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C–F activation reactions at germylium ions: dehydrofluorination of fluoralkanes†

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Reactions of the trityl cations with germanes afford the germylium ions $[R_3Ge][B(C_6F_5)_4]$ (1a: R = Et, 1b: R = Ph, 1c: R = *n*Bu). These compounds react with germane or fluorogermane to give polynuclear species, which are sources of the mononuclear ions, The latter convert with phosphines to yield the $[R_3Ge\text{-}PR_3]^+$ (4a: R = Et, 4b: R = Ph) cations. Catalytic dehydrofluorination reactions were observed for the C–F bond activation of fluoroalkanes when using germanes as hydrogen source.

Fluorinated compounds play an important role in everyday life in terms of agrochemicals, pharmaceuticals, liquid crystals and cooling agents.[1] Catalytic C–F activation reactions to access fluorinated building blocks open up opportunities in synthetic chemistry, but can often be considered as a major challenge,[2] which is frequently overcome by the formation of strong H–F, B–F, Al–F, Si–F or Ge–F bonds.[2,3] In this regard, strong Lewis-acidic main-group compounds such as silylium ions[4] were used to induce C–F activation reactions resulting often in hydrodefluorinations in the presence of hydrogen sources.

During the last years, germylium ions[4g,5] have been obtained *via* different synthetic approaches. They often bear bulky substituents and are stabilized by weakly coordinating anions. One of the most used methodologies consists of a hydride transfer reaction at germanes to a trityl cation. Thus, in 2013 Müller *et al.* described the syntheses of sterically bulky germylium ions such as $[Mes_3Ge]^+$, where the latter is formed from Mes_2MeGeH by a rearrangement reaction.[4g] One year later, they synthesized a hydrogen bridged naphtyldigermylium ion capable of performing catalytic hydrodefluorination reactions at $C(sp^3)$–F bonds using Et_3SiH as hydrogen source with comparable turnover numbers than those found for similar silylium ions as catalyst.[5i] Catalytic hydrodefluorination reactions have also been recently published by Weinert and co-workers using *in situ* formed $[Ph_3Ge][B(C_6F_5)_4]$ ions in neat substrates.[6] However, literature known trialkyl germylium ions are limited to $[R_3Ge]^+$ (R = Me, Et) stabilized by carborane anions and no studies on bond activation reactions are known.[5d,g] In general, investigations on the reactivity of germylium ions towards organic compounds are very scarce[5i,l,n,o,6] and so far, stoichiometric C–F bond activation reactions have not been studied.

Herein, we describe the generation and identification of the germylium ions $[R_3Ge]^+$ with $[B(C_6F_5)_4]^-$ as counteranion (**1a**: R = Et, **1b**: R = Ph, **1c**: R = *n*Bu) and their role in the C–F bond activation reactions of fluorinated alkanes. The reactions led not to hydrodefluorination reactions, but instead to unprecedented dehydrofluorination reactions at molecular main group compounds.

Treatment of $[Ph_3C][B(C_6F_5)_4]$ with one equivalent of triethyl-, triphenyl- or tributylgermane gave $[R_3Ge][B(C_6F_5)_4]$ (**1a:** R = Et, **1b**: R = Ph, **1c**: R = *n*Bu) as well as Ph_3CH (Scheme 1). NMR spectroscopic data confirmed the consumption of the corresponding germane due to the abstraction of a hydride by the trityl cation. In the case of the cation in **1a**, the quartet for the CH_2 moiety appears $\Delta\delta$ = 0.5 ppm shifted towards higher field with respect to the previously synthesized $[Et_3Ge][CHB_{11}H_5Br_6]$ germylium ion.[5g] LIFDI-TOF mass spectra show the isotopic pattern and molar masses of $[R_3Ge]^+$ (see ESI†).

As it has been previously reported by Reed *et al.* that with carboranes as counteranions, digermylium ions might be generated in the presence of an excess of germane.[5g] On treatment of $[R_3Ge][B(C_6F_5)_4]$ (**1a–c**) with one equivalent of germane the formation of polynuclear species such as the digermylium ions $[R_3Ge\text{–}H\text{–}GeR_3][B(C_6F_5)_4]$ (**2a–c**) can be assumed (Scheme 2). Broad signals at δ = 2.08 ppm (for R = Et), δ = 5.40 ppm (for R = Ph)

$$R_3GeH + [Ph_3C][B(C_6F_5)_4] \xrightarrow[-\ Ph_3CH]{C_6H_6,\ rt,\ 5\ min} \underset{\textbf{1a-c}}{[R_3Ge][B(C_6F_5)_4]}$$

Scheme 1 Formation of the germylium ions **1** (**1a**: R = Et, **1b**: R = Ph, **1c**: R = *n*Bu).

