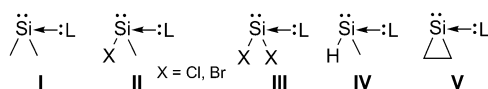


Synthesis and Characterization of an Isolable Base-Stabilized Silacycloprop-1-ylidene**

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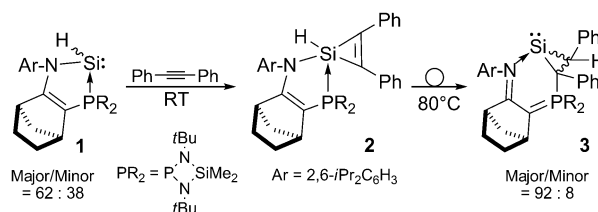
The chemistry of stable silylenes has been the subject of considerable research since the isolation of silicocene^[1] and N-heterocyclic silylene.^[2] To date, several stable silylenes,^[3–5] including kinetically stabilized dialkylsilylene,^[6] have been synthesized and their chemical properties have been extensively investigated.^[7] A novel silylene stabilized by ylidic carbon centers has also recently been reported.^[8] However, the structural modifications of stable silylenes are still far more limited than those of their lighter analogues, the carbenes.^[9]



Recently, silylenes **I** stabilized by the coordination of a donating ligand to the silicon(II) atom have attracted much attention owing to their high reactivity, which is strongly related to the nature of the ligands.^[10–13] In particular, this stabilization method allows for easy functionalization of the Si(II) atom. Indeed, silylenes with reactive Si–X bonds **II** (X = Cl, Br)^[11,14] and even dihalogenosilylene complexes **III**^[12] have been isolated as stable crystalline materials and have been used as precursors for preparing unique molecules.^[14,15] We have also successfully synthesized the first base-stabilized silicon(II) hydride species **IV**,^[16] which are difficult to prepare in the absence of steric protection.^[17] In this series, the small highly strained cyclic silylenes, such as the silacycloprop-1-ylidenes **V**, remain challenging target molecules.^[18]

Herein, we report the first synthesis of a base-stabilized silacycloprop-1-ylidene **3**.

We recently reported the synthesis of the first phosphine-stabilized silicon(II) hydride **1** and studied the reactivity of the species with olefins.^[16] Compound **1** similarly reacts at room temperature with diphenylacetylene through a [2+1] cycloaddition reaction to give the corresponding pentacoordinate silirene **2**, which was fully characterized by NMR spectroscopy in solution. A ²⁹Si NMR analysis of silirene **2** shows a high-field doublet (–135.2 ppm, ¹J_{SiP} = 58.9 Hz), which is characteristic of this type of structure.^[19] In the ¹H NMR spectrum, the Si–H fragment appears as a doublet at 6.25 ppm (²J_{PH} = 96.4 Hz) with the characteristic ²⁹Si satellites (ca. 4.7%, ¹J_{HSi} = 286.1 Hz), confirming a direct silicon–hydrogen bond in **2** (Scheme 1).



Scheme 1. Synthesis of base-stabilized silacycloprop-1-ylidene **3**.

Silirene **2** is thermally labile and quantitatively isomerizes in toluene at 80°C into silacycloprop-1-ylidene **3**, in which the Si^{II} atom is stabilized by the intramolecular coordination of the imine fragment. Compound **3** was successfully isolated as colorless crystals in 92% yield from pentane at room temperature (Scheme 1). Although the mechanism of the reaction is still unclear, this transformation formally involves two 1,2-shifts of silicon ligands, hydride and phosphine, to each of the carbon atoms of the silirene ring. Contrary to the previous cases, neither an alkyne-insertion into the Si^{II}–H bond^[15] nor tricyclic phosphine formation^[19] was observed. In the ³¹P NMR spectrum, **3** displays two singlets (46.5 and 42.8 ppm), which is in agreement with the presence of two diastereomers (92:8). In the ²⁹Si NMR spectrum, two high-field doublets were observed in the same ratio (–87.5 ppm, ²J_{SiP} = 2.9 Hz, for the major one), which is in agreement with a silicon atom in a small three-membered ring. The cyclopropylidene ring proton appears as doublets (3.57 ppm, ³J_{PH} = 30.8 Hz, and 3.02 ppm, ³J_{PH} = 31.1 Hz) in the ¹H NMR spectrum.

