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Silylene Compounds

An Acyclic Imino-Substituted Silylene: Synthesis, Isolation, and its Facile Conversion into a Zwitterionic Silaimine**

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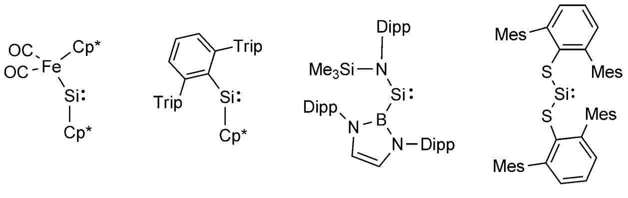
Dedicated to Professor Peter Jutzi

Silylenes, heavier analogues of carbenes, have attracted enormous research interest because of their interesting properties and reactivity.[1] Since the synthesis of the first N-heterocyclic silylene (NHSi) in 1994,[2] a number of isolable silylenes have been synthesized by taking advantage of thermodynamic stabilization of coordinating ligands and by the introduction of kinetic stabilization.[1,3] Despite significant advances made in the area of stable cyclic silylenes, which include donor-free silylenes,[4,5] acyclic silylenes are notoriously difficult and challenging synthetic targets. The acyclic diaminosilylene $[(Me_3Si)_2N]_2Si$: was reported by West and co-workers and is stable in solution at low temperatures, although it decomposes at 0 °C.[6] In fact, only a few examples of stable acyclic silylenes are known. For example, Jutzi and co-workers reported that the two acyclic silicon(II) compounds (**I** and **II**, Scheme 1) could be synthesized by a salt metathesis reaction of the silyliumylidene cation $[Cp^*Si]^+[B(C_6F_5)_4]^-$[7] with the corresponding anionic nucleophiles R^- ($R = [Cp^*Fe(CO)_2]$, 2,6-$Trip_2C_6H_3$).[8] Very recently, two stable acyclic two-coordinate silylenes (**III** and **IV**; Scheme 1) were successfully synthesized and their reactivity was investigated.[9,10] However, the chemistry of acyclic silylenes is largely unexplored.



I **II** **III** **IV**

Scheme 1. Stable acyclic, monomeric silicon(II) compounds **I**–**IV**. $Cp^* = Me_5C_5$, Trip = 2,4,6-$i$$Pr_3C_6H_2$, Dipp = 2,6-$i$$Pr_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$.

Recently, the isolation of small reactive molecules, such as B_2H_2,[11] Si_2,[12] Ge_2,[13] P_2,[14] As_2,[15] and PN,[16] was accomplished by employing elegant procedures using N-heterocyclic carbenes (NHCs).[17] One such reactive species, which has yet to be isolated, is the elusive silylene–nitrene species, R−Si−N, which is isoelectronic with silanitrile R−Si≡N.[18] This silylene–nitrene species has only been studied by theoretical calculations but a stable derivative may be accessible using carbenes, which have stabilizing properties. Generally, the free carbene is used when generating these types of species; however, in this case, an alternative approach using the imidazolin-2-iminato ligand as a precursor to the N-carbene moiety may be more convenient. This is because there are two coordination sites for a free carbene, one at the silicon atom (R(NHC)SiN) and the other at the nitrogen atom (R−SiN←NHC).[19] Preliminary computational studies showed that coordination to the nitrogen atom yields a product that is more stable than that derived from coordination to the silicon atom (for details see the Supporting Information). It is certain that this order of stability exists because of the strong C=N bond that is formed upon coordination as well as the steric congestion at the silicon center. Regardless, by using the imidazolin-2-iminato ligand, the preexisting bond assures that the carbene will be coordinated to the nitrogen atom in the product.

Tamm and co-workers have isolated and characterized numerous imidazolin-2-iminato transition-metal complexes.[20] In these cases the imidazolin-2-iminato ligands act as a 2σ- and either a 2π- or a 4π-electron donor, which results in some multiple-bond character in the interaction between the nitrogen atom and the metal center.[20,21] Therefore, we reasoned that the bis(2,6-diisopropylphenyl)imidazolin-2-iminato ligand would be an ideal bulky electron-donating group for the synthesis of an an NHC-stabilized silylene–nitrene compound. Notably, the resultant compound **A** can be described by several mesomeric structures, which include silylene–nitrene $\mathbf{A^{I}}$, the acyclic silylene $\mathbf{A^{II}}$, the zwitterionic silylene amide $\mathbf{A^{III}}$, and the 1-sila-2-azaallene $\mathbf{A^{IV}}$ (Scheme 2). In addition, because it is well known that the Cp* group is a good electron-donating group, sterically protects silicon(II) compounds, and shows variable bonding modes,[22] we employed it to stabilize the new silylene **A**. Herein, we report the synthesis, structure, and reactivity of a novel species of type **A**.

