Carbene Analogues

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Oligomerization of N-Heterocyclic Silylene into Zwitterionic Silenes

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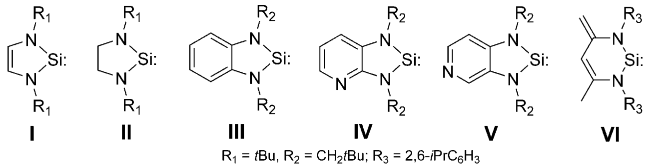
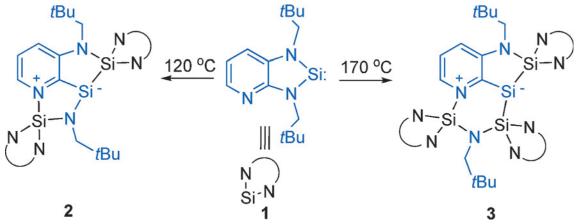
Abstract: *N-Heterocyclic carbenes (NHC's) are known to serve as efficient substrates for the stabilization of various transient species possessing low-valent Group 14 elements and for the generation of double E=C bonds. Herein, we report that the thermal tri- and tetramerizations of pyridoannulated silylene* ***1*** *lead to the formation of remarkably stable silenes* ***2*** *and* ***3*** *featuring zwitterionic distribution of electron density. Co-oligomerization of* ***1*** *and its germanium analogue gives a related tetrameric product* ***4*** *containing low-valent germanium atom stabilized by binding with the partial carbene-character C atom. Bonding situations in* ***2–4*** *are best described as silene or germene with the significant zwitterionic distribution of electron density. The singlet diradical electronic state of* ***2*** *is 10 $\text{kcal}\,\text{mol}^{-1}$ higher than the ground state configuration.*

The first representative of stable N-heterocyclic silylenes (NHSi's) was prepared in 1994 (**I**, Scheme 1),[1] shortly after the discovery of the analogous stable carbene by Arduengo et al.[2] Since then a great variety of cyclic systems with divalent silicon atoms has been prepared and their reactivity towards different substrates and coordination properties have been investigated.[3] The reactivity and stability of NHSi's can be tuned by a careful choice of substituents at low-valent silicon and overall cyclic backbones.[4] The recent applications of NHC's and their silicon analogs include the isolation of various elusive species including :EH$_2$, H$_2$E=EH$_2$,[5] cyclic triatomic Si$_3$ molecule,[6] and "neutral" atomic E (E = Si, Ge).[7]



Scheme 1. Silylenes **I–VI**.

For further development of the chemistry of NHSi's, it is highly important to understand the key factors leading to their stabilization or destabilization. The silicon analogue **I** of Arduengo's carbene did not show any decomposition even at 150 °C for a long period of time.[1] In contrast, the saturated silylene **II** dimerized at room temperature with the generation of N,Si-substituted silylene and a subsequent formation of a disilene.[8] Benzannulated silylene **III** showed a similar stability to that for silylene **I**,[9] whereas pyridoannulation in **IV** and **V** led to the destabilization of the resulting species.[10] The sublimation of **IV** at 120 °C resulted in significant decomposition of the silylene and reduced its overall yield to 6 %. Attempts to synthesize pyridoannulated silylene **V** were unsuccessful.[10] The instability of **IV** and **V** falls out of the trend observed for their lighter and heavier analogues: the corresponding heterocycles with the C^{II}, Ge^{II}, Sn^{II}, and Pb^{II} atoms are stable at ambient conditions.[10,11] Synthesis of silylene **VI**, stabilized by zwitterionic distribution of electron density, was reported by Driess and co-workers.[12]



Scheme 2. Preparation of **2** and **3**.

We found that the thermal transformation of solid silylene **IV** with CH$_2$*t*Bu substituents (**1**) at temperatures above 60 °C resulted in the generation of intensively purple product of oligomerization of three silylene moieties through the formation of new Si–Si, Si–C, and Si–N bonds (**2**, Scheme 2). Product **2** possesses two tetravalent and one tri-coordinated silicon atoms. The oligomerization of **1** was accelerated by heating silylene **1** in a sealed ampoule at 120 °C. The NMR spectra for the crude mixture demonstrated complete disappearance of the parent silylene **1** and the presence of **2** as the main product in the reaction mixture after 12 h. The recrystallization of the product from *n*-hexane yielded dark purple trimer **2** in a yield of 60 %.

