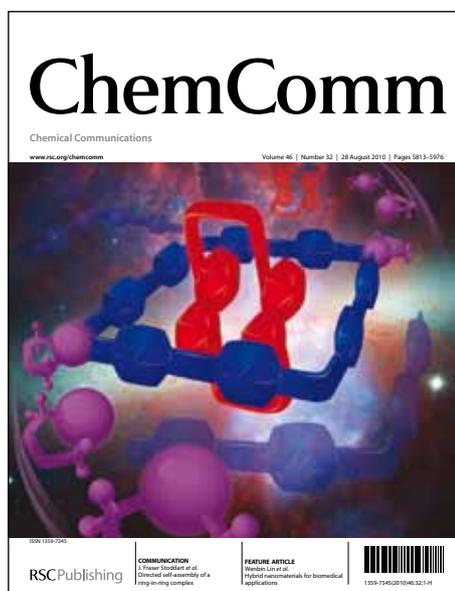


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COMMUNICATION

Lewis Base Mediated Dismutation of Trichlorosilane^{†‡}Amit Pratap Singh,^a Rajendra S. Ghadwal,^a Herbert W. Roesky,^{a*} Julian J. Holstein,^a Birger Dittrich,^{a*} Jean-Philippe Demers,^b Veniamin Chevelkov^b and Adam Lange^b

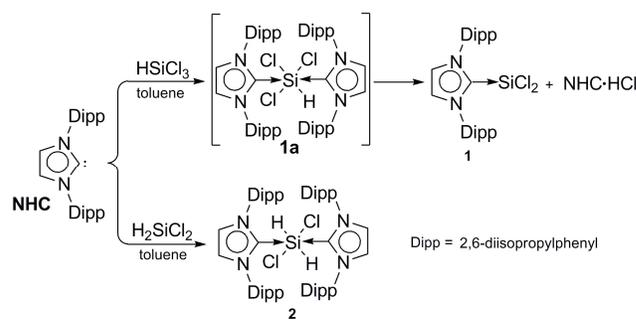
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An abnormal N-heterocyclic carbene (aNHC) has been used as a Lewis base to initiate dismutation of trichlorosilane. This report presents the reactivity differences of a normal N-heterocyclic carbene (NHC) versus aNHC with heavier group 14 elements. Three novel compounds (NHC)₂·SiCl₂H₂ (2) aNHC·SiCl₂H₂ (3), and aNHC·GeCl₂ (4) have been synthesized and characterized by single crystal X-ray analysis, solid-state NMR and DFT calculations.

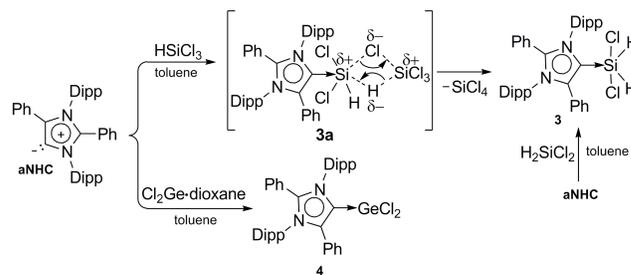
Trichlorosilane (HSiCl₃) is the most important precursor for the synthesis of numerous organosilicon derivatives and plays a significant role in the process of producing ultrapure silicon (Siemens process).¹ Moreover, it is well known that the highly reactive trichlorosilane tends to dismutate in the presence of a base or at higher temperatures. These dismutation reactions often afford Lewis acid-base adducts as intermediates leading to the formation of silicon halides and silane (SiH₄).² In the 1960s, Wannagat *et al.*³ reported on the first 1:2 adduct of trichlorosilane and pyridine (py) which undergoes the H versus Cl redistribution of HSiCl₃(py)₂ in the presence of polar solvents to form the pyridine adducts of H₂SiCl₂ and SiCl₄. In 1996, Fleischer *et al.*⁴ described the dismutation of bis(dichlorosilyl)amine in the presence of substituted pyridines (Rpy) to yield H₃SiCl, H₂SiCl₂, and HSiCl₃ adducts. However, Boudjouk *et al.*⁵ reported the first structurally characterized dichlorosilane [(teeda)·SiCl₂H₂] adduct, obtained from the dismutation of HSiCl₃ in the presence of N,N,N',N'-tetraethyl-1,2-ethanediamine (teeda). In a more recent report, Kroke *et al.*⁶ described the dismutation reaction of HSiCl₃(Rpy)₂, which exhibits various substitution patterns (R = H, 3-Br, 4-CHCH₂, 4-CH₃, 4-C(CH₃)₃, 4-N(CH₃)₂, and 4-CH₂CH₃) on the pyridine molecule (py). In all these investigations, the dismutation of trichlorosilane results in octahedral adducts of dichlorosilane. On the contrary, we have selectively synthesized a five coordinate aNHC·SiCl₂H₂ (3) adduct of dichlorosilane under mild conditions during the dismutation of trichlorosilane in the presence of aNHC as a Lewis base. We are not aware of any five coordinate dichlorosilane adduct during the dismutation of trichlorosilane.

