Isolation of a Stable, Acyclic, Two-Coordinate Silylene

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ABSTRACT: The synthesis and characterization of a stable, acyclic two-coordinate silylene, Si(SArmès)₂, (Armès = CsH₃-2,6(C₆H₅-2,4,6-Me₃)₃) by reduction of Br₂Si(SArmès)₂, with a magnesium(I) reductant is described. It features a v-shaped silicon coordination with a S-Si-S angle of 90.52(2)° and an average Si-S distance of 2.158(3) Å. Although it reacts readily with an alkyl halide, it does not react with hydrogen under ambient conditions probably as a result of the ca. 4.3 eV energy difference between the frontier silicon lone pair and 3p orbitals.

For several decades, silylenes, the silicon analogues of carbenedes, had been known only as transient species either in the gas phase, in solution, or trapped in frozen matrices.¹ ² ³ In 1986, Jutzi and coworkers reported the isolation of decamethylsilycencene which was the first monomeric, divalent silicon(II) compound that was stable at room temperature.⁴ The formally ten-coordinate Si(η³-C₅Me₅)₂ exists as two conformers; a centrosymmetric species with parallel C₅Me₅ rings or a bent form with a 25.3° interplanar angle. In 1994, the synthesis and structure of a two-coordinate, N-heterocyclic silylene, in which silicon is single bonded to two nitrogens, was reported by West and coworkers.⁵ Currently, numerous stable divalent silicon species are known⁶ ⁷ ⁸ ⁹ ¹⁰ but strictly two-coordinate species invariably involve silicon as part of a ring with the most common being the aforementioned N-heterocyclic silylenes.¹⁰ A cyclic alkyl silylene, which is stable at 0 °C, was reported by Kira but it isomerizes in solution via a 1,2-migration of an adjacent trimethylsilyl group to give a silene.¹¹ Other examples include the bisamido derivative Si[NPr']₂, which exists in a monomer/dimer equilibrium with the SiSi double-bonded disilene [Si[NPr']₂]₂,¹² as well as Si[NSiMe₅]₂, which persists for more than 12 h at -20 °C but decomposes into a complex mixture of products at increased temperatures.¹³ We now report that the reduction of the silicon(IV) precursor, Br₂Si(SArmès)₂ (1) (Armès = CsH₃-2,6(C₆H₅-2,4,6-Me₃)₃), affords the silicon dithiolate, Si(SArmès)₂ (2), which has a monomeric, two-coordinate structure and is an example of a stable acyclic two-coordinate silylene. In addition, the Si(IV) bisthiolatosilane 3 was prepared in order to compare its structural and spectroscopic parameters with those of 2. Furthermore, 2 was characterized by its derivatization with MeI to afford Si(Me)(I)(SAr₆Me₅)₂ (4). An overview of the synthesis is given in Scheme 1.

![Scheme 1: Synthesis of Silylene 2 by Reduction of 1.](image)

