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Synthesis and Rearrangement of Stable NHC→Silylene Adducts and Their Unique Reactivity towards Cyclohexylisocyanide

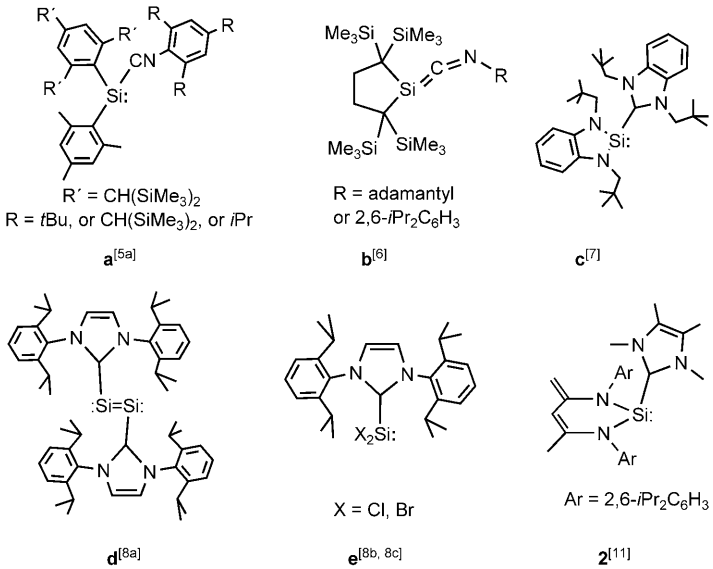
Yun Xiong, Shenglai Yao, and Matthias Driess*[a]

Abstract: The syntheses and reactivity of the two N-heterocyclic carbene (NHC)→ silylene complexes **2** and **4** have been investigated. The latter are easily accessible by reaction of the zwitterionic, N-heterocyclic silylene LSi: **1** [L = Ar-*N*-C(=CH_2)CH=C(Me)-*N*-Ar, Ar = 2,6-*i*$Pr_2C_6H_3$] with 1,3,4,5-tetramethylimidazol-2-ylidene and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, respectively. While compound **2** undergoes facile rearrangement above −20 °C to give the unsymmetrical N-heterocyclic silylcarbene **3**, the derivative **4** remains unchanged even after boiling in benzene. The remarkable reactivity of **3** and **4** towards cyclohexylisocyanide has been examined which leads in a unique series of C–H, Si–H, and C–N bond activations to the new triaminosilanes **5** and **6**, respectively. The novel compounds **3**, **4**, **5**, and **6** were fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, EI-MS, elemental analysis, and single-crystal X-ray diffraction.

Keywords: C-H activation · C-N activation · hydrosilylation · ketenimines · silicon

Introduction

There has been increasing interest over the last two decades in the study of stable silylene species (divalent, two-coordinate silicon compounds) in part owing to their carbene-like reactivites.[1] Silylenes, in contrast to the carbene homologues, have a singlet ground state with a lone pair of electrons (mainly 3s character) and a vacant 3p orbital at the Si^{II} site and thus can act either as Lewis bases or Lewis acids toward substrates.[2] In terms of their Lewis base reactivity, silylenes can serve as strong donor ligands as shown in numerous metal–silylene complexes which represent versatile functional systems in catalysis and beyond.[3] On the other hand, although many complexes in which silylenes serve as Lewis acids have been reported, they are too reactive to be isolable at ambient temperature and thus could only be observed spectroscopically in cryogenic matrices.[4] Rare exceptions of stable examples of the latter type comprise complexes with bulky substituted isocyanides and N-heterocyclic carbenes (NHCs) as depicted in Scheme 1. It is noteworthy that using less bulky isocyanides such as *t*BuNC: and MesNC: (Mes = 2,4,6-trimethylphenyl) leads to transient silylene–isocyanide complexes which afford C–H or C–C and Si–C activation species as final products.[5a]



Scheme 1. Several NHC- and RNC-stabilized low-coordinate silicon species and a silaketenimine.

