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Isolation of a Stable, Acyclic, Two-Coordinate Silylene

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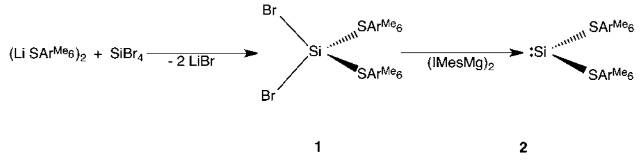
Supporting Information

ABSTRACT: The synthesis and characterization of a stable, acyclic two-coordinate silylene, $Si(SAr^{Me_6})_2$ [Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$], by reduction of $Br_2Si(SAr^{Me_6})_2$ 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 carbenes, had been known only as transient species either in the gas phase, in solution, or trapped in frozen matrices.[1−3] In 1986, however, Jutzi and co-workers reported the isolation of decamethylsilicocene, which was the first monomeric, divalent silicon (II) compound that was stable at room temperature.[4] The formally 10-coordinate Si(η^5-C_5Me_5)$_2$ exists as two conformers: a centrosymmetric species with parallel C_5Me_5 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 co-workers.[5] Currently, numerous stable divalent silicon species are known,[2,6−8] but strictly two-coordinate species invariably involve silicon as part of a ring,[9] 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 $Si(NPr^i_2)_2$, which exists in a monomer/dimer equilibrium with the SiSi double-bonded disilene $\{Si(NPr^i_2)_2\}_2$,[12] as well as $Si\{N(SiMe_3)_2\}_2$, 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, $Br_2Si(SAr^{Me_6})_2$ (**1**) [Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$), affords the silicon dithiolate, $Si(SAr^{Me_6})_2$ (**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 $Si(Me)(I)(SAr^{Me_6})_2$ (**4**). An overview of the synthesis is given in Scheme 1.

Scheme 1. Synthesis of Silylene 2 by Reduction of 1



The precursor, **1**, was obtained by reaction of $SiBr_4$ with $(LiSAr^{Me_6})_2$ in diethyl ether,[14,15] and **2** was synthesized by reduction with Jones's complex, $(IMesMg)_2$ (IMes = [(2,4,6-trimethylphenyl)NC(CH_3)]$_2$CH), in toluene.[16,17] The yellow solution of $Br_2Si(SAr^{Me_6})_2$ 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 90.519(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 involve C(7) and C(12) at 3.004(1) and 3.232(1) Å as well as C(31) and C(32) at

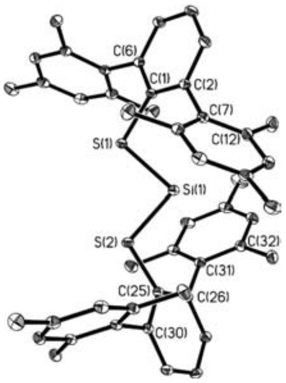


Figure 1. Thermal ellipsoid (30%) plot of **2** without H atoms. Selected bond lengths (Å) and angles (°): Si(1)−S(1) 2.1607(5), Si(1)−S(2) 2.1560(5), S(1)−C(1) 1.7916(13), S(2)−C(25) 1.7902(13), Si(1)−centroid(1) 3.453, Si(1)−centroid(2) 3.419, S(1)−Si(1)−S(2) 90.519(19), C(1)−S(1)−Si(1) 100.85(5), C(25)−S(2)−Si(1) 105.01(4).

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

	1	2		3	
	exptl	exptl	calcd	exptl	calcd
Si−S	2.113(1)	2.158(3)[a]	2.153	2.139(1)[a]	2.143
S−C	1.791(2)[a]	1.791(2)[a]	1.775	1.787(3)[a]	1.778
Si−centroid	4.452[a]	3.431[a]	3.606	3.546[a]	3.649
S−Si−S	100.05(2)	90.52(2)	90.04	93.5(0.9)[a]	95.74
C−S−Si	110.44(8)[a]	102.9(2.1)[a]	104.36	107.8(1.5)[a]	107.05

[a] Average.