Heating of the ampoule with solid **1** at an even higher temperature (170 °C) initially resulted in the formation of a purple liquid with a subsequent crystallization of the violet product of silylene tetramerization (**3**, Scheme 2). Tetramer **3** was formed in the reaction mixture upon the insertion of

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silylene **1** into the Si−N bond between tri-coordinated silicon and the attached nitrogen atom of trimer **2**. Heating of trimer **2** at 170 °C without addition of silylene **1** did not yield the product of tetramerization **3**. This showed irreversible character of thermal oligomerization of silylene **1**. In contrast to **1**, silylene **IV** with more sterically demanding *N*-*t*Bu substituents (**1**-*t*Bu) could be distilled around 120 °C in vacuo without any transformations. Moreover, the prolonged storage of a sealed ampoule loaded with **1**-*t*Bu at 170 °C did not lead to decomposition of the silylene either. Thus, this demonstrates the significance of the bulkier N-substituents on the stabilization of NHSi's and the possibility of tuning their reactivity.

Single-crystals of compound **2** were obtained upon slow evaporation of solvent from its *n*-hexane solution. An X-ray diffraction study of **2**[13] showed the compositional disorder at sites of atoms N5/C9 and N9/C34, that have equal contributions of carbon and nitrogen (Figure 1 a–c).

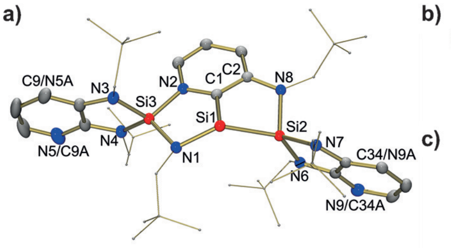


Figure 1. Molecular structure of **2** (a; N5, C9, N9, and C34 have occupancy of 0.5) and views for the environment at the tri-coordinated Si1 atom (b and **c**). Neopentyl groups are shown using wire depiction. Selected bond distances (Å) and angles: Si1−Si2 2.3530(5), Si1−C1 1.8410(13), Si1−N1 1.8004(11), Si2−N 1.7530(11)–1.8021(11), Si3−N 1.7104(11)–1.7870(11), C1−N2 1.369(2), C1−C2 1.429(2); N1-Si1-Si2 130.51(4)°, N1-Si1-C1 92.07(5)°, C1-Si1-Si2 82.62(4)°, N2-C1-Si1 117.61(9)°, N2-C1-C2 119.75(11)°.

The tri-coordinated Si1 atom in **2** exhibits substantial pyramidalization. The Si1−C1 bond length (1.8410(13) Å) is notably longer than Si=C double bonds measured in silenes (1.76 Å),[14] but shorter than Si−C single bonds (1.96 Å). The Si1−C1 bond distance is similar to the ones observed in silylone (1.824(2) Å, $^{\mathrm{NHC}}$C:Si:C$^{\mathrm{NHC}}$, NHC = :C(CCy$_2$)$_2$-(CH$_2$)*N*-2,6-*i*Pr$_2$-C$_6$H$_3$)[15] and in 1,4-diamino-2,3-disila-1,3-butadiene (1.826(3) Å), where the partial double character of the Si−C bond was postulated.[16] The plane of the central pyridine ring is almost perpendicular to the Si1Si2N1 plane (89.62(6)°). This type of arrangement was previously observed for the adducts of NHC's with their Group 14 element analogues.[17] The Si1−Si2 bond length (2.3530(5) Å) suggests single-bond character. The C−C bond distances within the central pyridine ring (1.356(2)–1.428(2) Å) are indicative of the retention of its aromatic character. The N1-Si1-Si2 angle (130.51(4)°) significantly deviates from that of idealized angles for sp^2- or sp^3-hybridized atoms.

