Silenes

DOI: 10.1002/anie.201304594

# A Stable Silene Substituted by Strong π-Donors at the Silicon Center**

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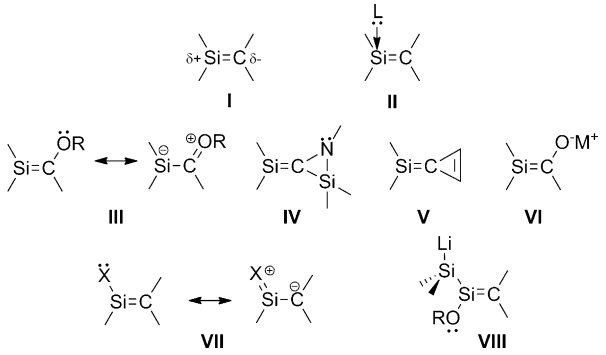
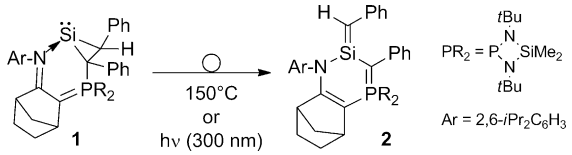
Since the first isolation of a stable silene by Brook et al. in 1981,[1] the chemistry of these species featuring a silicon–carbon double bond has been the subject of many studies.[2] The high reactivity of silenes **I** is mainly due to the SiC double




bond, which is naturally polarized towards carbon ($Si^{\delta+}=C^{\delta-}$), as C is more electronegative than Si. Therefore, the electrophilic silicon center can be stabilized by Lewis bases, leading to adducts **II**.[3] However, silenes with a reversed SiC bond polarization, arising from the presence of π-donating substituents at C (**III**[1,4,5] and **IV**),[6] or to the fulvalene-type structure **V**,[7] show a considerably enhanced stability and an elongated SiC double bond. It is clear that the substitution pattern considerably influences the reactivity and the stability of silenes derivatives.

Despite intense research efforts over the past three decades, only a few types of stable silenes are available. Particularly, although there are several C-substituted silenes by π-donors **III** and **IV**,[6] including anionic 2-silenolates **VI**,[8] very few studies on related Si-substituted silenes **VII** have been realized. Only one example of a silene featuring two potentially π-donors on silicon (**VIII**) has been isolated. However, in this silyl-anion-Si-substituted silene **VIII**, the π-interaction between the substituents and the silene moiety is not significant.[9] Herein, we report a synthesis of a stable and isolable silene **2** (type **VII**) by an isomerization of sila-cyclopropylidene **1**. This silene **2** substituted at silicon by two strong π-donating substituents, such as amino- and phosphonium ylide groups, possess unique properties and is an excellent ligand for transition metals.

We recently reported the synthesis of the base-stabilized sila-cyclopropylidene **1**.[10] Despite its strained cyclic structure, **1** is quite stable and can be easily handled at room temperature under inert conditions. However, simply by heating a few hours a toluene solution of **1** at 150 °C, under pressure, an original isomerization, involving a ring-opening reaction of sila-cyclopropylidene fragment, led to the formation of silene **2**, which was isolated as orange crystals in 76 % yield (Scheme 1). The same result was obtained by the




***Scheme 1.*** Synthesis of silene **2**.

photolysis of **1** ($\lambda = 300$ nm) in toluene solution at room temperature. The stereoselectivity of the rearrangement was indicated by the presence of only one singlet in $^{31}P$ NMR at $\delta = 27.4$ ppm. The $^{29}Si$ NMR spectrum exhibits a doublet signal at $\delta = 74.7$ ppm ($^2J_{PSi} = 24.0$ Hz), which is within the range of values previously observed for silenes ($\delta = 41$–145 ppm).[2a] However, the resonances observed for the silene carbon ($\delta = 60.9$ ppm, $^3J_{CP} = 6.1$ Hz), and the C–H proton ($\delta = 3.15$ ppm), appear at significantly higher field compared to those observed for other silenes, in $^{13}C$ and $^1H$ NMR, respectively.[11] These NMR data clearly suggest an enhanced polarization of the silene moiety Si=C towards the carbon atom, which is probably due to the presence of the π-donating substituents on the silicon atom (resonance structures **A** and **B** in Scheme 2).

