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Striking Reactivity of a Stable, Zwitterionic Silylene Towards Substituted Diazomethanes, Azides, and Isocyanides

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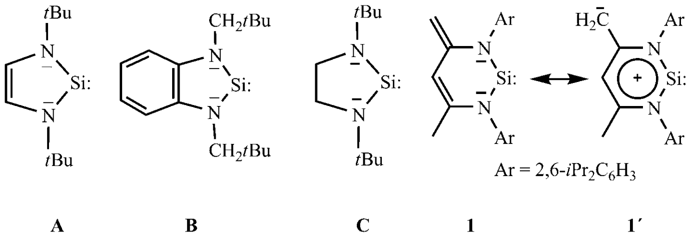
Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday

Abstract: The reactivity of the zwitterionic N-heterocyclic silylene (NHS) LSi: **1** (L = Ar−N−C(Me)=CH−C(=CH$_2$)−N−Ar, Ar = 2,6-iPr$_2$C$_6$H$_3$), towards diphenyldiazomethane (Ph$_2$CN$_2$), trimethylsilyl azide (Me$_3$SiN$_3$), and cyclohexyl isocyanide (C$_6$H$_{11}$−NC) is reported. The addition of Ph$_2$CN$_2$ to **1** leads to the diiminylsilane LSi(N=CPh$_2$)$_2$ **2** (80 % yield), whereas the treatment of **1** with Me$_3$SiN$_3$ gives the spirobicyclic silatetrazoline LSi(NNSiMe$_3$)$_2$ **3** (67 % yield), and addition of C$_6$H$_{11}$−NC gives the silyl cyanide LSi(R)CN (R = cyclohexyl) **4** (32 % yield) along with the unexpected azasilacyclobutane **5** (41 % yield). The novel compounds were fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, ESIMS, elemental analysis, and single-crystal X-ray diffraction.

Keywords: cyanides · diiminylsilanes · heterocycles · silatetrazolines · silylenes

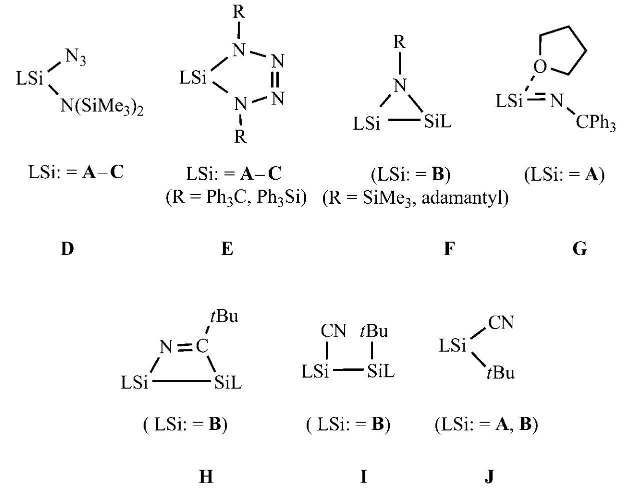
Introduction

Following the successful isolation of the thermally stable N-heterocyclic silylenes (NHSs) **A**–**C** in the last decade (Scheme 1),[1] their reactivities towards numerous unsaturated organic and organometallic substrates have been examined in detail.[2] Among these, the behavior of **A**–**C** towards organic azides, cyanides, and isocyanides has also been studied.[3]



Scheme 1. Isolable N-heterocyclic stable silylenes.

For azides, it has been shown that **A**–**C** readily react with Me$_3$SiN$_3$, Ph$_3$CN$_3$, Ph$_3$SiN$_3$, and AdN$_3$ (Ad = adamantyl) to give the different products **D**–**G** (Scheme 2), depending on the nature of the reactant and reaction conditions.[3] Similarly, the reactions of **A** and **B** with organic cyanides and isocyanides revealed significant differences (Scheme 2): Sily-



Scheme 2. Products resulting from the reactions between silylenes **A**–**C** and organic azides, cyanides, and isocyanides.

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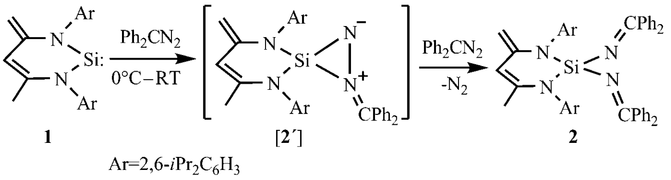
lene **A** is inert towards excess quantities of organic cyanides even at elevated temperature, whereas **B** readily reacts with *tert*-butyl cyanides to give the disilaazetine **H**.[3c] Moreover, silylene **B** reacts with isocyanide to give either the 1-cyano-2-organo disilane **I** or the silacyanide 1,1-adduct **J**, depending on the reaction conditions. In contrast, **A** undergoes conversion with organo isocyanides to give silacyanides of type **J**.[2a]