A single-crystal study of tetramer **3**,[13] grown from an *n*-hexane solution, demonstrated the presence of a related structural core consisting of a tri-coordinated silicon Si1 atom attached to the carbon atom of the pyridine ring (Figure 2) and to two tetravalent silicon Si2 and Si3 atoms. The Si1−Si2(3) bond lengths (2.2847(10) and 2.2754(9) Å) are shorter compared to that measured in **2** (2.3530(5) Å). This can be explained by bond and angle tensions of the molecule. The remaining distances in **3** were similar to those in **2**. The space filling models for **2** and **3** showed the partial exposition of the reactive tri-coordinated silicon atom in **2** and its full sterical protection in **3** (Figure 2b,c). Interestingly, the oligomerization reaction between **1** and its germanium analogue at 120 °C gave the mixed Si/Ge tetrameric product **4** with tri-coordinated germanium (Figure 3). The exclusive formation of **4** was attributed to the higher reactivity of the Ge−N bonds compared to the Si−N bonds towards Si$^{\mathrm{II}}$ centers.[18] In contrast, the reaction between pyridoannulated germylene-bearing sterically more demanding *N*-*t*Bu groups and **1** gave tetramer **3** and unreacted germylene.

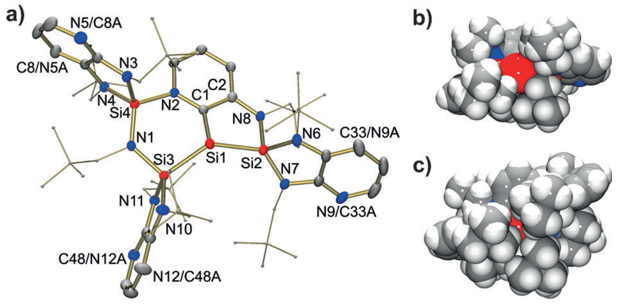


Figure 2. Molecular structure of **3** (a; neopentyl groups are shown using wire depiction; N9, C33, N5, C8, N12, and C48 reside at 1:1 compositionally disordered C/N sites) and space-filling models for **2** (b) and **3** (c). Selected bond distances (Å) and angles for **3**: Si1−Si2 2.2847(10), Si1−Si3 2.2754(9), Si1−C1 1.848(2), Si2−N 1.744(2)–1.773(2), Si3−N 1.749(2)–1.773(2), Si4−N 1.712(2)–1.813(2), C1−N2 1.379(2), C1−C2 1.451(2); Si3-Si1-Si2 130.12(3)°, C1-Si1-Si2 90.78(6)°, C1-Si1-Si3 101.61(6)°, C1-N2-Si4 125.11(11)°, N2-C1-Si1 124.19(12)°, N2-C1-C2 117.86(14)°.

Compound **4**, isolated from a toluene solution, is isostructural with **3**.[13] The molecules of **4** adopt essentially the same conformation as **3** (Figure 3). The Ge1−C1 bond length in **4** is 1.952(2) Å and is approximately 0.10 Å longer than the related Si1−C1 bond in **3**, whereas the Ge1−Si1(3) bonds are elongated by only 0.05 Å compared to Si1−Si2(3). The

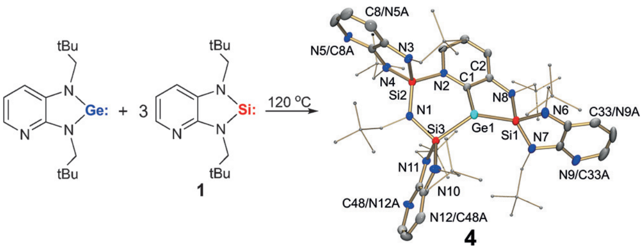
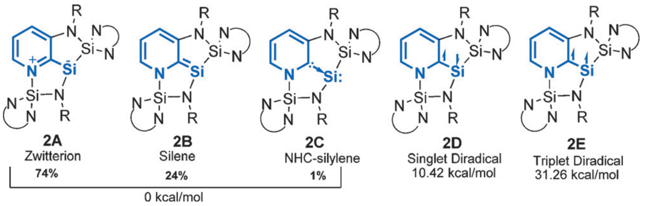


Figure 3. Synthesis and molecular structure of **4**. Neopentyl groups are shown using wire depiction; N9, C33, N5, C8, N12, and C48 are positionally disordered. Selected bond distances (Å) and angles: Ge1−Si1 2.3347(8), Ge1−Si3 2.3227(8), Ge1−C1 1.952(2), Si1−N 1.747(2)–1.779(2), Si2−N 1.713(2)–1.822(2), Si3−N 1.753(2)–1.780(2), C1−N2 1.373(3), C1−C2 1.440(3); Si3-Ge1-Si1 125.14(3)°, C1-Ge1-Si1 87.54(7)°, C1-Ge1-Si3 97.73(7)°, N2-C1-Ge1 122.8(2)°, Ge1-Si3-N1 101.21(7)°, N2-C1-C2 118.4(2)°.

