Silicon Chemistry

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From a Stable Silylene to a Mixed-Valent Disiloxane and an Isolable Silaformamide–Borane Complex with Considerable Silicon–Oxygen Double-Bond Character**

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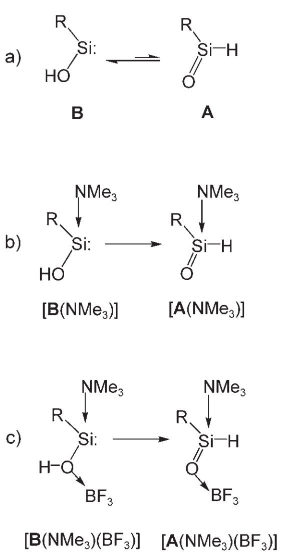
Dedicated to Professor Walter Siebert on the occasion of his 70th birthday

For a long time, unsaturated silicon compounds with multiple bonds to silicon have been thought to be unisolable at room temperature.[1] This situation changed profoundly in 1981.[2,3] During the past 25 years, intriguing progress has been achieved to generate a wealth of isolable compounds with silicon–heteroatom double bonds (heteroatom: elements from Groups 13,[4] 14,[5] and 15,[6–8] and sulfur[9]), and more recently even isolable compounds with a silicon–silicon triple bond have been reported[10] which represent unique and indispensable building blocks in organosilicon chemistry. However, the isolation of silanones ($R_2Si{=}O$) that are stable at room temperature ("Kipping's dream")[9d,e] has hitherto been unsuccessful. The absence of isolable silanones is probably a result of the lack of suitable synthetic methods as well as the difficulty in preventing oligomerization of the silicon–oxygen double bond.[11] Clearly, the pronounced polarity of the silicon–oxygen π bond, estimated by theoretical calculations,[12] accounts for the extraordinarily high tendency of silanones to undergo dimerization and trimerization. This proceeds with no barrier, in contrast to their carbon analogues or any other related silicon–heteroatom π system. Thus, taming the high polarity of the silicon–oxygen double bond is pivotal for the generation of an isolable silanone derivative.

Isolable silaformyl compounds R(H)Si=O (**A**) could be prepared by taking advantage of the tautomerization (hydrogen-atom migration) of suitable hydroxo silylenes RSi(OH) (**B**; i.e. RSi(OH)→R(H)Si=O)[12d] in the presence of donor and acceptor groups attached to the silicon and oxygen atom, respectively, which at the same time may reduce the polar nature and provide additional steric protection of the silicon–oxygen double bond (Figure 1). In fact, our calculations of the model series **B**, [**B**(NMe_3)], and [**B**(NMe_3)(BF_3)] (R = H, Me, SiH_3, NH_2; see Figure 1)[13a] revealed that the desired hydrogen migration from the OH group to the divalent silicon atom is adverse for **B** but strongly favored in the presence of suitable donor (e.g. amines) and acceptor groups (e.g. boranes) bound to silicon and oxygen, respectively.



R	A	B
H	0	-14.6
Me	0	-8.5
SiH_3	0	-5.7
NH_2	0	-38.2

R	[**A**(NMe_3)]	[**B**(NMe_3)]
H	0	30.4
Me	0	40.8
SiH_3	0	28.6
NH_2	0	31.7

R	[**A**(NMe_3)(BF_3)]	[**B**(NMe_3)(BF_3)]
H	0	109.5
Me	0	127.6
SiH_3	0	117.4
NH_2	0	115.7

Figure 1. a) Model study of the relative stability [kJ mol^{-1}] of silaformyl compounds **A** versus hydroxo silylenes **B**. The hypothetical silanones **A** result through hydrogen migration from the OH group to silicon in **B**. b) Generation and relative energies [kJ mol^{-1}] of the hypothetical N→Si silaformyl-amine adducts [**A**(NMe_3)] through the corresponding hydroxo silylene amine adducts [**B**(NMe_3)]. c) Generation and relative energies [kJ mol^{-1}] of the hypothetical N→Si and O→B donor–acceptor-supported silaformyl amine/boron trifluoride complexes [**A**(NMe_3)(BF_3)] through the corresponding hydroxo silylene amine/boron trifluoride complexes [**B**(NMe_3)(BF_3)]. Calculations were performed at the B3LYP/TZVP level of DFT.[13a]

These predictions prompted us to challenge the discouraging attempts to synthesize an isolable silaformamide complex by using the concept of donor–acceptor stabilization.

