reactions of $CHCl_3$ and CCl_4 are faster when the reaction is performed in Et_3GeH itself as solvent, which is reasonable due to the higher concentration of the germane. If the conversions were run in the presence of an excess of germane, in a subsequent reaction the polyhydrodechlorinated products were observed until germane is consumed.

$ACF \cdot Et_3GeH$ was investigated by NH_3-TPD, and for comparison an experiment was also run for ACF (Figure 1). Both samples are characterized by comparable weak and medium Lewis acidic sites, but the majority of Lewis acidic sites are very strong and no NH_3 desorption occurred until the decomposition temperature of ACF at approximately 400 °C. ACF then decomposes into AlF_3 and $AlCl_3$.[61] $ACF \cdot Et_3GeH$ shows an ammonia release at higher temperature than ACF, which can be explained by a slightly higher stability of $ACF \cdot Et_3GeH$ compared to ACF. In addition, ammonia release at ACF is more intense, which is consistent with lower number of very strong Lewis acidic sites at $ACF \cdot Et_3GeH$ due to the occupation by the germane.
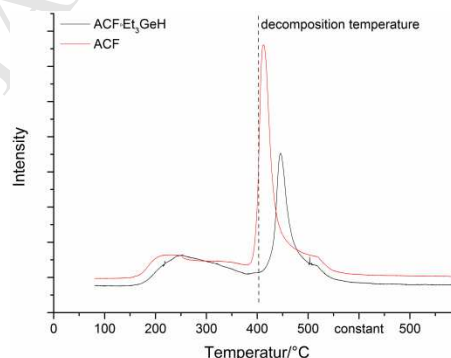

Figure 1. TPD profiles of adsorbed ammonia at the surface of $ACF \cdot Et_3GeH$ (black) and ACF (red).

Table 1. C–Cl bond activation reactions of chloromethanes at ACF with Et_3GeH.

| Entry	Substrate	Solvent	Main product	Minor products	T [°C]	Conv. [%][a]	TON[b]
1	CH_3Cl	–	CH_4	–	25	29	6
2	CH_3Cl	C_6D_6	CH_4	$PhCH_3$ (traces)	25	39	8
3	CH_2Cl_2	–	CH_3Cl	CH_4 (traces)	25	42	8
4	CH_2Cl_2	C_6D_6	CH_3Cl	CH_4 (traces), $PhCH_3$ (0.7%), Ph_2CH_2 (9%)	25	39	8
5	$CHCl_3$	–	CH_2Cl_2	CH_3Cl (22%)	70	78	16
6	$CHCl_3$	C_6D_6	CH_2Cl_2	Ph_2CH_2 (18%) $PhCH_3$ (0.8%),	70	50	10
7	CCl_4	–	$CHCl_3$	CH_2Cl_2 (8%)	70	100	20
8	CCl_4	C_6D_6	$CHCl_3$	CH_2Cl_2 (7%), Ph_2CH_2 (6%)	70	84	17

[a] Conversions were calculated after 72 h by integration of the ^1H NMR spectra and are based on the converted Et_3GeH into Et_3GeCl. [b] TONs were calculated based on the amount of converted chlorinated substrate and assuming that 1 g of ACF contains roughly 1 mmol of catalytically active sites. [60,67] Ph=C_6D_5.