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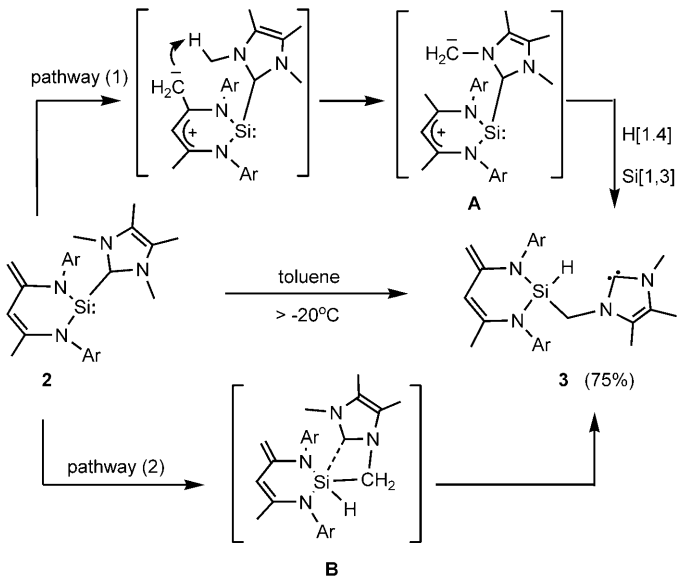
In line with that, the reactions of stable N-heterocyclic silylenes (NHSis) with *t*BuNC furnish silacyanides and/or 1-cyano-2-organo-disilanes under Me_3C–*N*C bond cleavage.[5b–d] Remarkably, using an electronically less disturbed dialkylsilylene, Kira et al. were able to obtain stable silaketenimines (Scheme 1, compound **b**).[6] In 1999 Gehrhus and Lappert reported a stable NHC-silylene adduct.[7] Very recently, the utilization of NHCs to stabilize low-valent silicon species has achieved a great progress. Presumably the most striking example is the synthesis of an isolable NHC→:Si=Si:←NHC species with silicon in the formal oxidation state zero (Scheme 1, compound **d**).[8a] Accordingly, the first related NHC-stabilized dihalosilylenes NHC→SiX_2 (X=Cl, Br) have also been synthesized (Scheme 1, compound **e**).[8b–c]

We have been engaged in exploring the chemistry of the thermally stable, partially zwitterionic, N-heterocyclic silylene LSi: **1** [L=Ar-*N*-C(=CH_2)CH=C(Me)-*N*-Ar, Ar=2,6-*i*$Pr_2C_6H_3$][9] which shows also a striking reactivity toward isocyanides and reacts with an excess of cyclohexylisocyanide, affording an unusual cycloaddition and C–H activation product along with a silacyanide.[10] More recently, we communicated the synthesis and structure of the 1:1 adduct **2**, starting from **1** and a NHC (Scheme 1).[11] We have now learned that **2** is thermolabile and undergoes unexpected tautomerization to give the unsymmetric N-heterocyclic silylcarbene **3**. The existence of **2** and **3** prompted us to explore its reactivity toward organoisocyanides which turned out to be very different from that of **1**. Herein we report on the formation of **3**, the synthesis and structure of the new NHC→silylene homologue **4**, and their unusual reactivity towards cyclohexylisocyanide.

Results and Discussion

As reported previously,[11] the NHC-silylene adduct **2** is accessible at −60 °C by direct conversion of silylene **1** with 1,3,4,5-tetramethylimidazol-2-ylidene in toluene and can be isolated in high yield by crystallization at low temperature. Dissolution of **2** in toluene revealed that it undergoes slowly rearrangement under intramolecular C–H activation above −20 °C to give the N-heterocyclic unsymmetric silylcarbene **3** (Scheme 2). Monitoring the reaction progress by ^{1}H NMR spectroscopy revealed that the conversion can be completed within 12 h at ambient temperature, and finally compound **3** can be isolated in the form of colorless crystals in 75% yield.

Although the mechanism is still unknown, we propose the two possible pathways (1) and (2) for the C–H activation and tautomerization of **2** which are sketched in Scheme 2. Pathway (1) involves deprotonation of a NMe group of the NHC donor in close proximity to the nucleophilic exocyclic methylene group of the partially zwitterionic silylene **1** which yields intermediate **A**. Subsequently, the latter undergoes H[1,4]- and Si[1,3]-shifts to yield the final product. Alternatively and according to pathway (2), the reactive silicon(II) center could be capable of insertion to a C–H bond



Scheme 2. Tautomerization of **2** to **3** via the proposed pathway (1) or (2).

of a NMe group to give **B**, which transforms to **3** under the cleavage of the NHC→Si dative bond.

Compound **3** has been fully characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, EI-MS, and elemental analysis. In the ^{1}H NMR spectrum of **3** the singlet at δ=6.17 ppm can be unequivocally assigned to the Si–H proton, and the respective ^{29}Si nucleus resonates at δ=−38 ppm in the ^{29}Si{H} NMR spectrum, indicating a four-coordinated silane species. The ^{13}C{H} NMR spectrum exhibits a characteristic low-field resonance for the two-coordinate sp^2 carbon atom of the NHC at δ=208.7 ppm. The structure of the silyl-substituted unsymmetrical NHC **3** has been confirmed by X-ray diffraction analysis (Figure 1). It crystallizes in the triclinic space group *P*1 with two independent molecules in the asymmetric unit. The carbene moieties of both molecules are disordered over two orientations (60:40). Compound **3** consists of a six-membered, puckered SiC_3N_2 ring and a five-membered, planar NHC skeleton which are bridged by a methylene group.