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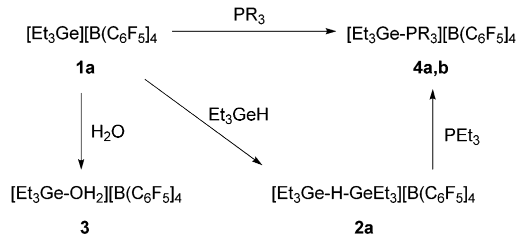


Scheme 2 Reactivity of **1a**. All reactions were performed in *ortho*-dichlorobenzene-d_4 at room temperature for 5 min (**4a**: R = Et, **4b**: R = Ph).

and δ = 1.97 ppm (for R = nBu) in the ^{1}H NMR spectra can be assigned to the proton bridging two germylium centres. In every case, the resonance appears shielded with respect to R_3GeH ($\Delta\delta$ = 1.88, 0.55 and 2 ppm for R = Et, R = Ph and R = nBu, respectively), which is in accordance with data for the previously described naphtyldibutyldigermylium cation.[5i] However, a DOSY NMR experiment of a product mixture of compound **1a** and Et_3GeH indicated that more than one species are present. Note that after adding more Et_3GeH to the mixture of **1a** and Et_3GeH a shift of the ^{1}H NMR signal to lower field as well as the formation of $GeEt_4$ was observed, which suggest the occurrence of rearrangement reactions.[4g]

The germylium ions in **1** are highly water-sensitive. Thus, **1a** reacts with water to yield $[Et_3Ge–OH_2][B(C_6F_5)_4]$ (**3**) (Scheme 2). The ^{1}H NMR spectrum of **3** reveals a very broad signal at 5.1 ppm due to the protons at the germanium bound water. The molecular structure of compound **3** was determined by single-crystal X-ray diffraction analysis (Fig. 1). Compound **3** crystallizes in a distorted tetrahedral structure. The sum of the C–Ge–C angles is 347.26°, which is consistent with literature-known structures for germanols or cations exhibiting hydroxo-bridged germanium centres.[5b,7] The Ge–O bond length in **3** of 1.923(2) Å is slightly longer than the distance in the hydroxo digermylium ion $[(Me_3Ge)_2OH]^+$ (1.897(4) and 1.903(4) Å)[5b] and around 0.15 Å longer than the Ge–O bond in Ph_3GeOH[7] or $(Ph_3Ge)_2O$.[8] Similar differences have been found for silicon analogues.[9] Additionally, the asymmetric unit shows a water molecule which binds *via* a hydrogen bond to the coordinated water molecule with a O–O separation of 2.492 Å.

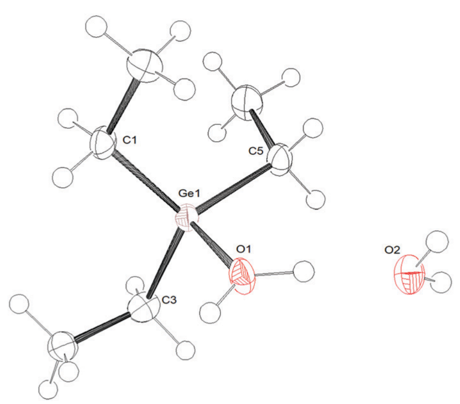


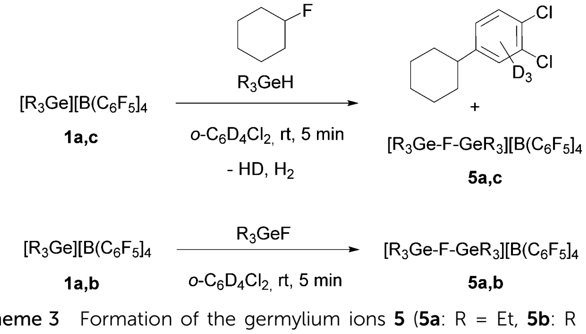
Fig. 1 ORTEP representation of the cation in $\mathbf{3}\cdot H_2O$; ellipsoids are drawn at a 50% probability level. Selected bonds lengths (Å) and angles (°): Ge1–O1 1.9247(14); Ge1–C1 1.932(2); Ge1–C3 1.9324(19); Ge1–C5 1.932(2); C3–Ge1–C5 116.42(9); C1–Ge1–C5 113.97(9); C1–Ge1–C3 116.89(9); C3–Ge1–O1 103.43(8); C5–Ge1–O1 101.47(8); C1–Ge1–O1 101.20(8).

