A Cyclic Silylone ("Siladicarbene") with an Electron-Rich Silicon(0) Atom**

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Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

There is a continuing increase in interest regarding the synthesis and reactivity of low-valent silicon species. Besides the successful access to two-coordinate cyclic^[1] and acyclic silylenes,^[2] even several donor-supported three-coordinate silicon(II) compounds could be isolated and structurally characterized. Striking examples are the chlorosilylene PhC[N(*t*Bu)]₂SiCl^[3] and the dichlorosilylene complex NHC-SiCl₂ **A** (Scheme 1; NHC = N-heterocyclic carbene, in **A**: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).^[4] The latter



Scheme 1. Selected low-valent silicon and germanium complexes stabilized through donor-acceptor coordination: the dichlorosilylene A, chlorosilyliumylidene B, silylones C–E, and the germylone F. Dip=2,6-diisopropylphenyl.

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donor-stabilized chlorosilylenes are long-sought-after convenient building blocks for the syntheses of new siliconcontaining functional groups. For instance, the NHC ligand in **A** can be replaced by a chelate ligand 1,8-bis(tributylphosphazenyl)naphthalene to yield the first chlorosilyliumylidene complex **B** (Scheme 1).^[5] Remarkably, the Si^{II} center in **B** remains three-coordinate and prefers ion-pair formation.

Along with those divalent silicon species, two-coordinate Si^0 species L: \rightarrow Si \leftarrow :L, termed as silvlones, have also attracted significant attention (L=N-heterocyclic carbenes, phosphanes, etc.). This new class of silicon compounds and their heavier homologues have been theoretically investigated by the group of Frenking.^[6] Results from calculations predict that, in contrast to linear allenes, silvlones adopt a bent molecular geometry, which is in accordance with the VSEPR theory because the central Si atom has two lone pairs of electrons and two dative electron pairs from the donor ligands L:. Accordingly, the previously reported trisilaallene C and digermasilaallene **D** (Scheme 1)^[7,8] with E-Si-E angles of 136.5° (E = Si) and 125.7° (E = Ge) should rather be silvlones with a central Si atom in the formal oxidation state zero that is stabilized by two silylene or germylene moieties, respectively. The results from calculations have inspired experimentalists to synthesize other types of silylones and examine their fascinating chemical behavior. Very recently, Roesky and coworkers prepared and isolated the siladicarbene (silylone) E (Scheme 1),^[9a] which represents a Si⁰ species stabilized by two cyclic alkyl amino carbene (cAAC) molecules.

The seminal work by Robinson and co-workers has demonstrated that even NHCs can serve as efficient donor ligands for the stabilization of Si⁰ species, as shown by the successful dechlorination of NHC \rightarrow SiCl₄ (in this case NHC is 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), affording the fascinating isolable disilicon(0) species NHC \rightarrow Si= Si \leftarrow NHC.^[10] Inspired by the latter results and Roesky's siladicarbene **E**, we employed the chelate N-heterocyclic carbene **1** (Scheme 2) for the synthesis of the first cyclic bis-NHC-stabilized silylone. Recently we have shown that the bis(carbene) **1** is suitable for the synthesis of an isolable cyclic germadicarbene **F** (Scheme 1).^[11] We wish to report herein straightforward access to the new chlorosilyliumylidene precursor **2**, which can be reduced to the desired cyclic siladicarbene (silylone) **3** (Scheme 2).

Analogous to the synthesis of **B** and $(cAAC)_2SiCl_2^{[9b]}$ (the precursor of **E**), we examined the reactivity of the ligand **1** toward NHC-SiCl_2 **A**. The experiment revealed that the reaction of equimolar amounts of **1** with NHC-SiCl_2 in THF at room temperature leads to the desired new chlorosilyliumy-

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Scheme 2. Synthesis of the cyclic bis-NHC stabilized silylone **3**, starting from the bis-NHC ligand **1** and the chlorosilyliumylidene precursor **2**.

