N-Heterocyclic Carbenes

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C–N Bond Cleavage and Ring Expansion of N-Heterocyclic Carbenes using Hydrosilanes**

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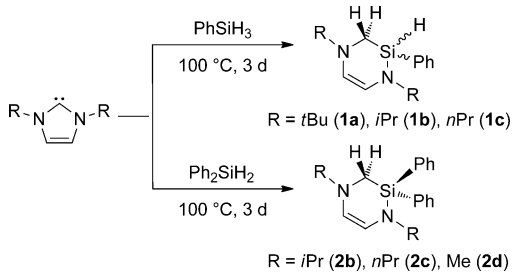
Dedicated to Dieter Fenske on the occasion of his 70th birthday

Since the isolation of stable N-heterocyclic carbenes (NHCs) in 1991,[1] the chemistry of NHCs and related molecules[2] has grown rapidly, and numerous applications of NHCs in main-group[3] and transition-metal chemistry,[4] as well as catalysis,[5] have been reported. In particular, NHCs are extensively used as ligands for transition-metal complexes because of their strong two-electron donor character.[6] Furthermore, NHCs have found wide application in main-group chemistry research in recent years. Among others, there are three important fields in main-group chemistry where NHCs and related molecules had a significant impact over the last few years: 1) the stabilization of low-coordinate main-group element compounds;[7,8] 2) element–element bond activation;[9] and 3) the application of NHCs in FLPs (molecules with "frustrated" Lewis pairs).[10] The strong σ-donation of NHCs has been applied to stabilize low-coordinate main-group element compounds, as exemplified by the isolation of NHC-supported **:**Si=Si**:** compounds with formally zero-valent silicon by Robinson et al.[7a] NHC-stabilized dihalosilylenes (SiX_2) as well as a NHC-stabilized silanones with a Si=O double bond have also been reported.[8] Similarly interesting is the activation of small molecules such as dihydrogen, ammonia, and silanes, which was achieved using the closely related cyclic alkyl amino carbenes (CAACs)[9] or "frustrated" NHC–borane Lewis pairs.[11]

In all these cases, the NHCs seem to provide a robust environment. Within the coordination sphere of transition metals, however, constructive and destructive decomposition pathways of NHC ligands are well-established, which mainly involve C–H,[12] C–N,[13] C–C,[14] and N–H[15] bond activation of the nitrogen alkyl, aryl, or hydrogen substituents. During our studies on the reactivity of $[Ni_2(iPr_2Im)_4(cod)]$[16] (iPr_2Im = 1,3-diisopropylimidazolin-2-ylidene, cod = 1,5-cyclooctadiene) with hydrosilanes H_nSiR_{4-n}[17] and on the catalytic hydrodefluorination of polyfluorinated aromatics using hydrosilanes,[18] we became aware of the formation of side products at higher reaction temperatures that originate from the dissociation of the NHC ligand and the reaction of the NHC with the hydrosilane employed. We report herein the C–N bond cleavage of NHC imidazoline cores accompanied by reductive ring opening and silylene ring expansion of the NHCs, which should be of particular relevance for NHC-based catalyst degradation as well as for main-group NHC chemistry. During the final stage of our work, Hill et al.[19] reported the closely related insertion of a BeH_2 unit into the C–N bond of $Dipp_2Im$ under mild conditions.

Based on our observations from nickel chemistry, and recent reports that some carbenes may undergo insertion into the Si–H bond of several silanes,[9] we were interested in the reactivity of selected NHCs towards phenyl-substituted silanes of the type $Ph_{4-n}SiH_n$ (n = 1, 2, 3). Treatment of the alkyl-substituted NHCs tBu_2Im, iPr_2Im, and nPr_2Im with one equivalent of phenylsilane $PhSiH_3$ in toluene at 100 °C for three days afforded in all cases pale yellow residues, which were obtained in low yields after work-up. These compounds were identified as derivatives of 3,4-dehydro-2,5-diazasilinanes **1** (R = *t*Bu **1a**, *i*Pr **1b**, *n*Pr **1c**; Scheme 1). Formally, two



Scheme 1. Reaction of different 1,3-dialkylimidazolin-2-ylidenes with $PhSiH_3$ and Ph_2SiH_2.

hydrogen atoms of the phenylsilane have been transferred to the NHC carbene carbon atom and the remaining silylene fragment has been inserted into one of the NHC C–N bonds with the formation of a six-membered heterocycle.

