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Silicon Chemistry

Aromatic Ylide-Stabilized Carbocyclic Silylene**

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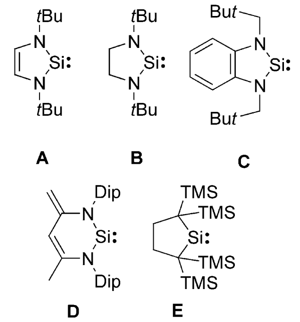
Dedicated to Professor Gottfried Huttner

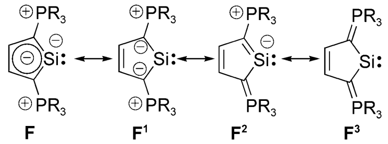
The chemistry of stable silylenes has been the subject of considerable research since the first isolation of the N-heterocyclic silylene (NHSi) **A** in 1994 (Scheme 1).[1] However, while the chemistry of stable carbenes, which began only a few years earlier, has led to a wide array of systems using a variety of stabilization modes,[2] silylene systems are less developed. To date cyclic silylenes have been limited to the three five-membered NHSis **A**,[1,3] **B**,[4] and **C**[5], the six-membered NHSi **D**[6], and the cyclic dialkylsilylene **E**.[7] In addition to these more classical silylenes there are also several examples of stable Si^{II} silylenoid species, wherein the silicon center has a coordination number greater than two.[8]



Scheme 1. N-heterocyclic silylenes **A**–**D**, and the cyclic dialkylsilylene **E**. Dip = 2,6-diisopropylphenyl, TMS = trimethylsilyl.

Among stable cyclic silylenes, the most common mode of stabilization, as with carbenes, is the use of nitrogen substituents, which act as excellent π donors and strong σ acceptors because of their lone pair of electrons and high electronegativity, respectively. The one exception is silylene **E**, which is stabilized sterically through protection of Si by the four trimethylsilyl groups and electronically by hyperconjugation of the Si–C bonds into the vacant 3p orbital on the silicon center as well as decreased σ-acceptor properties of the alkyl groups. These different methods of stabilization lead to significantly different properties and reactivities. The reactivities of both NHSis and cyclocarbosilylene **E** have been extensively studied and reviewed.[9]

Considering the significant chemistry that has already been developed for stable silylenes given their unique and varied reactivity, and potential as ligands for transition metals,[9] we set out to develop a new type of silylene having more electropositive carbon-based π-donating substituents, which should lead to an electronic stabilization intermediate to those of NHSis and the cyclic carbosilylene **E**. Carbanionic substituents were targeted because the π donation of such a substituent should match that of the nitrogen atom in NHSis and the less electronegative carbon atom is a poorer σ acceptor.[10] For the silylene to be neutral the carbanionic substituents can be additionally stabilized as part of a phosphous ylide. In fact, the use of a single ylide has been exploited in carbene chemistry to synthesize amino ylide carbenes.[11] With these constraints in mind the silylene **F** would be an ideal target (Scheme 2). In this case, not only is the low-valent silicon center electronically stabilized by the anionic carbon atoms of the two ylide groups as in $\mathbf{F^1}$, but the formally vacant 3p orbital at silicon is additionally stabilized by the aromaticity of the 6π-electron system. A further look at the resonance structures of **F** shows a silacyclopentadiene dianion,[12] which emphasizes the aromatic character,[13] the anionic sila vinyl betaine-like $\mathbf{F^2}$, and the neutral $\mathbf{F^3}$. Each of these resonance forms highlights potentially interesting chemical and physical properties that such a silylene may have and therefore we set about to develop a suitable synthetic route to such a species.



Scheme 2. Resonance structures of the carbocyclic ylide-stabilized silylene **F**.