For a better understanding of the reaction pathways of the monohydrodechlorinations, the interaction of the germane with the solid catalyst ACF·Et$_3$GeH and CH$_2$Cl$_2$ were studied by a *Pulse*TA® (PTA)[68] method. In the past, PTA analyses have been successfully employed for the investigation of solid-gas interactions, e.g. for ACF with Et$_3$SiH.[54] The kind of information that can be deduced from PTA experiments is shown in Figure 2 for the further loading of ACF·Et$_3$GeH with Et$_3$GeH. It is interesting that ACF·Et$_3$GeH[69], which was prepared by treatment of ACF with germane and a subsequent drying of the bulk sample in vacuum, absorbs further gaseous Et$_3$GeH. This is certainly due to active sites which remained at the surface even after the initial preparation of ACF·Et$_3$GeH. It can be assumed, that some of the active sites were desorbed by drying the ACF·Et$_3$GeH sample in vacuum. The immobilization of Et$_3$GeH to ACF·Et$_3$GeH completes the previously reported strong interaction between ACF and Et$_3$GeH as primary interaction, for which a surface coverage of 0.48 mol%[70] Et$_3$GeH was established.[71]
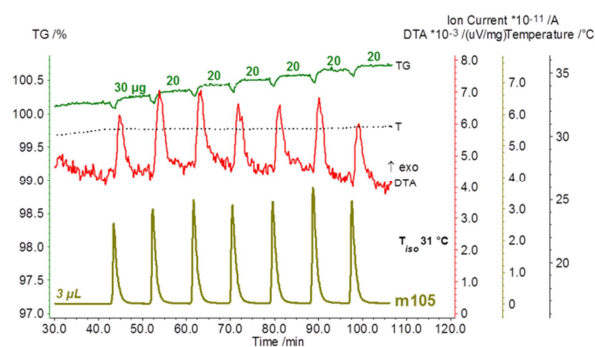
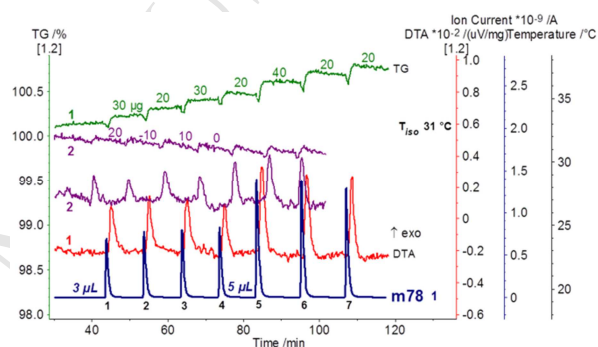**Figure 2.** Isothermal PTA curves for a sequence of 7 pulses of 3 μL liquid Et$_3$GeH (m/z=105, EtGeH$^+$) to ACF·Et$_3$GeH (27.3 mg) in Argon. The curve shapes of the exothermal DTA peaks and the TG steps are characteristic for chemisorption[72,73] A total mass gain of 150 μg (0.28 mol%[70]) was observed, but the Et$_3$GeH loading is not yet completed. Note that the TG spikes preceding the persistent mass gain steps are due to the high density of the injected germane (buoyancy effects).

Some of the catalytic reactions with ACF·Et$_3$GeH were run in benzene as solvent. Therefore, both reactants might compete for the adsorption sites at the ACF surface. This was confirmed by additional MAS NMR spectroscopic studies of benzene-loaded ACF which reveal also the immobilization of benzene at the surface, because of resonances which are in the range for aromatic compounds. The ^{1}H MAS NMR spectrum shows a broad resonance with the maximum at δ = 7.7 ppm (Figure 3, left) and two features at δ = 130 ppm and δ = 142 ppm in the ^{1}H-^{13}C CP MAS NMR spectrum (Figure 3, right).
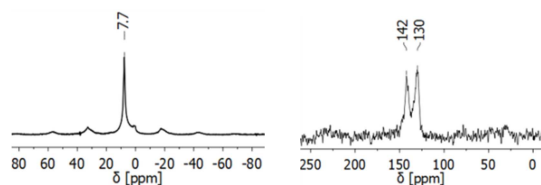
**Figure 3.** ^{1}H MAS NMR (left) and ^{1}H-^{13}C CP MAS NMR (right) spectra of benzene-loaded ACF.

The comparison of two PTA experiments clearly demonstrates the remarkable differences in the adsorption behavior of ACF and ACF·Et$_3$GeH for benzene (Figure 4). ACF shows a constant loading of benzene which was not completed in this sequence of 7 injections, whereas ACF·Et$_3$GeH exhibits only a very weak temporary adsorption, together with an underlying mass loss due to a benzene release in the dry purge gas flow. The benzene uptake of ACF is strong with 20-40 μg per pulse and the total uptake of 180 μg yields a benzene immobilization of 0.7 mol%.[70] Note further that benzene desorbs slightly from ACF after its loading (above 80 °C, TA curves in supplementary data). This also indicates a stronger interaction of Et$_3$GeH with the ACF surface (no desorption of Et$_3$GeH until 150 °C)[71] compared with that one of benzene and it is also in accordance with the intensities of the DTA signals for Et$_3$GeH and benzene. The average DTA signal area clearly indicates a greater exothermicity for the loading pulses of Et$_3$GeH (0.80 μVs/mg)[71] than for those of benzene (0.33 μVs/mg).