deviation of the Ge1 atoms from the Si1Si3C1 plane (0.90 Å) is greater than the related distance measured for the low-valent silicon atoms in **3** and **4** (0.80 Å and 0.75 Å, respectively). The angle Si3-Ge1-Si1 125.14(3)° is larger than in digermenes (113°)[19] and in the adducts of NHCs with germylenes (117°).[20]

The VT ^{1}H NMR study of **2** showed dependence of the multiplicity for the resonance signals of the N-$CH_2C(CH_3)_3$ protons on the temperature used (Figure S1) because of obstructed rotations about N−C and C−C bonds at low temperatures on the NMR time-scale. The resonance signals of the carbon atom attached to the tri-coordinated Si or Ge appeared in the range of $\delta = 186$–195 ppm in the ^{13}C NMR spectra, indicating a significant amount of positive charge at this atom or/and its carbene-type character. The ^{29}Si NMR spectra of **2** and **3** showed the signals of tri-coordinated silicon at $\delta = 10.8$ ppm and 3.6 ppm, respectively. The maximum of the absorbance band in the UV/Vis spectrum of a THF solution of **2** appeared at $\lambda_{max} = 525$ nm. The presence of an additional SiN_2-ring in **3** leads to a bathochromic shift of this band to $\lambda_{max} = 570$ nm (Figure S2).

To further investigate the electronic structure and bonding situation in oligomers **2**–**4**, we carried out computational investigations at the DFT level with help of hybrid exchange–correlation functional PBE0. We have considered the following possible electronic configurations of the ground and excited states: zwitterion (**2A**), silene (**2B**), carbene–silylene adduct (**2C**), and singlet and triplet diradicals (**2D** and **2E**, Scheme 3).



Scheme 3. Possible ground (**2A**–**2C**) and excited (**2D** and **2E**) electronic states, their relative energies, and contributions of the resonance forms **2A**–**2C** to the ground state of **2** (NRT).

Geometries and energetics for **2** were found to be very close for the models with N-Me or N-CH_2*t*Bu substituents (see the Supporting Information, here we discuss only the models with the N-Me groups). It was estimated that the forms **2A**–**2C** with a leading contribution of **2A** (see later) were lower in energy compared to the closest excited electronic state, singlet diradical **2D**, by 10.42 kcal mol^{-1}. Interestingly, the triplet state **2E** appeared to be higher in energy by 20.84 kcal mol^{-1} than **2D**. Altogether, it revealed the relatively low stability of the high-spin-state (**2E**) in comparison with the different singlet states. A zwitterionic stabilization, similar to **2A**, was previously observed for the adducts of a cyclic N,C-substituted carbene with silicon chlorides[21] and NHC's with acyclic silylenes.[22] Configurations **2A**, **2B**, and **2C** represent possible resonance structures for system **2**. Evaluation of their contributions to the ground state within the Natural Resonance Theory (NRT) framework revealed the dominant term (74%) coming from the resonance structure **2A**, whereas structure **2B** contributes 24%. The contribution of carbene–silylene structure **2C** was found to be below 1%.

The natural bond-orbital charge distribution analysis performed for the ground electronic state **2** unambiguously showed a substantial concentration of negative charge on the tri-coordinated silicon atom (+ 0.61). In accordance with this model, a significant reduction of negative charge on the C1 atom was also observed. For the same reason, the negative charge on N2 was found to be notably decreased, indicating some delocalization of the positive part of the zwitterionic pair. The negative part was also delocalized and resulted in a decrease of positive charge of Si2 (+ 1.57). For comparison, the charge on Si3, which is not involved in any charge delocalization (positive or negative), was found to be + 2.15. Delocalization of positive and negative parts of the zwitterionic pair is depicted graphically by a 3D map of molecular electrostatic potential in Figure 4 for **2**.

