N-Heterocyclic Silylenes

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Dichotomic Reactivity of a Stable Silylene toward Terminal Alkynes: Facile C–H Bond Insertion versus Autocatalytic Formation of Silacycloprop-3-ene**

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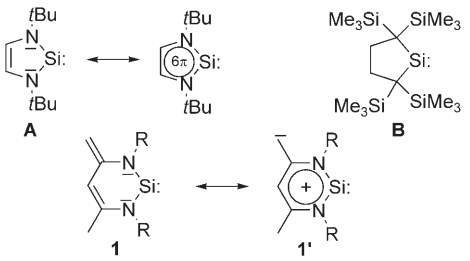
Dedicated to Professor Philip P. Power

Silylenes, the silicon analogues of carbenes, are key intermediates in numerous thermal and photochemical reactions.[1] They are indispensable building blocks for the synthesis of organosilanes through X–Y insertion reactions (X–Y = C–H, C–C, C–O, C–Cl, Si–H, O–H, for example).[1b–h] Until two decades ago, silylenes were generally considered to be extremely unstable species, decomposing readily at low temperature (> −196 °C). The situation changed profoundly in 1994, when West et al. described the synthesis of the first stable N-heterocyclic silylenes **A** with two-coordinate silicon which were persistent at room temperature (Scheme 1).[2a,b] Following the successful isolation of stable silylenes **A**, only a few other stable silylenes have been reported as yet,[2c–e] including the remarkable nonsupported dialkylsilylene **B** (Scheme 1).[2f] The latter systems benefit from π-donor stabilization of the low-valent silicon by the nitrogen atoms, pseudoaromaticity (**A**), and/or steric protection through bulky organic groups (**A**, **B**). Recently we described the stable ylide-like silylene **1**, in which significant participation of the 6π-aromatic resonance form **1′** is found in the electronic ground state (Scheme 1).[3]



Scheme 1. Stable silylenes **A** and **B**, and mesomeric forms of **1**. R = 2,6-*i*Pr$_2$C$_6$H$_3$.

Owing to its unusual ylide-like character, silylene **1** shows a remarkably distinct reactivity toward both electrophiles and nucleophiles, in comparison with **A** and **B**, respectively. Striking results include the facile formation of silyliumylidene cations by addition of H^+ or other Lewis acid centers at the nucleophilic carbon atom of the terminal C=C moiety in **1**,[4a] synthesis of a stable siloxysilylene through heterolytic addition of water to **1**,[4b] and insertion of the divalent silicon atom in **1** into P–P bonds of P_4.[4c] Another specific feature represents the addition of simple electrophiles RX (R = H, Me_3Si; X = halogen, OSO_2CF_3) to **1**, which resulted in the isolation of the corresponding 1,1-adducts (insertion products).[3] Similarly, the 1,4-dipolar nature of **1** could for the first time facilitate a marked preference for C–H insertion of divalent silicon versus C≡C-π bond addition with terminal alkynes. To our knowledge, neither facile silylene C–H bond insertion for terminal alkynes[5] nor formation of isolable silacycloprop-3-enes, starting from isolable silylenes **A** have been reported.[2f] Herein we report the remarkably different reactivity of **1** toward terminal alkynes. although conversion at room temperature results solely in the formation of the C–H insertion adducts **2a**, **2b**, and **3** as thermodynamic products, the same starting materials surprisingly undergo [2+1] cycloaddition after a induction period of a few hours at low temperature (−78 °C) to furnish the corresponding silacycloprop-3-enes **4a** and **4b** in high yield (Scheme 2).