Figure 4. Comparison of the isothermal PTA curves for pulses of 3 μL and 5 μL liquid benzene (m/z=78, C$_6$H$_6$$^+$) to ACF (**1**) (28.6 mg) and ACF·Et$_3$GeH (**2**) (26.4 mg) in Argon. The total uptake of C$_6$H$_6$ is 180 μg for ACF, whereas for ACF·Et$_3$GeH two weak temporary mass gains are overcompensated by an underlying mass loss that is due to a certain benzene loss in the purge gas flow. The IC curve for m/z=78 is shown only for ACF. Note the lower exothermicity for ACF·Et$_3$GeH and the different time intervals between the 7 injections which were performed both for ACF and ACF·Et$_3$GeH.

The interaction between CH$_2$Cl$_2$, as an example for the halomethanes, and ACF·Et$_3$GeH was additionally investigated with PTA (Figure 5). The first two pluses exhibit the characteristics of pure, but weak chemisorption with a first indication of an increasing overlap by physisorption (TG curve shape; see discussion above). Therefore, as an attempt to enhance the interaction, the pulse volume was increased from 3 to 5 μL within the experiment. The adsorption, however, was not promoted. As for the absorption of additional germane (Figure 1), ACF·Et$_3$GeH is apparently also able to load additional substrate CH$_2$Cl$_2$. Even if this interaction revealed to be weaker than in the case of ACF·Et$_3$GeH with Et$_3$GeH, it proves that an interaction between ACF·Et$_3$GeH and CH$_2$Cl$_2$ is possible, which is a prerequisite for a C–Cl bond activation step.
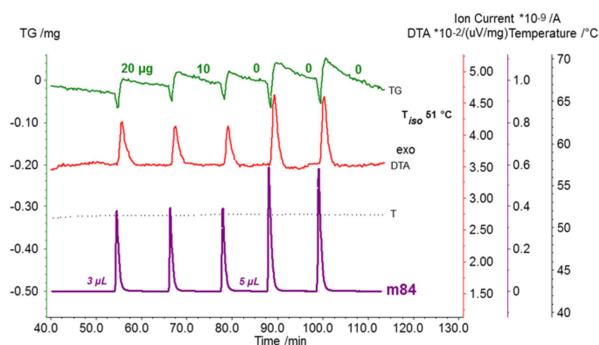
Figure 5. Isothermal PTA curves for a sequence of 5 pulses of 3 µL and 5 µL liquid CH_2Cl_2 (m/z= 84, $CH_2Cl_2^+$) to ACF·Et_3GeH (25.5 mg) in Argon. The adsorption of CH_2Cl_2 is rather limited. Note that the TG downwards spikes (cf. Figure 2) are stronger here due to the higher density of CH_2Cl_2.

A proposed mechanism for the monohydrodechlorination reaction involves the interaction of Et_3GeH with the ACF surface, which results in a polarization of the H—Ge bond. The formed germylium-like species at the surface is able to initiate a C—Cl bond cleavage at the surface of ACF·Et_3GeH. After release of Et_3GeCl, a generated carbenium ion-like surface species gives together with the surface-bound hydrogen atom the monohydrodechlorinated product. Finally, in the presence of additional germane, ACF·Et_3GeH is regained (Scheme 2). An alternative mechanism involves an initial activation of the C—Cl bond at the surface. Then, a subsequent reaction of Et_3GeH as hydrogen source with the surface gives the monohydrodechlorinated product in addition to Et_3GeCl (Scheme 2). However, the latter reaction pathway might favor Friedel-Crafts reactions.[71]
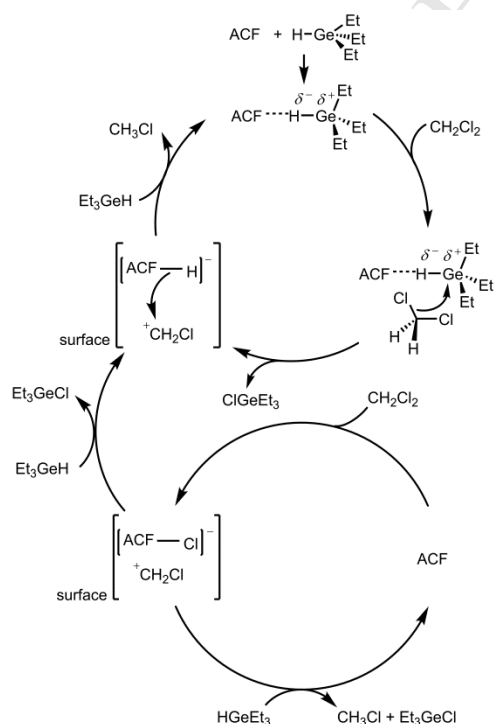

Scheme 2. Simplified mechanisms of the ACF catalysed monohydrodechlorination for CH_2Cl_2 with Et_3GeH.