In order to learn something about the influence of steric congestion on adduct formation, the more crowded 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene has been employed as NHC ligand. In fact, while the latter reacts with equimolar amounts of **1** in toluene at −60 °C, leading to the corresponding adduct **4** (Scheme 3), further increase of the steric congestion of the NHC ligand precludes adduct formation with **1**. Thus, 1,3-bis(tert.-butyl)imidazol-2-ylidene and its heavier homologue, the silylene L′Si: (L′=*t*Bu-*N*-CH=CH-*N*-*t*Bu), are chemically inert towards **1** (Scheme 3).

In contrast to **2**, the adduct **4** is even stable in boiling benzene. Compound **4** can be isolated as yellow crystals in 87% yield. Its composition is proven by multinuclear NMR, IR spectroscopy, elemental analysis, and EI-MS. The ^{29}Si NMR spectrum of **4** exhibits a slight shielding for the three-coordinate, divalent ^{29}Si atom in comparison to the situation ob-

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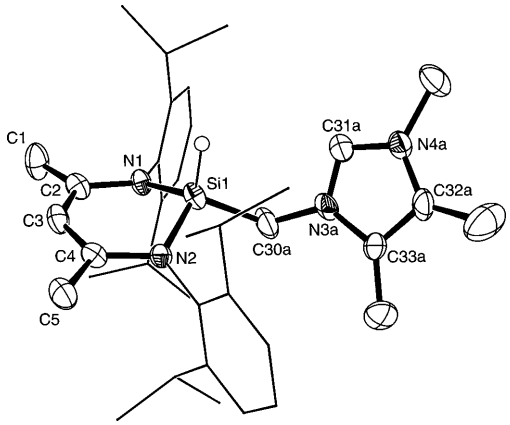
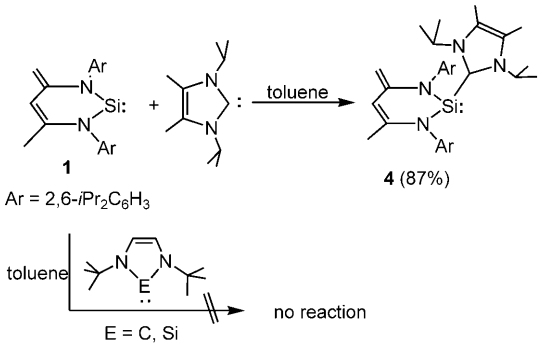


Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for that at Si1) are omitted for clarity. Two independent molecules in the asymmetric unit were observed. Additionally, the carbene moieties are statistically disordered over two orientations in a population ratio of 60:40 and 44:56, respectively. Only one of the two molecules with one orientation is shown. Selected bond lengths (pm) and bond angles (°): Molecule 1: Si1-N1 172.8(4), Si1-N2 173.1(4), Si1-C30a 187.2(5); N1-Si1-N2 104.1(2); Molecule 2: Si1–N1 176.3(4), Si1–N2 175.7(4), Si1–C30a 185.0(6); N1-Si1-N2 102.1(2).



Scheme 3. Reactivity of **1** toward bulkier NHCs and an NHSi.

served in **2** ($\delta = -7.6$ for **4** vs. -12 ppm for **2**). The molecular structure of **4** has been established by X-ray analysis (Figure 2). As expected, the silicon atom in **4** features a pyramidal coordination similar to the structure of **2**, with a five-membered, planar NHC ring and a six-membered SiN_2C_3 ring which is slightly puckered. In comparison to **2**, both the longer Si1−C30 distance of 206.5(2) pm (vs. 201.6(3) pm in **2**) and the larger sum of bond angles of 300.51° (vs. 295.9° in **2**) reflect the larger steric congestion of the NHC and the weaker coordination of the NHC to the silicon(II) atom in **4**. However, owing to the electron donation of the NHC, the two Si−N bonds in **4** (182.0(2) and 179.4(2) pm) become longer than in **1** (173.4 and 173.5(1) pm),[9a] but are similar to those in **2** (180.2 and 180.5(3) pm).[11]

The marked nucleophilic character of the Si^{II} center in **2** and **4** prompted us to investigate the reactivity towards organoisocyanides, which is expected to be different from that of **1**. At first, we probed the reactivity of **2** with equimolar amounts of cyclohexylisocyanide at −40 °C, but no conversion could be detected after several days. However, if the reaction mixture was allowed to warm up to ambient temperature, **2** and the isocyanide react solely to the tricyclic triaminosilane **5** (Scheme 4), which can be isolated in the form of