Recently, we reported a room temperature stable Lewis base stabilized dichlorosilylene NHC·SiCl₂ (1) by reductive elimination of HCl from HSiCl₃ in the presence of NHC (Scheme 1).⁷ NHCs have been extensively used as versatile ligands in main group as well as in transition metal chemistry.^{8,9} Typically NHCs form metal complexes through the carbene center adjacent



Scheme 1 Synthesis of compounds 1 and 2

to two nitrogen atoms. In 2009, Bertrand *et al.*¹⁰ reported an abnormal N-heterocyclic carbene (aNHC) where the carbene center has only one adjacent nitrogen atom. Experimental data suggest that the aNHC is a strong nucleophile as well as an electrophile and may be a better substitute for NHCs. Therefore we became interested to explore the chemistry of aNHC with heavier group 14 elements such as silicon and germanium.



Scheme 2 Synthesis of compounds 3 and 4

The reaction of aNHC with HSiCl₃ gives the 1:1 aNHC·SiCl₂H₂ (3) adduct under elimination of SiCl₄. A similar reaction with NHC produces dichlorosilylene 1. We assume that in case of NHC, the six coordinated intermediate 1a is formed (Scheme 1) which undergoes reductive elimination of HCl to produce compound 1. However, in the case of aNHC, the presence of bulkier substituents resists the formation of a six coordinate intermediate with another molecule of aNHC. Moreover, the strong nucleophilic nature of aNHC favours the formation of an intermediate 3a involving two molecules of HSiCl₃ (Scheme 2), resulting in the formation of 3 under elimination of SiCl₄. The formation of compound 2 by the reaction of H₂SiCl₂ with NHC (Scheme 1) strongly supports the

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formation of a six coordinated intermediate during the reaction of NHC with HSiCl_3 . Furthermore, we obtained the five coordinated adduct **3** from the reaction of aNHC with H_2SiCl_2 . For a comparative study aNHC· GeCl_2 (**4**) was synthesized by the addition of Cl_2Ge -dioxane to the toluene solution of aNHC in 1:1 molar ratio. All compounds have been characterized by their ^1H and ^{13}C NMR spectra and show resonances for their respective ligands. Additionally, the ^1H NMR spectra of compounds **2** and **3** show a slightly broad resonance for the two Si–H protons at 5.58 and 6.14 ppm, respectively. To investigate the electronic environments around the silicon center for compounds **2** and **3** solid- and solution-state ^{29}Si NMR spectra were recorded. The solution-state ^{29}Si NMR spectra show the resonances at -225.2^{11} and -118.2 ppm for **2** and **3**, respectively. The ^{29}Si solid-state NMR spectrum of **2** shows a resonance with an isotropic chemical shift of -225.2 ppm (Fig. 1 and S1). Two ^{29}Si resonances are found for **3**, at -118.0 ppm and -120.4 ppm, which could be due to polymorphism in the sample. The chemical shift anisotropy (CSA), determined from the intensity of the MAS spinning sideband pattern is $+24$ ppm for **2** and $+112$ ppm for **3**. The very negative chemical shift of **2** arises as both NHC ligands contribute to the electron-rich environment at the Si nucleus. Furthermore, in contrast to **2**, which has a small CSA due to the molecular symmetry, the single aNHC ligand in **3** generates a large anisotropy of the electronic distribution at the Si nucleus (See ESI, table S1). Cross-polarization build-up curves for **2** and **3** reach their maximal intensity within 200 μs , confirming the presence of directly bonded proton on Si atoms (see ESI, Fig. S2). The elimination of SiCl_4 during the dismutation reaction of trichlorosilane was confirmed by recording the ^{29}Si NMR spectrum of the reaction mixture which shows an additional resonance at -18.0 ppm corresponding to SiCl_4 .¹²

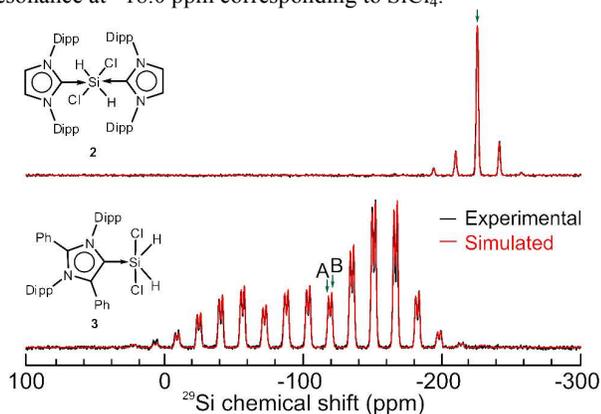


Fig. 1 ^{29}Si solid-state NMR cross-polarization spectra of **2** (top) and **3** (bottom) recorded at 1250 Hz MAS. Isotropic peaks are indicated by green arrows and back-calculated spectra are displayed in red. The high number of spinning sidebands for **3** illustrates the large anisotropy of the electronic environment at the silicon nucleus.