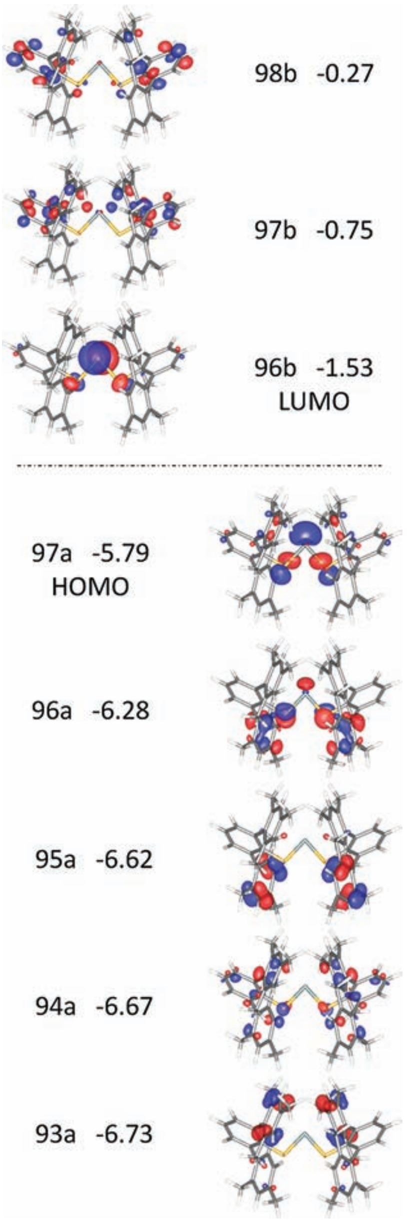

Figure 2. Kohn−Sham molecular orbitals for **2** (orbital energies are given in eV).

3.052(1) and 3.293(1) Å, respectively. The Si−centroid distances to the rings are 3.453 and 3.419 Å.

The Si−S bonds are mainly single in character, as indicated by the calculated Wiberg bond index of 0.95 for the Si−S bonds,[18] although weak Si−S π-bonding may exist, as indicated by computations (vide infra) and the low average torsion angle (13.4(2.1)°) between the coordination plane of silicon and those at the sulfurs.[7a,19,20] The Si−S distances in **2** are longer than those reported for the bisthiolatosilylene platinum complex, *trans*-$(Cy_3P)_2Pt(H)Si(SEt)_2OTf$, by ca. 0.07 Å,[7a] but are comparable to those predicted for 1,2-ethanedisulfide silylene.[20] DFT calculations,[21] using the hybrid PBE1PBE exchange-correlation functional[22] in combination with the def2-TZVP basis set for the whole molecule of **2** and **3**,[23] afforded structural parameters very close to those experimentally measured (Table 1).

The ^{29}Si NMR spectrum of **2** revealed a downfield signal at $\delta = 285.5$ (cf. $\delta = -23.1$ for **1**). The signal is farther downfield than those of cyclic amidosilylenes ($\delta = 78-119$),[5,10] Driess's ylide-stabilized silylenes ($\delta = 212.4, 213.3$),[17] and the thermally unstable silylene, $Si\{N(SiMe_3)_2\}_2$ ($\delta = 223.9$);[13] however, it is well upfield of that reported for the dialkylsilylene ($\delta = 567$).[11] The downfield shift of **2** is consistent with a two-coordinate silicon since an increased coordination number produces a significant upfield shift, as observed in $(C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2)Si(\eta^5\text{-}C_5Me_5)$ ($\delta = 51.6$) (four-coordinate silicon)[24] and decamethylsilicocene ($\delta = -577$) (10-coordinate silicon).[4,25] The ^1H and ^{13}C NMR spectra suggest free rotation around the C−S bond due to the observation of only two signals for the *o*- and *p*-methyl groups of the flanking arene rings.