Compared with the stable NHSs **A**–**C**, the N-heterocyclic zwitterionic stable silylene LSi: **1**[4] (L = Ar−N−C(Me)=CH−C(=CH$_2$)−N−Ar, Ar = 2,6-iPr$_2$C$_6$H$_3$), (Scheme 1) possesses a remarkably different reactivity pattern towards saturated and unsaturated substrates owing to the contribution of the ylide-like resonance structure **1′** (Scheme 1) to the electronic ground state. This implies the presence of two reactivity sites in the molecule with an electrophilic silicon site and a nucleophilic exocyclic methylene group. In fact, the zwitterionic nature of **1** causes a fascinating reactivity pattern: i) 1,4-addition with HX (X = B(C$_6$F$_5$)$_4$,[5a] OH,[5b] or triflate[4]), that is, electrophilic addition of H$^+$ to the exocyclic methylene group in **1** and addition of the nucleophile X to the silicon(II) center; ii) facile insertion reactions of silicon (II) into element–element bonds, for example, the reaction of **1** with white phosphorus,[5c] halosilanes and halocarbons,[5d] ammonia,[5e] terminal alkynes,[5f] as well as primary NHC to Si addition and subsequent oxygenation of Si to form isolable silanones[5g] and dioxasiliranes,[5 h] respectively; iii) cycloadditions with unsaturated organic substrates, for example, the [2 + 1] cycloaddition of **1** to alkynes[5f] and benzylideneacetone;[5i] iv) facile coordination to transition-metal centers in low oxidation state;[5j,k] and v) silicon-mediated C−H activation and tautomerization processes.[5l,m] The unusual electronic features of **1** prompted us to include reactivity studies employing unsaturated organic nitrogen substrates for the exploitation of novel building blocks. Herein, we wish to report the remarkable reactivity of **1** towards diphenyldiazomethane (Ph$_2$CN$_2$), trimethylsilyl azide (Me$_3$SiN$_3$), and cyclohexyl isocyanide (C$_6$H$_{11}$NC).

Results and Discussion

Treatment of an equimolar amount of **1** with diphenyldiazomethane at 0 °C affords a red solution from which the diiminylsilane LSi(N=CPh$_2$)$_2$ **2** was isolated in the form of orange-red crystals in 40 % yield (Scheme 3). Note that the expected silaethene LSi=CPh$_2$ could not be detected in the reaction mixture (by using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy). Compound **2** was obtained in almost quantitative yield through conversion of **1** with diphenyldiazomethane in the molar ratio of 1:2. The reactivity of **A**–**C** towards Ph$_2$CN$_2$ is currently unknown.



Scheme 3. Formation of **2**.

Compound **2** represents the first example of a diiminylsilane. Interestingly, the analogous diiminylaluminum(III) compound L′Al(N=CPh$_2$)$_2$ (L′ = Ar−N−C(Me)=CH−C(Me)=N−Ar, Ar = 2,6-iPr$_2$C$_6$H$_3$) was obtained by Roesky and co-workers from the reaction of the low-valent L′Al(I) compound with Ph$_2$CN$_2$ at 60 °C.[6] Its formation was assumed to result from the primary conversion of two molar equivalents of Ph$_2$CN$_2$ to Ph$_2$C=N−N=CPh$_2$ and subsequent insertion of Al(I) into the N−N bond, which was proven by carrying out reliable experiments.[6] In contrast, we can conclude that the formation of **2** does not result from an insertion reaction of **1** to the primarily generated Ph$_2$C=N−N=CPh$_2$ moiety, because **1** is resistant towards Ph$_2$C=N−N=CPh$_2$, even after boiling in toluene for several hours. Although the mechanism is still unknown, we suggest that the reaction of **1** with Ph$_2$CN$_2$ occurs through the diazasilacyclopropen [**2′**] as the initial product (Scheme 3). The formation of related and even isolable diazametallacyclopropenes containing NiN$_2$ and TiN$_2$ cores have been reported for the reaction of Ph$_2$CN$_2$ with corresponding transition-metal-complex precursors.[7] Subsequently, the proposed diazasilacyclopropen intermediate [**2′**] could be attacked by Ph$_2$C:, which is produced in situ from Ph$_2$CN$_2$ to give product **2** (Scheme 3). A related conversion was observed that involved titanium complexes.[8]

Compound **2** has been fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis. The formation of **2** is accompanied by a large shift in the ^{29}Si NMR spectrum of $\Delta\delta = -160$ ppm relative to **1** ($\delta = 88$ ppm). The molecular structure of **2** was confirmed by single-crystal X-ray diffraction analysis. The silicon atom in **2** is tetrahedrally coordinated by four nitrogen atoms (Figure 1). The endocyclic Si−N (ring) bond lengths in **2** (Si1−N1 173.5(2), Si1−N2 174.1(2) pm) are almost identical to the corresponding values in **1** (173.4(2), 173.5(2) pm), but are slightly longer than those of terminal Si−N bond lengths (Si1−N3 170.5(2), Si1−N4 170.0(2) pm). Whereas the N1−C6, and N2−C18 bond lengths (145.1(3), 145.6(2) pm) are typical for N−C single bonds, the much shorter N3−C30 and N4−C43 bond lengths (127.0(2), 127.4(2) pm) are indicative of N=C double bonds.