The crystal structure of **3** reveals a cyclopropylidene ring featuring a divalent silicon atom complexed by the imine

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fragment (Figure 1).^[20] The three-membered ring has a small bond angle around the silicon center (C1–Si1–C2 43.33°) and the two Si–C bonds (Si1–C1 1.993 Å, Si1–C2 1.920 Å) are

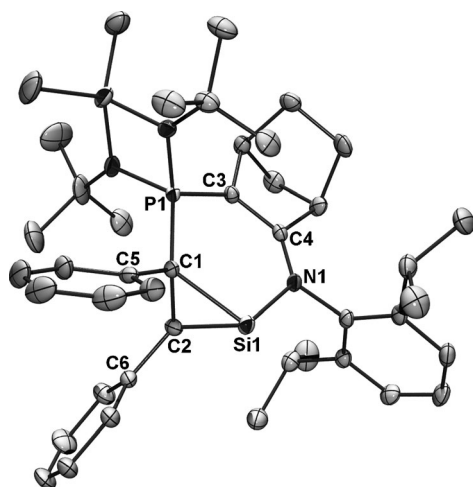


Figure 1. Crystal structure of **3**. Thermal ellipsoids set at 30% probability. H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.993(3), Si1–C2 1.920(3), C1–C2 1.572(3), Si1–N1 1.857(2), C1–P1 1.763(2), P1–C3 1.728(3), C3–C4 1.382(3), C4–N1 1.343(3); C1–Si1–C2 47.33(10), Si1–C1–C2 63.90(13), Si1–C2–C1 68.77(13), N1–Si1–C1 102.02(10), N1–Si1–C2 98.96(10).

longer than usual for Si–C bonds (ca. 1.89 Å).^[21] The silicon–nitrogen distance is also quite long (Si–N1 1.857 Å). The long bond distances around the tri-coordinate silicon center can probably be rationalized by the enhanced p character of these bonds as a consequence of the strong pyramidalization of the silicon center ($\Sigma^\circ_{\text{Si}} = 248.3^\circ$). The P–C bond (P1–C1 1.763 Å) is on the short end of the range expected for phosphoniocyclopropanes (1.759–1.780 Å).^[22] The geometry of the α -iminophosphorus ylide fragment (P1–C1–C2–N1) complexing the Si(II) center is similar to that observed in the corresponding transition-metal complexes.^[23]

To obtain more information about **3**, calculations were performed at the B3LYP/6-31G(d,p) level of theory (Figure 2). The optimized structure of **3** agrees quite well with the experimental data.^[24] The HOMO of **3** corresponds mainly to the lone pair orbital on the silicon atom. Natural bonding orbital (NBO) analysis reveals a very high-level of s character for the nonbonding orbital localized on the silicon

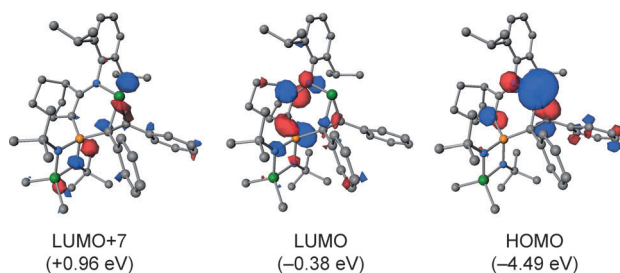


Figure 2. Calculated molecular orbitals of **3** at a 0.05 cut-off level. Energy levels of orbitals are given in parentheses.

atom (s: 75.4%, p: 24.6%). Despite this result, the energy level of the HOMO (−4.49 eV) remains quite high, suggesting a strong nucleophilic character. The LUMO does not localize on the Si^{II} atom, but rather corresponds to the π conjugate system of the α -iminophosphorus ylide fragment. The vacant orbital of the Si^{II} atom is much higher in energy (LUMO + 7), resulting in a large energy gap between LUMO + 7 and HOMO (5.45 eV), which suggests a decreasing silylenoid character for **3**.