There are only two methods by which free, stable silylenes can be formed. The most common method is the reduction of a dihalosilane precursor with elemental alkali metals. Recently, it has been shown that the treatment of monohalosilane precursors with strong bases can generate certain silylenes although the limitations of this methodology have not been fully explored.[14] In our case we opted to first explore the more common reduction method. Therefore the dibromosilanes **2** would be ideal precursors for the desired silylenes **3**. We applied a known synthetic methodology that could be modified to generate the desired dibromosilanes **2**

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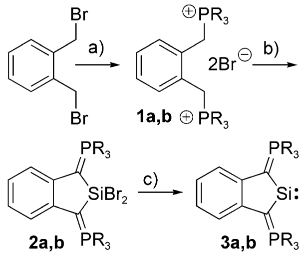


1a, 2a, 3a: R = Ph
1b, 2b, 3b: R = *m*-tol

Scheme 3. Synthesis of silylene **3**. a) PR_3 in refluxing toluene; b) KHMDS, $SiBr_4$ in toluene at −78°, c) KC_8 in THF or DME. DME = dimethoxyethane, THF = tetrahydrofuran. Experimental details are given in the Supporting Information.

from the corresponding bisphosphonium salts **1** (Scheme 3).[15] The synthesis is straightforward, starting from α,α′-dibromo-*ortho*-xylene, which, upon addition of two equivalents of triaryl phosphane, leads to the diphosphonium salts **1** in high yield (**1a** = 94 %, **1b** = 94 %). The next step is a one-pot reaction of **1** with four molar equivalents of potassium hexamethyldisilazide (KHMDS) in the presence of $SiBr_4$. The resultant dibromosilanes **2** can be isolated in good yield (**2a** = 72 %, **2b** = 86 %) and were fully characterized by multinuclear NMR spectroscopy, as well as by X-ray crystallography in the case of **2a** (Figure 1).[16]

Initial efforts to reduce the dibromosilane **2a** led to mixed results. The reduction of **2a** using two equivalents of KC_8 in THF led to a color change from orange to dark red. The crude reaction mixture was analyzed by ^{31}P NMR spectroscopy, and a mixture of starting material ($\delta = 12.0$ ppm) and a new product ($\delta = 17.3$ ppm) were observed. However, extended reaction times did not lead to complete conversion but rather decomposition into a compound having a very broad signal at $\delta \approx 8$ ppm in the ^{31}P NMR spectrum. Such broad signals are typical of polymeric species and indicate that perhaps the new species was not stable in THF because of its highly basic character. Therefore efforts were made to perform the reduction in other solvents using different reducing agents. The best results were achieved using Jones's $LMg^I–Mg^IL$ (L = $[(Mes)NC(Me)]_2CH$, Mes = 2,4,6-trimethylphenyl) as a reducing agent in benzene.[17] The benzene solution of the reaction mixture was analyzed by ^{31}P NMR spectroscopy and found to contain almost exclusively the desired product as indicated by the signal at $\delta = 17.3$ ppm. Furthermore this product was stable in a benzene solution, which allowed the ^{29}Si NMR spectrum to be measured, the result of which was observation of a new signal at $\delta = 213.3$ ppm with a large coupling constant (triplet, $^2J_{SiP} = 38.5$ Hz). As expected for **3a** the signal is shifted significantly downfield from the starting material ($\delta = -16.0$ ppm, triplet, $^2J_{SiP} = 29.3$ Hz). However, this is also far downfield compared to that of the reported NHSis ($\delta = 78$-119 ppm).[1,3–6] The only stable cyclic silylene with a chemical shift further downfield is **E**, which has a signal that appears at $\delta = 567$ ppm.[7] The calculated chemical shift of **3a** does correspond well with the experimental value ($\delta = 243$ ppm).[18] Unfortunately the silylene could not be separated from the LMgBr, thus making characterization by ^1H and ^{13}C NMR spectroscopy impossible.[19] By changing the phenyl groups on phosphorus to a 3-methylphenyl group, the more soluble dibromosilane **2b** could be synthesized. Subsequent efforts to reduce **2b** using KC_8 in DME proved successful. The best results were obtained using a significant molar excess of KC_8 (3 equiv) and the reaction had to be monitored by ^{31}P NMR spectroscopy. Upon completion (ca. 2–3 hr) the DME was immediately removed in vacuo and the silylene **3b** was extracted in toluene. The ^{29}Si and ^{31}P NMR spectra and respective coupling constants were nearly identical to those of **3a** ($\delta = 212.4$ and 18.6 ppm, respectively). In this case ^1H and ^{13}C NMR spectra of pure **3b** could be measured. The only signal of particular note is that of the ylidic carbon atom in the ^{13}C NMR spectrum. In **2b** the ylidic carbon atom has a chemical shift of $\delta = 37.2$ ppm and is coupled to both phosphorus nuclei ($^1J_{CP} = 114.7$ Hz and $^3J_{CP} = 10.3$ Hz) to give a doublet of doublets. In the silylene **3b** the ylidic carbon atom appears downfield at $\delta = 90.3$ ppm as a doublet of doublets ($^1J_{CP} = 75.0$ Hz and $^3J_{CP} = 16.1$ Hz), which is atypical for the carbanionic center of a phosphorus ylide, but does corresponds well with the calculated value ($\delta = 97.5$ ppm).[18] Such a change in chemical shift is easily understood by the generation of a ring current in the silacyclopentadienide-like system as highlighted by the resonance structure **F**^{1}. In fact the chemical shift is remarkably similar to that of cyclopentadienide ($\delta = 95$ ppm). Furthermore, the silylene **3b** could be characterized by atmospheric pressure chemical ionization HRMS (APCI/HRMS), where the protonated silylene $\mathbf{3b}{\cdot}H^+$ could be observed (calculated = 737.2922—Found = 737.2928) with the appropriate isotopic distribution.