Treatment of **1** with excess trimethylsilyl azide at ambient temperature quantitatively afforded the silatetrazoline **3** (Scheme 4). The iminosilane [**3′**] has been proposed as a reactive intermediate, which undergoes immediate conversion with trimethylsilyl azide in a [3 + 2] cycloaddition process to give the silatetrazoline **3** (Scheme 4). The formation of **3** is reminiscent of the result of the reaction of L′Al(I) with Me$_3$SiN$_3$.[9]

Notably, and in contrast to the result mentioned above, the reactions of the stable silylenes **A**–**C** with an excess of Me$_3$SiN$_3$ exclusively afforded the corresponding azido(trimethylsilylamido)silanes **D**[3] (Scheme 2). The formation of a si-

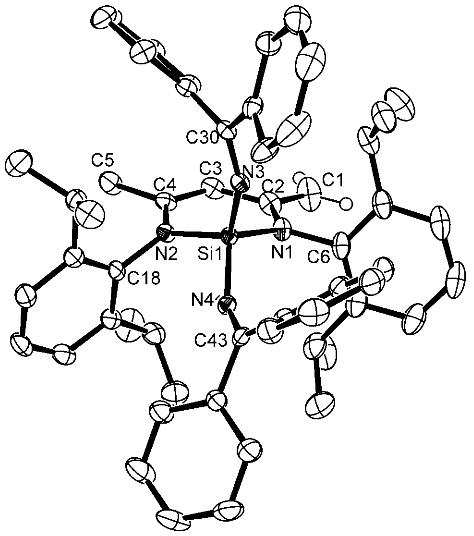


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for those at C1) are omitted for clarity. Selected bond lengths (pm): Si1−N4 170.00(2), Si1−N3 170.6(2), Si1−N1 173.5(2), Si1−N2 174.1(2), N1−C2 142.2(2), N1−C6 145.1(3), N2−C4 140.7(2), N2−C18 145.6(2), N3−C30 127.0(2), N4−C43 127.4(2), C1−C2 134.4(3), C2−C3 145.9(3), C3−C4 134.4(3), C4−C5 149.4(3); N1-Si1-N2 103.48(8), N3-Si1-N4 110.01(8), N1-Si1-N3 109.31(8), N1-Si1-N4 113.24(8), N2-Si1-N3 117.52(8), N2-Si1-N4 103.19(8).

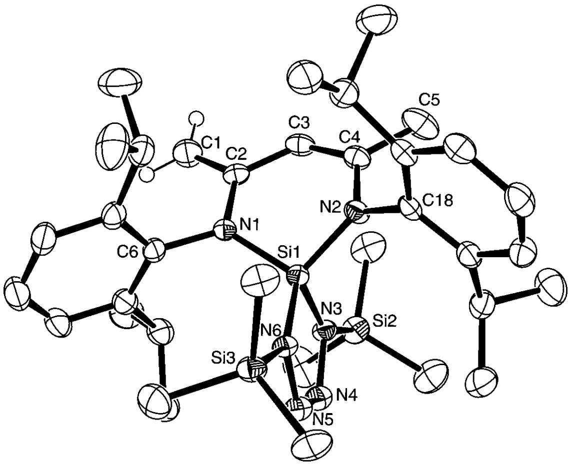
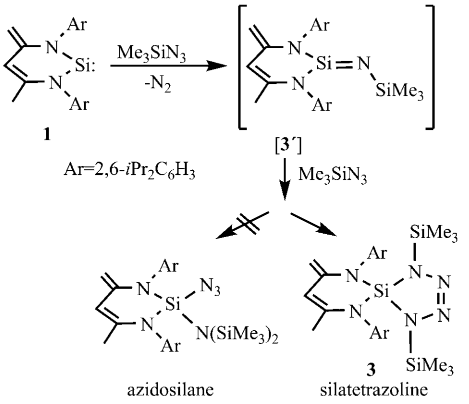


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for those at C1) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1−N1 173.9(2), Si1−N2 173.07(1), Si1−N3 175.7(1), Si1−N6 172.1(1), N1−C2 141.7(2), N1−C6 145.8(2), N2−C4 143.1(2), N2−C18 146.3(2), Si2−N3 178.1(1), Si3−N6 176.9(1), N3−N4 140.7(2), N4−N5 125.9(2), N5−N6 142.6(2), C1−C2 139.6(3), C2−C3 141.5(2), C3−C4 138.1(3), C4−C5 144.6(3); N1-Si1-N2 103.07(7), N3-Si1-N6 89.81(6).