lidene precursor 2 (Scheme 2). Compound 2 is insoluble in THF, but soluble in acetonitrile, and could be isolated in 57 % yield. It has a similar electronic nature as **B**, but is remarkably different from that of the neutral biradical tetravalent $(cAAC)_2SiCl_2\!,^{[9b]}$ which results from the reaction of two molar equivalents of cAAC with NHC-SiCl₂ A. Unexpectedly, the three-coordinate Si^{II} atom in 2 exhibits a drastic upfield shift in the ²⁹Si NMR spectrum at $\delta = -58.4$ ppm in CD₃CN, and similarly in the solid-state CP/MAS ²⁹Si NMR spectrum at $\delta = -57.8$ ppm, in comparison to those of **B** ($\delta =$ -3.30 ppm in CD₂Cl₂)^[5] and other related three-coordinate silicon(II) compounds LSi(Ar)Cl (L=1,3,4,5-tetramethylimidazol-2-ylidene, $Ar = 2,6-Mes_2C_6H_3$, $\delta = 1.34 \text{ ppm}$ in C_6D_6 ; $Ar = 2,6-Trip_2C_6H_3$ (Trip = 2,4,6-*i*Pr₃C₆H₂), $\delta =$ 0.77 ppm in C_6D_6 ^[12] $\delta = 19.1$ ppm in C_6D_6 for A^[4] and $\delta =$ 14.6 ppm for PhC[N(*t*Bu)]₂SiCl in C_6D_6),^[3] respectively. The calculated ²⁹Si chemical shift (GIAO/B3LYP/6-311(d) for (H, C, N), and 6-311G(3d) for Si) of the bare silvliumylidene cation of **2** confirms the relatively large shielding of the ²⁹Si nucleus ($\delta = -66.3$ ppm), which is in reasonable agreement with the experimental value. Remarkably, the ²⁹Si NMR chemical shift of 2 falls even in the range of four-coordinate Si species ($\delta = -20$ to -80 ppm).^[13] The strong upfield shift of the ²⁹Si NMR signal of 2 indicates a much stronger electrondonation effect of the bNHC chelate ligand **1** to the Si^{II} atom than those of 1,8-bis(tributylphosphazenyl)naphthalene in **B** and by other ligands mentioned above.

The yellow compound **2** crystallizes in the orthorhombic space group *Pbca*. Akin to **B**, the Si^{II} atom of the silyliumylidene cation of **2** is three-coordinate, namely by the two carbene carbon atoms of the chelate ligand **1** and one chlorine atom (Figure 1), featuring a trigonal-pyramidal coordination geometry with the sum of bond angles around Si atom of 282.13°. The counteranion (Cl⁻) is located far away from the silicon atom, with the smallest distance of 6.424(2) Å. Owing to the chelate coordination, the Si atom resides in a puckered six-membered C₃N₂Si ring with boat conformation, and the C1-Si1-C2 bond angle is 88.7(2)°. The dihedral angle between the plane defined by C1, Si1, C2 and the plane defined by C1, N2, N3, C2 is 8.1°, whereas the dihedral angle between the



Figure 1. Molecular structure of the chlorosilyliumylidene cation of **2**. Ellipsoids are set at 50% probability. H atoms and one acetonitrile lattice solvent molecule are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1–Cl1 2.139(2), Si1–Cl 1.960(4), Si1–C2 1.963(4), Cl–N1 1.348(5), Cl–N2 1.355(5), C2–N3 1.356(5), C2–N4 1.342(5); Cl-Si1-C2 88.7(2), Cl-Si1-Cl1 95.8(1), C2-Si1-Cl1 97.6(1), Si1-C1-N1 126.4(3), Si1-C1-N2 127.9(3), N1-C1-N2 105.2(3), Si1-C2-N3 127.3(3), Si1-C2-N4 127.1(3), N3-C2-N4 104.9(3).

plane defined by N2, C3, N3 and the plane defined by C1, N2, N3, C2 is 35.8°. The sum of angles around each carbene carbon atom in **2** is 359.53° and 359.31°, respectively, indicating nearly ideal trigonal-planar coordination geometry. The Si1–Cl1 distance of 2.139(2) Å in **2** is slightly shorter than those in **A** (2.158(2), 2.174(2) Å),^[4] in **B** (2.172(2) Å),^[5] and in PhC[N(*t*Bu)]₂SiCl (2.156(1) Å).^[3] The two long Si–C distances in **2** (average 1.961(4) Å vs. 1.985(4) Å in **A**)^[4] fall in the normal range for dative C→Si donor–acceptor bonds.