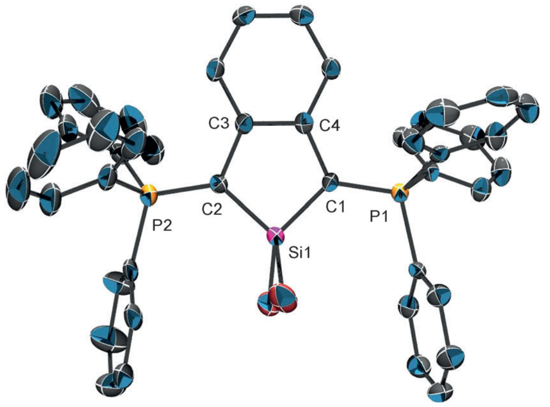
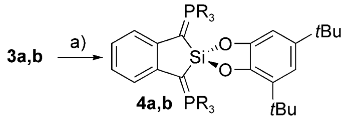


Figure 1. Molecular structure of **2a**. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Repeated efforts to grow single crystals suitable for X-ray diffraction analysis were unfortunately unsuccessful. Whereas the silylenes **3** appear to be remarkably stable in aromatic solvents (no significant change observed by NMR spectroscopy after three months at room temperature), slow decomposition occurs in some ethereal solvents (especially THF, but also slowly in DME) and they are highly sensitive to oxygen and moisture. Therefore to further confirm the generation of the silylenes **3**, several trapping reactions were performed. Interestingly, the silylene **3b** is stable for several days at 60 °C



Scheme 4. Synthesis of compound **4a**,**b**. a) 3,5-di-*tert*-butyl-*ortho*-benzoquinone in THF (**4a**) or toluene (**4b**) at −78 °C. Experimental details are given in the Supporting Information.

