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Cleavage of a N−H Bond of Ammonia at Room Temperature by a Germylene

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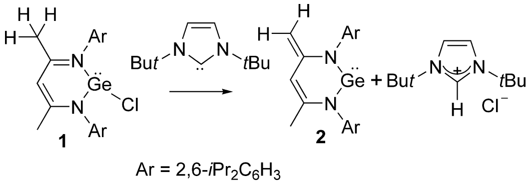
The reaction of LGeCl [**1**; L = CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)}$_2$] with 1,3-di-*tert*-butylimidazol-2-ylidene results in the formation of the germylene L′Ge [**2**; L′ = CH{(C=CH$_2$)(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$}]. **2** reacts with ammonia under N−H cleavage to give LGeNH$_2$ (**3**). This type of reaction can also be used to activate primary amines. **3** is characterized by microanalysis, multinuclear NMR spectroscopy, and X-ray structural analysis. The single-crystal X-ray structural analysis indicates **3** to be a monomer, and the germanium atom shows a trigonal-pyramidal environment with a stereochemically active lone pair.

In recent years, we have been interested in the synthesis of low-valent germanium compounds and reported on the preparation and structural characterization of LGeCl,[1] LGeF,[2] LGeOH,[3] and LGeH[4] [L = CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)}$_2$]. These small reactive molecules are ideal precursors for the preparation of heterometallic germylenes, which are active catalysts in olefin polymerization reactions.[5] One important missing species in this series is LGeNH$_2$. To date, there is only one example known of a stable germanium(II) amide featuring the parent NH$_2$ group.[6] A conventional route for the preparation of GeNH$_2$-containing compounds is the ammonolysis of the corresponding halide.[7] Therefore, it was expected that the reaction of LGeCl with an excess of ammonia leads to the product LGeNH$_2$. However, in a broad temperature range (−40 to +25 °C), the starting material does not react with ammonia. From our previous experience for the preparation of LGeOH[3] and LAl(NH$_2$)$_2$[8] using LGeCl and LAlCl$_2$, respectively, we employed N-heterocyclic carbenes (NHCs) as HCl acceptors. Herein we follow the route for the preparation of LGeNH$_2$ from LGeCl, NH$_3$, and NHC.

Scheme 1. Preparation of **2**



A toluene solution of 1 equiv of LGeCl and 1 equiv of 1,3-di-*tert*-butylimidazol-2-ylidene[9] under stirring immediately changed the color from yellow to brown-red after a few minutes, and a white precipitate is formed[10a] (Scheme 1). There was no reaction when a solution of 1 equiv of LGeCl and 1 equiv of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene was used.

The insoluble white precipitate was identified as 1,3-di-*tert*-butylimidazolium chloride and the soluble part as the germylene **2**, which was confirmed by NMR spectroscopy and compared to a previously reported sample.[11] We postulate that the reaction proceeds via cleavage of a C−H methyl bond and formation of the C−H carbonium ion (Scheme 1). This type of C−H cleavage reaction was reported for nucleophilic carbenes.[12] The proof for C−H

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bond cleavage at the backbone methyl group of **1** by 1,3-di-*tert*-butylimidazol-2-ylidene is shown by the formation of **2** and the elimination of HCl under isolation of 1,3-di-*tert*-butylimidazolium chloride. The previously reported germylene **2** was formed by the reaction of **1** with $LiN(SiMe_3)_2$. Similar deprotonation reactions at the backbone have been observed for the borane-stabilized germylene hydride,[2] the tautomerization of a iminogermane bearing the β-diketiminato ligand,[13] a cyclodiazaborane analogue,[14] and related calcium complexes.[15] This is so far a unique example where the deprotonation reaction at the backbone has been demonstrated using 1,3-di-*tert*-butylimidazol-2-ylidene.