Figure 2 shows the shapes of the frontier orbitals of the chlorosilyliumylidene cation of **2**. The HOMO has mainly σ lone-pair orbital character at the Si^{II} center. It becomes obvious that compound **2** has at the same time silylium-like and silylene character. On the other hand, the LUMO shows



Figure 2. HOMO (left) and LUMO (right) of 2.

significant π -type contribution at the Si atom. A similar π -type LUMO was also determined by DFT calculation of the cyclic chlorogermyliumylidene analogue,^[11] indicating that compound **2** could be an excellent precursor for the synthesis of the target silylone **3** (Scheme 2) through dechlorination.

When a freshly prepared THF solution of sodium naphthalenide was cooled down to -60 °C and added into a suspension of **2** in THF (-60 °C) in a 2:1 mol ratio, the reaction mixture immediately turned dark red, indicating that a reduction process took place. In fact, the desired silylone **3** could be isolated from the reaction mixture in the form of a dark red powder in 68 % yield. The ¹H and ²⁹Si NMR spectra and also the IR spectrum clearly rule out the existence of

a Si-H bond in 3 (see the Supporting Information). Strikingly, the chemical shift of the two-coordinate silicon atom in 3 in the ²⁹Si NMR spectrum appears at much higher field ($\delta =$ -83.8 ppm in [D₈]THF and $\delta = -80.1$ ppm in C₆D₆) than that of the acyclic siladicarbene Si(cAAC)₂ E ($\delta = 66.7$ ppm in C_6D_6). The enormous upfield shift observed for 3 is in accordance with GIAO calculations ($\delta = -78.7$ ppm). We reasoned that the remarkable shielding of the ²⁹Si nucleus in 3 results from a stronger σ -donor but weaker π -acceptor ability of the two NHC moieties towards silicon and the acute C-Si-C angle caused by the cyclic structure. To gain insights into the electronic differences, we carried out additional computational investigations of the related model compounds 3' (with a chelate bis-NHC), 3" (with two NHCs), and E' (bearing two cAAC ligands). Selected results of the calculations are summarized in Table 1. Whereas the C-Si-C angle of the cyclic silylone model 3' is smaller than that of acyclic silylone 3'' and E', the Si-C bond length of 3' is slightly longer than

Table 1: Calculated distances and angles, ²⁹Si chemical shifts, NBO charges at Si, and the first and second proton affinities (PAs) of model compounds 3', 3", and \mathbf{E}' .^[a]

	N N N H Si		
	3′	3″	Ε′
C-Si-C [°]	88.2	94.7	100.0
Si-C [Å]	1.880	1.877	1.861
δ (²⁹ Si) [ppm]	-69.2	-67.2	+25.5
NBO charge at Si	+0.191	+0.163	+0.315
1st PA [kcal mol ⁻¹]	273.8	283.4	268.8
2nd PA [kcal mol ⁻¹]	164.0	168.3	155.3

[a] Calculated at B3LYP/6-31G(d) level of theory. GIAO/B3LYP/6-311(d) [H, C, N]: 6-311G(3d) [Si].

that of acyclic silylones. The calculated ²⁹Si chemical shifts and NBO charges at silicon clearly support that the two NHC ligands in **3'** and **3''** are much stronger σ -donors towards silicon than the cAAC ligands in **E'**. In other words, the Si⁰ atoms in **3'** and **3''** are more electron-rich, which explains their larger first and second proton affinities (PA) in comparison to **E'** (Table 1). The presence of electron-rich silicon(0) in **3** could also explain its extreme sensitivity towards air and moisture, which is in contrast to the behavior of **E**.

The UV/Vis spectrum of **3** in toluene solutions exhibits absorption maxima at $\lambda = 345$ ($\varepsilon = 4.6 \times 10^3$), 415 ($\varepsilon = 3.5 \times 10^3$), and 547 nm ($\varepsilon = 7.5 \times 10^3$), which are comparable to those observed for the analogous germylone **F** ($\lambda = 286, 420, 564$ nm),^[11] the bent trisilallene **C** ($\lambda = 390, 584$),^[7] bent digermasilaallene **D** ($\lambda = 272, 383, 432, 488, and 612 nm),^{[8]}$ and **E** ($\lambda = 270, 327, 392, 570, 611 nm).^{[9]}$ TD-DFT calculations of compound **3** revealed the longest absorption maximum at $\lambda = 544$ nm with an oscillator strength of f = 0.0814, which can be assigned to the electronic HOMO \rightarrow LUMO transition.