No C—F bond activation of CH_2F_2 was observed with ACF·Et_3GeH as catalyst. This is in contrast to the conversions reported for ACF and silane.[62] Note also that at BaF_2[74] and Pd/C[75] a dehydrochlorination is preferred over a dehydrofluorination. Therefore, $CHCl_2F$ and $CHClF_2$ were tested as chlorofluoromethanes for selective hydrodechlorinations. Nevertheless, in the presence of a very strong Lewis acid such as ACF,[57,60,61] both substrates undergo in addition chlorine fluorine exchange reactions[76-83], i.e. dismutation reactions. The activation of $CHCl_2F$ at ACF·Et_3GeH gave CH_2F_2 and CH_2Cl_2 as main products of hydrodechlorination as well as CHF_3 and CH_3Cl as minor products next to $CHClF_2$ (Scheme 3; Table 2, entry 1). However, C—F bond activations occurred only in terms of dismutation reactions.
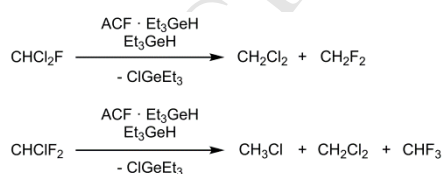
Scheme 3. Main products of the ACF catalysed C—Cl bond activation reactions of $CHCl_2F$ and $CHClF_2$ with ACF·Et_3GeH and Et_3GeH.

For the reaction of $CHCl_2F$ as substrate possible dismutation and hydrodechlorination products are shown in Scheme 4. Because of the presence of CHF_3, rather than CH_2F_2, the dismutation reaction pathway seems to be faster than the hydrodechlorination reaction. Note that due to the dismutation pathway, the comparable reaction pathways are observed when $CHClF_2$ was activated. The reaction of $CHCl_2F$ is faster when compared to the conversion of its dismutation product $CHClF_2$, although both activations occur at room temperature (Scheme 3; Table 2, entries 1 and 3). Both substrates $CHCl_2F$ and $CHClF_2$ undergo a dismutation before the products of isomerization undergo indeed hydrodechlorination reactions. The reactions reveal that the dismutation reaction is more rapid than the hydrodechlorination. In literature are some examples for the preferred activation of one carbon halogen bond of bromofluoromethanes[84-87] or chlorofluoro-methanes[88-97] described, but they are usually performed under very harsh reaction conditions.
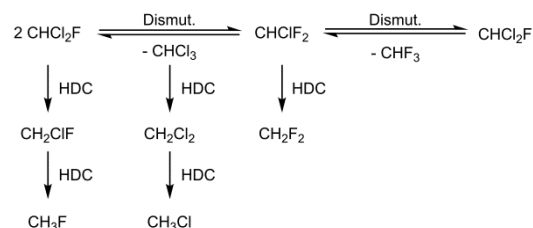
Scheme 4. Reaction pathways of ACF catalysed dismutation and hydrodechlorination reactions (HDC) of $CHCl_2F$ and $CHClF_2$ in the presence of Et_3GeH.

Table 2. ACF catalysed C–Cl bond activation reactions of chlorfluoromethanes with Et$_3$GeH.

Entry	Substrate	Solvent	Main products	Minor products	T [°C]	t [h]	Conv. [%][a]	TON[b]
1	CHCl$_2$F	–	CH$_2$Cl$_2$, CH$_2$F$_2$ (2.5:1.0)	CHF$_3$, (22%), CHClF$_2$ (16%), CH$_2$ClF (4%), CH$_2$F$_2$ (traces)	25	3d	72	16
2	CHCl$_2$F	C$_6$D$_6$	CH$_2$ClF (50%), Ph$_2$CH$_2$ (39%), CH$_2$Cl$_2$ (11%)	CHClF$_2$ (traces), CH$_3$Cl (traces), PhCH$_3$ (traces)	70	9d	44	10
3	CHClF$_2$	–	CH$_3$Cl (41%), CH$_2$Cl$_2$ (32%), CHF$_3$ (27%)	CHCl$_2$F (traces)	25	3d	19	5
4	CHClF$_2$	C$_6$D$_6$	CHF$_3$	Ph$_2$CH$_2$ (5%), CHCl$_2$F (1.3%), PhCH$_3$ (traces), CH$_3$Cl (traces)	70	9d	10	4