The molecular structure of **2**[12] reveals an essentially planar six-membered heterocycle (sum of interior angles: 719.2°), including a trigonal planar silicon atom ($\Sigma°_{Si\alpha} =$

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[**] We are grateful to the CNRS, the ANR (NOPROBLEM) and the European Research Council (ERC Starting grant agreement no. 306658) for financial support of this work. N.N. acknowledges the JSPS for Young Researcher Overseas Visits Program for Vitalizing Brain Circulation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304594.


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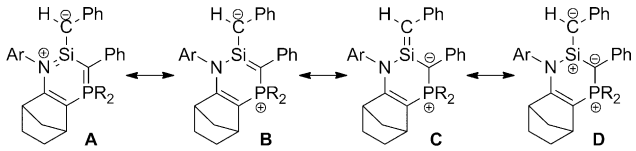



***Scheme 2.*** Important resonance structures of **2** (other than the structure given in Scheme 1).

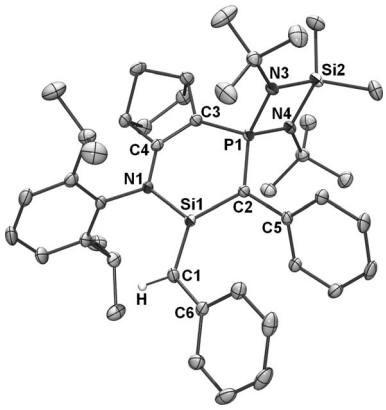



***Figure 1.*** Molecular structure of **2**. Ellipsoids are set at 30% probability; H atoms except for that on C1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.725(2), Si1–C2 1.766(2), C2–P1 1.706(2), P1–C3 1.748(2), C3–C4 1.363(3), C4–N1 1.380(2), Si1–N1 1.739(2); Si1-C1-C6 126.97(15), C1-Si1-N1 116.77(8), C1-Si1-C2 131.48(9), N1-Si1-C2 111.76(8), Si1-C2-P1 121.77(10), C5-C2-P1 118.58(13), C5-C2-Si1 119.64(13).

360.0°, Figure 1). The silene presents a *trans*-configuration between amino group on the silicon atom and the phenyl group on the carbon atom. The phenyl group is oriented to the less-hindered side. The *exo*-cyclic SiC-bond distance (Si1−C1 1.725 Å) is at the short end of those observed for SiC double bonds (1.702–1.778 Å).[2a,6,13,14] The *endo*-cyclic SiC bond is also quite short (Si1−C2 1.766 Å) and is as short as those observed for Brook's silenes (1.764 Å),[4] indicating a strong π-delocalization of ylidic lone pair (resonance structure **B** and **C**, Scheme 2). In contrast, the relatively long Si1−N1 bond (1.739 Å)[15] suggests a weak π-donation of the amino group (resonance structure **A**). Of particular interest, despite the presence of two strong π-donating substituents on silicon atom, there is no significant elongation of the *exo*-cyclic Si=C bond.

To gain more insight into silene **2**, DFT calculations at the M06/6-31G** level were performed.[16] The calculated geometry of **2** is in good agreement with the experimental structure.[17] The HOMO of **2** (Figure 2) corresponds mainly to the exocyclic Si−C π-bonding system. The HOMO−1 is localized on the endocyclic Si=C bond as a consequence of an important interaction of the phosphonium ylide function with the silene moiety. Probably because of this interaction, the energy level of the HOMO (−4.11 eV) is considerably high implying the enhancement of the nucleophilicity of **2**. The LUMO is not localized on the Si−C fragment but it corresponds to the π-conjugating system of the enamine fragment. The antibonding $\pi^*_{SiC}$ orbital is slightly higher in

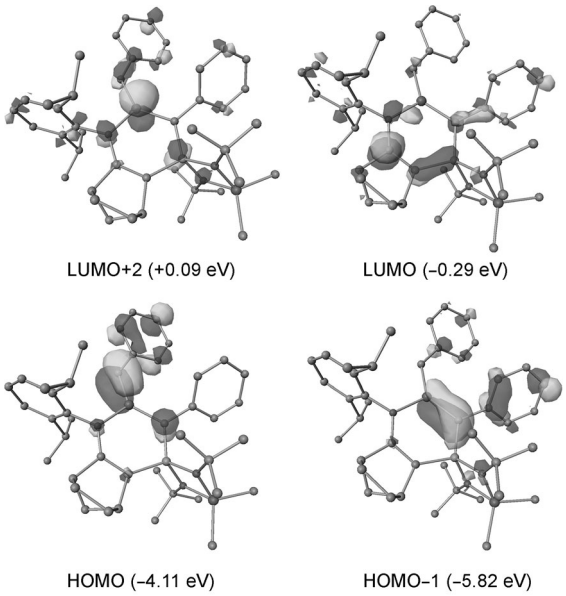
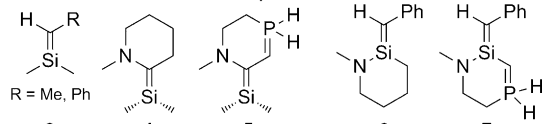



