Low-Valent Silicon Cations with Two-Coordinate Silicon and Aromatic Character

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Dedicated to Professor Robert West

The parent silylium cation H_3Si^+[1] and the silyliumylidene cation HSi^+[2] are the simplest polyatomic silicon cations with low-coordinate silicon atoms. Because of their kinetic lability, they are very reactive species that can only be detected under mass spectrometric[1,3] and related astrophysical conditions.[2,4] However, because of their importance as basic building blocks in silicon chemistry, the quest for isolable derivatives of the free cations is one of the current challenges in contemporary silicon chemistry.

The isolation of free cations is particularly difficult in the case of silyliumylidene derivatives RSi^+ because of the redox lability of divalent versus tetravalent silicon in R_3Si^+. One successful method for the stabilization of low-coordinate silicon cations in the condensed phase is provided by using sterically encumbering substituents and/or π-donor ligands attached to the silicon in a noncoordinating environment. In line with that, the presence of a preferably weakly ("non"-) coordinating anion turned out to be crucial for the kinetic stability of highly Lewis acidic "free" cations in the solid state.[5] This has been impressively shown with the isolation of stable silylium salts that contain "free" R_3Si^+ cations,[6] including the remarkable synthesis of the first salt with a cyclotrisilylenium cation $[(RSi)_3]^+$.[7]

Recently, the concept of kinetic stabilization through the presence of appropriate bulky substituents has also paved the way to the isolation of the intriguing $[(\eta^5\text{-}C_5Me_5)Si]^+$ cation (**A**), the first and hitherto only known derivative of the elusive HSi^+ ion.[8] Apparently, the divalent (silylene-like) silicon atom in **A** benefits from the η^5-coordination mode of the C_5Me_5 ligand ("half-sandwich"), which leads to formally eight valence electrons and a lone electron pair at silicon ($\lambda^5\text{-}Si^{II}$). According to the Jemmis–Schleyer interstitial electron rule for half-sandwich (nido-cluster) species,[9] the cation **A** can be described as a 3D-aromatic compound. The existence of **A** prompted us to investigate whether HSi^+ derivatives **B** with two-coordinate Si^{II} atoms ($\lambda^2\text{-}Si^{II}$) are accessible by using
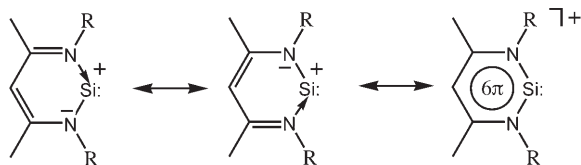
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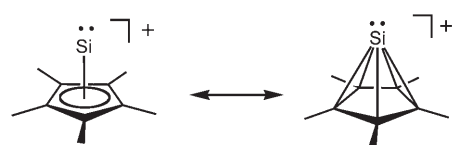
A: λ^5-Si^{II}, "half-sandwich"; nido-SiC$_5^+$ cluster, 3D aromatic

B: λ^2-Si^{II}, planar, 2D aromatic

sterically encumbered β-diketiminate ligands. The kinetic stabilization of the low-coordinate, divalent silicon center in **B** could be achieved by favorable N-coordination and a planar (Hückel-like) aromatic 6π-electron delocalization. Here we report the unexpected simple access and structural character-ization of the novel silyliumylidene-like species **1** and **2**, starting from the potentially zwitterionic N-heterocyclic silylene **3** (Scheme 1).[10]

3: R = 2,6-iPr$_2$C$_6$H$_3$
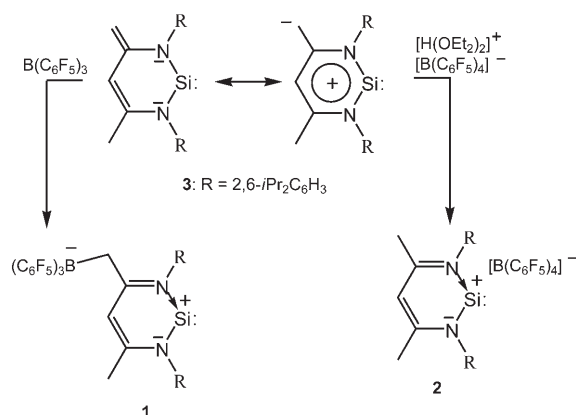
Scheme 1. Synthesis of the silyliumylidene compounds **1** and **2**.