[a] Conversions were calculated by integration of the ^{1}H NMR spectra and are based on the converted Et$_3$GeH into Et$_3$GeCl. [b] TONs were calculated based on the amount of converted chlorinated substrate and assuming that 1 g of ACF contains roughly 1 mmol of catalytically active sites. [60,67] Ph=C$_6$D$_5$.

If the reactions of CHCl$_2$F and CHClF$_2$ are performed in C$_6$D$_6$ as solvent, deuterated diphenylmethane and deuterated toluene were also detected in traces as Friedel-Crafts products in addition to the dismutation and hydrodechlorination products (Table 2, entries 2 and 4). The reactivity of the chlorofluoromethanes might show these differences, because of the formation of carbenium-like ions as intermediates within the dismutation reaction pathways at ACF. These species behave presumably different than the carbenium-like surface species formed during the hydrodechlorinations of chloromethanes at ACF · Et$_3$GeH. The reactions of CHClF$_2$ and CHCl$_2$F with germane itself as solvent are again faster than the reactions in benzene because of a higher concentration of the germane. The former reaction can be performed already at room temperature, whereas the reaction in benzene requires 70 °C and a longer reaction time (Table 2).

3. Conclusion

In conclusion, we have shown that the combination of ACF, as a very Lewis acidic aluminum chlorofluoride, with germane forms a suitable catalytic system for the selective activation of C–Cl bonds. The reactions proceed at very mild conditions. The material ACF · Et$_3$GeH promotes a unique monohydro-dechlorination of polyhalogenated methanes with high selectivity towards the activation of C–Cl bonds. There is no evidence for C–F bond activation, which enables a hydrodechlorination of hydrochlorofluoromethanes. At the same time it is remarkable, that Friedel-Crafts-like conversions with benzene as a solvent are suppressed in the presence of Et$_3$GeH, although such reaction routes are typically for strong Lewis acids. PTA experiments give information about the interaction between benzene or CH$_2$Cl$_2$ at the ACF · Et$_3$GeH surface.

4. Experimental

4.1 General

All reactions were performed in JYoung NMR tubes prepared in a glovebox and using conventional Schlenk techniques. C$_6$D$_6$ was dried over K-Solvona® and distilled before usage. Et$_3$GeH was purchased from Alfa Aesar and was used as received and stored in a glovebox. The liquid substrates CH$_2$Cl$_2$ (Sigma Aldrich), CHCl$_3$ (Sigma Aldrich) and CCl$_4$ (Sigma Aldrich) as well as the gaseous substrates CH$_3$Cl (Linde), CHCl$_2$F (abcr) and CHClF$_2$, (Merck) were used as received.

The experimental setup for performing a *Pulse*TA® (PTA) measurement can be understood as an extension of usual TA-MS devices by a gas dosing unit allowing for the injection of gases into the purge gas thus enabling an interaction with the solid. The measurements have to be prepared as usually in the case of simultaneously coupled TA-MS investigations.[68,72,73] One obtains the thermoanalytical curves (DTA, TG) both under heating or isothermally whereby their interpretation is supported by additionally recorded ionic current (IC) curves in the multiple ion detection mode. For the present study, a NETZSCH thermoanalyzer STA 409 C Skimmer® system, equipped with a BALZERS QMG 421, was used. Further experimental details are as follows: DTA-TG sample carrier system, platinum crucibles (0.8 mL beaker), Pt/PtRh10 thermocouples, constant purge gas flow 70 mL/min Argon 5.0 (MesserGriesheim), isothermal temperature plateau, raw data evaluation with the manufacturer's software PROTEUS® (v. 4.3) and QUADSTAR® 422 (v. 6.02) with no further data treatment. ACF samples were measured versus empty reference crucible. Substrates were injected either by using the commercially available PTA box or manually by using simple plastic syringes. Evaporable liquids can be pulsed as well by using a septum-tightened heated (120 °C) GC injector and ordinary micro litre glass syringes. Isothermal PTA revealed to be of extraordinary sensitivity for enthalpic effects and mass changes. The injection pulses as well as changes of the product composition of the gas phase are monitored by the IC curves of pre-chosen characteristic mass numbers for the injected agent.

