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

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Reactions of the trityl cations with germannes afford the germium ions [R₃Ge][B(C₆F₅)₄] (1a: R = Et, 1b: R = Ph, 1c: R = nBu). 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 [R₃Ge–PR₃]⁺ (4a: R = Et, 4b: R = Ph) cations. Catalytic dehydrofluorination reactions were observed for the C–F bond activation of fluoralkanes 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. 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, which is frequently overcome by the formation of strong H–F, B–F, Al–F, Si–F or Ge–F bonds. In this regard, strong Lewis-acidic main-group compounds such as silylium ions were used to induce C–F activation reactions resulting often in hydrofluorination in the presence of hydrogen sources.

During the last years, germium ions 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 germium ions such as [Mes₂Ge]⁺, where the latter is formed from Mes₂MeGeH by a rearrangement reaction. One year later, they synthesized a hydrogen bridged naphthylgermylium ion capable of performing catalytic hydrodefluorination reactions at C(sp³)–F bonds using Et₃SiH as hydrogen source with comparable turnover numbers than those found for similar silylium ions as catalyst. Catalytic hydrodefluorination reactions have also been recently published by Weinert and co-workers using in situ formed [Ph₃Ge][B(C₆F₅)₄] ions in neat substrates. However, literature known trialkyl germium ions are limited to [R₃Ge]^+ (R = Me, Et) stabilized by carborane anions and no studies on bond activation reactions are known. In general, investigations on the reactivity of germium ions towards organic compounds are very scarce and so far, stoichiometric C–F bond activation reactions have not been studied.

Herein, we describe the generation and identification of the germium ions [R₃Ge]^+ with [B(C₆F₅)₄]^− as counteranion (1a: R = Et, 1b: R = Ph, 1c: R = nBu) 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 [Ph₃C][B(C₆F₅)₄] with one equivalent of triethyl-, triphenyl- or tributylgermane gave [R₃Ge][B(C₆F₅)₄] (1a: R = Et, 1b: R = Ph, 1c: R = nBu) as well as Ph₃CH (Scheme 1). NMR spectroscopic data confirmed the consumption of the corresponding germane to the abstraction of a hydride by the trityl cation. In the case of the cation in 1a, the quartet for the CH₂ moiety appears δ = 0.5 ppm shifted towards higher field with respect to the previously synthesized [Et₃Ge][CHB₁₁H₅Br₆] germium ion. LIFDI-TOF mass spectra show the isotopic pattern and molar masses of [R₃Ge]^+ (see ESI†).

As it has been previously reported by Reed et al. that with carboranes as counteranions, digermium ions might be generated in the presence of an excess of germane, on treatment of [R₃Ge][B(C₆F₅)₄] (1a–c) with one equivalent of germane the formation of polynuclear species such as the digermium ions [R₃Ge–H–GeR₃][B(C₆F₅)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)
and $\delta = 1.97$ ppm (for $R = n$Bu) 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 $R = n$Bu, respectively), which is in accordance with data for the previously described naphthylidibutylgermylium cation.5 However, a DOSY NMR experiment of a product mixture of compound 1a and Et$_3$GeH indicated that more than one species are present. Note that after adding more Et$_3$GeH to the mixture of 1a and Et$_3$GeH 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.4 The germylium ions in 1 are highly water-sensitive. Thus, 1a reacts with water to yield [Et$_3$Ge–OH$_2$][B(C$_6$F$_5$)$_4$] (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 germylium centres.6,7 The Ge–O bond length in 3 of 1.923(2) Å is slightly longer than the distance in the hydroxygermylium ion [(Me$_3$Ge)$_2$OH]$^+$ (1.897(4) and 1.903(4) Å)$^{5b}$ and around 0.15 Å longer than the Ge–O bond in Ph$_3$GeOH$^-$ or (Ph$_3$Ge)$_2$O.$^8$ 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.