In order to establish unambiguously the structural features of compounds **2–4**, single crystal X-ray structural analyses were carried out. The molecular structure of **2** reveals that two NHCs are coordinated to the H_2SiCl_2 molecule to affords a six coordinated (NHC) $_2$ · SiCl_2H_2 (**2**) adduct with an octahedral geometrical environment around the silicon center (Fig. 2). The

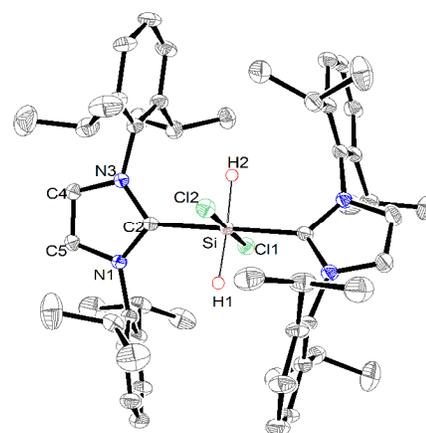


Fig. 2 ORTEP-representation of the molecular structure of (NHC) $_2$ · SiCl_2H_2 (**2**). ADPs are depicted at the 50% probability level. All C–H hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–C(2) 2.0494(15), Si–Cl(1) 2.2871(5), Si–Cl(2) 2.2850(5), C(2)–Si–Cl(1) 89.64(4), C(2)–Si–Cl(2) 90.23(4), Cl(1)–Si–Cl(2) 179.25(2).

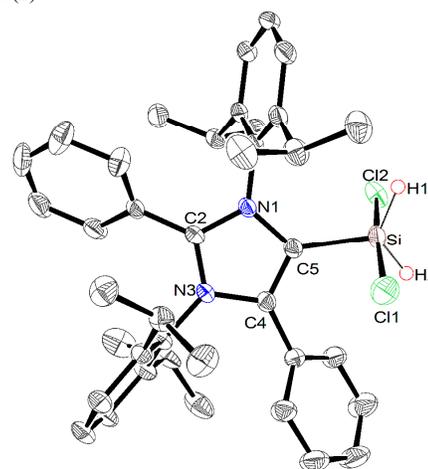


Fig. 3 ORTEP-representation of the molecular structure of aNHC· SiCl_2H_2 (**3**). ADPs are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–C(5) 1.908(2), Si–Cl(1) 2.2977(14), Si–Cl(2) 2.2992(11), C(5)–Si–Cl(1) 91.42(8), C(5)–Si–Cl(2) 91.98(8), Cl(1)–Si–Cl(2) 174.08(5).

NHCs, hydrogen and chlorine atoms are coordinated through the trans positions. Both NHCs makes an angle of 179.18 (5)° with C2–Si bond length of 2.0494(15) Å. The molecular structures of compounds **3** and **4** show that aNHC is coordinated to the metal ion (Si for **3** and Ge for **4**) through the carbene center C5. In the structure of **3** aNHC forms a five coordinated adduct with H_2SiCl_2 moiety resulting in trigonal bipyramidal geometry around the silicon center (Fig. 3). The carbon C5 and two hydrogen atoms (H1 and H2) are found in the trigonal plane, while the chlorine atoms (Cl1 and Cl2) occupy the axial positions. The average Si–Cl bond lengths for compounds **2** and **3** are 2.286 and 2.298 Å, respectively. The chlorine atoms Cl1 and Cl2 form angles of 179.25 (2)° (**2**) 174.08 (5)° (**3**) with silicon. In both **2** and **3** hydrogen atoms (H1 and H2) coordinated to the silicon were located in the difference Fourier map (see ESI, Fig.