Exposure of yellow solutions of **1** in hexane to HC≡CH at room temperature leads to colorless solutions within a few minutes from which the C–H insertion product **2a** can be isolated in the form of colorless crystals in 82 % yield.[6] Additionally, prolonged reaction time with molar excess of **1** or conversion of **2a** with **1** in molar ratio of 1:1 affords the double insertion product **3** which was isolated in 85 % yield. Furthermore, addition of PhC≡CH to **1** leads exclusively to the corresponding alkynylsilane **2b**, which was isolated in 93 % yield. The composition and constitution of the products was confirmed by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si), mass spectrometry, and elemental analysis (C, H, N). The six-membered C_3N_2Si rings in **2a** and **3** are only slightly puckered, and the Si–C and C≡C bond lengths (Figures 1 and 2) are similar to those reported for other alkynylsilanes.[7] As expected, the most important geometrical features of **2b** are practically identical to those of **2a**.[6]

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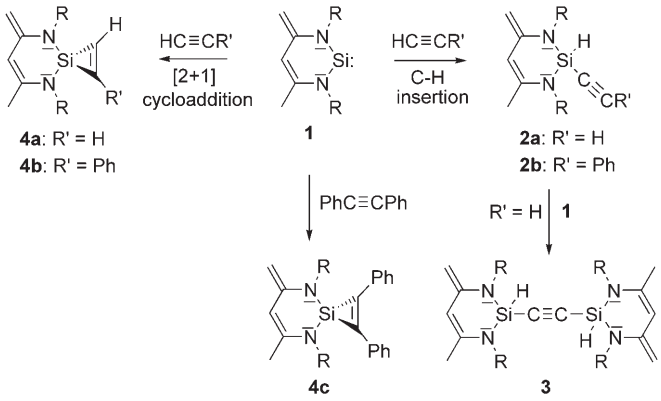


Scheme 2. Synthesis of **2a**, **2b**, **3**, and **4a**–**4c** from reaction of **1** with the corresponding alkynes. R = 2,6-*i*Pr$_2$C$_6$H$_3$.

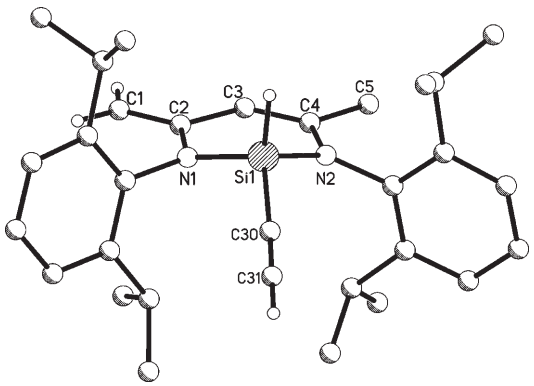


Figure 1. Molecular structure of **2a**. Hydrogen atoms (except for those at C1, C31, and Si1) omitted for clarity. Selected bond lengths [pm] and angles [°]: C30–C31 115.5(4), Si1–N1 170.3(2), Si1–N2 172.2(2), Si1–C30 182.1(3), N1–C2 141.9(3), N2–C4 141.0(3); N1-Si1-N2 104.7(1), N1-Si1-C30 110.3(1), N2-Si1-C30 112.0(1), C31-C30-Si1 175.6(3).

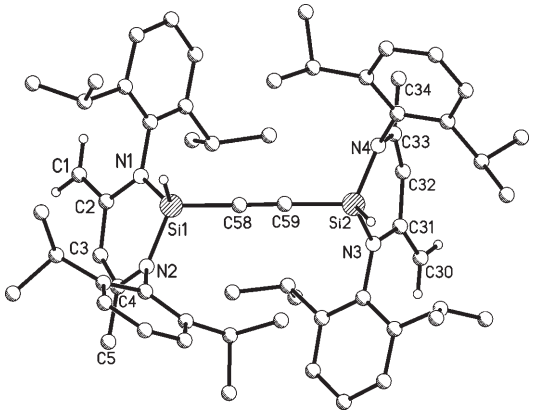


Figure 2. Molecular structure of **3**. Hydrogen atoms (except for those at C1, C30, Si1, and Si2) omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1–N1 171.6(2), Si1–N2 171.7(2), Si2–N4 171.3(2), Si2–N3 171.3(2), Si1–C58 183.0(3), Si2–C59 183.8(3), C58–C59 121.1(3); N1-Si1-N2 105.7(1), N4-Si2-N3 105.2(1), C59-C58-Si1 178.5(3), C58-C59-Si2 176.7(3).