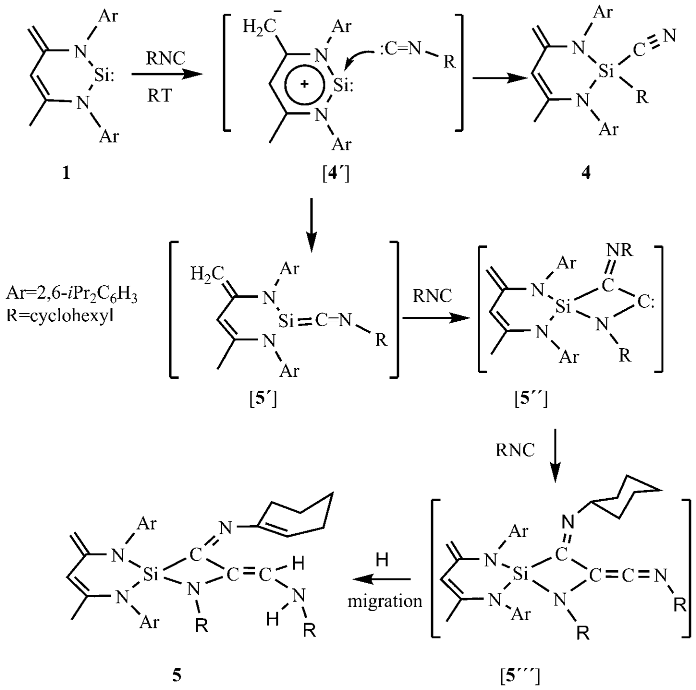
Scheme 4. Treatment of **1** with trimethylsilyl azide.

latetrazoline **3**, instead of the corresponding azido(amido)silane (Scheme 4), could be rationalized through the larger steric congestion of **1** compared with those of **A**–**C**. This is supported by the fact that **A**–**C** react similarly with more bulky substituted azides such as Ph_3CN_3 and Ph_3SiN_3 to give silatetrazolines.

The ^{29}Si NMR spectrum of **3** shows three resonances at $\delta = 9.45$ and 11.5 ($SiMe_3$) and −40.8 ppm ($Si_{silylene}$), respectively. An X-ray diffraction analysis proves that **3** consists of a spirobicyclic skeleton (Figure 2) with two SiN_2C_3 and SiN_4 rings orthogonal to each other (dihedral angle = 89.5°). The Si−N bond lengths of the C_3N_2Si ring in **3** (Si1−N1 173.9(2), Si1−N2 173.1(2) pm) are similar to those in **1** (173.4(2), 173.5(2) pm), whereas those of the Si−N bond lengths of the SiN_4 ring in **3** (Si1−N3 175.7(2), 172.1(2) pm) vary a little. The six-membered SiN_2C_3 ring is puckered with a folding angle of 41.6° between the plane defined by the Si1, N1, and N2 atoms and that by the N1, C2, C3, C4, and N2 atoms. In contrast, the five-membered SiN_4 ring is almost planar (mean deviation from the plane = 2.2 pm.). The N3−N4 and N5−N6 bond lengths (140.6(3) and 142.6(2) pm) are typical of N−N single bonds, whereas the much shorter N4−N5 bond length of 125.9(2) pm is indicative of a N=N double bond. The N-Si-N angles are in the range of 89.8 to 119.07°, and thus the Si atom is coordinated in a distorted tetrahedral fashion.

Similar to silylene **A**,[2a] **1** is chemically inert towards organic cyanides (MeCN, *t*BuCN). However, **1** readily reacts with cyclohexyl isocyanide in hexane solutions at room temperature, affording the orange silacyanide **4** and the red azasilacyclobutane **5**, which can be isolated by fractional crystallization in 32 and 41 % yield, respectively (Scheme 5). Interestingly, the formation of **5** encompasses a silicon-mediated coupling of three isocyanide molecules and twofold C−H activation.