***Figure 2.*** Calculated molecular orbitals of **2** at 0.05 cut-off level. Energy levels of Kohn–Sham orbitals are in parentheses.

energy (LUMO + 2). Nevertheless, the π–π*(Si=C) energy gap is still very small (3.82 eV). The high stereoselectivity observed in the formation of **2** can be explained by an easy *cis–trans* isomerization, which is due to a relatively small energy barrier for rotation of Si=C fragment to 90° (30–36 kcal mol$^{-1}$).[18]

Of particular interest, the NBO charge analysis indicates no significant increase of the negative charge on the terminal carbon atom, despite the presence of two strong π-donating substituents on silicon. In fact, the charge distribution within the silene fragment in **2** ($q_C$ −1.08, $q_{Si}$ +1.83) is almost the same as those for the silene **3-Ph** without donating substituents ($q_C$ −0.96, $q_{Si}$ +1.60, Table 1). Besides, a large negative charge remains on the ylidic carbon of **2** ($q_{C2}$ −1.32). These results are in agreement with the absence of any significant π-donating effects of the substituents on silicon atom. Thereby,

***Table 1:*** Structural and electronic parameters of different silenes.[a]




**3** **4** **5** **6** **7**

| Entry | Si=C [Å] | $q_C$[b] | $q_{Si}$[b] | $E_{HOMO}$ [eV] | $E_{HOMO-LUMO}$ [eV] |
|---|---|---|---|---|---|
| **3-Me** | 1.709[c] | −0.96 | 1.54 | −5.35 | 5.67 |
| **4** | 1.816[d] | −0.28 | 1.14 | −4.32 | 3.91 |
| **5** | 1.914[d] | −0.19 | 0.93 | −3.83 | 3.09 |
| **3-Ph** | 1.719[c] | −0.96 | 1.60 | −5.16 | 4.51 |
| **6** | 1.718[c] | −1.04 | 1.79 | −4.77 | 4.54 |
| **7** | 1.721[c] | −1.07 | 1.84 | −4.19 | 4.40 |
| **2** | 1.727[c] | −1.08 | 1.83 | −4.11 | 4.20[e] |

[a] Calculated at the M06/6-31G** level. [b] NBO charges of silene fragment. [c] Silene fragment is essentially planar [d] Si center is pyramidalized: $\Sigma°_{Si}$ = 334.0 (**6**), 308.2 (**7**). [e] $\Delta E_{(HOMO-LUMO+2)}$.

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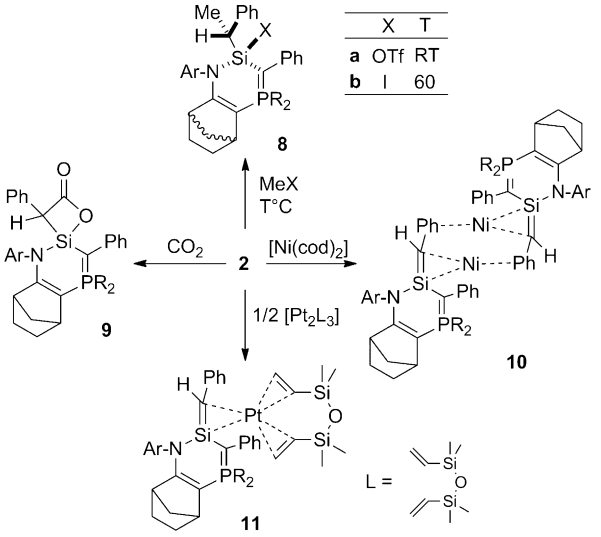
the two considerably short Si–C bond distances would be probably attributed to a coulombic stabilization resulting from the strongly polarized C1-Si1-C2 fragment (**D**; Scheme 2). A similar alternation of charges, with a weak allylic resonance contribution, was theoretically predicted for the 2-sila-allyl anion,[19] as well as for the related bis(methylene)phosphoranes.[20]