S3c and S4c) and were freely refined. The experimental Si–H lengths (1.477(19) and 1.461(18) Å) in **2** are in good agreement with theoretical predicted value (1.478 Å). However, due to disorder or large amplitude vibrations, the experimentally determined Si–H bond lengths (1.32(3) and 1.14(3) Å) in **3** are different from the theoretically calculated value (1.470 Å). The molecular structure of **4** reveals that a distorted trigonal pyramidal geometry has been adopted by the coordinated germanium with the lone pair of the electrons at the apex (Fig. 4, ESI S5). Two chlorine atoms C11 and C12 are attached to the metal center with an average Ge–Cl bond length of 2.301 Å, which is longer than that found in the analogous compound NHC·GeCl₂ (2.277 Å).¹³ Both chlorine atoms C11 and C12 are

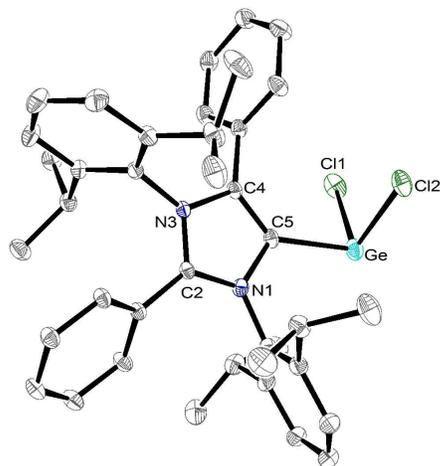


Fig. 3 ORTEP-representation of the molecular structure of aNHC·GeCl₂ (**4**). ADPs are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge–C(5) 2.071(2), Ge–Cl(1) 2.2856(7), Ge–Cl(2) 2.3157(6), C(5)–Ge–Cl(1) 92.91(6), C(5)–Ge–Cl(2) 93.33(6), Cl(1)–Si–Cl(2) 98.19(2)

nearly perpendicular (93.12°) to the Ge–C5 bond. The bond angle between the two chlorine atoms C11–Ge–Cl2 (98.19°) is a little larger than that for the reported C11–Ge–Cl2 (95.13°) of NHC·GeCl₂. The aNHC coordinated compounds have shorter M–C_{carbene} bond lengths (1.908(2) Å (**3**) and 2.071(2) Å (**4**)) in comparison with that of NHC coordinated **2** and the reported NHC·GeCl₂ (2.112(2) Å).¹³ This is due to the strong nucleophilic nature of aNHC, resulting in a stronger M–C bond. The DFT geometry optimization results confirm that the calculated deformation densities show the expected electron density accumulations in the bonding regions (for more details see ESI†).

In summary, we have studied the reactivity differences of aNHC versus NHC towards HSiCl₃ and H₂SiCl₂. A dismutation reaction of HSiCl₃ occurred in presence of aNHC resulting in a five coordinated aNHC·SiCl₂H₂ (**3**) adduct under elimination of SiCl₄. However, a similar reaction of NHC with HSiCl₃ produces dichlorosilylene by reductive elimination of HCl. In addition, a six coordinated **2** and a five coordinated **3** adduct was obtained by the reaction of NHC and of aNHC with H₂SiCl₂, respectively. This shows that aNHC is more nucleophilic as well as electrophilic in comparison to the NHC. Furthermore, dichlorogermylene aNHC·GeCl₂ (**4**) was synthesized by the treatment of Cl₂Ge-dioxane with aNHC in 1:1 molar ratio. The molecular structures of **2–4** were determined by single crystal X-

ray analysis and supported by DFT geometry optimizations. Compounds **2–4** might prove to be promising candidates for the synthesis of other potentially important compounds with low-valent silicon and germanium. Such type of investigations will be reported in due course from our laboratory.

Notes and references

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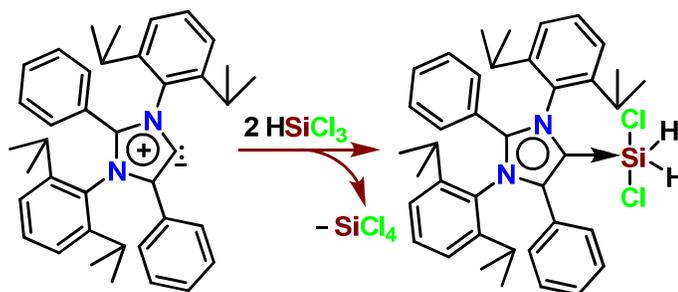
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⁵¹ †Electronic Supplementary Information (ESI) available: Experimental details, Solid-state NMR and theoretical details. Crystal data in CIF, CCDC No.: 883982 (**2**), 876665 (**3**), 876666 (**4**). For ESI and crystallographic data in CIF see DOI: 10.1039/b000000x. Financial support from the Deutsche Forschungsgemeinschaft (Emmy Noether Fellowship to A.L. and B.D.) and the NSERC of Canada (Postgraduate Scholarship to J.P.D.) is gratefully acknowledged.

⁵² ‡This paper is dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday.

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Abnormal N-heterocyclic carbene (aNHC) initiates the dismutation reaction of trichlorosilane to afford aNHC·SiCl₂H₂ adduct under elimination of SiCl₄.