Figure 3. Molecular structure of **3**. Ellipsoids are set at 50% probability. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1–C1 1.864(1), Si1–C2 1.874(1), C1–N1 1.383(2), C1–N2 1.382(2), C2–N3 1.374(2), C2–N4 1.377(2); C1-Si1-C2 89.1(1), Si1-C1-N2 128.9(1), Si1-C1-N1 127.9(1), N1-C1-N2 103.1(1), Si1-C2-N3 128.4(1), Si1-C2-N4 127.8(1), N3-C2-N4 103.7(1).

Crystals of **3** in the monoclinic space group C2/c could be obtained in toluene solutions at -20 °C. The X-ray diffraction analysis (Figure 3) reveals that the Si atom in **3** is two-coordinate with a C-Si-C angle of $89.1(1)^\circ$, which is much smaller than those in **C** (136.5°),^[7] **D** (125.7°),^[8] and **E** (117.9°),^[9] but is comparable to those in the germylone analogue **F** (86.6°)^[11] and in its precursor **2** (88.7(2)°).

The six-membered C₃N₂Si ring is puckered and adopts a boat conformation. The dihedral angle between the plane defined by N2, C3, N3 and the plane defined by C1, C2, N3, N2 is 50° (versus 46.0° in $\mathbf{F}_{11}^{[11]}$ and 35.8° in **2**), whereas Si1 is only slightly deviated from the plane defined by C1, C2, N3, N2 with corresponding dihedral angle of 10.7° (versus 13° in **F**,^[11] and 8.1° in **2**). The sum of angles around C1 (359.96°) and C2 (359.85°) indicates almost ideal trigonal-planar coordination geometry of two carbene carbon atoms. The Si-C bond distances in 3 (average 1.869 Å) are significantly shorter than those in **2** (average 1.962 Å), and in **A** (1.985(4) Å).^[4] However, they are distinctly longer than Si-C double bonds in silaethenes (1.702–1.775 Å).^[14] In fact, they are slightly longer than that in the siladicarbene (cAAC)₂Si E (1.841(2) Å),^[9a] and close to the calculated value for Si-(NHC)₂ (1.869 Å).^[6]

Further insights into the electronic structure of 3 stem from DFT calculations, which have been carried out for the silylone 3 at the B3LYP/6-31G(d) level. The optimized geometry of 3 in the singlet ground state closely reproduced the experimental data. The energetic gap between singlet ground state and triplet first excited state is 33.0 kcalmol⁻¹. Compound 3 exhibits similar features to those of the germylone analogue F. For example, the HOMO represents the silicon π -orbital, whereas the HOMO-1 is the silicon σ lone-pair orbital (Figure 4). The silicon π -bonding orbital with Si-C bonds presents an evidence for the relatively short Si-C bond length in 3 in comparison to precursor 2. This is supported by the calculated Si-C bond lengths (average 1.888 Å) and the relatively large WBI (Wiberg Bond Index) values of the Si-C bonds (average 1.002). The electronic nature of silvlones has been well-described by Frenking and



Figure 4. HOMO (left) and HOMO-1 (right) of 3.

co-workers using several methods.^[6] The fact that compound **3** has a large value for the first (281.7 kcal mol⁻¹) and second PA (189.4 kcal mol⁻¹) definitely indicates a silylone character of compound **3**, which is similar to compound **E**. However, the results of the values for the first and second PA of model compounds (Table 1) clearly indicate that compound **3** has a stronger silylone character with a more nucleophilic silicon site than that of **E**, which is due to a more pronounced σ -donor vs. π -acceptor ability of the NHC ligand towards silicon.

In summary, by employing the neutral bidentate bis-NHC ligand **1** the unprecedented bis(carbene) chlorosilyliumylidene complex **2** could be isolated, in which both HOMO and LUMO are mainly localized on the silicon(II) atom according to DFT calculations. Dechlorination of **2** by sodium naphthalenide led to the first isolable cyclic siladicarbene (silylone) **3**. The bent geometry (C-Si-C angle 89.1°) and the average Si-C distances of 1.869 Å in **3** are in good agreement with the DFT calculated values. Furthermore, DFT calculations of model silylones with two NHC versus two cAAC ligands revealed that bis-NHC silylones possess a larger nucleophilicity at the Si⁰ atom, which is due to the weaker π -acceptor character of the NHC ligand. The remarkably high reactivity of **2** and **3** towards electrophiles and nucleophiles is currently under investigation.

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