The reaction of Cp^*SiBr_3 (**1**)[23] with one equivalent of the lithium reagent LLi (L = bis(2,6-diisopropylphenyl)imidazo-

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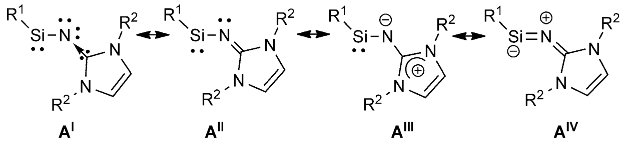
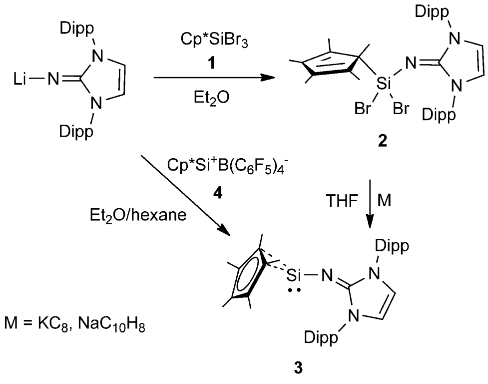


Scheme 2. Mesomeric structures of **A** (R^1 = Cp*, R_2 = Dipp).

lin-2-iminato)[24] in diethylether gives dibromosilane **2** as colorless crystals in 71% yield (Scheme 3). Compound **2** crystallized with two independent molecules in the unit cell but the geometries are almost identical to each other (see also the Supporting Information, Figure S1).[25] In the solid state, the geometry of the imidazolin-2-iminato moiety of **2** is similar to that of reported compounds $LSiMe_3$ and $LSiMe_2$-(C_5Me_4H).[24a,29a,c] The Cp* ligand in **2** is coordinated to the silicon atom in an η^1 mode (σ bonded). The methyl groups of the Cp* moiety appear as three broad signals in the ^{1}H NMR spectrum in the ratio 1:2:2. The broadening of the peaks is presumably due to the slow rotation of the Cp* ligand on the NMR time scale in solution. In accordance with the above results, three signals for the methyl groups of the Cp* moiety and three signals for the quaternary carbon atoms of the Cp* ring were observed in the ^{13}C NMR spectrum.



Scheme 3. Synthesis of **3**.

Our initial attempts to prepare imino–silylene **3** by reacting dibromosilane **2** with various reducing reagents, such as $NaC_{10}H_8$ or KC_8, led to the formation of the desired product **3** in only trace amounts (less than 10%) as observed by NMR spectroscopy (Scheme 3). Alternatively, the direct use of a silicon(II) precursor in the one-step reaction of $[Cp^*Si]^+[B(C_6F_5)_4]^-$ (**4**)[7] with LLi in a mixture of Et_2O/hexane afforded **3** as colorless crystals in a much higher yield of 57%.

X-ray analysis of **3** revealed a monomeric structure (Figure 1).[25] According to the geometry, the nitrogen atom (N1) of the imidazolin-2-iminato ligand and the Cp* ligand are coordinated to the silicon atom. The distances between the silicon center and the Cp* moiety in **3** (Si−C28 2.218(6) Å and Si1−C29 2.124(6) Å) clearly slow an η^2 coordination of the Cp* moiety to the silicon atom. The N1-Si1-C28 and N1-Si1-C29 bond angles of **3** are 103.9(2)° and 99.5(3)°, respectively. Interestingly, the Si1−N1 bond length of **3**

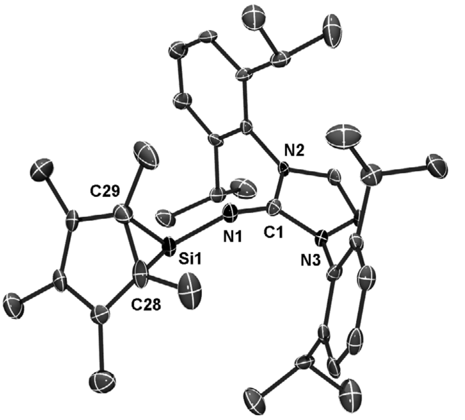


Figure 1. Molecular structure of compound **3**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1−N1, 1.691(5); Si1−C28, 2.218(6); Si1−C29, 2.124(6); C1−N1, 1.280(6); C1−N2, 1.377(6); C1−N3, 1.387(6); N1-Si1-C28, 103.9(2); N1-Si1-C29, 99.5(3); Si1-N1-C1, 136.6(4).