It is reasonable to assume that the initial step for the formation of both **4** and **5** is a Lewis acid–base reaction between **1** and cyclohexyl isocyanide, leading to the silylene–isocyanide adduct [**4′**] as an initial intermediate (Scheme 5). The formation of [**4′**] appears to be favored owing the high electrophilicity of Si(II) and the ylide-like structure of **1**. Likewise, related silylene–isocyanide adducts were previously observed by Tokitoh and co-workers.[10] Moreover, employing the cycloorganosilylene reported by Kira and coworkers led to the isolation of a [**5′**]-type adduct (Scheme 5) that contains a heteroallenic Si=C=N moiety.[11] Apparently, in the case of **1**, the adducts [**4′**] and [**5′**] undergo further re-



Scheme 5. Formation of **4** and **5** through the proposed intermediates [**4′**], [**5′**], [**5″**], and [**5‴**].

actions either to afford compound **4** through cyclohexyl migration to the divalent silicon center, or they react with two isocyanide molecules to yield the novel azasilacyclobutane **5**. We assume that the adduct [**5′**] initially reacts with one molecule of isocyanide through [2+2] cycloaddition to give the transient carbene [**5″**], which couples to one molecule of isocyanide to yield the transient species [**5‴**] that contains an excocyclic C=C=N moiety at the SiC$_2$N ring (Scheme 5). The mechanism for the twofold C–H activation of a cyclohexyl group and the concomitant dihydrogen transfer to a C=N moiety in hypothetical [**5‴**] to give the final product **5** remains unknown. The driving force for the latter process could be attributed to the close proximity of the basic C=C=N group to the cyclohexyl group attached to the exocyclic C=N group in [**5‴**]. Clearly, further investigations are necessary to elucidate the mechanism.

Both products **4** and **5** were fully characterized by NMR spectroscopy, ESIMS, and elemental analysis. Their molecular structures were established by single-crystal X-ray diffraction analyses as shown in Figures 3 and 4, respectively. Compound **4** crystallizes in the monoclinic space group $P2_1$. As expected, the silicon atom adopts a tetrahedral coordination geometry. The SiN$_2$C$_3$ heterocycle is puckered with a folding angle of 25.2°. The Si–N bond length of the C$_3$N$_2$Si ring are similar to the corresponding values in **2** and **3** and those in the precursor **1**. The Si1–C30 and Si1–C31 lengths represent common values for Si–C single bonds, whereas the C30–N3 bond length of 111.3(2) pm is typical of a cyanide group.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$. The structure of **5** consists of a spirobicyclic skeleton with a strongly puckered six-membered SiN$_2$C$_3$ ring and a planar four-membered SiNC$_2$ ring, which are orthogonal to each other. Remarkably, the C50, C45, N4, C32, and N5 atoms, as well as the four-membered SiNC$_2$ ring have a co-planar orientation to each other, which implies the presence of a conjugated π system. Accordingly, the respective C–C and C–N bond lengths show expected alternations.

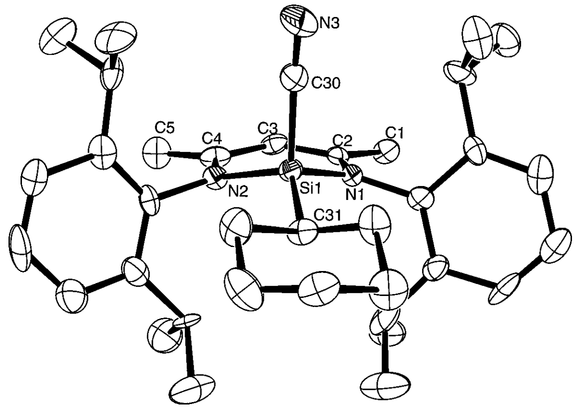


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1–N1 172.0(4), Si1–N2 172.5(4), Si1–C30 188.5(2), Si1–C31 187.4(2), N3–C30 111.3(2), N1–C2 138.4(5), N2–C4 145.6(5), N2–C18 145.8(5), N1–C6 144.8(6); C30-Si1-C31 104.69(7), N1-Si1-N2 104.67(6), N2-Si1-C31 116.4(2), N1-Si1-C31 115.7(2), N2-Si1-C30 107.5(2), N1-Si1-C30 107.5(2).

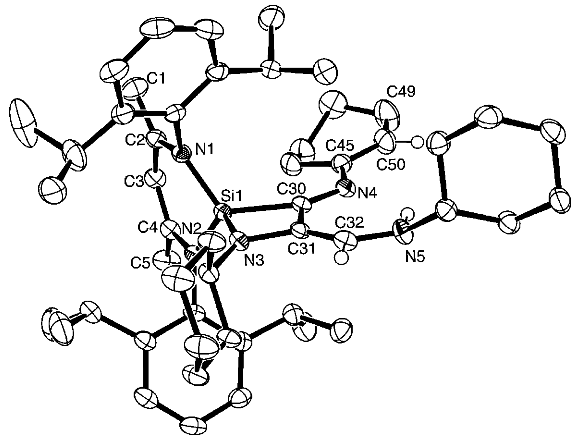


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for those at N5, C32, and C50) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1–N1 173.0(2), Si1–N2 172.6(2), Si1–N3 170.6(2), Si1–C30 190.6(2), C30–C31 147.0(3), C31–C32 134.7(3), N4–C30 129.6(3), N5–C32 138.3(3), N4–C45 142.2(3), C45–C50 133.0(3), N3–C31 144.8(2), N1–C2 142.3(2), N2–C4 141.7(2), C1–C2 137.4(3), C2–C3 143.0(3), C3–C4 136.7(3), C4–C5 146.1(3); N3-Si1-N2 117.36(8), N3-Si1-N1 118.00(8), N2-Si1-N1 103.83(8), N3-Si1-C30 76.34(8), N2-Si1-C30 120.71(9), N1-Si1-C30 119.83(8), C31-N3-Si1 96.12(12), C30-N4-C45 120.50(18).