In contrast, the related stable silylenes **A** and **B** do not lead to C–H insertion products with terminal alkynes, and only **B** is capable of generating an isolable silacycloprop-3-ene.[2a,f] Additionally, gas-phase studies of transient silylenes in the presence of terminal alkynes revealed that C–H bond insertion is not facile and results merely from rearrangement of silacycloprop-3-enes as primary intermediates at relatively high temperature (> 500 °C).[5] To probe whether silacycloprop-3-enes are possible intermediates for the generation of **2a** and **2b**, reaction of **1** with HC≡CH and PhC≡CH was also carried out at lower temperature (−78 °C). The reaction does take a different course, which can be monitored by ^{1}H NMR spectroscopy. It turns out that conversion proceeds slowly, and is still incomplete even after 5 h, affording the corresponding silacycloprop-3-enes **4a** and **4b** as sole products (Scheme 2). To our surprise, completion of the reaction at room temperature leads exclusively to **4a** and to **4b**, which can be isolated in the form of colorless cubes in high yield (82 % (**4a**), 85 % (**4b**)). Accordingly, conversion of **1** with HC≡CH at room temperature in the presence of **4a** (initial molar ratio **1**:**4a** = 5:1) is complete after about 3 h to give **4a** in quantitative yield (^{1}H, ^{13}C NMR); **4a** appears to play an autocatalytic role. The same is true for **4b**, which autocatalyzes the transformation of **1** with PhC≡CH to **4b** at room temperature.[6] The formation of **4a** and **4b** can be seen in the characteristic deshielding of the vinylic protons at the SiC_2 ring in the ^{1}H NMR spectrum[8] ($\delta(^1H) = 7.91$ (**4a**), 7.86 ppm (**4b**)) and by the typical upfield signal in the ^{29}Si NMR spectrum at $\delta = -91.9$ (**4a**) and −86.4 ppm (**4b**).[8] Remarkably, the synthesis of **4a** and **4b** can even be catalyzed using the related silacycloprop-3-ene **4c** (Scheme 2). The latter is easily accessible from **1** and PhC≡CPh at room temperature in quantitative yield. The composition of the novel silacycloprop-3-enes **4a**–**4c** was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, EI-MS, and correct combustion analyses (C, H, N). Their molecular structures have been established by single-crystal X-ray diffraction.[6] Although a few silacycloprop-3-enes have already been characterized by X-ray diffraction,[9,10] **4a** and **4b** represent the first structurally characterized derivatives with hydrogen attached to the olefinic carbon atoms in the three-membered SiC_2 ring. The C_3N_2Si-ring in **4a** (and in **4b**) is practically planar and perpendicular to the SiC_2 ring (Figure 3).

The SiC_2 ring in **4a**–**4c** is strikingly stable and survives prolonged heating of solutions at 110 °C for several hours. This can be explained by pronounced σ* aromaticity of the SiC_2-ring, in accordance with theoretical calculations.[11] This implies some masked silacyclopropenylium ylide-like character of **4a**–**4c**, as depicted in the resonance structures in Scheme 3. However, the high stability clearly precludes that **4a** and **4b** play any role as intermediates for the formation of the respective C–H insertion products **2a** and **2b**. Accordingly, attempts to generate **2a** and **2b** by thermolysis of **4a** and **4b** were unsuccessful. Although the pathway to **4a** and **4b** is dominant at low temperatures, it plays no role at higher temperatures, which implies a lower (i.e., more negative) activation entropy. In other words, the conversion of **1** into the C–H insertion products **2a** and **2b** proceeds by a completely different mechanism than previously reported for transient