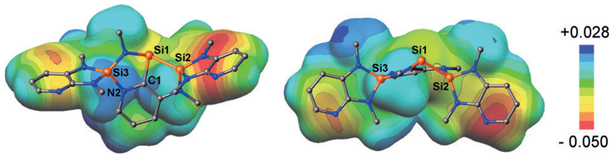
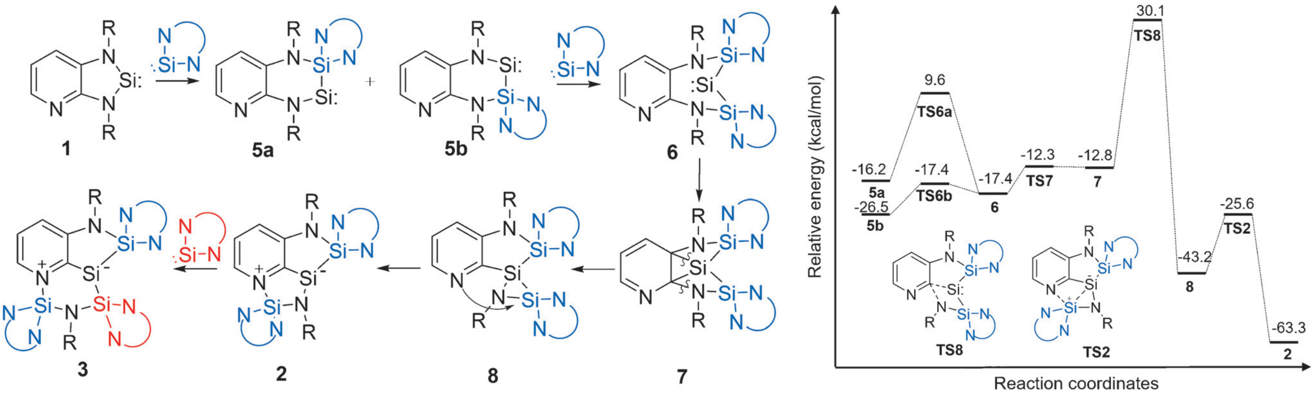


Figure 4. Map of molecular electrostatic potential for **2**.

The HOMO and HOMO-1 unambiguously indicate the localization of the electron density on the Si1 atom (Figure S3). Moreover, they show involvement of the Si2 and connected aromatic systems on the delocalization of negative charge. The LUMO shows the delocalization of a positive charge within the central pyridine ring. All of these findings are in good agreement with previous observations and strongly support the zwitterionic nature of the ground state for **2**.

The mechanism for the formation of **2** initially includes the insertion of the reactive Si^{II} center into one of the Si−N bonds of the neighboring molecule to give N,Si-substituted silylenes **5a,b** (Scheme 4). Similar reactivity was previously observed for saturated silylene **II**.[8] The resulting Si,Si′-substituted silylene **6** undergoes the intramolecular [1+2] addition of Si^{II} into the closest C=C bond of the pyridine ring with the formation of constrained polycyclic product **7**. The activation energy of this transformation is less than 6 kcal mol^{-1}. The following exothermic rearomatization of **7** into intermediate **8** proceeds through a high-energy transition state (**TS8**) requiring approximately 43 kcal mol^{-1}. It should be noted here that the related transformation via dearomatization/rearomatization of the pyridine ring was documented for the reaction of benzannulated silylene **III** with pyridine.[23] Consequently, one of the Si−Si bonds in **8** is broken, generating a positive center on the Si atom (**TS2**). Finally, the attachment of the cationic silicon center to the nitrogen of the pyridine ring gives trimer **2**. The insertion of silylene **1** into the Si−N bond between tri-coordinated silicon and nitrogen in **2** leads to tetramer **3**. An analogous reaction pathway is expected for the formation of mixed Si−Ge tetramer **4**.



Scheme 4. Proposed mechanism of the formation of **2** and **3** (all energies are shown with respect to monomeric **1**).

In conclusion, silylene **1** transforms upon heating into oligomers **2** and **3**, representing new types of silenes stabilized by zwitterionic distribution of electron density. The co-oligomerization reaction of **1** with its germanium analogue gave the related germene **4**. The dominant zwitterionic resonance form provides remarkable stability for molecules **2**–**4**. The resulting data are useful for further understanding the reactivity of NHSi's and NHGe's, and for the design of appropriate substrates for the stabilization and trapping of reactive intermediates, as well as for the tuning reactivity of the divalent derivatives of silicon and germanium.

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[13] See the Supporting Information for crystallographic details. CCDC 1485756 (**2**), 1485757 (**3**), and 1485758 (**4**) 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.

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