In order to get more insight on the structure and reactivity of **1a**, it was also reacted with PEt_3 or PPh_3 in deuterated *ortho*-dichlorobenzene. After 5 minutes, signals at 1.9 ppm and 2.3 ppm for $[Et_3Ge–PR_3][B(C_6F_5)_4]$ (R = Et (**4a**), Ph (**4b**)) in the $^{31}P\{^1H\}$ NMR spectra were observed (Scheme 2). Further support for the presence of these compounds was provided by the LIFDI-TOF spectrum of **4b**, which reveals a peak at m/z 423 with the corresponding isotopic pattern for the cation (see ESI†).

The mixture of **1a** and Et_3GeH was also treated with one equivalent of PEt_3 (Scheme 2). Again, compound **4a** was obtained together with Et_3GeH, $GeEt_4$ and Et_2GeH_2 in an approximate ratio of 8 : 2.4 : 1. This again indicates the occurrence of rearrangement reactions, but also that a mixture of **1** and germanes shows a comparable reactivity to those of **1**.

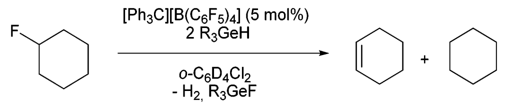
Treatment of $[R_3Ge][B(C_6F_5)_4]$ (**1a**: R = Et, **1c**: nBu) with fluorocyclohexane in a 1 : 1 ratio in deuterated 1,2-dichlorobenzene gave the Friedel–Crafts product, 1,2-dichloro-4-cyclohexylbenzene-d_3.[10] In addition, a broad peak at δ = −200 ppm in the ^{19}F NMR spectrum was observed, which might be assigned to polynuclear species such as $[R_3Ge–F–GeR_3][B(C_6F_5)_4]$ (**5**), although a second fluorine containing product was not detected. However, the chemical shift in the ^{19}F NMR spectrum slightly varies over time or after addition of further fluorocyclohexane suggesting the formation of various fluoride-bridge germylium compounds. Additionally, the reaction of a mixture of **1a,c** with R_3GeH and fluorocyclohexane provided the same result (Scheme 3), giving a signal in the ^{19}F NMR spectrum of the product reaction solution at δ = −196.9 ppm (R = Et) or δ = −201.6 ppm (R = nBu). Note that HD and H_2 formation was observed in the ^{1}H NMR spectrum. The presence of fluoride-bridged cations is further supported by a reaction of the compounds **1a,b** with R_3GeF (R = Et, Ph), which resulted in resonances at δ = −196.9 ppm for R = Et and δ = −170.4 ppm for R = Ph, which appear at lower field than the signals for R_3GeF in the ^{19}F NMR spectra (Scheme 3).

The *in situ* generated ions **1** were then used as catalysts (5 mol%) for the C–F bond activation of 1-fluorocyclohexane. In a very different outcome, the presence of two equivalents of Et_3GeH or nBu_3GeH in deuterated 1,2-dichlorobenzene as solvent promoted the formation of the dehydrofluorinated



Scheme 3 Formation of the germylium ions **5** (**5a**: R = Et, **5b**: R = Ph, **5c**: R = nBu).

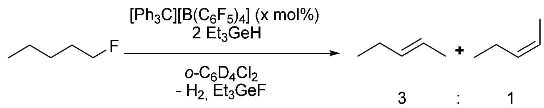
Table 1 C–F activation of fluorocyclohexane by germylium ions



R	T (°C)	Time	Conversion[a] (%)	Products ratio
Et	rt	30 min	100	7 : 1
Et[b]	rt	5 h	99	12 : 1
Et[c]	100	1 d	100	10 : 1
nBu	rt	4 d	23	1 : 0
nBu	65	2 h	100	3 : 1

[a] Based on the consumption of fluorocyclohexane by integration of the ^{19}F NMR spectra. [b] 2.5 mol% of catalyst. [c] Compound **4b** as catalytic precursor.

Table 2 Dehydrofluorination of 1-fluoropentane



x (mol%)	T (°C)	Time	Conversion[a] (%)
5	rt	1 d[b]	62
10	rt	1 d[c]	73
5	65	6 h 30 min	99
10	65	3 h	100
10[d]	65	4 h	99

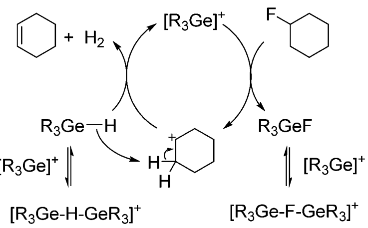
[a] Based on consumption of fluoropentane by integration of the ^{19}F NMR spectra. [b] 3 d, 66% conversion. [c] 3 d, 77% conversion. [d] nBu$_3$GeH used as hydrogen source.