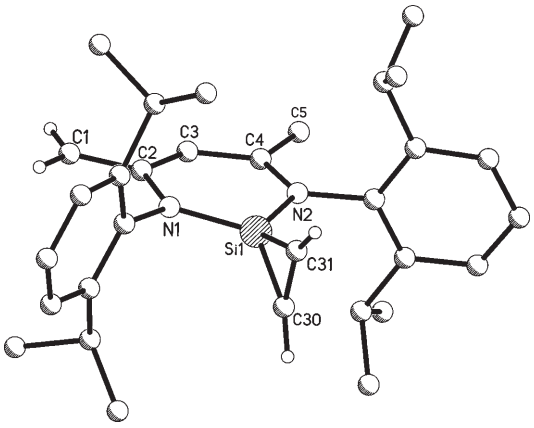


Figure 3. Molecular structure of **4a**. Hydrogen atoms (except for those at C1, C30, and C31) omitted for clarity. Selected bond lengths [pm] and angles [°]: C30–C31 131.1(5), Si1–N1 170.7(2), Si1–N2 170.9(2), Si1–C30 173.7(4), Si1–C31 177.1(4), N1–C2 140.9(3), N2–C4 140.7(3); N1-Si1-N2 105.1(1), C30-Si1-C31 43.9(2), C31-C30-Si1 69.4(3), C30-C31-Si1 66.7(3).

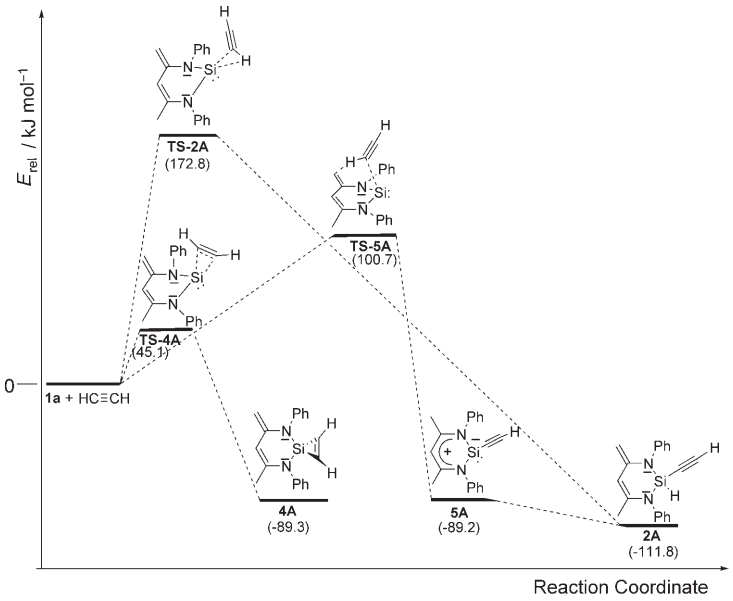
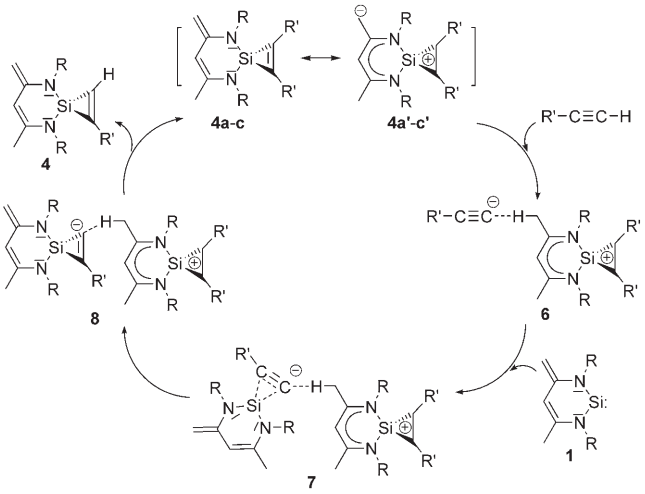