The electronic transitions were calculated by the TD-DFT approach using the same functional−basis set combination as employed in the geometry optimization.[21−23] The Kohn−Sham orbitals for **2** are shown in Figure 2. The calculations reveal several excitations at wavelengths between 250 and 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 ($\varepsilon = 8300\ M^{-1}\ cm^{-1}$).[26] A more intense absorption at 318 nm ($\varepsilon = 23\,000\ M^{-1}\ cm^{-1}$) (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 and the arene π^* orbitals. The absorptions at 291 ($\varepsilon = 20\,000\ M^{-1}\ cm^{-1}$) and 269 nm ($\varepsilon = 25\,000\ M^{-1}\ cm^{-1}$) are due to an arene π-to-silicon p transition and transitions 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 $\pi\rightarrow\pi^*$ 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 (Supporting Information).

The bisthiolatosilane, **3** (Figure 3), was obtained from H_2SiCl_2 and $(LiSAr^{Me_6})_2$. The structural data reveal a relatively close resemblance between the structural parameters for the $Si[S(C\text{-}ipso)]_2$ moiety and those of silylene **2**, with very similar

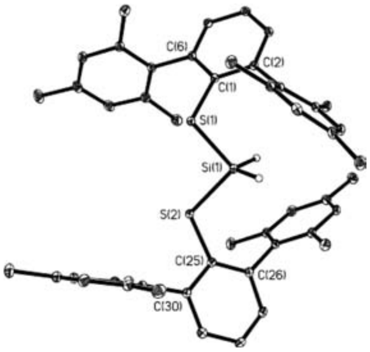

Figure 3. Thermal ellipsoid (30%) drawing of one of the crystallographically independent molecules of **3**. Selected bond lengths (Å) and angles (°): Si(1)−S(1) 2.1372(6), Si(1)−S(2) 2.1403(6), S(1)−C(1) 1.7859(15), S(2)−C(25) 1.7892(16), Si(1)−centroid(1) 3.500, Si(1)−centroid(2) 3.591, S(1)−Si(1)−S(2) 94.41(2), C(1)−S(1)−Si(1) 104.97(5), C(25)−S(2)−Si(1) 108.79(5).

Si−S distances and a small, ca. 3°, difference in the S−Si−S bond angle. The Si−centroid distances differ by ca. 0.11 Å. However, the compounds **2** and **3** were unequivocally distinguished by the location and refinement of the two Si−H hydrogens in **3**. The presence of the Si−H hydrogens was also confirmed by the observation of a 1:2:1 triplet signal in the ^{29}Si NMR spectrum at $\delta = -13.22$ ($^1J_{\mathrm{SiH}} = 256$ Hz).[27] In addition, the Si−H signal in the ^{1}H NMR spectrum was observed at 4.11 ppm, and two satellite signals corresponding to the natural abundance of ^{29}Si were also identified ($^1J_{\mathrm{SiH}} =$ 256 Hz). Two partially overlapped absorptions at 2182 and 2168 cm^{-1} in the IR spectrum are characteristic of a and b Si−H stretching modes.[27,28]

The addition of MeI to **2** afforded the iodomethyl bisthiolatosilane, **4**.[6,29] Its ^{29}Si NMR spectrum revealed an upfield quartet at $\delta = -5.88$ ($^2J_{\mathrm{SiH}} = 8.3$ Hz) A methyl group signal at $\delta = 2.01$ ($^2J_{\mathrm{SiH}} = 8.7$ Hz) in the ^{1}H NMR spectrum and a signal at $\delta = 11.39$ in the ^{13}C NMR spectrum are comparable to those for compounds with similar moieties.[30,31]

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 increases the energy separation (4.26 eV) of the silicon lone pair and the 3p orbitals and makes a synergic interaction between the frontier orbitals of **2** and H_2 less likely. In effect, the electronegative character of the thiolate ligands is a key factor in both the stability of **2** (with some help from Si−S π-bonding) and its reluctance to react with hydrogen. Geometric constraints of the ligands may also hinder the reactivity of **2**.[32]

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 second 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.[33]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files for **1**−**3**; experimental details and ^{1}H, ^{13}C, and ^{29}Si NMR spectra for **1**−**4**; infrared spectra of **2** and **3**; UV−vis spectrum and table of experimental and calculated electronic spectra of **2**; computational results on the models of **2** and **3**; tables of crystallographic data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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