Silylene **3** reacted gently with B(C$_6$F$_5$)$_3$ at ambient temperature to afford the zwitterionic adduct **1**, which was isolated as air- and moisture-sensitive colorless crystals in 69% yield. The structure of **1** was determined by a single-crystal X-ray diffraction analysis (Figure 1)[11] and NMR spectroscopy (see below). The zwitterion crystallizes in the triclinic space group $P\bar{1}$ and consists of a planar six-membered SiC$_3$N$_2$ ring with an exocyclic B(C$_6$F$_5$)$_3$ group attached to the C1 atom. The lengths of the C1–C2 (149.4(2) pm), C4–C5 (149.9(2) pm), and C1–B1 (165.6(2) pm) bonds indicate that they are single bonds, while those for C2–C3 (139.2(2) pm), C3–C4 (137.6(2) pm), N1–C2 (136.6(2) pm), and N2–C4 (136.4(2) pm) bonds are significantly shorter than those in **3**,[10] suggesting the presence of strongly conjugated π bonds. The Si–N bond lengths of 177.22(15) and 176.28(13) pm in **1** are approximately 3 pm longer than those in **3**. Additionally,
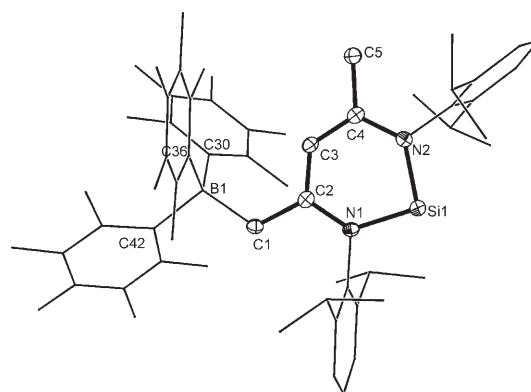

Figure 1. Molecular structure of **1**. Thermal ellipsoids (C1–C5, N1, N2, and Si1) are drawn at 50% probability level. Hydrogen and fluorine atoms are omitted for clarity. Selected distances [pm] and angles [°]: Si1–N1 177.22(15), Si1–N2 176.28(13), N1–C2 136.6(2), N2–C4 136.4(2), C1–C2 149.4(2), C2–C3 139.2(2), C3–C4 137.6(2), C4–C5 149.9(2), C1–B1 165.6(2), B1–C30 166.0(2), B1–C36 166.2(2), B1–C42 166.6(2); N1-Si1-N2 96.50(6), C2-N1-Si1 129.01(11), C4-N2-Si1 127.76(11, C2-C3-C4 127.16(14).

the endocyclic N1-Si1-N2 angle is only 3° smaller than that in **3**.

Crystals of **1** were insoluble in hydrocarbons but readily dissolved in ethereal solvents, whereas dissolution of **1** in CH$_2$Cl$_2$ led immediately to decomposition. Interestingly, dissolution of **1** in THF at room temperature led to an equilibrium mixture of **1** and silylene **3** in a molar ratio of 10:7 (^{1}H, ^{29}Si NMR spectroscopy), together with the (F$_5$C$_6$)$_3$B-THF adduct (^{1}H, ^{11}B NMR spectroscopy; see Supporting Information). However, the ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{29}Si NMR signals of **1** could be unequivocally assigned and "extracted" from the difference spectra. Surprisingly, the ^{29}Si NMR spectrum of **1** revealed a resonance signal at $\delta = 40.5$ ppm, that is, the ^{29}Si nucleus is more shielded than that in **3** ($\delta = 88.4$ ppm) by about 48 ppm,[10] in contrast to the expected higher Lewis acidity (electron-deficiency) of the low-valent Si atom in **1**. This can be explained by the presence of a stronger p$_\pi$–p$_\pi$ donor–acceptor interaction between the π-electron system of the β-diketiminate ligand and the Si atom. In line with that, the ^{1}H NMR chemical shift of the γ-CH proton of the SiC$_3$N$_2$ ring at $\delta = 6.79$ ppm was significantly different from the respective value for **3** ($\delta = 5.44$ ppm) and thus indicative for the presence of an aromatic 6π-electron system.