(1.691(5) Å) is shorter than that of the acyclic silylene **III** (1.731(1) Å) and those of other two-coordinate N-heterocyclic silylenes (1.696(3)–1.774(4) Å),[4a–d,f,g,9] thus indicating some π donation from the nitrogen atom to the silicon atom, a type of donation that was also observed for the imidazolin-2-iminato ligand. The Si1-N1-C1 angle of **3** (136.6(4)°) is smaller than those of compound **2** (141.2(3)° and 145.1(3)°). The N1−C1 bond length of **3** (1.280(6) Å) is, within experimental accuracy, the same as those of carbene-stabilized phosphorus mononitride PN (1.282(3) Å)[16] and in the range of those of reported for transition-metal complexes using imidazolin-2-iminato ligands;[20,24] however, the bond length is slightly longer than those of $LSiMe_3$ and $LSiMe_2$-(C_5Me_4H).[20a,c,24a]

The ^{1}H and ^{13}C NMR spectra of **3** show averaged resonance signals for the methyl and ring carbon atoms of the Cp* group; this observation is consistent with the fluxional behavior of these types of compounds in solution.[22] The ^{29}Si NMR chemical shift observed for **3** ($\delta = -43.8$ ppm) is shifted upfield relative to that found for $Cp^*SiN(TMS)_2$ (TMS = trimethylsilyl; $\delta = -10.2$ ppm), which was reported by Jutzi and co-workers,[7,26] thus implying that there is more electron donation from the ligand to the silicon center in **3** than in $Cp^*SiN(TMS)_2$. This hypothesis is also consistent with the Si−N bond length of both compounds (1.691(5) Å for **3**; 1.7476(10) Å and 1.7483(10) Å for $Cp^*SiN(TMS)_2$). Interestingly, the amino–silylene compound $Cp^*SiN(TMS)_2$, exhibits a monomeric structure only in solution, but exists as a dimer (a disilene with a Si=Si bond) in the solid state.[7,26] Furthermore, this ^{29}Si NMR resonance of **3** is significantly upfield relative to that of other reported silylenes,[4,5] thus indicating that the relatively high electron density on the silicon center is a result of not only electron donation from the imidazolin-2-iminato ligand, but also that from the Cp* ligand.

To gain more insight into compound **3**, DFT calculations were performed at the B3LYP/6-31G(d) level (see the Supporting Information). The optimized structure of **3** was in good agreement with the X-ray data. The lone-pair orbital on the silicon atom is clearly present in the HOMO (Figure 2, left) and the vacant 3p orbital of the silicon atom is located in the LUMO + 4 (Figure 2, right). The HOMO-1 shows the σ-bonding interaction of the π orbitals of the Cp* group with the vacant p orbital of the silicon(II) center (see the Supporting Information, Figure S5). On the other hand, the HOMO-2 indicates the presence of a σ-bonding orbital between C28 and Si1 (Figure S5). Furthermore, an orbital corresponding to π donation from the nitrogen atom to the silicon atom was also observed (HOMO-7; Figure S5), however, the calculated WBI (Wiberg Bond Index) value for the Si1−N1 bond (0.798) indicates single-bond character. The multiple-bond character of the N1−C1 bond in **3** is also supported by the WBI value (1.551) and by the presence of a π-bonding orbital between the N1 and C1 atoms (this can also be seen in the HOMO-11; Figure S5). Although some contribution from silylene–nitrene ($\mathbf{A^{I}}$) and silylene-ylide ($\mathbf{A^{III}}$ and $\mathbf{A^{IV}}$) resonance forms may exist, all theoretical and experimental results indicate that the imino-substituted silylene structure ($\mathbf{A^{II}}$) is dominant in **3** (Scheme 2). This result is unlike the corresponding result obtained for a carbene-stabilized P_2 and As_2,[14,15] a difference that can be explained by the fact that a nitrogen atom can make much stronger multiple bond with a carbon atom.

