From an N-Heterocyclic Silacyclopropene to Donor-Supported Silacyclopropenylium Cations

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Summary: Addition of equimolar amounts of $B(C_6F_5)_3$ to the N-heterocyclic silacyclopropenes $[LSi(C_2H_2)](2; L=CH\{(C=CH_2)-(CMe)(2,6^{-i}Pr_2C_6H_3N)_2\})$ affords the first isolable, zwitterionic silacyclopropenylium—boranide compounds **3**. Protonation of **2** with the convenient Brønsted acid $H(OEt_2)_2^+B(C_6F_5)_4^-$ leads to quantitative formation of the corresponding silacyclopropenylium salt $[4-B(C_6F_5)_4]$.

Silicon-containing small-ring compounds are of interest because of their versatile role as building blocks in organosilicon chemistry.¹ Among those, silacyclopropenes and silacyclopropenylium cations, in which the skeletal carbon atoms are fully or partially replaced by silicon, represent the most strained cycloorganosilanes. While silacyclopropenes have been investigated extensively,² little is known about the corresponding silacyclopropenylium cations, owing to synthetic difficulties. In contrast, cyclopropenylium cations, the smallest members of Hückel aromatic systems, have been considerably studied.³ Recently, even heavier congeners of the cyclopropenylium cations have been synthesized by Sekiguchi and co-workers.

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Striking examples comprise the cyclotrigermenylium cation $({}^{'}Bu_{3}Si)_{3}Ge_{3}^{+}, {}^{4b-d}$ the cyclotrisilenylium cation $\{({}^{'}Bu_{2}MeSi)(Si'Bu_{3})_{2}\}Si_{3}^{+}, {}^{4e}$ and the disilacyclopropenylium cation $\{({}^{'}Bu_{3}Si)_{2}\}Si_{2}CR^{+}$ (R = adamantyl).^{4f} To our knowledge, neither an isolable monosilacyclopropenium cation nor related donor-supported silacyclopropenylium cations have been reported to date.

Very recently, we reported on the N-heterocyclic silacyclopropenes **2a** and **2b**⁵ (Scheme 1) as new types of SiC₂ cycles which are formed by the [2 + 1] cycloaddition of the zwitterionic silylene **1**^{6a,b} with alkynes. Remarkably, the electronic nature of **2a** and **2b** implies σ^* aromaticity⁷ and a significant contribution of the ylide-like resonance structures **2a'** and **2b'**, respectively, in the electronic ground state (Scheme 1). In the preliminary communication,⁵ we proposed that the resonance ylide structures **2a'** and **2b'** might play a crucial (autocatalytic) role in their formation from **1** and the respective acetylene. According to the calculation (see the Supporting Information), the proton affinity of the terminal H₂C group in the model compound of **2a**, in which the 2,6-*i*Pr₂C₆H₃ groups on the nitrogen atoms were replaced by phenyl groups, amounts to 1111.6 kJ mol⁻¹. This implies that the basicity of **2a** is even

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Figure 1. Molecular structure of compound **3a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except for those at C30 and C31) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Si1-N2 = 1.736(2), Si1-N1 = 1.745(2), Si1-C30 = 1.746(3), Si1-C31 = 1.756(3), N1-C2 = 1.368(2), N2-C4 = 1.366(2), C1-C2 = 1.487(3), C1-B1 = 1.656(3), C2-C3 = 1.388(3), C3-C4 = 1.378(3), C4-C5 = 1.491(3), C30-C31 = 1.330(3); N2-Si1-N1 = 102.17(8), N2-Si1-C30 = 126.4 (1), N1-Si1-C30 = 125.6(1), N2-Si1-C31 = 123.8(1), N1-Si1-C31 = 126.3(1), C30-Si1-C31 = 44.7(1).

Scheme 2. Synthesis of 3a, 3b, and 4



greater than that of its precursor 1 and is comparable to that of the bent allenes calculated by Frenking^{8a} and at the same time synthesized by Bertrand and co-workers.^{8b} The zwitterionic character of the N-heterocyclic silacyclopropenes 2a and 2b prompted us to synthesize the first silacyclopropenylium systems, simply by addition of suitable Lewis acids. Herein we report the formation of the intramolecularly donor-supported silacyclopropenylium cations 3a, 3b, and 4 and the striking reactivity of 4 toward diethyl ether.