Although hydroxo silylenes are promising starting materials, isolable derivatives are currently unknown. Recently, we prepared the stable zwitterion-like silylene [LSi:] **1**,[14] which could be a suitable starting material for the generation of the desired hydroxo silylene (HL)Si(OH) (**2**) by 1,4-addition of H_2O (Figure 2); alternatively, 1,1-addition of water at the divalent Si atom could lead to the tautomer LSiH(OH) (**2′**; Figure 2).

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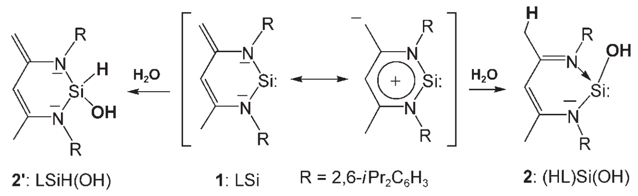

Figure 2. Proposed access to the hydroxo silylene (HL)Si(OH) (**2**) (1,4 adduct) and/or its 1,1 tautomer hydroxo silane LSiH(OH) (**2'**) by addition of water to the mesomeric forms of the potentially zwitterionic silylene **1**.

Thus, solutions of **1** in hexane at 4°C were exposed to oxygen-free water vapor. Notably, the reaction of **1** with water proceeds in the molar ratio of 2:1, leading solely to the unexpected siloxy derivative of the desired hydroxo silylene **2**, that is, the siloxy silylene **4** (Figure 3). The latter was isolated in the form of brown-red crystals in 52 % yield. In contrast, reactions of **1** in the presence of more water molecules (e.g. 1:1 molar ratio) afford merely unidentified hydrolysis products. The siloxy silylene **4** represents an unprecedented type of mixed-valent disiloxane, which contains di- and tetravalent silicon atoms that are bridged by an oxygen atom. Its composition was proven by multinuclear NMR spectroscopy, mass spectrometry, and elemental (C,H,N) analysis. The ^{1}H and ^{29}Si NMR spectra revealed that **4** is a mixture of two rotational isomers as a result of the presence of a tetracoordinate stereogenic Si atom and hindered rotation around the Si–O bonds. Thus, the ^{29}Si NMR spectrum shows two singlet resonance signals at $\delta = -7.9$ and -9.6 ppm, which can be unequivocally assigned to the silylene, and two doublets at $\delta = -53.7$ and -54.2 ppm for the siloxy ^{29}Si nuclei.[14]

