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Oxidative Addition of Ammonia at a Silicon(II) Center and an Unprecedented Hydrogenation Reaction of Compounds with Low-Valent Group 14 Elements Using Ammonia Borane

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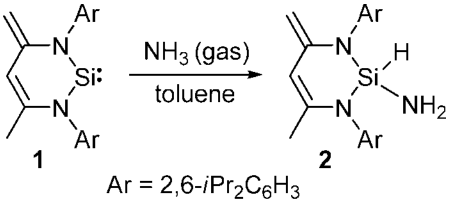
Activation of the N−H bonds of ammonia is rare. The first example of ammonia splitting by transition metals under the formation of an amido hydride complex was only recently reported by Hartwig and co-workers.[1] Studies of the corresponding chemistry with main-group compounds have been explored to a lesser extent. In 2007, Bertrand and co-workers[2] showed that the facile splitting of ammonia by nucleophilic activation at a single carbon center is possible. Last year Power and co-workers[3] and Stephan's group[4] independently showed that the activation of ammonia occurred when a diarylstannylene or a frustrated Lewis pair were involved. We very recently reported the cleavage of a N−H bond of ammonia by a germylene.[5] In general, oxidative addition of the N−H bond of ammonia to unsaturated species could be very important in generating new products. For example, the catalytic addition of ammonia to olefins and the coupling of ammonia with arenes are considered to be two of the 10 greatest current challenges for catalytic chemistry.

Herein we report the oxidative addition of ammonia at the silicon(II) center of a silylene, L′Si (**1**)[6] (L′ = CH{(C=CH$_2$)(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}), which occurs under mild conditions with the formation of L′Si(H)NH$_2$ (**2**). The addition of an excess of dry ammonia gas to a yellow solution of **1** in toluene led to a rapid color change from yellow to colorless (Scheme 1).[7] The solution was evaporated and extracted with *n*-hexane. Concentration of the solution yielded colorless crystals of **2** in 90% yield. Single crystals of **2** were obtained from a saturated *n*-hexane solution at −32 °C after 2 days. Compound **2** crystallizes in the orthorhombic space group *Pbca,* with one monomer in the asymmetric unit. X-ray crystal structure analysis afforded a monomeric structure, as illustrated in Figure 1.[7] Surprisingly, **2** is monomeric in the solid state, and even more striking is the fact that the NH$_2$ group is not involved in any kind of hydrogen bonding, as shown by X-ray structural analysis and IR spectroscopy. Compound **2** is stable in the solid state as well as in solution for a long time without any decomposition under an inert atmosphere. The coordination polyhedron around the silicon atom features a distorted tetrahedral geometry. The silicon is attached to the NH$_2$ group, a hydrogen atom, and two nitrogen atoms from the backbone of the chelating ligand. The Si−N2 bond lengths and N2−Si−N3 angle are 1.7237 Å and 103.11(8)°, respectively. These data are comparable with those of related compounds.[8] A noteworthy feature of compound **2** is the Si(H)NH$_2$ moiety; the Si−N1 bond length [1.653(3) Å] can be compared with the slightly longer Si−N bond lengths in RSi(NH$_2$)$_3$[9] [R = 2,4,6-Ph$_3$C$_6$H$_2$, av 1.709(7) Å; R = 2,6-iPr$_2$C$_6$H$_3$NSiMe$_3$, av 1.709(2) Å; R = 2,4,6-tBu$_3$C$_6$H$_2$O, av 1.692(6) Å].

Scheme 1. Preparation of **2**



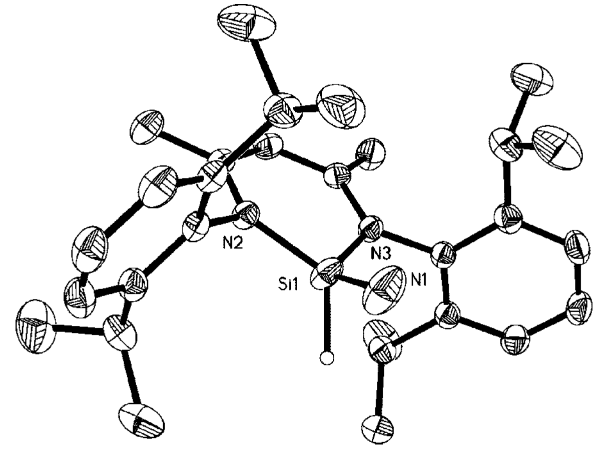


Figure 1. Thermal ellipsoid (50%) drawing of **2**. Hydrogen atoms, except the one at silicon, have been omitted for clarity.

Its composition was further proven by multinuclear NMR and IR spectroscopy, mass spectrometry, and elemental (C, H, N) analysis. The ^{1}H and ^{29}Si NMR spectra revealed that **2** has a Si(H)NH$_2$ moiety. The Si−H proton shows a triplet (δ = 4.97 ppm) with a coupling constant of $^3J_{\mathrm{H-H}}$ = 4.5 Hz. Thus, the ^{29}Si{^{1}H} proton-decoupled spectrum exhibits a singlet resonance (δ = −45.00 ppm) while the proton-coupled spectrum shows a doublet resonance (δ = −43.74 and −46.27 ppm) with a coupling constant of $J_{\mathrm{Si-H}}$ = 251.72 Hz. In addition, the ^{1}H NMR spectrum exhibits the expected pattern for the ligand, with a singlet at 5.31 ppm for the γ-C*H* proton.