This hypothesis was additionally corroborated by the synthesis of the separated ion pair [**2**{B(C$_6$F$_5$)$_4$}$^-$] through protonation of **3** with the convenient Brønsted acid H(OEt$_2$)$_2$$^+$[B(C$_6F_5$)$_4$]$^-$.[12] The desired product afforded color-less crystals, which were isolated in 61% yield. Its structure was elucidated by single-crystal X-ray diffraction analysis (Figure 2).[11] The salt [**2**{B(C$_6$F$_5$)$_4$}$^-$] crystallizes in the monoclinic space group $P2_1/n$ and consists of separated ion pairs (shortest Si–F distance 429.7 pm). As expected, the Si–N bond lengths and the N1-Si1-N2 angle (96.2(1)°) are almost identical with those observed in **1**. The same is true for the exocyclic C1–C2 and C4–C5, as well as the endocyclic C–C and C–N bond lengths, respectively. The geometrical para-meters of the cation were very similar to those observed for
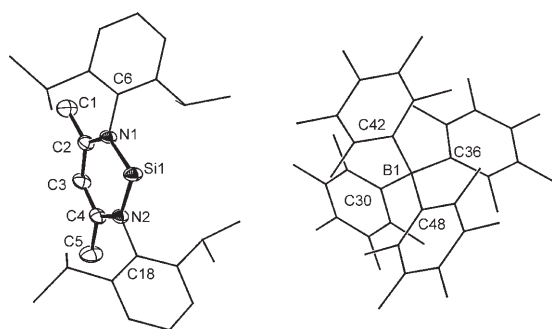
Figure 2. Molecular structure of the ion pair [**2**{B(C$_6$F$_5$)$_4$}$^-$]. Thermal ellipsoids (C1–C5, N1, N2, and Si1) are drawn at 50% probability level. Hydrogen atoms of the cation **2** and the fluorine atoms in the [B(C$_6$F$_5$)$_4$]$^-$ anion are omitted for clarity. Selected distances [pm] and angles [°]: Si1–N1 177.0(3), Si1–N2 176.0(3), N1–C2 136.1(4), N2–C4 136.0(4), C1–C2 148.9(5), C2–C3 138.9(5), C3–C4 137.5(5), C4–C5 149.6(5), B1–C30 164.8(5), B1–C36 165.3(5), B1–C42 162.2(5), B1–C48 165.3(5); N1-Si1-N2 96.18(13), C2-N1-Si1 128.4(2), C4-N2-Si1 128.6(2), N1-C2-C3 119.8(3), C3-C2-C1 120.4(3), C4-C3-C2 126.6(3).

the germanium homologue.[13] Crystals of [**2**{B(C$_6$F$_5$)$_4$}$^-$] were slightly soluble in ethereal solvents, but readily dissolved in CH$_2$Cl$_2$ without decomposition. Its ^{29}Si NMR spectrum showed a singlet resonance signal at $\delta = 69.3$ ppm, indicating that the ^{29}Si nucleus in the cation **2** is less shielded than that in **1** by about 29 ppm.

It is also striking to compare the chemical shifts of the ^{29}Si nucleus in **1** and the cation **2** with that observed for the isovalent but λ^5-coordinate Si atom in the silyliumylidene cation [(η^5-C$_5$Me$_5$)Si]$^+$ (**A**). The latter shows a resonance signal at extremely high field ($\delta = -400.2$ ppm).[8] Apparently, the drastic shielding of the ^{29}Si nucleus in **A** is due to the higher coordination number and 3D-aromatic cluster stabilization. The similar ^{1}H NMR chemical shift of the γ-CH proton of the SiC$_3$N$_2$ ring in **2** ($\delta = 6.92$ ppm) and **1** ($\delta = 6.79$ ppm) suggests the presence of aromatic 6π-electron stabilization. This is supported by density functional theory (DFT) calculations of the model cation **2′**, in which the 2,6-diisopropylphenyl groups at nitrogen are replaced by 2,6-dimethylphenyl substituents (see Supporting Information).[14] The geometric parameters of the model cation **2′** were in good agreement with those for **2**. The calculation of the ^{29}Si NMR chemical shift of **2′** revealed a value of $\delta = 93.9$ ppm (IGLO B3LYP, TMS referenced), about 24.6 ppm lower than the experimental value of **2** as a result of typical overestimation of paramagnetic contributions to the chemical shielding in divalent silicon compounds.[15] The calculation of magnetic properties of **2′** clearly suggests the presence of some aromatic stabilization (i.e., a significant contribution of the resonance form **2B** with cyclic delocalization; Scheme 2), which is further supported by the negative nucleus-independent chemical shift (NICS) values calculated for **2′** (NICS(0) = −1.4 ppm, NICS(1) = −3.9 ppm).