The effects of π-donating substituents on silene fragment are totally different depending on their positions (Si or C atom). Indeed, one or two π-donors, such as amino and phosphonium ylide groups, on the carbon atom considerably alter both structural and electronic properties of the corresponding silenes (**4**, **5** in Table 1). This C-substitution with π-donating substituents induces a significantly elongated Si=C bond with a pyramidalized silicon center.[5] Besides, this effect results in a significant diminution of polarity of Si=C fragment and a decrease of HOMO–LUMO gap. In marked contrast, the introduction of the same type of substituents on silicon atom (**6**, **7**) does not induce detectable changes in the silene function. Indeed, in the case of silenes (**6**, **7**), there is no significant alterations neither in their geometry nor in the charge distributions ($q_C$ and $q_{Si}$) compared to those of **3-Ph**. It affects only the HOMO energy level, which is significantly increased, but the HOMO–LUMO gap remains approximately the same.

The nucleophilic character of the silene **2** was confirmed by its reactions with different electrophilic reagents (Scheme 3). In particular, silene **2** readily reacts with methyl




***Scheme 3.*** The reaction of **2** with $CO_2$, electrophiles (RX), $[Ni(cod)_2]$, and $[Pt_2L_3]$. cod = cyclooctadiene.

trifluoromethanesulfonate to give the corresponding C-methylated 1,2-adduct **8a** with the triflate group on the silicon center. The reaction affords exclusively the *anti* adduct as a mixture of two diastereomers (55:45). This was confirmed by the X-ray diffraction analysis of **8a**, which shows the co-crystallization of the two diastereomers in the same single crystal (Figure 3).[12] Silene **2** also reacts with the less reactive methyl iodide, at 60 °C, to give the corresponding *anti* adduct

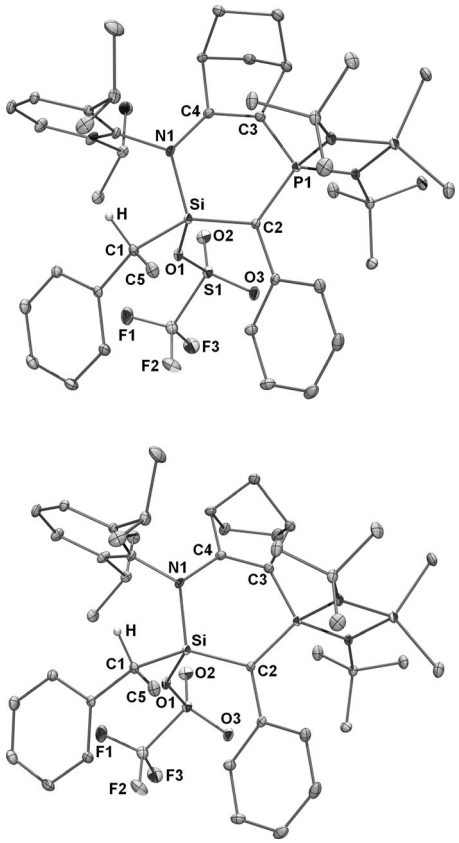



***Figure 3.*** Molecular structures of **8a** (two diastereomers). Ellipsoids are set at 10% probability; H atoms, except for that on C1, are omitted for clarity.

**8b** also as a mixture of two diastereomers (57:43). An original [2+2] cycloaddition was observed with $CO_2$, leading to the formation of a silicon-containing β-lactone **9**.[12] A similar type of cycloaddition, involving a silene and an aldehyde, has already been reported.[21]

Of particular interest, silene **2** appears to be an interesting new ligand for transition-metal complexes and it readily reacts with $[Ni(cod)_2]$ and Karstedt's $Pt^0$ species[26] to afford the corresponding $\eta^2$-silene–$Ni^0$($\eta^6$-arene) complex **10**[22] and $\eta^2$-silene–$Pt^0$ complex **11**, respectively. Both complexes were isolated in crystalline form in relatively good yields (**10**, red crystals, 78%; **11**, yellow crystals, 56%). Both complexes **10** and **11** were characterized in the solid state by an X-ray diffraction analysis (Figure 4 and 5). It is worth noting that this is the first example of a direct synthesis of silene–transition metal complexes involving a stable and isolable silene ligand.[23]

The X-ray diffraction analysis of silene–$Ni^0$ complex **10** reveals a dimeric structure involving the $\eta^6$-coordination of the phenyl groups to the Ni centers (Figure 4). The exocyclic SiC bond (1.825 Å) is considerably elongated compared to free ligand **2** (1.725 Å), and the silicon center is strongly pyramidalized ($\Sigma_{Si}° = 343.6°$). The remarkably short Ni–Si1 bond length (2.181 Å) is at the long end of those observed for silylene–$Ni^0$ σ-complexes (2.06–2.22 Å),[22,24] although the Ni–C1 bond length (2.000 Å) is typical for $\eta^2$-olefin–Ni com-