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 1.99 ppm and 2.3 ppm for [Et$_3$Ge–PR$_3$][B(C$_6$F$_5$)$_4$] ($R = Et$ (4a), Ph (4b)) in the $^{13}$P($^1$H) 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$_3$GeH was also treated with one equivalent of PEt$_3$ (Scheme 2). Again, compound 4a was obtained together with Et$_3$GeH, GeEt$_4$ and Et$_3$GeH$_2$ 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$_3$Ge][B(C$_6$F$_5$)$_4$] (1a: $R = Et$, 1c: $n$Bu) with fluorocyclohexane in a 1:1 ratio in deuterated 1,2-dichlorobenzene gave the Friedel–Crafts product, 1,2-dichloro-4-cyclofluorocyclohexane in a 1:1 ratio in deuterated 1,2-dichlorobenzene. After 5 minutes, signals at 1.9 ppm and 2 ppm were observed (Scheme 3). 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 presence of fluoride-bridged cations is further supported by a reaction of the compounds 1a,b with R$_3$GeF ($R = Et$, Ph), which resulted in resonances at $\delta = −196.9$ ppm for $R = Et$ or $\delta = −201.6$ ppm for $R = n$Bu. 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$_3$GeF ($R = Et$, Ph), which resulted in resonances at $\delta = −196.9$ ppm for $R = Et$ and $\delta = −170.4$ ppm for $R = Ph$, which appear at lower field than the signals for R$_3$GeF in the $^{19}$F NMR spectra (Scheme 3).

The $\textit{in situ}$ 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$_3$GeH or nBu$_3$GeH in deuterated 1,2-dichlorobenzene as solvent promoted the formation of the dehydrofluorinated...
product cyclohexene (Table 1) together with the corresponding fluorogermane species and dihydrogen. The formation of small amounts of cyclohexene could also be detected. A reaction of Et₃GeH or nBu₃GeH with fluorocyclohexane in presence of [Ph₃C]⁺ 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 HGePh₃ without solvent or by using a naphthylgermylium ion and silanes as hydrogen source.⁵ Note that when 1a was used as catalyst and HSiEt₃ as the hydrogen source, only hydrodefluorination of fluorocyclohexane is observed, which is consistent with the reactivity pattern of silylium ions.⁴,⁵,⁶,⁷

When Et₃GeH was used as hydrogen source a TON of 40 could be obtained after five hours. In contrast, nBu₃GeH 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 countere-ion as well as to the generation of Friedel–Crafts products with the solvent. [Et₃Ge-PPh₃][B(C₆F₅)₄] (4b) was also tested in the catalytic reaction, which results in a comparable outcome as with [Et₃Ge][B(C₆F₅)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), Et₃GeF and dihydrogen, the latter converted to GeEt₄, ethane and Et₃GeF. Difluoroethane, trifluoroethane and 1,1,1,2,3,3-hexafluoropropane did not react, which suggest that the activation of any CF₂ or CF₃ 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 silium ions was proposed for hydrodefluorination reactions by Ozerov and Müller,⁴ but the presence of germanes in solution obviously favours a dehydrofluorination pathway.

The germylium ion reactivity resembles the behaviour of germanes in heterogeneous reactions using the Lewis-acid aluminum chlorofluoride ACF (AlCl₃-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 fluorogermanyl 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

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### 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 |
| Et² | rt | 5 h | 99 | 12:1 |
| 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 ¹⁹F NMR spectra. ² 2.5 mol% of catalyst. ^ Compound 4b as catalytic precursor.

### Table 2 Dehydrofluorination of 1-fluoropentane

| x (mol%) | T (°C) | Time | Conversion a (%) |
|---|---|---|---|
| 5 | rt | 1 d | 62 |
| 10 | rt | 1 d | 73 |
| 5 | 65 | 6 h 30 min | 99 |
| 10 | 65 | 3 h | 100 |
| 10⁴ | 65 | 4 h | 99 |

*a Based on consumption of fluoropentane by integration of the ¹⁹F NMR spectra. ² 3 d, 66% conversion. ⁴ 3 d, 77% conversion. ⁵ nBu₃GeH used as hydrogen source.

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**Scheme 4** Simplified mechanism of the catalytic dehydrofluorination of fluorocyclohexane by germylium ions (R = Et, nBu).
using Et₂GeH or nBu₂GeH promote dehydrofluorination reactions instead of the hydrodefluorination products, which occur when silanes are used as hydrogen source. In addition, [Et₂Ge]⁺ or [nBu₂Ge]⁺ favour a reaction pathway towards the dehydrofluorination, although under near conditions with [Ph₂Ge]⁺ selectivity towards hydrodefluorination was reported. 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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