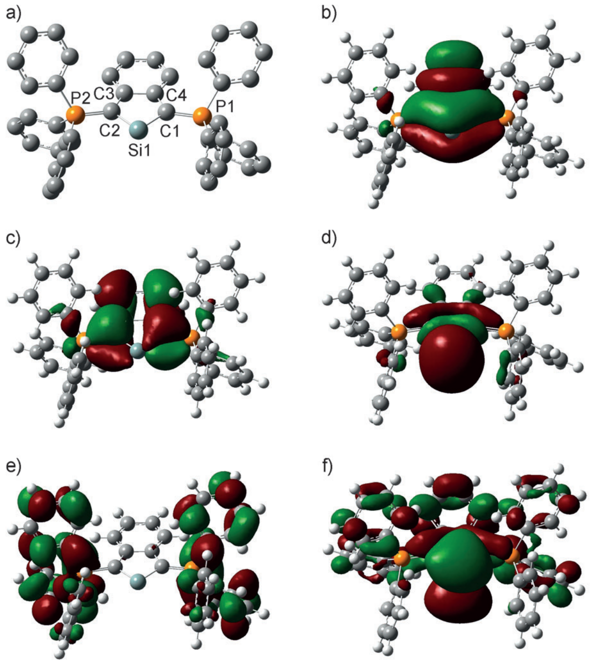


Figure 2. a) Calculated structure of silylene **3a** [B3LYP/6-31G(d) level]. Calculated molecular orbitals of silylene **3a** [HF/6-311G(d)//B3LYP/6-31G(d)]. b) HOMO, c) HOMO−1, d) HOMO−2, e) LUMO, f) LUMO+8.

in the presence of triethylsilane. Some decomposition occurs slowly (indicated by the broad peak at $\delta \approx 8$ ppm in ^{31}P NMR spectra) but no insertion product could be seen observed from the ^{31}P and ^{1}H NMR spectra. Treatment of silylenes **3** with 3,5-di-*tert*-butyl-*o*-benzoquinone, on the other hand, generated the [4+1] cycloaddition products **4** (Scheme 4). This type of cyclization reaction has been demonstrated with several other silylene systems.[20] In the case of **3a** we found that use of a large excess of KC_8 (3–4 equiv) in THF would generate the silylene rapidly enough to obtain near complete conversion with minimal decomposition. Thus this THF solution could be added immediately to a solution of the *ortho*-benzoquinone at −78 °C. In the case of **3b** the silylene was extracted in toluene and added to the *ortho*-benzoquinone at −78 °C. The ^{31}P NMR spectra of **4a**–**b** show a single peak (singlets at $\delta = 11.4$ and 10.7 ppm, respectively) as does the ^{29}Si NMR spectrum (triplets at $\delta = 15.4$ and 15.5 ppm; $^{2}J_{SiP} =$ 26.2 and 25.3 Hz, respectively). As expected, these signals are similar to those of **2** and indicate a phosphorus ylide system with a tetracoordinated Si center. Compounds **4a**–**b** were also fully characterized by ^{1}H and ^{13}C NMR spectroscopy and APCI/HRMS. Of note is the shift of the signal for the ylidic carbon atom from $\delta \approx 90$ ppm to a chemical shift more typical of such ylide species (**4a**: $\delta = 30.7$ ppm and **4b**: $\delta = 31.8$ ppm). The formation of spirocyclic silanes **4** is further evidence that silylenes **3** are generated.

To have a better understanding of the structural and electronic properties of this new type of carbocyclic silylene DFT calculations [B3LYP/6-31G(d)] of compounds **2a** and **3a** were performed. The calculated structural parameters of **2a** closely matched those found in the crystal structures. The optimized structure of **3a** is shown in Figure 2a.[18]

A closer look at the electronics of the silylene **3a** shows some interesting features. The HOMO is comprised of the 10-electron system and appears to include the P−C ylide bond (Figure 2b). This orbital is similar to the HOMO of the unsaturated NHSi **A**.[21] The HOMO−1 orbital is also a π-bonding orbital of the ring system (Figure 2c). The orbital containing the lone pair of electrons is the HOMO−2 orbital (Figure 2d), which is different from that of NHSis where the orbital containing the lone pair of electrons is the HOMO−1. This difference indicates that the π system significantly stabilizes the lone pair of electrons in **3a**. Another significant difference is the LUMO, which for NHSis has significant π character that is located principally at the Si center. The LUMO of **3a** on the other hand is restricted to the triphenylphosphine substituents (Figure 2e). The lowest unoccupied molecular orbital with significant π character on silicon is the LUMO+8 (Figure 2 f; 0.34 eV higher in energy than the HOMO), which is an indication that the silylene center may be electron-rich compared to that of NHSis and is thus less electrophilic.