The reaction products can be easily distinguished spectroscopically from the starting material. Most notably, in the proton NMR spectra of the compounds **1a–c**, two sets of multiplets can be observed in the range between 2.29 ppm and 2.50 ppm for the diastereotopic NCH_2Si protons. The remaining Si*H* protons of **1a–c** give rise to signals in the region between 5.25 and 5.46 ppm, with $^1J_{SiH}$ coupling constants of 205.9 (**1a**), 205.5 (**1b**), and 206.9 (**1c**) Hz, respectively. The characteristic NHC carbene signals at approximately 212 ppm

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in the $^{13}C\{^1H\}$ NMR spectra of the starting compounds are absent and these carbon atoms give rise to significantly high-field shifted signals at 32.4 (**1a**), 31.7 (**1b**), and 36.7 ppm (**1c**) for the N*C*H$_2$Si carbon atoms of the product. In the ^{29}Si NMR spectra, signals were observed at −25.4 (**1a**), −24.9 (**1b**), and −21.6 ppm (**1c**), and Si−H stretch vibrations were detected in the IR spectra of the compounds at 2129 (**1a**), 2115 (**1b**), and 2115 (**1c**) cm^{-1}. Furthermore, the composition of all of the compounds was confirmed by mass spectrometry (EI-MS) and elemental analysis.

To demonstrate the generality of this reaction, the same set of NHCs (*t*Bu$_2$Im, *i*Pr$_2$Im, and *n*Pr$_2$Im) was reacted with diphenylsilane under identical conditions (3 d at 100 °C). For *i*Pr$_2$Im and *n*Pr$_2$Im, the corresponding insertion products **2b** and **2c** were isolated in moderate yields (48 and 61 %). In the case of *t*Bu$_2$Im, no conversion was observed, which presumably arises from the steric hindrance of the bulky *tert*-butyl substituents and the phenyl groups of the silane in the course of the reaction. However, for the sterically much less-hindered NHC 1,3-dimethyl-imidazolin-2-ylidene (Me$_2$Im) the corresponding methyl-substituted 3,4-dehydro-2,5-diazasilinane **2d** was formed (Scheme 1). In the proton NMR spectra, the NC*H*$_2$Si signals for the products appear as singlets at 2.59 (**2b**), 2.89 (**2b**), and 2.56 ppm (**2d**), and no signals for Si−*H* could be found. Similarly to **1a-c**, the carbon nuclei signals of N*C*H$_2$Si were detected at 33.0 (**2b**), 51.4 (**2c**), and 41.5 ppm (**2d**) in the $^{13}C\{^1H\}$ NMR spectra, and the silicon atoms gave rise to signals at −20.8 (**2b**), −20.4 (**2b**), and −19.4 ppm (**2b**) in the ^{29}Si NMR spectra.

To unequivocally determine the connectivity of the reaction products obtained, single crystals of **2b** were grown by cooling a boiling hexane solution of the compound slowly to room temperature. The result of the X-ray analysis as well as selected bond lengths and bond angles are given in Figure 1.

The molecular structure of **2b** confirms that the ring expansion is the result of a formal twofold hydrogen atom transfer from diphenylsilane to the carbene carbon atom with insertion of the remaining formal silylene fragment into the NHC C–N bond. The bond lengths Si–C1 (1.872(2) Å) and Si–N2 (1.718(2) Å) lie in the range typically observed for Si–C or Si–N single bonds in six-membered rings.[20] The C–C double bond of the NHC backbone is still intact (C2–C3 1.337(3) Å), and the torsion angle N1-C2-C3-N2 of 1.995(40)° confirms the coplanar alignment at the C2–C3 double bond. The carbon atom C1 lies 0.576 Å above, and the silicon atom Si 0.121 Å below, the plane defined by the atoms N1-C2-C3-N2, leading to a twisted six-membered ring.