Figure 4. Energy profile for the reaction of **1a** with HC≡CH, including DFT-calculated structures of the model compounds **2A**, **4A**, and **5A** as well as their corresponding transition states **TS-2A**, **TS-4A**, and **TS-5A**, respectively.[6]

silylenes. This fact is supported by theoretical calculations using the model system **1a**, in which the 2,6-iPr$_2$C$_6$H$_3$ groups at nitrogen have been replaced by phenyl groups.[6] We initially considered concerted [2+1] cycloaddition versus C–H insertion of the divalent silicon in **1a** towards HC≡CH (Figure 4): whereas the calculations revealed a relatively small barrier of 45.1 kJ mol^{-1} for the [2+1] cycloaddition to give the corresponding silacycloprop-3-ene **4A**, direct insertion into the C–H bond in HC≡CH to form **2A** encounters a much higher barrier of 172.8 kJ mol^{-1}. As expected, **2A** is thermodynamically favored by 22.5 kJ mol^{-1} over **4A**.[6] Consistent with the experimental results, there is also no facile interconversion **4A**→**2A** under thermal conditions.[6] Thus it seems reasonable to assume that the mechanism for C–H insertion must be at least a two-step process. We propose the ylide-like structure **5A** (Figure 4) as a key intermediate, which is virtually as stable as **4A** ($\Delta E <$ 0.1 kJ mol^{-1}).[6] Compund **5A** is most likely formed after deprotonation of HC≡CH by the basic terminal CH_2 group of **1a**, followed by a transfer of the C≡CH anion to the silicon atom. In the gas phase, charge separation is disfavored, thus our calculations find a transition state 100.7 kJ mol^{-1} above the starting compounds, and the proton is transferred relatively late on the reaction coordinate.[6] In the condensed phase, deprotonation will occur much earlier, and formation of **5A** be even more facile. Contrary to the direct formation of **2A** from **1a** and HC≡CH, our DFT calculations neither find excessive barriers nor instable intermediates along this pathway. Subsequently, 1,4-adduct **5A** could easily tautomerize to **2A**. This is also consistent with previous experimental results, in which the comparatively basic terminal CH_2 group at the zwitterionic silylene **1** plays an important role toward electrophiles.[3] How can the astonishing autocatalytic role of the silacycloprop-3-enes **4a–4c** on the conversion of **1** with terminal alkynes be explained? Although the mechanism is still unknown, the resonance ylide structures **4a′–4c′** could play a crucial role (Scheme 3). This is in accordance with the prediction of relatively large proton affinities of the terminal H_2C group in the model compounds **4A**, **1a**, and in the



Scheme 3. Proposed autocatalytic cycle of **4a–c** for the conversion of **1** with terminal alkynes. R′ = H, Ph.

corresponding silicon dibromide [**1a**Br_2] in the order **4A** (1111.6) > **1a** (1099) > [**1a**Br_2] (1088.1 kJ mol^{-1}).[3,6] Thus, the latter compounds are relatively strong neutral bases.

In turn, this suggests that the alkyne is preferably captured in terminal fashion by **4a** to give the intermediate complex **6**, but then no 1,4-adduct can be formed. Thus we believe that **4a–4c** can serve as auxiliary bases which are capable of mediating the [2+1] cycloaddition of **1** via the postulated complexes **6**, **7**, and **8** (Scheme 3). Accordingly, conversion of

1 with R′C≡CH (R′ = H, Ph) at room temperature in the presence of similarly strong neutral bases such as the dibromide [**1**Br_2] leads also exclusively to **4a** and to **4b**. In contrast, organic nitrogen-containing bases with significantly lower proton affinities, such as NEt_3 and pyridine, show no catalytic activity. However, further experiments are necessary to elucidate the mechanism of the autocatalytic process.

In summary, we report the unprecedented reactivity of the ylide-like silylene **1** toward terminal alkynes. The first facile silylene C–H bond insertion for terminal alkynes was thereby discovered, and, at the same time, a unique autocatalytic generation of the stable silacycloprop-3-enes **4a** and **4b**. The easily accessible compounds **4a**–**4c** are promising building blocks for cyclopropene syntheses by catalytic σ-bond metathesis.[12] Respective investigations to elucidate the autocatalytic formation of **4a** and **4b** are currently underway.

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[6] Experimental and computational details as well as X-ray diffraction analyses and geometrical parameters of **2a** **2b**, **3**, and **4a–c** are provided in the Supporting Information.

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