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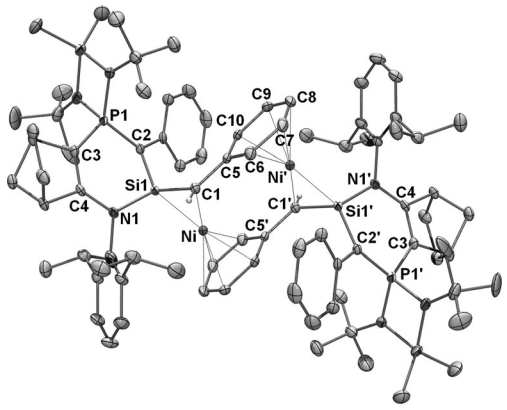


***Figure 4.*** Molecular structure of **10**. Ellipsoids are set at 30% probability; H atoms, except for that on C1 and disorder are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.825(3), Ni–C1 2.000(3), Ni–Si1 2.181(1), Si1–N1 1.787(2), Si1–C2 1.824(3), C2–P1 1.699(3); C1-Si1-Ni 59.10(8), Si1-C1-Ni 69.36(9), C1-Ni-Si1 51.54(7), N1-Si1-C2 109.15(11), N1-Si1-C1 110.02(11), C2-Si1-C1 124.40(11).

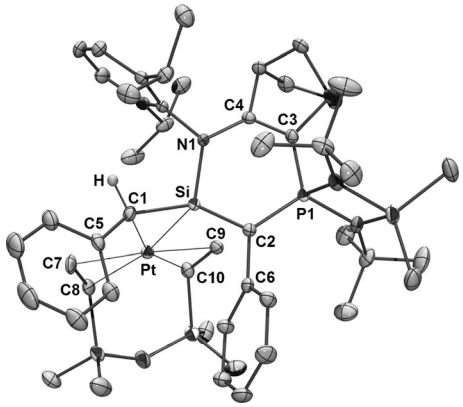


***Figure 5.*** Molecular structure of **11**. Ellipsoids are set at 30% probability; H atoms except for that on C1, disorder and solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Si1 1.802(3), Si1–N1 1.772(2), Si1–C2 1.812(3), C1–C5 1.470(4), Si1–Pt 2.440(1), C1–Pt 2.236(3), C2–P1 1.705(3); C1-Si1-Pt 61.47(9), Si1-C1-Pt 73.45(9), C1-Pt-Si1 45.07(7), N1-Si1-C2 110.71(11), C1-Si1-N1 108.92(12), C1-Si1-C2 131.42(13).

plexes.[25] These results are in agreement with a π-coordination of silene on the Ni center with significant π-back donation. Indeed, similar structural data were observed in the case of the previously reported $\eta^2$-silene–$Pt^0$ complex (Si–C: 1.838 Å, $\Sigma_{Si}° = 353°$), which presents a hybrid structure between π-complex and σ-bonded compound.[23] In contrast, silene–$Pt^0$ complex **11** presents a higher π-complex character (Figure 5).[12] Indeed, the Pt–silene distances are quite long (Si1–Pt 2.440 Å, C1–Pt 2.236 Å) and the Si1–C1 bond length remains relatively short (1.802 Å) compared to those observed in the related complex with a $PCy_3$ ligand.[23] This different bonding situation could be attributed to the presence in **11** of an electron-withdrawing vinyldisiloxane ligand on Pt, instead of a strong electron-donating phosphine ligand, which decreases the π-back-donation from the metal to the silene ligand.

In conclusion, we have successfully synthesized a stable and isolable silene with two strongly π-donating groups on the silicon center. This Si-substituted silene clearly shows particular π-substituent effects, which are completely different to those observed in the case of C-substituted silenes. Indeed, the presence of π-donating substituents on the silicon atom only affects the energy level of molecular orbitals (increased HOMO level). In other words, the Si-substituted silene presents intrinsic silene properties with a strong electron-donating character. Probably because of these unique properties, silene **2** is a stable and excellent π-coordinating ligand for transition metals. Currently, we are exploring the coordination chemistry of silenes, which was underdeveloped up to now, using the new stable silene **2**.

Received: May 28, 2013
Revised: July 15, 2013
Published online: September 2, 2013

**Keywords:** complexes · silenes · silylenes · transition metals · ylides

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