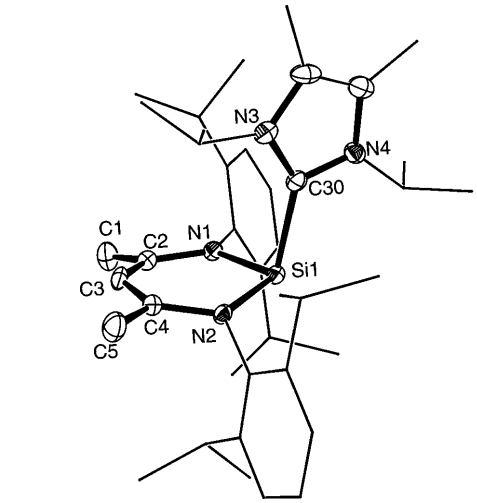
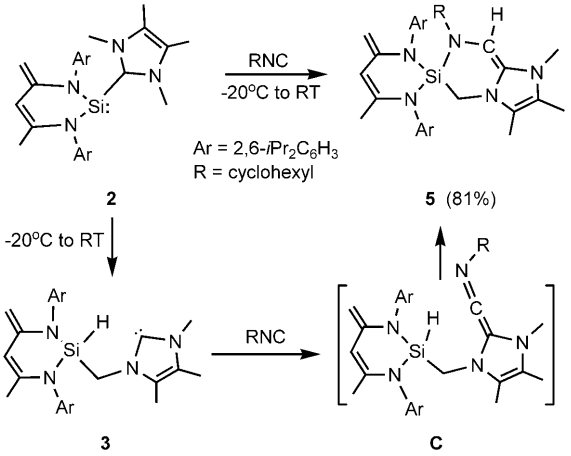


Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability level. H atoms and a cocrystalized toluene molecule are omitted for clarity. Selected distances (pm) and angles (°): Si1-N2 179.4(2), Si1-N1 182.0(2), Si1-C30 206.5(2), N1-C2 139.6(3), N2-C4 140.3(3), N3-C30 136.4(3), N3-C31 139.2(3), N4-C30 136.4(3), N4-C32 139.8(3), C1-C2 136.7(3), C2-C3 144.8(3), C3-C4 135.4(3), C4-C5 148.9(3), C31-C32 134.3(3); N2-Si1-N1 97.64(8), N2-Si1-C30 105.4(1), N1-Si1-C30 97.47(8).



Scheme 4. The formation of **5** from **2** via **3**.

yellow crystals in 81% yield. The formation of **5** can be explained through prior rearrangement of **2** to **3** and subsequent conversion of **3** with isocyanide. This was proven by authentic experiments upon treatment of equimolar amounts of **3** with cyclohexylisocyanide under similar reaction conditions. Although the mechanism is currently unknown, we reason that the ketenimine **C** is an intermediate which than undergoes intramolecular hydrosilylation of the C=N double bond and ring closure to furnish **5**. In line with that, it is well known that carbenes can react with organoisocyanides to form ketenimines,[12a,b] and even a silaketeni-

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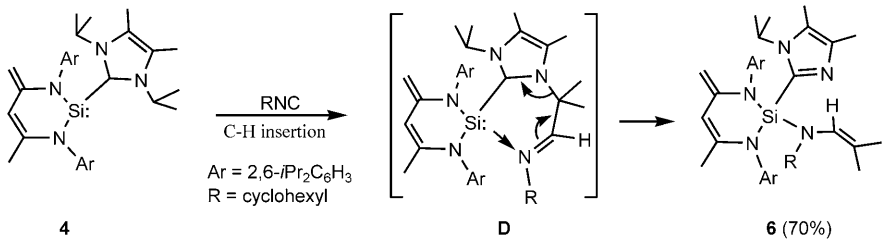
mine, related to the proposed intermediate **C**, has been isolated previously (Scheme 1).[6] The proposed mechanism to give **5** is reminiscent of a hydrosilylation of a imine catalyzed by NHC which has been reported recently.[12c]



Scheme 5. Formation of **6** from **4** and cyclohexylisocyanide, probably via **D**.