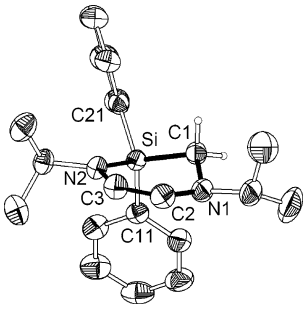
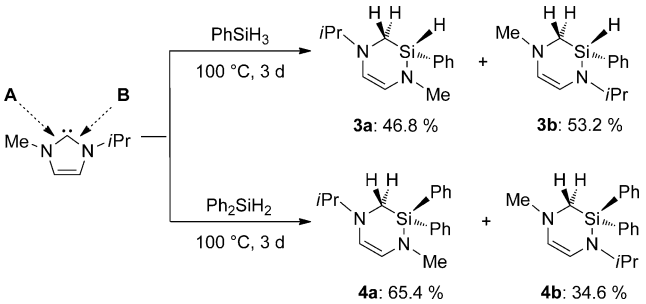


Figure 1. ORTEP diagram of the molecular structure of **2b**[21] in the solid state (ellipsoids set at 50% probability). Hydrogen atoms have been omitted for clarity, with the exception of those located at C1 (the NHC carbene carbon atom of the starting compound). Selected bond lengths [Å], angles [°], and dihedral angles [°]: Si–C1 1.872(2), C1–N1 1.463(3), N1–C2 1.398(3), C2–C3 1.337(3), C3–N2 1.410(3), N2–Si 1.718(2); C1-Si-N2 101.83(9), N1-C1-Si 110.72(15), N1-C1-Si-N2 46.915(17), N1-C2-C3-N2 1.995(40), C3-C2-N1-C1 27.352(34), C2-C3-N2-Si 6.013(31).

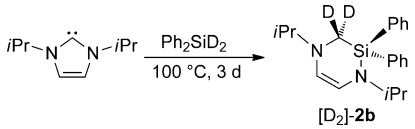
As no reaction between diphenylsilane and the *tert*-butyl-substituted NHC *t*Bu$_2$Im was observed, the influence of the NHC alkyl substituents and the number of phenyl groups of the silane used for the reaction was further analyzed. Treatment of asymmetrically substituted 1-isopropyl-3-methylimidazolin-2-ylidene (*i*PrMeIm) with mono- and diphenylsilane led to two different insertion products (denoted as **A** and **B** in Scheme 2). The use of PhSiH$_3$ leads to the isomers **3a** and **3b** in a ratio of 0.88:1.00 according to ^{1}H NMR spectroscopy, affording the sterically unfavorable **3b** as the major product. The reaction of *i*PrMeIm with Ph$_2$SiH$_2$ gave a 1.00:0.53 mixture of **4a** and **4b** in favor of the sterically less-crowded **4a**.



Scheme 2. Reaction of 1-isopropyl-3-methylimidazolin-2-ylidene with PhSiH$_3$ and Ph$_2$SiH$_2$.

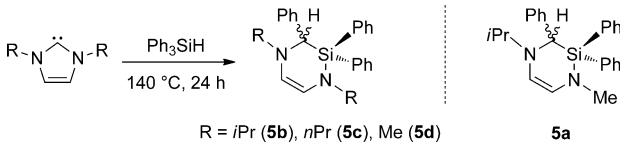
NMR spectroscopy experiments were performed to elucidate mechanistic details of the reaction of *i*Pr$_2$Im and Ph$_2$SiH$_2$. A vacuum-sealed NMR tube containing equimolar amounts of *i*Pr$_2$Im and Ph$_2$SiH$_2$ in C$_6$D$_6$ was slowly heated in steps of five degrees per 30 min until the reaction initiated at a temperature of approximately 75 °C. Furthermore, the reaction was monitored at 90 °C in [D$_8$]toluene (Supporting Information, Figure S1). In these spectra, only signals for *i*Pr$_2$Im, Ph$_2$SiH$_2$, and the reaction product **2b** were observed. This finding basically confirms the quantitative formation of **2b** from the starting material on an NMR scale, but gave no information on possible intermediates of the reaction. However, concerning the mechanism, these experiments suggest that the initial step of the reaction has a high activation barrier. In another experiment, we reacted *i*Pr$_2$Im with deuterated Ph$_2$SiD$_2$ and obtained [D$_2$]-**2b** (Scheme 3), exclusively deuterated at the NHC carbene carbon atom (C1 in Figure 1). The reaction of *i*Pr$_2$Im with a 1:1 ratio of Ph$_2$SiH$_2$ and Ph$_2$SiD$_2$ afforded a mixture of **2b** and [D$_2$]-**2b**, and no H/D cross products were observed.