5

The ^{1}H and [1]H-^{13}C CP (cross polarization) solid state NMR experiments were recorded on a Bruker AVANCE 400 spectrometer (B_0=9.4 T) at room temperature using a 4.0 mm magic angle sample spinning (MAS) probe head. The experiments were performed with a rotation frequency of 10 kHz. ^{1}H-^{13}C CP MAS NMR experiments were performed with a contact time of 1 ms, a recycle delay of 5 s and an accumulation number of 4914. Chemical shift values (δ) of ^{1}H and ^{13}C MAS NMR spectra are given with respect to TMS and are measured against adamantane as secondary standard.

NMR spectra in solution (^{1}H, ^{19}F, [13]C{[1]H}) were recorded at room temperature on a Bruker DPX 300 or a Bruker AVANCE II 500 spectrometer with tetramethylsilane as external standard. ^{1}H NMR chemical shifts (δ) were referenced to residual C_6D_5H (δ = 7.16 ppm) and ^{13}C{^{1}H} NMR spectra were referenced to the deuterated solvent (C_6D_6: δ = 128.1 ppm). ^{19}F NMR spectra were externally calibrated to $CFCl_3$ (δ = 0 ppm) and the measured spectra were referenced to $PhCF_3$ (δ = −63.7 ppm) in a capillary. Characteristic NMR resonances of substrates and products are summarized in Table 3.

Table 3. NMR resonances in C_6D_6 of substrates and products.

Reactant	δ(^{1}H NMR) [ppm]	δ(^{19}F NMR) [ppm]	$^2J_{H,F}$ [Hz]	δ(^{13}C NMR) [ppm]
Et_3GeH	1.06 (t, 9H, CH_3, $^3J_{H,H}$ = 7.8 Hz)	–	–	10.3 (s) 3.8 (s)
Et_3GeCl	0.99 (t, 9H, CH_3, $^3J_{H,H}$ = 6.6 Hz)	–	–	10.4 (s) 8.1 (s)
CH_4	0.16 (s)	–	–	n.d.
CH_3Cl	2.34 (s)	–	–	25.3
CH_2Cl_2	4.28 (s)	–	–	53.3
$CHCl_3$	6.20 (s)	–	–	77.3
CCl_4	–	–	–	96.3
$PhCH_3$	2.12 (s, 3H, CH_3)	–	–	n.d.
Ph_2CH_2	3.75 (s, 2H, CH_2)	–	–	41.9 (s, CH_2)
$CHCl_2F$	6.38 (d)	-81.0 (d)	53.7	104.4 (d, $^1J_{C,F}$=294.5 Hz)
$CHClF_2$	6.02 (t)	-72.1 (d)	63.1	116.4 (t, $^1J_{C,F}$=289.7 Hz)
CH_2ClF	5.05 (d)	-170.1 (t)	47.9	n.d.
CH_2F_2	4.76 (t)	-142.9 (t)	50.3	108.0 (t, $^1J_{C,F}$=236.0 Hz)
CHF_3	5.29 (q)	-78.8 (d)	79.5	n.d.

n.d.=not determined. Ph=C_6D_5.

For temperature progammed desoption (TPD) experiments, samples (ACF 37.8 mg, ACF · Et_3GeH 25.2 mg) were preheatet for 1 h from 50 °C to 120 °C (5 °C/min) under an argon atmosphere and the Lewis acidic sites were loaded afterwards in a NH_3 gas flow. The desorption of NH_3 was followed by the deformation band of NH_3 at 930 cm^{-1} using the FTIR spectrometer Excalibur 300 digilab.

4.1 Synthesis of ACF and ACF · Et_3GeH

Synthesis of ACF (Aluminum chlorofluoride, $AlCl_xF_{3-x}$, x = 0.05-0.3): According to the literature[55,56] CCl_3F (Fluka) was added to $AlCl_3$ (99.99%, anhydrous powder, Sigma Aldrich, lot number MKBQ7519V) in CCl_4, which was stored over molecular sieves. NH_3-TPD measurements show that 1 g ACF contains roughly 1 mmol of Lewis acidic sites.[60,67]

Synthesis of ACF · Et_3GeH: ACF (300 mg) was suspended in an excess of Et_3GeH (300 μL, 1.85 mmol). The reaction mixture was stirred for 2 h at room temperature. Then, the Et_3GeH excess was removed under dynamic vacuum and the resulting powder was stored in a glovebox. A mass weight increase of approximately 10% indicates a coverage of Lewis acidic sites of 62%, based on the assumption that roughly 1 mmol/g[60,67] catalytically active sites are present.