The ^{1}H NMR spectrum of **5** shows, besides other signals, a characteristic singlet at $\delta =$ 3.98 ppm which can be assigned to the proton of the RNC*H*=C moiety. The corresponding ^{13}C nucleus of the RN*C*H=C subunit resonates at $\delta = 65.9$ ppm in the ^{13}C{^{1}H} NMR spectrum, and the singlet at $\delta = -43.2$ ppm in the ^{29}Si NMR spectrum indicates the presence of a four-coordinate silicon species. An X-ray diffraction analysis revealed that the compound consists of a tricyclic, N-heterocyclic triaminosilane skeleton with a tetrahedrally coordinated silicon atom as a spirobicyclic center (Figure 3). Both six-membered, spirobicyclic connected SiN_2C_3 rings are puckered whereas the five-membered C_3N_2 ring is planar. The short C37–C33 distance of 133.4(3) pm is indicative of a new-formed C=C double bond. The C33–N3 distance of 141.0(3) pm as well as the C33–N4 distance of 139.2(3) pm are significantly shorter than a C–N single bond but longer than a C=N double bond, presumably because of π delocalization within the five-membered, heterofulvene-like C_3N_2 ring.

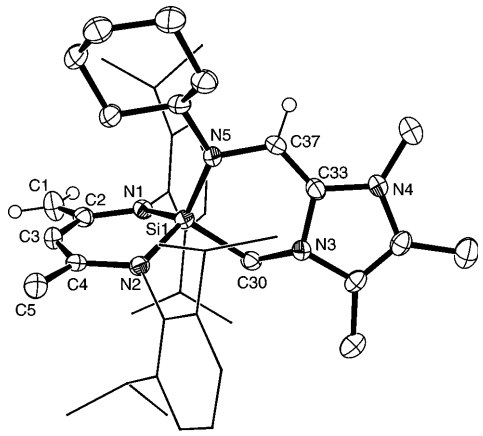


Figure 3. Molecular structure of **5** Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for those at C1 and C37) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1-N1 174.0(2), Si1-N2 174.2(1), Si1-N5 172.0(2), Si1-C30 186.3(2), N5-C37 143.7(3), C37-C33 133.4(3), C33-N4 139.2(3), C33-N3 141.0(3), N3-C30 146.3(3); N5-Si1-C30 103.3(1), N1-Si1-N2 102.7(1).

Interestingly, treatment of **4** with an equimolar amount of cyclohexylisocyanide at ambient temperature takes a completely different course, affording the novel compound **6** in 70% yield (Scheme 5). Usually an isocyanide acts as electron donor;[5a,6,10] however, because of the strong electron donor ability of the NHC, the cyclohexylisocyanide here acts as electron acceptor to give the proposed intermediate **D** (Scheme 5). The latter involves insertion of the terminal carbon(II) atom of the isocyanide into the C–H bond of an N*CH*Me$_2$ group to give **D**, which rearranges to form the final product **6**. The C–H bond cleavage of a NHC alkyl group is reminiscent of the formation of **3** as shown in Scheme 2. A related base-induced but metal-mediated C–H activation has also been described recently.[12d]

In the ^{1}H NMR spectrum of **6** the C–H proton of the RNC*H*=CMe$_2$ moiety is observed at $\delta = 5.52$ ppm, and the respective carbon atom exhibits a resonance at $\delta = 62.8$ ppm in the ^{13}C NMR spectrum. The ^{29}Si NMR spectrum of **6** shows as expected a high-field resonance relative to the precursor **4** ($\delta = -58$ ppm for **6** vs. -43 ppm for **5**, and -7.6 ppm for **4**). An X-ray analysis revealed that compound **6** contains a tetrahedrally coordinated silicon atom as part of a SiN_3C group (Figure 4). The transferred CMe$_2$ group from N4 of the former NHC ligand is now part of a C=C double bond with a C38–C39 distance of 133.1(3) pm. The N4–C30 distance of 133.8(3) pm in the modified C_3N_2 heterocycle is indicative of a C=N double bond. The Si1–N5 distance of 170.4(2) pm is slightly shorter than those of Si1–N1 (176.0(2) pm) and Si1–N2 (175.0(2) pm). The Si1–C30 distance of 189.4(2) pm falls into the normal range for a Si–

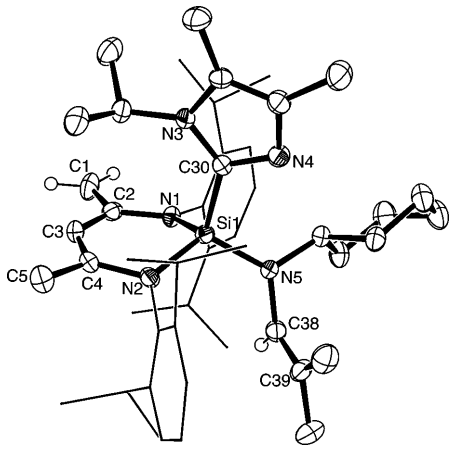


Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except for those at C1 and C38) and two cocrystallized toluene molecules are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1-N1 176.0(2), Si1-N2 175.0(2), Si1-N5 170.4(2), Si1-C30 189.4(2), C30-N4 133.8(3), C30-N3 138.9(3), N5-C38 144.3(3), C38-C39 133.1(3); N1-Si1-N2 101.2(1), C30-Si1-N5 105.8(1).