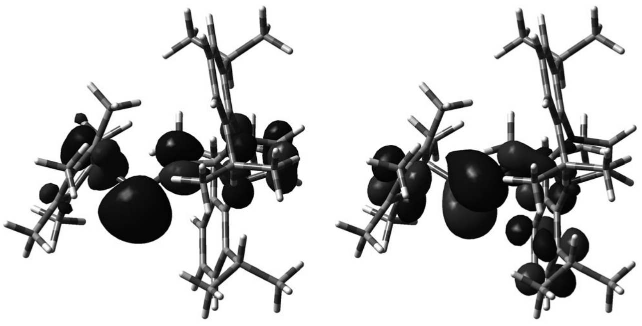
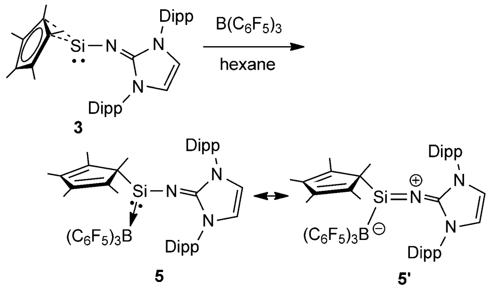


Figure 2. Molecular orbitals of **3**, HOMO (left, −0.1637 eV) and LUMO + 4 (right, −0.001 eV).

To date, only a few borane adducts of silylenes have been characterized. The only example of a silylene coordinated to a borane was reported by Metzler and Denk, who observed reversible formation of the adduct between $[CHN(tBu)]_2Si$ and $B(C_6F_5)_3$; however, the compound was unstable and slowly rearranged to a silylborane.[27] There are several other examples of silylene–borane adducts but they were synthesized using coordinated silylenes or by using other forms of reactivity.[28] However, in the case of silylene **3**, its reaction with $B(C_6F_5)_3$ in hexane results in the formation of the borane adduct **5** in 89 % yield (Scheme 4).

The coordination of the boron atom to the silicon atom in compound **5** was confirmed by the ^{29}Si NMR spectrum where a quartet appears at $\delta = 114.5$ ppm ($^{1}J_{Si,B} = 70$ Hz). In the ^{29}Si NMR spectra, the resonance of **5** is significantly more downfield shifted than that of compound **3** (ca. 158 ppm), a fact that is attributable to the change in coordination number of the silicon atom along with a decreased electron density at the silicon atom, upon coordination of the boron species. The observed signal is also significantly more downfield than that of the carbene-stabilized silylene–borane adducts, $NHC \rightarrow SiH_2 \rightarrow BH_3$ ($\delta = -55.6$ ppm) and $NHC \rightarrow SiCl_2 \rightarrow BR_3$ ($R = C_6F_5$, $\delta = 53.2$ ppm; $R = H$, $\delta = 30.7$ ppm).[28] The ^{11}B NMR spectrum of **5** shows one signal at $\delta = -21.5$ ppm, which is more upfield than that of $[CHN(tBu)]_2Si \rightarrow B(C_6F_5)_3$ ($\delta = -14.3$ ppm).[27] Compound **5** is stable in C_6D_6 solution for at least one month.



Scheme 4. Synthesis of borane adduct **5**.

The molecular structure of borane adduct **5** was also determined by single-crystal X-ray diffraction analysis (Figure 3).[25] The silicon(II) atom in **5** is three-coordinate: it is bound to the boron atom of the borane, the nitrogen atom of the imidazolin-2-iminato ligand, and the C28 atom of the Cp* ligand. It should be noted that the Cp* ligand is coordinated in an η^1 mode with only a σ bond between the C28 and Si1 atoms (1.905(4) Å). The Cp* ring and one of the C_6F_5 rings in **5** are almost parallel and exhibit intramolecular π–π stacking (the distance between the rings varies from 3.325 to 3.542 Å). The B1−Si1 bond length (2.080(5) Å) is shorter than that of $NHC \rightarrow SiCl_2 \rightarrow B(C_6F_5)_3$ (2.1135(6) Å) and longer