Isomerization of 1,2-dibromohexafluoropropane into 2,2-dibromohexafluoropropane: As an indication for the activity of the catalyst this reaction is used, because only very strong Lewis acids perform this reaction at 25 °C.[57] ACF (25 mg) or ACF · Et_3GeH (25 mg) were suspensed in 1,2-dibromohexafluoropropane (250 μL). After 2 h at 25 °C, $CDCl_3$ was added and the isomerization reaction was monitored by ^{19}F NMR spectroscopy. For ACF, the measurement revealed 100% conversion in constrast to the ACF · Et_3GeH sample with 0% of conversion.

4.2 Activation of the liquid substrates CH_2Cl_2, $CHCl_3$, CCl_4

In a JYoung NMR tube, ACF · Et_3GeH (20 mg) was suspended in Et_3GeH (0.4 mmol) and C_6D_6 (0.6 mL) before the substrate (0.4 mmol) was added. The reaction progress was monitored by ^{1}H NMR spectroscopy. If the reaction is performed in Et_3GeH as solvent, C_6D_6 (0.6 mL) was condensed to the reaction mixture for NMR spectroscopic analysis after the reaction was stopped. Conversions were calculated based on signal integration of the consumed Et_3GeH (C_6D_6: δ = 1.06 (t, 9H, CH_3, $^3J_{H,H}$ = 7.8 Hz) ppm) into Et_3GeCl (C_6D_6: δ = 0.99 (t, 9H, CH_3, $^3J_{H,H}$ = 6.6 Hz) ppm). TONs were calculated based on the amount of chlorinated substrate assuming ACF reveals 1 g/mmol catalytically active sites.[60,67]

4.3 Activation of the gaseous substrates CH_3Cl, $CHCl_2F$, $CHClF_2$, CH_2F_2

In a JYoung NMR tube ACF·Et_3GeH (20 mg for CH_3Cl, 25 mg for $CHCl_2F$, $CHClF_2$, CH_2F_2) was suspended in Et_3GeH (0.4 mmol for CH_3Cl, 0.5 mmol for $CHCl_2F$, $CHClF_2$, CH_2F_2) and C_6D_6 (0.6 mL). Then a defined volume of the substrate (1.72 mmol CH_3Cl, 0.54 mmol $CHCl_2F$, 0.68 mmol $CHClF_2$) was condensed into the reaction mixture from a small glass bulb filled with 1 atm of the gaseous substrate. For the reaction of CH_2F_2, the argon atmosphere in the NMR tube was exchanged with CH_2F_2. Note the dissolved amount of gaseous substrates is limited by their solubility in the solvent. The reaction progress was monitored by ^{1}H NMR spectroscopy. If the reaction is performed in Et_3GeH as solvent, C_6D_6 (0.6 mL) was condensed to the reaction mixture for NMR spectroscopic analysis after the reaction was stopped. Conversions were calculated based on signal integration of the consumed Et_3GeH (C_6D_6: δ = 1.06 (t, 9H, CH_3, $^3J_{H,H}$ = 7.8 Hz) ppm) into Et_3GeCl (C_6D_6: δ = 0.99 (t, 9H, CH_3, $^3J_{H,H}$ = 6.6 Hz) ppm). TONs were calculated based on the amount of chlorinated substrate assuming ACF reveals 1 g/mmol catalytically active sites. [60,67]

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Highlights of the publication:

Selective Reduction of a C−Cl Bond in Halomethanes with Et$_3$GeH at Nanoscopic Lewis Acidic Aluminium Fluoride

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- Selective monohydrodechlorination reactions of polychlorinated alkanes were achieved.

- Hydrodechlorination of CHCl$_2$F and CHClF$_2$ occurs with selectivity towards C−Cl activation.

- Heterogeneous catalytic reactions were developed.

- PTA studies give information about the interaction between the substrates at ACF · Et$_3$GeH.