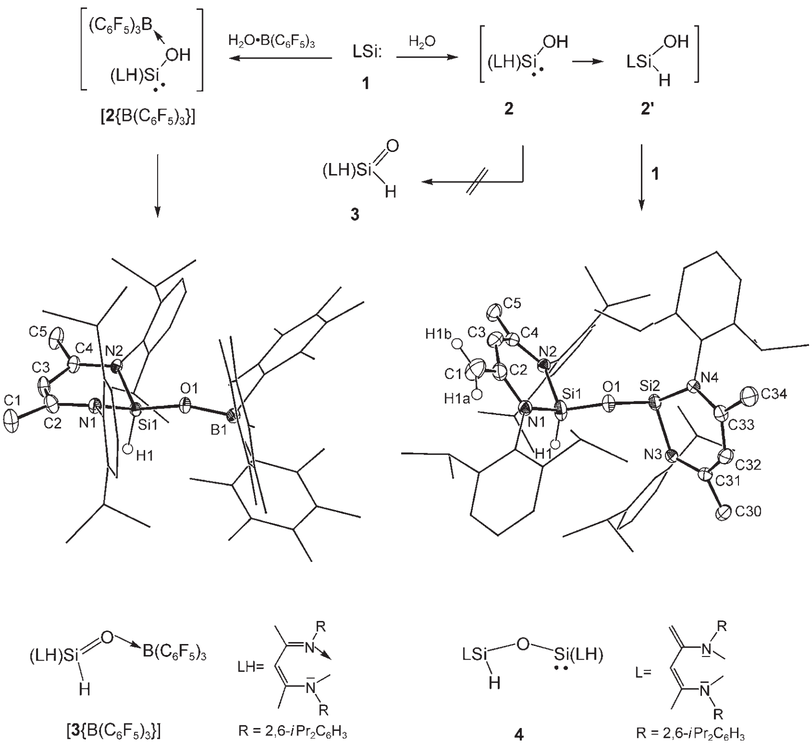

Figure 3. Generation of the silaformamide-borane complex [**3**{B(C_6F_5)$_3$}] and the mixed-valent disiloxane (siloxy silylene) **4** by addition of $H_2O{\cdot}B(C_6F_5)_3$ and H_2O to the silylene **1**, respectively. The compounds **2**, [**2**{B(C_6F_5)$_3$}], as well as **2'** are proposed as reactive intermediates for the formation of [**3**{B(C_6F_5)$_3$}] and **4**, respectively. Molecular structure representations of [**3**{B(C_6F_5)$_3$}] and **4** derived from X-ray diffraction studies are included.[13a]

One of the two isomeric forms could be enriched by fractional crystallization and was characterized by X-ray diffraction analysis. In the solid state (Figure 3), the two almost-planar C_3N_2Si rings in **4** prefer a *gauche* conformation relative to each other. The Si–O bonds are somewhat short compared to silicon–oxygen single bonds observed in common disiloxanes;[15] in the present case, the Si2–O1 bond (165.6(1) pm) with the coordinatively unsaturated divalent silicon is slightly longer than the Si1–O1 bond (163.2(1) pm) involving the tetravalent silicon atom. The Si1-O1-Si2 bond angle of 137.08(5)° is similar to values observed for other disiloxanes.

The mechanism is still unknown, however, the formation of **4** suggests that the proton migration from a terminal methyl group in the proposed reactive intermediate **2** seems to be much faster than the proton transfer from the OH group to the divalent silicon atom, preventing the formation of the desired silaformamide **3**. The migration of the proton from OH to the divalent silicon in **2** should be on a competitive basis if the acidity of the OH group is drastically increased by the presence of a strong Lewis acid bound to oxygen. In fact, addition of the water–borane adduct $H_2O{\cdot}B(C_6F_5)_3$ to **1** in a molar ratio of 1:1 affords exclusively the desired silaformamide-borane complex [**3**{B(C_6F_5)$_3$}] (Figure 3). The latter complex was isolated in the form of colorless, air-stable crystals in 67 % yield. Their composition was confirmed by correct elemental analysis and electron-impact mass spectrometry (EI-MS). The structure of [**3**{B(C_6F_5)$_3$}] was established by means of multinuclear NMR spectroscopy and confirmed by single-crystal X-ray crystallography (Figure 3). The compound consists of a puckered six-membered C_3N_2Si ring with an exocyclic OB(C_6F_5)$_3$ group attached to silicon. The silicon atom of the silaformyl group (Si(H)O) is tetrahedrally coordinated because of an intramolecularly dative N→Si bond. Because of the relatively large intrinsic Si–O and B–O σ-bond polarity, the Si-O-B bond angle is widened to 163.7(1)°, which minimizes the dipole moment, releases steric congestion, and supports Si–O π interaction.

The structure is most notable for its unique short silicon–oxygen interatomic distance of 155.2(2) pm, about 7 % shorter than those observed in silyl ethers (Si-O-C) and common disiloxanes (Si-O-Si)[15] and only marginally longer than the value of 153.7 pm calculated for the parent silaformamide, $H_2N(H)Si{=}O$, by density functional theory

(DFT).[13a,b] This observation indicates that multiple bonding between silicon and oxygen in [**3**{B(C_6F_5)$_3$}] is not significantly disturbed. In line with this suggestion, the B–O distance of 150.3(3) pm is significantly longer than a covalent B–O bond (ca. 131 pm) but close to the value of the coordinative O→B bond in $H_2O{\cdot}B(C_6F_5)_3$ (159.7(2) pm).[16a] Likewise, and in accord with DFT calculations of the related silaformyl derivatives **A** and their donor–acceptor adducts [**A**(NMe_3)] and [**A**(NMe_3)(BF_3)], respectively, the Si–O bond reveals a small elongation (ca. 4%) upon additional N→Si donor and O→B acceptor coordination.[15] The electronic features of the silicon–oxygen functionality in [**3**{B(C_6F_5)$_3$}] are similar to that described for related Lewis acid stabilized monomeric boron–oxygen[16b] and aluminum–oxygen complexes,[16c] which reveal also unusually short B–O and Al–O bond lengths, respectively, suggesting considerable double-bond character. However, a relatively short element–oxygen distance as in the aforementioned cases and in [**3**{B(C_6F_5)$_3$}] is a unreliable criterion for the assessment of the bond order. Alternatively, the short distances could be explained by the intrinsically high bond polarity and the contribution of polar resonance structures as previously suggested.[16b]