In fact, reaction of the silacyclopropene **2a** with 1 molar equiv of B(C₆F₅)₃ in toluene at ambient temperature affords the desired zwitterionic adduct **3a** (Scheme 2). It can be isolated in the form of air- and moisture-sensitive colorless crystals in 61% yield. The composition and constitution of compound **3a** have been proven by elemental analysis and ¹H, ¹³C, ²⁹Si, ¹¹B, and ¹⁹F NMR spectroscopy (see the Supporting Information). The NMR data suggest that the ring π electrons of the C₃N₂ moiety are more delocalized than in the starting material **2a**. Accordingly, the γ -H atom of **3a** resonates at δ 6.28, about 1 ppm downfield shifted in comparison to that in **2a**. Since the Si atom is tetracoordinated, the six π ring electrons are merely delocalized in the C₃N₂ diazapentadienylium π system: that is, the ring system is nonaromatic. This is supportedby nucleus-independent chemical shift (NICS) values from DFT calculation of a model



Figure 2. Molecular structure of compound **3b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Si1-N2 = 1.748(3), Si1-N1 = 1.755(3), Si1-C30 = 1.765(4), Si1-C31 = 1.776(4), N1-C2 = 1.358(4), C1-C2 = 1.495(4), C1-B1 = 1.659(6), N2-C4 = 1.371(4), C2-C3 = 1.407(5), C3-C4 = 1.366(5), C4-C5 = 1.504(5), C30-C31 = 1.367(5); N2-Si1-N1 = 102.6(1), N2-Si1-C30 = 129.3(2), N1-Si1-C30 = 120.6(2), N2-Si1-C31 = 124.9(2), N1-Si1-C31 = 126.3(2), C30-Si1-C31 = 45.4(2).

system of **3** ((NICS(0) = 1.6 ppm; NICS(1) = 0.4 ppm; see the Supporting Information). In contrast, related silyliumylidene cations with two-coordinate silicon featuring a six- π -electron heteroaromatic C₃N₂Si system are aromatic (calculated NICS(0) = -1.4 ppm; NICS(1) = -3.9 ppm).^{6c} The structure of **3a** has been confirmed by a single-crystal X-ray diffraction analysis (Figure 1).

Compound **3a** crystallizes in the triclinic space-group PI and consists of a nearly planar six-membered SiC₃N₂ ring with an exocyclic B(C₆F₅)₃ group attached to the C1 atom and a threemembered SiC₂ ring. These two cycles are perpendicular to each other and share one (spiro) silicon atom. As expected, the C1-C2 (1.487(3) Å) and C4-C5 distances (1.491(3) Å) represent single bonds due to the addition of the B(C₆F₅)₃ moiety. The Si-N bond lengths of 1.736(2) and 1.745(2) Å are ca. 3 pm longer than those observed in the precursor **2a**, while the C2-N1 (1.368(2) Å) and C4-N2 distances (1.366(2) Å) are about 4 pm shorter than the corresponding values in **2a**, in accordance with 6- π -electron aromatic delocalization. Slight changes of the structural parameters can also be observed for the three-membered ring in **3a**. Thus, the C30-C31 distance (1.330(3) Å) is slightly longer than that in **2a** (1.311(5) Å).

Similarly, the silacyclopropene derivative **2b** reacts gently with equimolar amounts of B(C₆F₅)₃, affording the analogous adduct **3b** (Scheme 2). Changing the solvent from toluene to *n*-hexane allows the isolation of **3b** in 88% yield in the form of colorless crystals. The molecular structure of **3b** has also been established by X-ray diffraction analysis (Figure 2). As expected, the characteristic metric features of **3b** are similar to those of **3a**, despite the additional phenyl groups attached to the C ring atoms of the SiC₂ cycle. The C30–C31 distance of 1.367 (3) Å in **3b** is slightly longer than the corresponding value in **3a**, probably due to a combination of electronic and steric factors. In line with that, the Si1–C30 (1.765(4) Å) and Si1–C31 (1.776(4) Å) distances are 2 pm longer than those observed in **3a**. Similar metric differences have been observed for the precursors **2b** vs **2a**.⁵ Because of the π electron delocalization,