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C single bond. The bond angles of the SiN_3C core are in the range of 101.2(1)–114.0(1)° and thus slightly distorted from a regular tetrahedron.

Conclusions

We prepared the new bulky substituted NHC→silylene adduct **4**. While the less sterically congested NHC-silylene adduct **2** undergoes rearrangement via C–H activation by the nucleophilic silicon(II) center to give the unsymmetrical N-heterocyclic silylcarbene **3** above −20 °C, the bulkier adduct **4** remains stable even in boiling benzene. Because of the strong nucleophilic character of the Si^{II} atom, the adducts **2** and **4** possess a very different reactivity towards cyclohexylisocyanide in comparison to **1**. At low temperature, compound **2** does not react with cyclohexylisocyanide. Instead compound **2** rearranges to **3** at elevated temperature, prior to reacting with cyclohexylisocyanide. However, the N-heterocyclic silylcarbene **3** reacts with cyclohexylisocyanide to give under formation of a ketenimime intermediate and subsequent intramolecular hydrosilylation the tricyclic triaminosilane **5**, bearing a spirocyclic tetracoordinate Si atom. The reaction of **4** with cyclohexylisocyanide proceeds at room temperature and leads in a unique intramolecular rearrangement sequence to the novel triaminosilane **6**, involving C–H and C–N bond activation and C=C coupling processes.

Experimental Section

General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material silylene **1**, **2**, NHCs, and NHS were prepared according to literature procedures.[9a,11,13a–c] NMR spectra were recorded with Bruker spectrometers ARX200, AV400 and with residual solvent signals as internal reference (^1H and $^{13}C\{^1H\}$) or with an external reference ($SiMe_4$ for ^{29}Si). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; m = multiplet; br = broad.

Single-Crystal X-ray Structure Determination

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of **3**, **4**, **5**, and **6** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[14] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 739318 (**3**), CCDC 731580 (**4**), CCDC 739319 (**5**), CCDC 739317 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

3: Triclinic, space group $P\bar{1}$, $a = 8.7223(4)$, $b = 12.1105(5)$, $c = 17.1446(4)$ Å, $\alpha = 103.360(3)$, $\beta = 101.828(3)$, $\gamma = 100.769(4)°$, $V = 1671.61(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.130$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.100$ mm^{-1}, 13949 collected reflections, 8441 crystallographically independent reflections [$R_{int} = 0.0295$], 7025 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0639$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.1543$ (all data), 846 refined parameters.

4: Triclinic, space group $P\bar{1}$, $a = 11.1382(4)$, $b = 14.2145(4)$, $c = 14.2274(5)$ Å, $\alpha = 75.283(3)$, $\beta = 80.647(3)$, $\gamma = 86.899(4)°$, $V = 2149.48(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.108$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.090$ mm^{-1}, 18120 collected reflections, 7522 crystallographically independent reflections [$R_{int} = 0.0439$], 5157 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0560$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.1114$ (all data), 485 refined parameters.

5: Triclinic, space group $P\bar{1}$, $a = 11.7216(5)$, $b = 12.0002(6)$, $c = 17.0485(9)$ Å, $\alpha = 101.360(4)$, $\beta = 97.438(4)$, $\gamma = 116.781(5)°$, $V = 2032.62(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.108$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.093$ mm^{-1}, 14803 collected reflections, 7073 crystallographically independent reflections [$R_{int} = 0.0599$], 4156 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0599$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.0996$ (all data), 454 refined parameters.

6: Monoclinic, space group $P2_1/n$, $a = 12.1569(5)$, $b = 25.0641(9)$, $c = 16.2116(7)$ Å, $\beta = 93.454(4)°$, $V = 4930.7(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.113$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.087$ mm^{-1}, 25314 collected reflections, 8666 crystallographically independent reflections [$R_{int} = 0.0532$], 4468 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0492$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.0994$ (all data), 622 refined parameters.