Bond lengths, angles, and the Wiberg bond index (WBI) for the calculated compounds **2a** and **3a** can be found in Table 1. Upon examination there are several interesting features that are apparent. First, the angle at the silylene center decreases significantly because of the lone pair of electrons, which causes the Si−C bonds to elongate somewhat. However, the WBI indicates these Si−C bonds actually have a slightly higher bond order, which is in agreement with a silacyclopentadienide-like structure **F**. Second, in both **2a** and **3a** the P−C ylide bonds are somewhat longer than typical unstabilized ylide bonds (ca. 1.66 Å)[22] but there is no significant difference between the dibromosilane and the silylene. However, upon inspection of the natural bonding orbitals (NBOs) some clarification of the nature of the bonding can be obtained. NBO analysis shows that the P−C ylide bond loses π-bonding character, while the C1−C4 and C2−C3 bonds become polarized π bonds. Additionally, the Si center has a partially occupied p orbital (classified as a lone-pair orbital at silicon with exclusively 3p character and an

Table 1: Selected bond lengths [Å], WBI, and bond angles [°] for the calculated compounds **2a** and **3a**.

	2a		**3a**	
	Bond length	WBI	Bond length	WBI
C1-Si1	1.814	0.7824	1.871	0.8869
C1-P1	1.709	1.1198	1.719	1.1359
C1-C4	1.477	1.1190	1.461	1.1637
C3-C4	1.441	1.2438	1.440	1.2337
C1-Si1-C2	95.69°		86.94°	
Si1-C1-C4	107.04°		113.70°	

occupancy of 0.499 electrons). These orbitals create the conjugated π system required for aromaticity. To further probe the aromatic character of **3a** nucleus-independent chemical shift (NICS)[23] calculations were performed. The NICS(1)[24] value of −4.0, does indicate aromatic character. As can be seen in the HOMO (Figure 2b) the π system is also delocalized into the phosphorus ylide moiety, which may explain the lack of a larger NICS(1) value; however, overall **3a** has the characteristics of an aromatic system.[11c]

In conclusion, the synthesis of a new type of carbocyclic silylene has been reported. This new type of silylene is stabilized by two phophorus ylide functionalities and has considerable aromatic character. Calculations indicate that this silylene should have an electron-rich silicon center. This characteristic in addition to the cyclopentadienide-like structure **F** suggest that the silylenes **3** should have reactivities and coordination properties that differ from other known silylenes (**A**–**E**). Studies of the reactivity as well as the use of **3** as a ligand to transition metals are currently underway.

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[19] A silylene→Mg complex could not be detected in solution at ambient temperature. Only "free" **3a** and LMgBr are observed by ^{1}H and ^{13}C NMR spectroscopy.

[20] Silylene **3b** also reacts with 2,3-dimethyl-1,3-butadiene to give complex reaction mixtures. The silylene **3b** was consumed but no product could be isolated and identified. For examples of [4+1] cyclization reactions, see: a) R. Azhakar, R. S. Ghadwal, H. W. Roesky, J. Hey, D. Stalke, *Organometallics* **2011**, *30*, 3853; b) M. Haaf, A. Schmiedl, T. A. Schmedake, D. R. Powell, A. J. Millevolte, M. Denk, R. West, *J. Am. Chem. Soc.* **1998**, *120*, 12714; c) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1998**, *17*, 1378; d) B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1997**, *16*, 4861.

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