In contrast to the phosphine-stabilized silylene **1**, which shows a silylene-like reactivity,^[16,19,25] **3** does not react with olefins or alkynes. However, it readily reacts with the Lewis acid BH₃·THF to give the corresponding borane complex **4**, which was isolated as colorless crystals in 93 % yield. The crystal structure of **4** reveals the coordination of BH₃ to the Si^{II} atom^[26] (Figure 3).^[20] The three bonds around the silicon

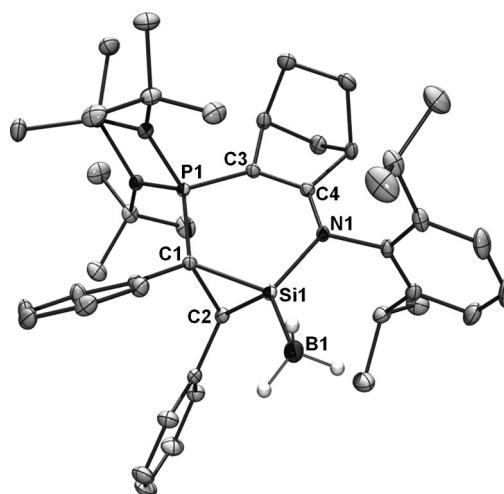
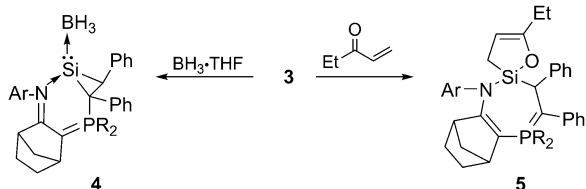


Figure 3. Crystal structure of **4**. Thermal ellipsoids set at 30% probability. H atoms (except for H atoms on B1) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–B1 1.987(2), Si1–C1 1.932(2), Si1–C2 1.868(2), C1–C2 1.610(2), Si1–N1 1.796(2), C1–P1 1.778(2), P1–C3 1.733(2), C3–C4 1.370(2), C4–N1 1.363(2); C1–Si1–C2 50.11(7), C2–C1–Si1 62.89(9), C1–C2–Si1 67.00(9), N1–Si1–C1 107.32(7), N1–Si1–C2 106.93(7).

atom are significantly shorter (Si1–C1: 1.932 Å, Si1–C2: 1.868 Å, Si1–N1: 1.796 Å) than those in **3**. These shorter bond lengths are probably due to the reduced p character of these bonds, which is induced by the coordination of the lone pair. Indeed, the sum of the bond angles for the SiX₃ subunit (X = N1, C1, and C2) in **4** (264.4°) is much larger than that observed for **3** (248.3°). Silacycloprop-1-ylidene **3** also reacts with polarized unsaturated molecules, such as ethyl vinyl ketone, to give spirocyclic silane **5** in 92 % yield (Scheme 2). The reaction probably involves an initial [4+1] cycloaddition reaction at the Si^{II} atom of **3** followed by a ring opening reaction of the three-membered silacyclopropane ring to afford **5**. This system features a bicyclic structure with a novel seven-membered ring that includes a phosphonium ylide fragment. The structure of this molecule was unambiguously confirmed by X-ray diffraction analysis.^[20,27]



Scheme 2. Reaction of **3** with $\text{BH}_3\cdot\text{THF}$ and ethyl vinyl ketone.

The isomerization of silirene **2** into silacyclopent-1-ylidene **3** involves a reduction of the silicon center from Si^{IV} to Si^{II} (Figure 4). Such an isomerization to give a stable lower-

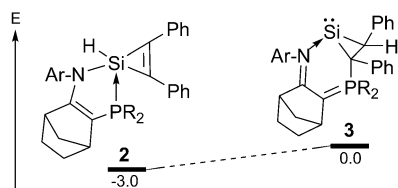


Figure 4. Relative energies (kcal mol^{-1}) of isomers **2** and **3**.

valent silicon species is, to the best of our knowledge, unprecedented. Calculations indicate that isomers **2** and **3** are very close in energy ($\Delta E_{3-2} = +3.2 \text{ kcal mol}^{-1}$). This is probably due to the efficient stabilization of the Si^{II} center in **3** by coordination of the iminophosphorus ylide fragment.

In conclusion, we have successfully synthesized an N-donor-stabilized silacyclopent-1-ylidene **3** through the isomerization of tetravalent silirene **2** under mild conditions. This process involves an unprecedented $\text{Si}^{\text{IV}} \rightarrow \text{Si}^{\text{II}}$ rearrangement. Further investigations on the reactivity of this new species are underway.

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