Syntheses

3: To a solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.14 g, 1.12 mmol) in toluene (5 mL) was added a solution of silylene **1** (0.50 g, 1.12 mmol) in toluene (5 mL) at −60 °C. The reaction mixture was allowed to warm to room temperature. After two days the reaction was completed and the colorless crystals of **3** at −20 °C isolated. Yield: 0.48 g (0.84 mmol, 75 %); m.p.: 85 °C (decomp.); ^1H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.00$–1.45 (m, 21H; CH*Me*$_2$), 1.20 (s, 3H, *Me*), 1.35 (s, 3H; *Me*), 1.55 (s, 3H, NC*Me*), 1.57 (d, ^3J (H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 2.79 (s, 3H; N*Me*), 3.08 (s, 1H; NC*H*$_2$), 3.12 (s, 1H; NC*H*$_2$), 3.32 (s, NCC*H*$_2$), 3.72 (m, 4H; C*H*Me$_2$), 3.99 (s, 1H; NCC*H*$_2$), 5.44 (s, 1H; γ-H), 6.17 (s, 1H; Si*H*), 7.02–7.19 ppm (m, br, 6H; 2,6-*i*Pr$_2$C$_6$H$_3$); $^{13}C\{^1H\}$ NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.18$, 8.57 (C$_2$*Me*$_2$), 22.1, 23.3, 24.3, 24.6, 25.0, 25.2, 25.4, 26.1, 26.6 (NC*Me*, CH*Me*$_2$), 28.3, 28.4, 28.6, 28.9 (*C*HMe$_2$), 33.9, 36.9 (N*C*H$_2$Si, N*Me*), 86.7 (NC*C*H$_2$), 104.2 (γ-*C*), 122.0, 122.4, 123.5, 123.9, 124.4, 124.8, 126.9, 139.5, 140.3, 141.8, 146.9, 148.4, 148.8, 148.9, 149.5 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$), 208.7 ppm (carbene C); $^{29}Si\{^1H\}$ NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -38.4$ ppm (s); EI-MS: *m*/*z* (%):568 (55) [*M*$^+$], 553 (100) [*M*$^+$−Me], 525 (77) [*M*$^+$−*i*Pr]; elemental analysis calcd (%) for $C_{36}H_{52}N_4Si$: C 76.00, H 9.21, N 9.85, found: C 75.87, H 9.26, N 9.53.

4: 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene (0.13 g, 0.72 mmol) in toluene (10 mL) was added to a solution of silylene 1 (0.32 g, 0.72 mmol) in toluene (10 mL) at −60 °C. After 10 min the reaction was completed and the solution was concentrated to about 10 mL and cooled at −20 °C. The product **4** crystallized as yellow crystals. Yield: 0.39 g (0.63 mmol, 87 %); m.p.: 78 °C (decomp.); ^1H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.38$ −1.66 (m, 45H; CH*Me*$_2$, C$_2$*Me*$_2$, NCH*Me*$_2$, NC*Me*), 3.20–4.27 (m, 6H; NC*H*Me$_2$, C*H*Me$_2$), 3.32 (s, 1H; NCC*H*$_2$), 3.94 (s, 1H; NCC*H*$_2$), 5.55 (s, 1H; γ-C*H*), 7.00–7.27 ppm (m, br, 6H; 2,6-*i*Pr$_2$C$_6$H$_3$); $^{13}C\{^1H\}$ NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 9.7$ (C$_2$*Me*$_2$), 21.4–28.4 (NCH*Me*$_2$, NC*Me*, C*HMe*$_2$), 49.0 (N*C*HMe$_2$), 82.9 (NC*C*H$_2$), 107.4 (γ-C), 123.9–148.2 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$); 149.7 ppm (Si*C*); $^{29}Si\{^1H\}$ NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -7.6$ ppm (s); EI-MS: *m*/*z* (%): 444 (5 [(*M*-NHC)$^+$]), 429 (100, [(*M*-NHC-Me)$^+$]), 180 (11, NHC$^+$); elemental analysis calcd (%) for $C_{40}H_{60}N_4Si{\cdot}C_7H_8$: C 78.71, H 9.56, N 7.81, found: C 78.37, H 9.70, N 7.57.

5: Method 1: Cyclohexylisocyanide (0.18 mL, $d = 0.88$ g mL^{-1}, 1.46 mmol) was added to a solution of **3** (0.83 g, 1.46 mmol) in diethyl ether (15 mL) at −20 °C. After three days yellow crystals of **5** formed at −20 °C with yield of 0.80 g (1.18 mmol, 81 %). Method 2: A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (0.16 g, 1.30 mmol) in toluene (5 mL) was added to a solution of silylene **1** (0.59 g, 1.30 mmol) in toluene (10 mL) at −40 °C under stirring. After 30 min. the reaction was completed. Cyclohexylisocyanide (0.16 mL, $d = 0.88$ g mL^{-1}) was added in situ to the reaction mixture at −40 °C. The reaction temperature was allowed to warm to room temperature and the solvent was changed from toluene to diethyl ether (5 mL), and the solution was cooled at −20 °C. After two days the product **5** crystallized at −20 °C as yellow crystals. Yield: 0.66 g