product cyclohexene (Table 1) together with the corresponding fluorogermane species and dihydrogen. The formation of small amounts of cyclohexane could also be detected. A reaction of Et_3GeH or nBu$_3$GeH with fluorocyclohexane in presence of $[Ph_3C]^+$ without using a solvent did not lead to any different outcome. The observations are in sharp contrast to the mentioned report on catalytic hydrodefluorination reactions at fluoroalkanes, which occur in the presence of $HGePh_3$ without solvent or by using a naphtyldigermylium ion and silanes as hydrogen source.[5i,6] Note that when **1a** was used as catalyst and $HSiEt_3$ as the hydrogen source, only hydrodefluorination of fluorocyclohexane is observed, which is consistent with the reactivity pattern of silylium ions.[4a,b,e,i]

When Et_3GeH was used as hydrogen source a TON of 40 could be obtained after five hours. In contrast, nBu$_3$GeH only gave a 23% of conversion at room temperature after four days, however, heating at 65 °C reduced the reaction time to two hours with full conversion of fluorocyclohexane. Note that the triphenylgermylium ions led to reactivity towards the counteranion as well as to the generation of Friedel–Crafts products with the solvent. $[Et_3Ge\text{-}PPh_3][B(C_6F_5)_4]$ (**4b**) was also tested in the catalytic reaction, which results in a comparable outcome as with $[Et_3Ge][B(C_6F_5)_4]$ (**1a**) when heating at 100 °C. Therefore, triethylgermane was chosen as the best hydrogen source for the following studies, using the trityl cation as pre-catalyst for the *in situ* formation of the catalyst **1a** (Table 2).

Treatment of a mixture of the trityl cation as catalytic precursor (10 mol%) and triethylgermane as hydrogen source with 1-fluoropentane gave at 65 °C in 3 hours 2-pentene isomers in a ratio of the *E*- and *Z*-isomer of 3 : 1. Other fluorinated compounds such as 1-fluoroheptane and fluoroethane were also tested. Whereas the former gave a mixture of *E*/*Z*-2-heptene isomers (3 : 1 ratio), Et_3GeF and dihydrogen, the latter converted into $GeEt_4$, ethane and Et_3GeF. Difluoroethane, trifluoroethane and 1,1,1,2,3,3-hexafluoropropane did not react, which suggest that the activation of any CF_2 or CF_3 moieties is difficult. However, 1,1,1,3,3-pentafluorobutane was converted to 2,4,4,4-tetrafluoro-1-butene in 4.6% after three days at 65 °C.

A tentative mechanistic proposal for the catalytic dehydrofluorination reactions involves the C–F activation of a fluoroalkene by a germylium ion-type species to give fluorogermane and a carbenium-like ion. In the presence of germane, an olefin and dihydrogen are generated in addition to the regeneration of the germylium ion (Scheme 4). The formation of intermediate carbenium-like ions as intermediates is also supported by the formation of 2-pentene isomers instead of 1-pentene when 1-fluoropentane is used as starting material. Note that a mechanism *via* carbenium-like species based on silylium ions was proposed for hydrodefluorination reactions by Ozerov and Müller,[4a,e,i] but the presence of germanes in solution obviously favours a dehydrofluorination pathway.



Scheme 4 Simplified mechanism of the catalytic dehydrofluorination of fluorocyclohexane by germylium ions (R = Et, nBu).

The germylium ion reactivity resembles the behaviour of germanes in heterogeneous reactions using the Lewis-acid aluminum chlorofluoride ACF ($AlCl_xF_{3-x}$, x = 0.05–0.3) as catalyst, for which germylium-type intermediates were proposed, and dehydrofluorination reactions were also found, although 70 °C and 4 d were required.[11] Note also that for homogeneous reactions, only very few examples of transition metal complexes of Sc, Ti and Ce have been reported to perform dehydrofluorination reactions *via* an initial C–H bond activation followed by β-fluoride elimination.[12]

In conclusion, the synthesis of germylium ions has been achieved and their reactivity towards fluorinated alkanes was studied. Although the structure of the polygermylium ions remains unclear, their reactivity towards phosphines demonstrate their applicability as sources of mononuclear species. The germylium-type ions react with fluoroalkanes to form fluorogermylium ions. When no excess of germane is present, Friedel–Crafts reactivity was observed. However, in the presence of germane the carbenium-like ion reactivity is diminished. Remarkably, catalytic C–F activation at monofluorinated alkanes using Et_3GeH or $n Bu_3GeH$ promote dehydrofluorination reactions instead of the hydrodefluorination products, which occur when silanes are used as hydrogen source. In addition, $[Et_3Ge]^+$ or $[nBu_3Ge]^+$ favour a reaction pathway towards the dehydrofluorination, although under neat conditions with $[Ph_3Ge]^+$ selectivity towards hydrodefluorination was reported.[6] Overall, the presented results open opportunities for the development of reactions routes for defluorination of fluorinated alkanes.

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Conflicts of interest

There are no conflicts to declare.

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