The IR spectrum displays two weak sharp bands ($\tilde{\nu}$ = 3477 and 3382 cm^{-1}) that are attributed to the NH$_2$ group and a band at 2633 cm^{-1} for the Si−H bond. The most intense peak in the electron-impact mass spectrum appeared at *m/z* 446 [M − CH$_3$]$^+$, and the signal at *m/z* 461 (15%) was assigned to the molecular ion [M]$^+$.

The results reported here show that the silylene can mimic to some extent the behavior of a transition metal. The oxidative addition of NH$_3$ under very mild conditions offers an alternative paradigm in the ongoing search for catalytic systems capable of efficiently transforming ammonia into useful amino compounds. Driess and co-workers[10] recently reported that L′Si adds water via formation of the intermediate L′Si(H)OH or LSiOH (L = CH{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$). However, this intermediate cannot be isolated and reacts further with L′Si, in contrast to compound **2**.

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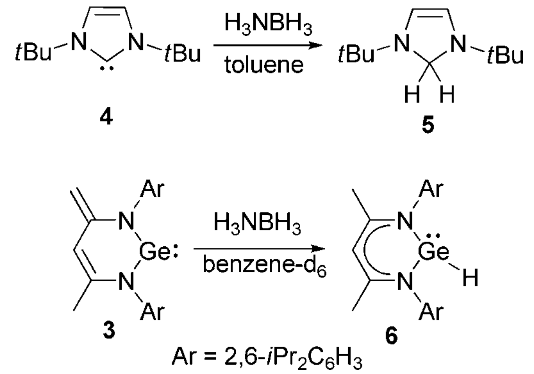
Furthermore, it should be emphasized that diaminocarbenes are inert toward dihydrogen,[11] whereas acyclic and cyclic alkylaminocarbenes undergo oxidative addition of dihydrogen at the carbene carbon atom.[2] In addition, dihydrogen reacts with digermynes[12] and stannylene[3] respectively. Consequently, we selected L′Si and the analogous germylene L′Ge (**3**)[5,13] for the reaction with dihydrogen. Unfortunately, neither compound reacted with dihydrogen under mild conditions. Next, as an alternative source of dihydrogen, we used ammonia borane (AB, H_3NBH_3), the preferred precursor for the preparation of boron nitride. AB, which has a hydrogen content of 19.6%, has recently attracted great interest because of its potential application in chemical hydrogen storage.[14] The AB molecule contains both hydridic B−H and protic polarized N−H bonds as well as a strong B−N bond, so hydrogen release from solid AB is more favorable than dissociation into ammonia and diborane under noncatalytic conditions.

N-heterocyclic carbenes (NHCs) are well-studied in terms of their use as ligands (organometallic chemistry) and in organocatalysis, including a number of reports of unique and unexpected reactivity.[15] The hydrogenation of 1,3-di-*tert*-butylimidazol-2-ylidene (**4**)[16] is exothermic. In the absence of a catalyst, **3** is inert toward hydrogen, but the presence of catalytic amounts of palladium or platinum leads to slow uptake of dihydrogen and formation of the 1,1-addition product.[17] The 1:1 reaction of AB with **4** at room temperature in toluene in the absence of any catalyst leads to compound **5** (Scheme 2, top).[17] We found that the C═C double bond present in **4** is unaffected even when an excess of AB is used. In the ^1H NMR spectrum, there are only three resonances, which appear at 5.4, 4.2, and 1.0 ppm in a 1:1:9 ratio, and they are in accordance with an original sample.[17] The conversion of **4** to **5** at room temperature is quantitative.

Scheme 2. Reactions of Ammonia Borane



The reaction of N-heterocyclic germylene **3** with AB is different. We recently reported on the synthesis of $LGeNH_2$,[5] which was formed by the reaction of ammonia with **3** through cleavage of one N−H bond. We reasoned that **3** may react like an NHC under oxidative addition at the germanium(II) atom. However, the 1:1 reaction of **3** with AB resulted in the formation of LGeH (**6**) (Scheme 2, bottom).[18] Even an excess of AB led only to LGeH. In the latter case, we also observed the addition of one molecule of dihydrogen, without oxidation of germanium(II). In comparison with the carbon(II) in an NHC, we found that the oxidation of the acyclic C═C double bond in **3** occurred. **6** is a known compound, and the ^1H NMR data were in agreement with those from the literature.[18]

In summary, we have shown that the silylene L′Si reacts with ammonia to afford compound **2** via oxidative addition at the silicon(II) atom. Moreover, ammonia borane can be used to add dihydrogen to N-heterocyclic carbenes and germylenes at room temperature by oxidative addition without any additional catalyst. The latter examples demonstrate that solid AB can be used instead of gaseous hydrogen for hydrogenation reactions without any additional catalyst.

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Supporting Information Available: Experimental synthesis details and X-ray data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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