To support whether the silicon–oxygen functionality in [**3**{B(C_6F_5)$_3$}] retains considerable double-bond character, we performed IR measurements. Previous experiments on low-temperature matrix-isolated silanones revealed characteristic Si=O stretching vibration modes (ν(Si=O)) in the region of 1200 cm^{-1},[17] whereas Si–O single bonds in organosilanols (R_3SiOH; R = alkyl, aryl) and siloxanes (R_3Si-O-X; R = alkyl, aryl; X = Me_3Si, organic group) exhibit peaks at much lower wavenumbers in the range of 800 to 900 cm^{-1}.[17b] The vibrational modes in the IR spectrum of [**3**{B(C_6F_5)$_3$}] were unambiguously assigned by means of isotope labeling experiments and respective DFT calculations.[13b] Accordingly, ^{18}O-labeled [**3**{B(C_6F_5)$_3$}] was prepared from **1** and $H_2{}^{18}O{\cdot}B(C_6F_5)_3$. Comparison of the observed spectra of these two isotopomers with the calculated IR spectra of the two respective slightly smaller substituted isotopomer models are nearly identical except for one band, which originates from Si=O stretching.[17c] This comparison allows us to assign the observed band at 1112 cm^{-1} for ^{18}O-labeled [**3**{B(C_6F_5)$_3$}] to a Si=^{18}O stretching mode. On the basis of the calculation as well as a wealth of experimental data,[13a] we conclude that the corresponding vibration of the ^{16}O isotopomer is shifted about 40 cm^{-1} towards higher wavenumbers and is part of the broad band at 1165 cm^{-1}, whose intensity decreases considerably upon ^{18}O labeling.

The calculated Si–O stretching frequencies (1122 cm^{-1} for Si=^{16}O, 1082 cm^{-1} for Si=^{18}O) are smaller than those found experimentally, most likely because the N-aryl substituents in the calculated model are smaller and thus lead to less steric repulsion with B(C_6F_5)$_3$. However, this does not question our assignment, which is primarily based on the *changes* in the spectra upon ^{18}O labeling. The observed Si–O stretching frequency (1165 cm^{-1} for the ^{16}O isotopomer) is somewhat smaller than for matrix-isolated silanones (about 1200 cm^{-1}) but clearly far above frequencies typical for Si–O single bonds. To derive a Si–O bond order from the frequency, we calculated Si–O stretching frequencies for prototypical molecules with Si–O single and double bonds and for silanones supported by N donors as well as stabilized both by amine donors and borane acceptors, including compounds which model the bonding situation in [**3**{B(C_6F_5)$_3$}]. From a plot of calculated Si–O force constant versus the square of the vibrational frequency,[13a] one can estimate that a $Si={}^{16}O$ stretching frequency of 1165 cm^{-1} corresponds to a Si–O force constant of about 800 $N\,m^{-1}$. The linear interpolation between the prototypes Me_3SiOMe ($k = 438\ N\,m^{-1}$, bond order set to 1.0) and $H_2Si{=}O$ ($k = 874\ N\,m^{-1}$, bond order set to 2.0) reveals 1.83 for the Si–O bond order in [**3**{B(C_6F_5)$_3$}]. In this interpolation, the bond order has been defined through the bond strength, but a claim for a partial silicon–oxygen double-bond character also calls for a rationalization in terms of molecular orbitals. Because the silicon atom is tetracoordinated, there is no classical Lewis structure featuring a double bond. However, a population analysis for [**3**{B(C_6F_5)$_3$}] in terms of natural atomic orbitals, performed with the NBO module of the Gaussian program,[13a] reveals a significant population for the two antibonding Si–N bonds (σ^*_π acceptor orbitals mainly located at silicon) and a decreased population for the two oxygen lone pairs (n_π donor orbitals) which indicates a substantial π-bonding interaction between these orbitals. Together with the large force constant (and bond order derived therefrom), this provides enough evidence that [**3**{B(C_6F_5)$_3$}] can faithfully be viewed as a silaformamide equivalent. Investigations on its reactivity are currently underway.

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