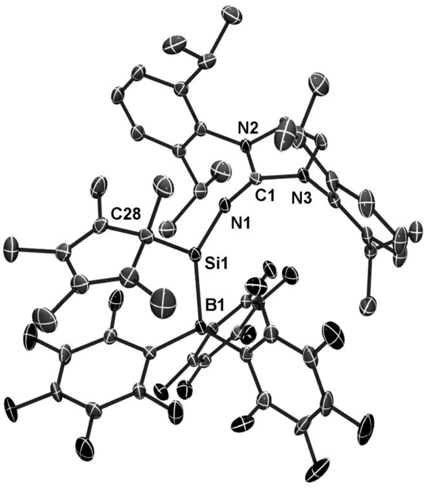


Figure 3. Molecular structure of compound **5**. Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles(°): Si1−N1, 1.605(3); Si1−C28, 1.905(4); Si1−B1, 2.080(5); C1−N1, 1.302(4); C1−N2, 1.372(4); C1−N3, 1.372(5); N1-Si1-C28, 108.69(18); N1-Si1-B1, 129.45(17); B1-Si1-C28, 121.81(17); C1-N1-Si1, 158.7(3).

than those of other reported silylene borane adducts (1.922(7)–1.996(4) Å).[28] This bond length is also comparable to those of boryl-substituted disilenes (1.996(4)–2.022(8) Å].[29] Notably, the Si1−N1 bond length of **5** (1.605(3) Å) is significantly shorter than that of silylene **3** (1.691(5) Å) and those of typical Si−N bonds (1.713–1.739 Å).[30] The Si1−N1 bond length in **5** is in the range of that reported for Si=N bonds.[31,32] In addition, the π-bonding interaction between the silicon and nitrogen atoms can be observed in the HOMO-13 of the optimized structure of **5** (see the Supporting Information, Figure S6). This increased interaction is also seen in the calculated WBI value for the Si1−N1 bond of **5** (0.900), which is larger than that of **3** (0.798). Moreover, the Si1-N1-C1 angle in **5** (158.7(3)°) is significantly larger than that of imino–silylene **3** (136.6(4)°), which indicates that the N1 atom has lower p character. The N1−C1 bond length of **5** (1.302(4) Å) is longer than those of its precursor **3** (1.280(6) Å) and other reported compounds containing imidazolin-2-iminato ligands.[20,24] The geometry around the silicon atom of **5** is planar, which was confirmed by the sum of the three bond angles around the Si1 atom (359.94°). Accordingly, the electronic environment of the silicon atom has clearly been changed through the addition of $B(C_6F_5)_3$. The increase in π donation from the nitrogen atom to the silicon atom, the decrease in p character at the nitrogen atom, and the planar structure of the Si1 atom, point to a 1-sila-2-azaallene resonance form **5′**. Similar π donation from a nitrogen atom to an sp^2-silicon atom and from an sp^2-silicon atom to a boron atom were also observed in the amino–disilenes and boryl–disilenes.[29,33]

In summary, we have synthesized a novel acyclic silylene **3** by the reduction of dibromosilane **2**. Compound **3** is also accessible in higher yield through the salt metathesis reaction of silyliumylidene cation **4** with the lithium reagent LLi. Although compound **3** may be considered as an NHC-stabilized silylene–nitrene derivative $\mathbf{A}^{\mathbf{I}}$, the structural and spectroscopic characterization as well as DFT calculation, indicate **3** is best described as an imino-substituted silylene with an N=C bond and a Si−N bond. This silylene readily reacts with $B(C_6F_5)_3$ to form the stable silylene–borane adduct **5** having significant 1-sila-2-azaallene **5′** character. Further reactivity studies of compound **3** are currently underway and will be reported in due course.

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Communications

Silylene Compounds

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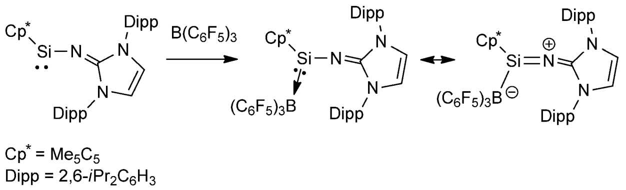
An Acyclic Imino-Substituted Silylene: Synthesis, Isolation, and its Facile Conversion into a Zwitterionic Silaimine



A new type of Si(II): A novel silylene stabilized by a Cp* and an imidazolin-2-iminato ligand has been prepared using two different methods (see scheme). The X-ray crystallographic structure shows that the silicon(II) center is coordinated to an η^2-Cp* ligand and the nitrogen atom of an imidazolin-2-iminato ligand. This silylene easily reacts with $B(C_6F_5)_3$ to give a stable borane adduct having a zwitterionic resonance structure.