Conclusion

We have found that the reaction of the zwitterionic stable silylene **1** with unsaturated nitrogen substrates opens facile access to unprecedented building blocks in organosilicon heteroatom chemistry. Thus, conversion of **1** with diphenyldiazomethane leads to the isolation of the first diiminylsilane LSi(N=CPh$_2$) **2**. In contrast to the behavior of the related stable NHSs **A**–**C**, reaction of **1** with trimethylsilyl azide solely affords the corresponding silatetrazoline **3**, instead of formation of the corresponding azido(amido)silane. Conversion of **1** with cyclohexyl isocyanide gives the silacyanide **4**, but also the remarkable azasilacyclobutane **5**. The latter results from a cascade of coupling reactions of three isocyanide molecules, twofold C−H activation, and intramolecular dihydrogen transfer.

Experimental Section

General methods and materials: All experiments and manipulations were carried out under dry oxygen-free nitrogen by using standard Schlenk techniques or in an MBraun inert atmosphere dry box, which contained an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting materials silylene **1** and Ph$_2$CN$_2$, as well as Ph$_2$C=N−N=CPh$_2$ were prepared according to the literature procedures in Refs. [4], [12], and [13], respectively. NMR spectra were recorded with Bruker spectrometers (ARX200, AV400) and with residual solvent signals as internal references (^{1}H and ^{13}C{H}) or with an external reference (SiMe$_4$ for ^{29}Si). Abbreviations: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad. High-resolution ESIMS were measured on a Thermo Scientific LTQ orbitrap XL.

Single-crystal X-ray structure determination: Crystals were each mounted on a glass capillary in perfluorinated oil and measured under a flow of nitrogen. The data of **2**, **3**, **4**, and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 123 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-732602, 732603, 732604, and 732605 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.

Compound **2**: Monoclinic; space group $P2_1/n$; $a = 19.7641(3)$, $b = 11.9909(2)$, $c = 20.2938(4)$ Å; $\beta = 107.144(2)°$; $V = 4595.72(4)$ Å^3; $Z = 4$; $\rho_{calc} = 1.164$ mg/m^3; μ (Mo$_{K\alpha}$) = 0.092 mm^{-1}; 41293 collected reflections; 8077 crystallographically independent reflections ($R_{int} = 0.0350$); 6964 reflections with $I > 2\sigma(l)$; $\theta_{max} = 25.00°$; $R(F_o) = 0.0567$ ($I > 2\sigma(l)$); $wR(F_o^2) = 0.1347$ (all data); 550 refined parameters.

Compound **3**: Monoclinic; space group $P2_1/n$; $a = 12.4172(3)$, $b = 21.7559(5)$, $c = 14.0023(3)$ Å; $\beta = 92.208(2)$; $V = 3776.83$ (15) Å^3; $Z = 2$; $\rho_{calc} = 1.138$ mg/m^3; μ (Mo$_{K\alpha}$) = 0.157 mm^{-1}; 23445 collected reflections; 6641 crystallographically independent reflections ($R_{int} = 0.0356$); 4545 reflections with $I > 2\sigma(l)$; $\theta_{max} = 25°$; $R(F_o) = 0.0352$ ($I > 2\sigma(l)$); $wR(F_o^2) = 0.0882$ (all data); 412 refined parameters.

Compound **4**: Monoclinic; space group $P2_1$; $a = 8.8465(3)$, $b = 20.1261(6)$, $c = 9.9234(3)$ Å; $\beta = 111.857(4)$; $V = 1639.81(9)$ Å^3; $Z = 2$; $\rho_{calc} = 1.122$ mg/m^3; μ (Mo$_{K\alpha}$) = 0.099 mm^{-1}; 9516 collected reflections; 5466 crystallographically independent reflections ($R_{int} = 0.0156$); 4421 reflections with $I > 2\sigma(l)$, $\theta_{max} = 25°$; $R(F_o) = 0.0347$ ($I > 2\sigma(l)$); $wR(F_o^2) = 0.0907$ (all data); 370 refined parameters.