The precursor, 1, was obtained by reaction of SiBr₄ with Li[SArmès]₂ in diethyl ether.¹⁴ ¹⁵ and 2 was synthesized by reduction with Jones’ complex (IMesMg)₂ (IMes = [(2,4,6-trimethylphenyl)NC(CH₃)]₂CH) complex in toluene.¹⁶ ¹⁷ The yellow solution of Br₂Si(SArmès)₂ became darker with concomitant precipitation of IMesMgBr upon stirring for 2 days at ca. 25°C. Workup afforded colorless crystals of 2 in moderate yield (51%). The silylene, 2, was found to be stable up to 146 °C. The X-ray crystal structure of 2 (Figure 1) showed that the silicon bonds to two thiolate sulfurs with a S-Si-S angle of 90.52(19)°. The Si-S distances are 2.1607(5) and 2.1560(5) Å and the Si-S-C angles are 100.85(5) and 105.01(4)°. The closest other approaches to silicon involving C(7) and C(12) at 3.004(1) and 3.232(1) Å as well as C(31) and C(32) at 3.052(1) and 3.293(1) Å respectively. The Si-centroid distances to the rings are 3.453 and 3.419 Å.
The electronic transitions were calculated by the TD-DFT approach using the same functional-basis set combination as employed in the geometry optimization. The Kohn-Sham orbitals for 2 are shown in Figure 2. The calculations reveal several excitations at wavelengths between 250-400 nm although only the five strongest predicted absorptions are discussed here. The calculated values may be compared to the four transitions observed in the electronic spectrum. The HOMO-LUMO (silicon n → 3p) absorption appears as a shoulder at 382 nm (ε = 8900 M·cm⁻¹). A more intense absorption at 318 nm (ε = 23,000 M·cm⁻¹) (HOMO-1 → LUMO) corresponds to a transition from a sulfur lone pair to the silicon 3p orbital. The calculated absorption at 296 nm corresponds to the HOMO → LUMO+1 transition but is partly obscured by other absorptions that are close in energy. It arises from transitions between the silicon lone pair to the arene π* orbitals. The absorptions at 291 (ε = 20,000 M·cm⁻¹) and 269 (ε = 25,000 M·cm⁻¹) are due to an arene π to silicon π transition and from both silicon and sulfur lone pairs to arene π* orbitals respectively. A series of very intense absorptions, centered at ca. 220 nm, correspond to arene π → π* transitions that partially mask the absorptions at 291 and 269 nm. Overall, the experimental and computational values for the spectral data are in good agreement (associated content).

The bisthiolatosilane, 3, (Figure 3) was obtained from HSiCl₃ and (Li₂SiMe₅)₂. The structural data reveal a relatively close resemblance between the structural parameters for the Si[S(C(CH₃)₂)₂]₂ (δ = 78.11) absorptions at 2182 and 2168 cm⁻¹ in the IR spectrum are characteristic of a and b Si-H stretching modes. The addition of Me₂Si to 2 afforded the iodo-methylbisthiolatosilane. Its ²⁹Si NMR spectrum revealed an upfield quartet at δ = -5.88 (J₆₋₅ = 8.3 Hz) A methyl group signal at δ = 2.01 (J₆₋₅ = 8.7 Hz) in the ¹H NMR spectrum and a signal at δ = 11.39 in the ¹³C NMR spectrum is comparable to compounds with similar moieties. Attempts to react 2 directly with hydrogen gas to afford 3 were unsuccessful, possibly because of the relatively high electronegativity of the thiolate substituents which increase the energy separation (4.26eV) of the silicon lone pair and the 3p orbitals and make the synergic interaction between the frontier orbitals of 2 and H₂ less likely. In effect, the electronegative character of the thiolate ligands is a key factor both in the stability of 2 (with some help from Si-S n-bonding), and its reluctance to react with hydrogen. Geometric constraints of the ligands may also hinder the reactivity of 2.

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Table 1: Selected Bond Lengths (Å) and Angles (°) for the Experimental and Calculated Structural Data for 1-3

<table>
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<td>Si-S</td>
<td>2.13(1)</td>
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<tr>
<td>S-C</td>
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<td>1.79(2)*</td>
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<td>3.430*</td>
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<tr>
<td>S-Si</td>
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<td>0.95(1)</td>
<td>0.904</td>
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<tr>
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<td>1.0436</td>
<td>1.078(1)*</td>
<td>1.0705</td>
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* Average.
In summary, a thermally stable, two-coordinate, acyclic silylene stabilized by a bulky terphenyl thiolate ligand has been synthesized and characterized. Until now, stable two-coordinate silylenes have been limited to cyclic systems in which silicon is bound to elements of the 2nd row of the periodic table. Future work will involve the investigation of further reactions of 2 as well as those of its heavier element analogues.

Note: The synthesis and structure of another type of acyclic silylene is given in the preceding paper.3)

ASSOCIATED CONTENT
Supporting Information
Crystallographic information files for 1-3. Experimental details and 1H, 13C and 29Si NMR spectra for 1-4, infrared spectra of 2 and 3, UV-Vis spectrum and table of the experimental and calculated electronic spectra of 2, computational results on the models of compounds 2 and 3, tables of crystallographic data for 1-3 (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES
14. For the synthesis and characterization of 1-4 see the Associated Content.
33. Please cite preceding paper here.