Bertrand and co-workers[9] previously reported that some CAACs and the saturated NHC bis(2,6-diisopropylphenyl)-



Scheme 3. Reaction of 1,3-diisopropylimidazolin-2-ylidene with Ph_2SiD_2.

imidazolidin-2-ylidene ($Dipp_2ImH_2$) react with hydrosilanes with the formation of the corresponding Si–H bond-activation products. As it seemed likely that Si–H activation products are decisive intermediates for the reaction observed here, we were led to react the NHCs with triphenylsilane in the hope of avoiding the transfer of two hydrogen atoms to the carbene carbon atom, and thus observing a product of Si–H addition to the NHC. Surprisingly, in all cases, analogues of **1** and **2** were isolated, which were presumably formed by transfer of one silane hydrogen atom and one silane phenyl substituent to the NHC carbene carbon atom with insertion of the remaining {$SiPh_2$} fragment into one of the C–N bonds of the NHCs (Scheme 4). By using the unsymmetrically substituted NHC *i*PrMeIm, insertion into the C–N(Me) bond was observed exclusively with formation of isomer **5a**.



Scheme 4. Reaction of various 1,3-dialkylimidazolin-2-ylidenes with Ph_3SiH.

Compared to compounds **1** and **2**, the N–C*H*(C_6H_5)–Si protons are shifted downfield in the proton NMR spectra of compounds **5** (**5b** 4.27, **5c** 4.23, **5d** 4.03 ppm) owing to the electron-withdrawing effect of the phenyl substituent. In the $^{13}C\{^1H\}$ NMR spectra, the N–*C*H(C_6H_5)–Si signals were observed at 53.1 (**5b**), 53.5 (**5c**), and 56.4 ppm (**5d**). The silicon nuclei of these compounds give rise to signals at −23.8 (**5a**), −22.7 (**5b**), and −22.2 ppm (**5c**) in the ^{29}Si NMR spectrum. X-ray analyses were performed on single crystals of **5b** (Figure 2) and **5c** (Supporting Information, Figure S3) to confirm phenyl group transfer from silicon to the NHC carbon atom. The substitution of C1 with a phenyl group has no significant influence on the diazasilinane core. The kinking within the ring is more pronounced (deviation of Si and C1 from the N1-C2-C3-N2 plane 0.580 Å and 0.249 Å, respectively) and the Si–C1 distance is slightly elongated (**5b** 1.912(2) Å, **2b** 1.872(2) Å).

In the search for isolable intermediates from Si–H bond activation, the reactions of the diisopropylphenyl-substituted imidazolin-2-ylidene $Dipp_2Im$ and imidazolidin-2-ylidene ($Dipp_2ImH_2$; saturated at the NHC backbone) with silanes were also investigated (Scheme 5). $Dipp_2Im$ does not react with $PhSiH_3$ in boiling toluene. However, a reaction leading to diazasilinane **6** was observed in neat phenylsilane at higher temperatures, which was complete after 5 h at 160 °C. In the case of $Dipp_2ImH_2$, complete conversion to the diazasilinane

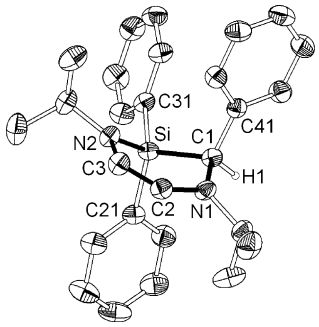
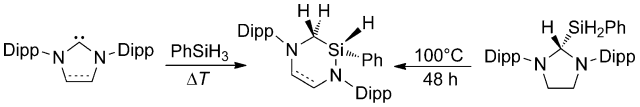