Activation of the ammonia molecule has attracted considerable interest over the years. Although ammonia usually forms simple Lewis acid−base adducts with transition-metal complexes, there is also some N−H activation of ammonia via transition-metal complexes known.[16,17] In contrast to these studies, the corresponding chemistry of stable main-group molecular compounds for activation of ammonia is virtually nonexistent. In 2007, the first example of ammonia splitting was reported by Bertrand and co-workers using stable carbenes.[18] Very recently, Power and co-workers reported the activation of ammonia by the heavier group 14 element carbene analogue $SnAr_2$ [$Ar = C_6H_3$-2,6(C_6H_3-2,6-$^iPr_2)_2$],[19] and Stephan and co-workers reported the activation of amine by a frustrated Lewis pair.[20]

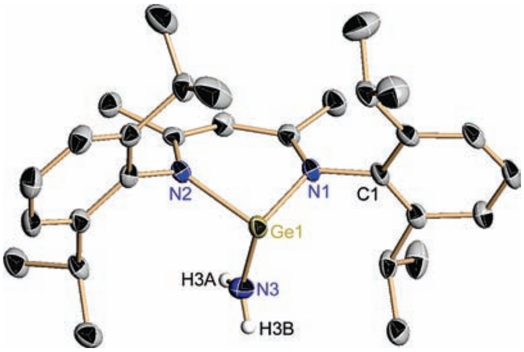
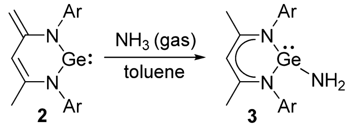


Figure 1. Anisotropic displacement parameters, depicted at the 50% probability level of **3**. Hydrogen atoms, except those vital at the nitrogen atom N3, are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge1−N3 1.845(2), Ge1−N1 2.030(2), Ge1−N2 2.030(2); N1−Ge1−N2 88.60(8), N3−Ge1−N1 95.52(10), N3−Ge1−N2 95.55(10).

Scheme 2. Preparation of **3**



Ar = 2,6-$i$$Pr_2C_6H_3$

Herein we show the N−H cleavage of ammonia by employing L′Ge [**2**; L′ = $CH\{(C{=}CH_2)(CMe)(2,6\text{-}{}^iPr_2C_6H_3N)\}_2$], which generates at mild conditions a terminal $GeNH_2$ group (Scheme 2).[10b] The addition of an excess of dry ammonia gas to a red solution of **2** in toluene leads to a rapid change of the color to orange. The solution was evaporated and extracted with *n*-hexane. Concentration of the solution yielded yellow crystals of $LGeNH_2$ (**3**). X-ray crystal structure analysis afforded a monomeric structure, as illustrated in Figure 1.[21] Surprisingly, **3** is monomeric in

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(10) All manipulations were carried out under anaerobic and anhydrous conditions with Schlenk techniques. (a) L′Ge (**2**): 1,3-di-*tert*-butylimidazol-2-ylidene (0.360 g, 2.0 mmol) and LGeCl (1.050 g, 2.0 mmol) were dissolved in toluene (30 mL) at room temperature. The reaction mixture was stirred, and the color of the solution changed from yellow to brown-red. A white precipitate was formed. The reaction mixture was stirred for another 1 h, then the white precipitate was separated by filtration, and the remaining red solution was evaporated. The residue was dissolved in *n*-hexane. Storage of the solution at −30 °C for 1 day yielded brown-red crystals suitable for a single-crystal X-ray diffraction experiment. Yield: 0.630 g (65%). ^1H NMR (500 MHz, C_6D_6): $\delta = 7.04-7.21$ (m, 6H, Ar−*H*), 5.43 (s, 1H, γ-C*H*), 3.91 (s, 1H, CH_2), 3.69 (sept, 2H, $CH(CH_3)_2$), 3.44 (sept, 2H, $CH(CH_3)_2$), 3.26 (s, 1H, CH_2), 1.41 (s, 3H, CH_3), 1.35 (d, 6H, $CH(CH_3)_2$), 1.29 (d, 6H, $CH(CH_3)_2$), 1.20 (d, 6H, $CH(CH_3)_2$), 1.15 (d, 6H, $CH(CH_3)_2$) ppm. (b) $LGeNH_2$ (**3**): Dry ammonia gas was added to a red solution of **2** (0.490 g, 1 mmol) in toluene (20 mL) at room temperature. The reaction mixture became orange. For a further 5 min, the ammonia gas was bubbled through the solution. After that, the solvent was removed in vacuum and the residue was extracted with *n*-hexane. The solution was reduced to half of the volume. Storage of the solution at −30 °C for 1 day yielded yellow crystals suitable for a single-crystal X-ray diffraction experiment. Yield: 0.455 g (95%). Mp: 162 °C. ^1H NMR (500 MHz, C_6D_6): $\delta = 7.12-7.18$ (m, 6H, Ar−*H*), 4.79 (s, 1H, γ-C*H*), 3.54 (sept, 2H, $CH(CH_3)_2$), 3.47 (sept, 2H, $CH(CH_3)_2$), 1.60 (s, 6H, CH_3), 1.35 (d, 6H, $CH(CH_3)_2$), 1.28 (d, 6H, $CH(CH_3)_2$), 1.24 (d, 6H, $CH(CH_3)_2$), 1.14 (d, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): $\delta = 163.20$ (*C*N), 145.95, 143.77, 142.74, 125.81, 124.66, 124.18 (Ar−*C*), 95.55 (γ-C), 29.19 ($CH(CH_3)_2$), 28.60 ($CH(CH_3)_2$), 28.25 ($CH(CH_3)_2$), 26.96 ($CH(CH_3)_2$), 24.76 ($CH(CH_3)_2$), 24.67 ($CH(CH_3)_2$), 23.40 (CH_3) ppm. IR (Nujol, KBr): $\nu = 3431$ vw, 3333 vw (N−H) cm $^{-1}$. EI-MS (70 eV): *m*/*z* (%): 507 (100) [M^+]. Anal. Calcd for $C_{29}H_{43}GeN_3$ (507.27): C, 68.79; H, 8.56; N, 8.30. Found: C, 69.25; H, 8.82; N, 7.66.

