N-Heterocyclic Silylenes

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, silvlenes 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



Scheme 1. Stable silylenes **A** and **B**, and mesomeric forms of 1. $R = 2,6 \cdot i Pr_2 C_6 H_3$.

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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 silvliumylidene 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 P₄.^[4c] Another specific feature represents the addition of simple electrophiles RX (R = H, Me₃Si; X = halogen, OSO₂CF₃) 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 $(-78^{\circ}C)$ 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 (1H, 13C, 29Si), mass spectrometry, and elemental analysis (C, H, N). The sixmembered 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. $R=2,6-iPr_2C_6H_3$.



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 silvlenes A and B do not lead to C-H insertion products with terminal alkynes, and only **B** is capable of generating an isolable silacycloprop-3ene.^[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 $(>500 \,^{\circ}\text{C})$.^[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 ¹H 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 4ain quantitative yield (¹H, ¹³C 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 SiC₂ ring in the ¹H NMR spectrum^[8] (δ (¹H) = 7.91 (**4a**), 7.86 ppm (4b)) and by the typical upfield signal in the ²⁹Si 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 ¹H, ¹³C, and ²⁹Si 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 SiC₂ ring. The C₃N₂Si-ring in 4a (and in 4b) is practically planar and perpendicular to the SiC_2 ring (Figure 3).

The SiC₂ 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 SiC₂-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

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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 **1** a 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-

*i*Pr₂C₆H₃ 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 4 A, direct insertion into the C-H bond in HC=CH to form 2 A 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 $4A \rightarrow 2A$ 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 vlide-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 CH₂ 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 CH₂ 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 vlide 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 $[\mathbf{1}\mathbf{a}Br_2]$ in the order $\mathbf{4}\mathbf{A}$ (1111.6) > $\mathbf{1}\mathbf{a}$ (1099) > $[\mathbf{1}\mathbf{a}Br_2]$ (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 $[1Br_2]$ leads also exclusively to **4a** and to **4b**. In contrast, organic nitrogen-containing bases with significantly lower proton affinities, such as NEt₃ 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 meta-thesis.^[12] Respective investigations to elucidate the autocatalytic formation of **4a** and **4b** are currently underway.

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