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Scheme 3. Proposed Mechanism for the Reaction of Cation 4 with Diethyl Ether To Give 5



the metric features of the C_3N_2 moiety in the SiC₃N₂ ring in **3a** and **3b**, respectively, are somewhat reminiscent of those observed in the zwitterionic silyliumylidene–boranide analogue.^{6c}

Additionally, we examined the protonation of 2a with the convenient Brønsted acid $H(OEt_2)_2^+B(C_6F_5)_4^{-9}$ in diethyl ether at low temperature. As expected, the reaction leads to the formation of the ion pair $[4-B(C_6F_5)_4]$ in quantitative yield (Scheme 2). The constitution of $[4-B(C_6F_5)_4]$ has been proven by ¹H, ¹³C, ²⁹Si, ¹¹B, and ¹⁹F NMR spectroscopy (see the Supporting Information). As expected, the ¹H NMR spectrum shows the presence of two identical terminal CH₃ groups attached to the SiC₃N₂ ring. The singlet resonance signal at δ 7.87 ppm can be unambiguously assigned to the two protons attached to the olefinic carbon atoms in the SiC₂ ring. Likewise, the $\gamma\text{-H}$ (δ 6.08 ppm), $\gamma\text{-}^{13}C$ (δ 102.8 ppm) and ^{29}Si NMR resonances (δ -84.8 ppm) are very close to the corresponding values observed for 3a. According to DFT calculations (see the Supporting Information), the most important geometric features of the model cation 4', in which the $2,6^{-i}Pr_2C_6H_3$ groups on the nitrogen atoms were replaced by phenyl groups, are practically identical with those of **3a**. Interestingly, cation **4** reacts with diethyl ether at ambient temperature to give $[5-B(C_6F_5)_4]$ and ethene (Scheme 3). The N-heterocyclic salt $[5-B(C_6F_5)_4]$ forms colorless crystals which can be isolated in 85% yield. An X-ray diffraction analysis confirms that the latter consists of separated ion pairs (Figure 3). The silicon atom in 5 adopts a tetrahedral geometry and bears a vinyl and an ethoxy group. The C30-C31 distance of 1.309(3) Å lies in the normal range observed for C=C double bonds of a vinyl group. The protons of the vinyl group show in the ¹H NMR spectrum a typical ABC spin pattern at δ 5.55, 5.95, and 6.23 ppm with J(H,H) coupling constants of 20.5, 15.0, and 2.6 Hz, respectively. These values are similar to those observed for terminal vinyl groups attached to related β -diketiminate aluminum compounds.¹⁰



Figure 3. Molecular structure of [**5**-B(C_6F_5)₄]. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except for those at C30 and C31) are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Si1–N1 = 1.756(2), Si1–N2 = 1.771(2), Si1–C30 = 1.800(3), Si1–O1 = 1.605(2), N1–C2 = 1.361(3), N2–C4 = 1.344(3), C1–C2 = 1.505(3), C2–C3 = 1.382(3), C3–C4 = 1.392(3), C4–C5 = 1.501(3), C30–C31 = 1.309(3); O1–Si1–N1 = 111.7(1), O1–Si1–N2 = 109.77(10), N1–Si1–N2 = 100.9(1), O1–Si1–C30 = 108.4(1), N1–Si1–C30 = 113.3(1), N2–Si1–C30 = 112.5(1), C31–C30–Si1 = 121.6(2).

Although the mechanism is still unknown, we propose that the initial step of the ether cleavage is a silicon–(Lewis acid) assisted β -H elimination process with release of ethene. Subsequently, a proton-induced Si–C ring-opening reaction occurs, presumably via silaoxonium,¹¹ to give the final tautomeric cation **5** (Scheme 3). The latter reaction demonstrates that the highly electrophilic silicon atom in the donor-supported silacyclopropenylium cation **4** could be very useful for the synthesis of other types of functionalized vinyl silanes, simply by electrophilic ring-opening reactions. Respective investigations are underway.

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Supporting Information Available: Text, tables, and figures giving experimental details of the synthesis and spectroscopic data of **3a**, **3b**, [**4**-B(C_6F_5)_4], and [**5**-B(C_6F_5)_4] and CIF files giving crystallographic data for **3a**, **3b**, and [**5**-B(C_6F_5)_4]. This material is available free of charge via the Internet at http://pubs.acs.org.

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