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(0.97 mmol, 73%); m.p.: 171°C (decomp.); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25°C): δ = 1.24–1.82 (m, 44H; C_2Me_2, $CHMe_2$, C_6H_{11}, NC*Me*), 2.27 (s, 3H; N*Me*), 3.03–3.10 (b, 2H; NCH_2Si), 3.32 (s, 1H; $NCCH_2$), 3.55 (m, 1H; $CHMe_2$), 3.78 (m, 1H, $CHMe_2$), 3.89 (m, 1H, $CHMe_2$), 3.98 (s, 1H; RNC*H*=C), 4.02 (m, 1H; $CHMe_2$), 4.04 (s, 1H; $NCCH_2$), 5.45 (s, 1H; γ-*H*), 7.08–7.27 ppm (m, br, 6H; 2,6-$iPr_2C_6H_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25°C): δ = 8.67 (C_2Me_2), 22.3, 24.6, 25.0, 25.3, 25.4, 25.7, 26.1, 26.4, 26.6, 26.9, 27.0, 28.4, 28.6, 28.8, 29.7, 32.3, 32.5, 35.4 (NC*Me*, NCH_2Si, N*Me*, $CHMe_2$, $CHMe_2$, $NCH(CH_2)_5$), 57.1 ($NCH(CH_2)_5$), 65.9 (RN*C*H=C), 87.3 ($NCCH_2$), 107.8 (γ-*C*), 116.9, 118.0, 124.6, 124.7, 124.9, 125.0, 139.0, 139.2, 142.9, 143.3, 148.1, 148.4, 148.5, 148.6, 150.3 ppm (N*C*Me, N*C*CH_2, C_2Me_2, *C*=*C*HN, 2,6-$iPr_2C_6H_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25°C): δ = −43.2 ppm (s); EI-MS: *m*/*z* (%): 677.63 (100) [M^+], 662 (5) [M^+−Me], 594 (70) [M^+−*i*Pr]; elemental analysis calcd (%) for $C_{43}H_{63}N_5Si$: C 76.17, H 9.36, N 10.33, found: C 76.29, H 9.34, N 10.16.

6: 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene (0.25 g, 1.39 mmol) was added to a solution of silylene **1** (0.62 g, 1.39 mmol) in toluene (10 mL) at −20°C. The reaction mixture was allowed to warm to room temperature. After 20 min. cyclohexylisocyanide (0.17 mL, d = 0.88 g mL^{-1}) was added to the reaction mixture at −20°C and the reaction was finished after 24 h. Colorless crystals of **6** result from the concentrated toluene solution at −20°C. Yield: 0.71 g (0.97 mmol, 70%); m.p.: 314°C (decomp.); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25°C): δ = 1.02–1.54 (m, 50H; C_2Me_2, $NCHMe_2$, $CHMe_2$, C_6H_{11}, NC*Me*), 2.12 (s, 3H; =CMe_2), 2.19 (s, 3H; =CMe_2), 2.90 (m, 2H; $CHMe_2$), 3.30 (s, 1H, $NCCH_2$), 3.81 (m, 2H, $CHMe_2$), 3.99 (s, 1H; $NCCH_2$), 5.31 (s, 1H; γ-*H*), 5.40 (m, 1H; $CHMe_2$), 5.52 (s, 1H; C*H*=CMe_2), 6.96–7.18 ppm (m, br, 6H; 2,6-$iPr_2C_6H_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25°C): δ = 11.6, 12.9 (C_2Me_2), 19.6, 21.4, 23.2, 23.4, 23.6, 23.7, 24.4, 24.6, 24.7, 25.4, 26.4, 26.6, 26.7, 27.2, 27.3, 27.6, 28.0, 28.4, 29.1, 29.5, 32.5, 33.2 ($CHMe_2$, $NCHMe_2$, NC*Me*, $NCH(CH_2)_5$), 49.8 ($NCH(CH_2)_5$), 62.8 (*C*H=CMe_2), 89.8 ($NCCH_2$), 105.1 (γ-*C*), 123.4, 124.1, 124.8, 125.2, 125.3, 125.4, 125.6, 127.2, 128.3, 129.3, 136.7, 136.8, 139.7, 139.9, 142.7, 148.0, 148.2, 148.3, 149.0, 150.4 ppm (N*C*Me, N*C*CH_2, =*C*Me_2, 2,6-$iPr_2C_6H_3$, *C*Si); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25°C): δ = −58.0 ppm (s); EI-MS: *m*/*z* (%): 733 (100) [M^+], 718 (18) [M^+−Me], 690 (70) [M^+−*i*Pr]; elemental analysis calcd (%) for $C_{47}H_{71}N_5Si{\cdot}C_7H_8$: C 78.49, H 9.64, N 8.48, found: C 78.46, H 9.66, N 8.68.

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