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(21) Single-crystal structure analysis of **3**: The data set was collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics (Mo Kα, $\lambda = 71.073$ pm). The crystal was mounted in a shock-cooled oil drop at the tip of a fibre.[22] The integration was performed with *SAINT V7.46A*, which was followed by an empirical absorption correction with *SADABS-2008/1*. The structure was solved by direct methods and refined with *SHELXL* against F^2.[23] The positions of the hydrogen atoms H3A and H3B at the amine nitrogen atom N3 were taken from the difference map and refined with distance restraints. $C_{29}H_{43}GeN_3$, $M = 506.25$ g/mol, crystal size 0.25 × 0.03 × 0.03 mm, monoclinic, $C2/c$, $a = 2490.2(5)$ pm, $b = 1516.7(3)$ pm, $c = 1467.2(3)$ pm, $\beta = 95.261(3)°$, $V = 5.5180(18)$ nm; $Z = 8$, $\rho_{calcd} = 1.219$ Mg/m^3, $\mu = 1.131$ mm^{-1}, $T = 100(2)$ K, $2\theta_{max} = 50.76°$, 25 829 reflections measured, of which 5069 were independent, $R_{int} = 0.0526$, $R1 = 0.0385$ [$I > 2\sigma(I)$], $wR2 = 0.1048$ (all data), +0.609/−0.799 e/Å^3 residual densities. Complete crystallographic data are deposited at the Cambridge Crystallographic Data Centre, where it can be downloaded free of charge from www.ccdc.cam.ac.uk/data_request/cif at CCDC 705305.

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the solid state, and what is even more striking is that the NH_2 group is not involved in any kind of hydrogen bonding, as shown by X-ray structural analysis and IR spectroscopy.

The IR spectrum displays two weak sharp bands at 3431 and 3333 cm^{-1} that are attributed to the two N−H stretching modes of the NH_2 group. These wavenumbers are close to those at 3380 and 3308 cm^{-1} observed for $(Ar^*GeNH_2)_2$ [$Ar^* = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}{}^iPr_2)$].[6]

In summary, we have shown that 1,3-di-*tert*-butylimidazol-2-ylidene cleaves the C−H bond of a methyl group of **1** and leads to the formation of the carbene analogue germylene **2**. Compound **2** reacts quantitatively with ammonia at room temperature under N−H bond cleavage and oxidative addition to **3**, demonstrating an example of sustainable chemistry. 1,3-Di-*tert*-butylimidazolium chloride can be converted to the starting material using a strong base. Preliminary studies of **2** with $2,6\text{-}{}^iPr_2C_6H_3NH_2$ show the complete conversion of **2** and afford $LGeN(H)\text{-}2,6\text{-}{}^iPr_2C_6H_3$. Other N−H and P−H cleavage reactions according to this route should be possible.

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Supporting Information Available: Crystallographic data for **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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