Figure 2. ORTEP diagram of the molecular structure of **5b**[21] in the solid state (ellipsoids set at 50% probability). Hydrogen atoms have been omitted for clarity, with the exception of that located at C1 (the former NHC carbene carbon atom). Selected bond lengths [Å], angles [°], and dihedral angles [°]: Si–C1 1.912(2), C1–N1 1.474(2), N1–C2 1.388(2), C2–C3 1.337(2), C3–N2 1.421(2), N2–Si 1.717(2); C1-Si-N2 101.95(7), N1-C1-Si 107.90(11), N1-C1-Si-N2 48.785(12), N1-C2-C3-N2 5.865(30), C3-C2-N1-C1 6.760(27), C2-C3-N2-Si 17.825(33).

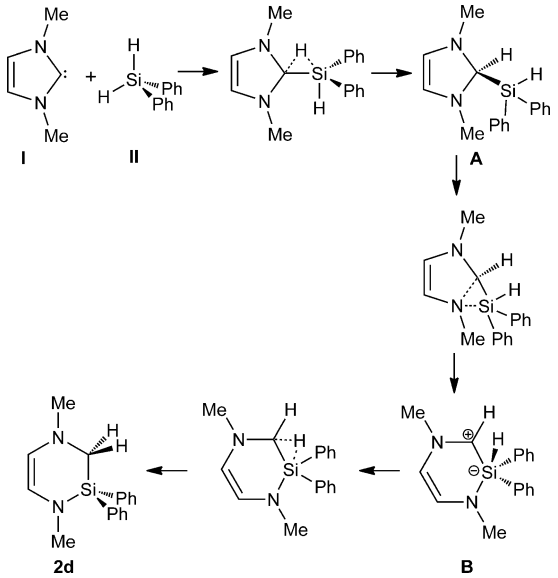


Scheme 5. Reaction of aryl-substituted NHCs with $PhSiH_3$. Dipp = 2,6-$iPr_2C_6H_3$.

7 was observed after 5 h in toluene at 100 °C. As already reported by Bertrand et al., $Dipp_2ImH_2$ cleanly reacts with $PhSiH_3$ at room temperature in hexane to give the Si–H activation product **9**, which can be isolated in pure form. After heating compound **9** for 5 h at 100 °C in toluene, the clean conversion to **7** was also observed (Scheme 5), which confirms the hypothesis that the reported ring expansion proceeds initially by insertion of the NHC into the Si–H bond, followed by a rearrangement of the Si–H bond activation product into the corresponding derivatives of the diazasilinane. However, no intermediates were detected using NMR techniques for the transformation of **9** to **7**.

For the formation of the diazasilinanes, we propose the pathway shown in Scheme 6 for the reaction of 1,3-dimethylimidazolin-2-ylidene (Me_2Im, **I**) with diphenylsilane (**II**) to give 1,1-diphenyl-2,5-dimethyl-3,4-dehydro-2,5-diazasilinane (**2d**). The first step of the reaction involves activation of one of the Si–H bonds of diphenylsilane at the NHC, that is, the insertion of the NHC carbene carbon atom of Me_2Im into the Si–H bond of the silane to give intermediate **A**, followed by amide transfer to the silicon atom to yield intermediate **B**. The final step of the reaction sequence involves hydrogen atom transfer from the silicon atom to the carbon atom to give **2d**.

In summary, the direct insertion of silylene moieties into the C–N bond of N-heterocyclic carbenes with ring expansion and formation of diazasilinanes has been achieved. These reactions are feasible using primary, secondary, and tertiary silanes $Ph_{4-n}SiH_n$ and a variety of NHCs; that is, saturated and unsaturated NHCs with N-alkyl and N-aryl substituents. This ring expansion should be of general interest for the different



Scheme 6. Proposed reaction path for the formation of **2d** from Me_2Im (**I**) and diphenylsilane (**II**).

areas of NHC-based chemistry of main-group elements and transition metals, and also for catalysis, especially if silanes are used in reactions with these species at higher temperature.

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[21] CCDC 884932 (**2b**), 884933 (**5b**), 884934 (**5c**), and 884935 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