Compound **5**: Triclinic, space group $P\bar{1}$, $a = 10.3377(3)$, $b = 12.7802(5)$, $c = 20.0685(8)$ Å; $a = 101.868(3)$, $\beta = 94.871(3)$; $\gamma = 109.864(4)°$; $V = 2405.59(15)$ Å^3; $Z = 2$; $\rho_{calc} = 1.066$ mg/m^3; μ (Mo$_{K\alpha}$) = 0.086 mm^{-1}; 21149 collected reflections; 8401 crystallographically independent reflections ($R_{int} = 0.0387$); 5612 reflections with $I > 2\sigma(l)$; $\theta_{max} = 25°$; $R(F_o) = 0.0491$ ($I > 2\sigma(l)$); $wR(F_o^2) = 0.0839$ (all data); 545 refined parameters.

Syntheses of 2: Ph$_2$CN$_2$ (0.60 g, 3.1 mmol) was added to a solution of **1** (0.68 g, 1.5 mmol) in *n*-hexane (10 mL)at 0 °C. The reaction mixture was allowed to warm to room temperature. Recrystallization of the crystalline material obtained from hexane at −20 °C in diethyl ether at room temperature yielded orange-red single crystals of **2** that were suitable for X-ray diffraction analysis. Yield: 1.00 g (1.24 mmol, 80 %); m.p. 158 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.79$ (d, ^3J(H,H) = 7.0 Hz, 9H; CH*Me*$_2$), 1.16 (s, 6H; CH*Me*$_2$), 1.40 (d, ^3J(H,H) = 7.0 Hz, 9H; CH*Me*$_2$), 3.22–3.35 (m, 1H; C*H*Me$_2$), 3.50 (s, 1H; NCC*H*$_2$), 3.50–3.74 (m, 3H; C*H*Me$_2$), 4.15 (s, 1H; NCC*H*$_2$), 5.62 (s, 1H; γ-C*H*), 6.29–7.27 ppm (m, br, 26H; *Ph*, 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 22.4$–28.8 (*C*H*Me*$_2$, NC*Me*), 86.9 (NC*C*H$_2$), 108.9 (γ-*C*), 124.5–150.1 ppm (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, N=*CPh*$_2$); ^{29}Si NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -72.0$ ppm (s); ESIMS: *m/z* (%): 804 (13) [M^+], 789.6 (100) [M^+−Me], 761.5 (98) [M^+ −*i*Pr]; elemental analysis calcd (%) for C$_{55}$H$_{60}$N$_4$Si: C 82.04, H 7.51, N 6.96; found: C 82.22, H 7.40, N 6.91.

Syntheses of 3: Trimethylsilyl azide (0.39 mL, $d = 0.88$ g mL^{-1}, 3.0 mmol) was added to a solution of silylene **1** (0.29 g, 0.65 mmol) in hexane (10 mL) at room temperature. The reaction was completed in three days. The solution was concentrated to approximately 5 mL and cooled to −20 °C. Product **3** crystallized as colorless crystals. Yield: 0.28 g (0.44 mmol, 67 %); m.p. 235 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = -0.32$ (s, 9H; Si*Me*$_3$), 0.55 (s, 9H; Si*Me*$_3$), 1.06 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.17 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.18 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.22 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.26 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.38 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.39 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.45 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.47 (s, 3H, NC*Me*), 3.25 (sept ^3J(H,H) = 7.0 Hz, 1H; C*H*Me$_2$), 3.44 (sept ^3J(H,H) = 7.0 Hz, 1H; C*H*Me$_2$), 3.46 (s, 1H; NCC*H*$_2$), 3.63 (sept ^3J(H,H) = 7.0 Hz, 1H; C*H*Me$_2$), 3.78 (sept ^3J(H,H) = 7.0 Hz, 2H; C*H*Me$_2$), 4.02 (s, 1H; NCC*H*$_2$), 5.25 (s, 1H; γ-C*H*), 7.02–7.16 ppm (m, 6H; *i*PrC$_6$H$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = -0.10$ (Si(*C*H$_3$)$_3$), 1.06 (Si(*C*H$_3$)$_3$), 23.0, 24.7, 24.8, 25.3, 25.4, 25.7, 26.1, 26.4, 27.2, 28.1, 28.5, 28.9, 29.0 (NC*Me*, *C*H*Me*$_2$), 91.1 (NC*C*H$_2$), 109.0 (γ-*C*), 124.7, 125.2, 125.3, 125.6, 127.5, 127.6, 137.0, 137.7, 144.0, 147.3, 148.0, 148.2, 148.3, 149.8 ppm (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -40.8$ (L*Si*), 9.45 (*Si*Me$_3$), 11.5 ppm (*Si*Me$_3$); ESIMS: *m/z* (%): 647.1 (3) [M^+], 632.3 (3) [M^+−Me], 604.3 (5) [M^+ −*i*Pr]; elemental analysis calcd (%) for C$_{35}$H$_{58}$N$_6$Si$_3$: C 64.96, H 9.03, N 12.99; found: C 64.96, H 8.84, N 12.96.