The cyclic delocalization of the π electrons in **2** also becomes evident from the shortening of the endocyclic N−C bonds (by 5 pm), concomitant with an elongation of the Si−N bond length (by 3 pm) when going from **3** to **2**. While this can hardly be explained by the mesomeric form **2A** alone, it
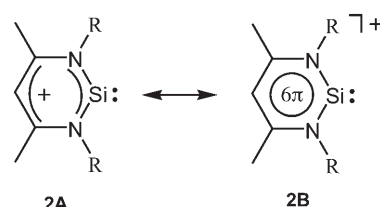
Scheme 2. Resonance structures **2A** and **2B**.

naturally follows from the changes in the π-bond orders when **2B** contributes. Additionally, the electronic situation of the cyclic cation **2** is similar to that for the known germanium homologue.[13a] In fact, this is clearly indicated by the similar negative NICS values (NICS(0) = −1.1 ppm, NICS(1) = −3.5 ppm; *zz* component of NICS(1) = −9.8 ppm) calculated for the germanium homologue of **2′** at the same theoretical level.[14] The highly electrophilic divalent silicon atom in the silyliumylidene cation in [**2**{B(C$_6$F$_5$)$_4$}$^-$] is expected to pave the way to new classes of divalent silicon compounds with terminal main-group and transition-metal substituents at the Si^{II} atom.

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[11] Compound **1**: Triclinic, colorless rod, space group $P\bar{1}$, $a = 12.099(3)$, $b = 13.740(5)$, $c = 15.0013(13)$ Å, $\alpha = 109.756(18)$, $\beta = 90.924(11)$, $\gamma = 108.95(3)°$, $V = 2197.4(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.446$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.154$ mm^{-1}, 24382 collected reflections, 7710 crystallographically independent reflections [$R_{int} = 0.0232$], 6120 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25.00°$, $R(F_o) = 0.0325$ $(I > 2\sigma(I))$, $wR(F_o^2) = 0.0496$ (all data), 604 refined parameters. Compound [**2**{B(C$_6$F$_5$)$_4$}$^-$]: Monoclinic, colorless rod, space group $P2(1)/n$, $a = 12.5960(6)$, $b = 24.2554(9)$, $c = 17.8847(7)$ Å, $\beta = 110.492(4)°$, $V = 5118.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.460$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.158$ mm^{-1}, 31527 collected reflections, 8885 crystallographically independent reflections [$R_{int} = 0.0747$], 6318 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25.00°$, $R(F_o) = 0.0706$ $(I > 2\sigma(I))$, $wR(F_o^2) = 0.1166$ (all data), 704 refined parameters. Crystals were mounted on a glass capillary and measured in a cold N$_2$ flow. The data of **1** and [**2**{B(C$_6$F$_5$)$_4$}$^-$] were collected on a Oxford Diffraction Xcalibur S Sapphire at 88 K (**1**) and 150 K ([**2**{B(C$_6$F$_5$)$_4$}$^-$]), respectively (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[16] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Absorption corrections were performed by using the SCALE3 ABSPACK program.[17] CCDC 607460 (**1**) and 607461 ([**2**{B(C$_6$F$_5$)$_4$}$^-$]) 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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[14] Geometry optimizations were performed with the TURBO-MOLE program (see Supporting Information) at density functional level using the B3LYP hybrid exchange-correlation functional and polarized valence triple zeta (TZVP)basis sets. Nucleus-independent chemical shifts (NICS) were calculated by the (B3LYP) IGLO method with its integral direct implementation. NICS values were obtained at the ring centers (NICS(0) value) as well as at 100 pm above (NICS(1) value). See Supporting Informations for details..

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