Syntheses of 4 and 5: Cyclohexyl isocyalide (0.53 mL, $d = 0.878$ g mL^{-1}, 4.3 mmol) was added to a solution of silylene **1** (0.63 g, 1.4 mmol) in hexane (10 mL) at room temperature. After three days at room temperature the solution was concentrated to 5 mL and cooled to −20 °C. The orange compound **4** (0.25 g, 0.45 mmol, 32 %) first crystallized, followed by the formation of red crystals of **5** (0.45 g, 0.58 mmol, 41 %).

4: M.p. 198 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.58$–1.07 (m, 7H; cyclohexyl), 1.14 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.20 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.27 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.31 (d, ^3J(H,H) = 7.0 Hz, 6H; CH*Me*$_2$), 1.35 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.43 (s, 3H; NC*Me*), 1.52 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 1.61 (d, ^3J(H,H) = 7.0 Hz, 3H; CH*Me*$_2$), 3.43 (s, 1H; NCC*H*$_2$), 3.50–3.60 (m, 1H; C*H*Me$_2$), 3.62–3.72 (m, 1H; C*H*Me$_2$), 3.71–3.85 (m, 2H; C*H*Me$_2$), 4.04 (s, 1H; NCC*H*$_2$), 5.36 (s, 1H; γ-H), 6.96–7.18 ppm (m, br, 6H; 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 21.4$, 23.8, 24.2, 24.3, 24.9, 25.1, 26.1, 26.2, 26.3, 26.4, 26.5, 26.6, 27.1, 27.4, 27.7, 28.6, 28.7, 29.1, 29.2 (cyclohexyl, NC*Me*, *C*H*Me*$_2$), 89.6 (NC*C*H$_2$), 106.2 (γ-*C*), 124.0, 124.2, 124.5, 125.4, 126.0, 128.5, 128.6, 136.0, 141.1, 147.0, 147.1, 148.2, 149.0, 149.7 ppm (N*C*Me, N*C*CH$_2$, N*C*, 2,6-*i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -45.3$ ppm (s); ESIMS: *m/z* (%): 553.4 (18) [M^+], 538.4 (100) [M^+−Me], 10.3 (75) [M^+−*i*Pr]; elemental analysis calcd (%) for C$_{36}$H$_{51}$N$_3$Si: C 78.06, H 9.28, N 7.59; found: C 77.86, H 9.15, N 7.74.

5: M.p. 238 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.38$–2.85 (m, 33 H; cyclohexyl), 1.21 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.31 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.33 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.34 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.36 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.43 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.44 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.47 (d, ^{3}J(H,H) = 7.0 Hz, 3 H; CHMe_2), 1.48 (s, 3 H; NCMe), 3.27–3.37 (m, 1 H; CHMe$_2$), 3.35–3.45 (m, 1 H; CHMe$_2$), 3.42 (s, 1 H; NCCH_2), 3.67–3.77 (m, 1 H; CHMe$_2$), 3.79–3.89 (m, 1 H; CHMe$_2$), 4.02 (s, 1 H; NCCH_2), 5.29 (s, 1 H; γ-H), 5.53 (d, ^{3}J(H,H) = 10.0 Hz, 1 H; C=CH-NHR), 6.13 (t, ^{3}J(H,H) = 3.9 Hz, 1 H; SiC=N−C=CHCH$_2$), 7.00–7.19 (m, br, 6 H; 2,6-iPr$_2$C$_6$$H_3$), 7.52 ppm (t, ^{3}J(H,H) = 10.0 Hz, 1 H; NH); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C): $\delta = 21.2$–29.2 (cyclohexyl, NCMe, CHMe_2), 35.0, 53.6, 56.6 (−CH(CH$_2$)$_5$), 89.6 (NCCH$_2$), 105.0 (γ-C), 117.6 (C=CH−NHR), 120.5 (NC=CHCH$_2$), 123.6–149.7 (NCMe, NCCH$_2$, CNSi, NC(CH$_2$)(=CHCH$_2$), 2,6-iPr$_2$$C_6H_3$), 178.0 ppm (Si$C$NR, R = cyclohexyl); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]benzene, 25 °C): $\delta = -42.9$ ppm (s); ESIMS: m/z (%): 771.6. (100) [M^+], 728.5 (7.7) [M^+-iPr], 688.5 (13.6) [M^+-C$_6$H$_{11}$]; elemental analysis calcd (%) for $C_{50}H_{73}N_5Si$: C 77.77, H 9.53, N 9.07; found: C 77.58, H 9.30, N 9.07.

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