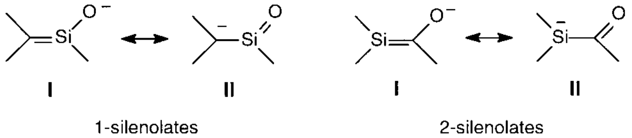
Stable Silenolates

The First Isolable 2-Silenolate**

*Tamaz Guliashvili, Ibrahim El-Sayed, Andreas Fischer, and Henrik Ottosson**

Enolates hold a central position in organic chemistry.[1] However, there has been much less focus on silenolates, that is, Si analogues of enolates (Scheme 1). So far 1-silenolates have not been made, and even computational studies of these species are absent. With regard to 2-silenolates, there are only a handful of reports from the groups of Bravo-Zhivotovskii and Apeloig[2,3] and Ishikawa and Ohshita.[4] It was found that 2-silenolates with bulky alkyl or aryl substituents on the carbonyl carbon atom are moderately stable at low temperatures, thus allowing their characterization by NMR spectroscopy. At room temperature these compounds undergo degradation within a few hours, presumably preceded by dimerization.[4]



Scheme 1. The resonance structures of silenolates.

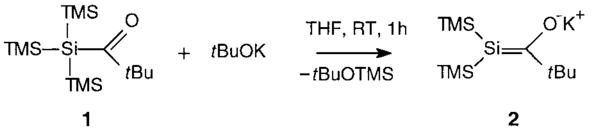
Our interest lies in silenes that display reversed Si=C bond polarity (Si$^{\delta-}$=C$^{\delta+}$),[5] which is enabled by delocalization of the negative charge from π-electron-donating substituents in the 2-position to the silene Si atom.[6] These reverse-polarized silenes are less reactive towards moisture and alcohols than naturally polarized silenes (Si$^{\delta+}$=C$^{\delta-}$), and addition of alcohol proceeds by an unexpected regiochemistry because C–O instead of Si–O bonds are formed.[5,7,8] The reverse-polarized silenes also react selectively with dienes to yield only [4+2] adducts.[4,5,7] This is in contrast to the naturally polarized silenes, which give [2+2] and ene adducts as well.[9]

The negative charge in 2-silenolates resides on the O and/or Si atom (Scheme 1). If resonance structure **II** dominates, then the electronic structure resembles that of a reverse-polarized silene. Such 2-silenolates should contain Si–C single bonds (≈1.87 Å),[10] and the Si atoms will be similar to those of silyl anions, that is, strongly pyramidal.[11] On the other hand, if 2-silenolates are dominated by structure **I** the SiC bond lengths will be close to that of a Si=C double bond (1.704 Å in H$_2$Si=CH$_2$),[12] and the Si atoms will be planar.

There is very little structural information available on 2-silenolates. According to HF/6-31G(d) calculations, [(H$_3$Si)$_2$SiC(O)Me]$^-$ has a SiC bond of 1.926 Å, corresponding to a Si–C single bond.[4b] However, can Hartree–Fock correctly describe 2-silenolates, and how does the result obtained for the gas phase transfer to condensed phases? Indeed, variable temperature ^{1}H NMR spectroscopy suggests a partial Si=C double bond with an activation energy for bond rotation of 14.3 kcal mol^{-1}.[4b]

As part of our study on how reversed polarization affects Si=C-bonded compounds, we have now generated a crystallizable 2-silenolate. This is also the first experimentally determined crystal structure of a heavy Group 14 enolate.

We started from tris(trimethylsilyl)acylsilane (**1**, Scheme 2), but instead of applying a silyllithium reagent for abstraction of a trimethylsilyl group we used *t*BuOK.[13] This procedure leads to facile and quantitative formation of 2-silenolates at room temperature, in contrast to the more difficult preparation of lithium 2-silenolates using silyllithium. The products prepared by our method are resistent to decomposition. For instance, [(TMS)$_2$SiC(O)*t*Bu]$^-$K$^+$ (**2**) formed by application of *t*BuOK in THF can be kept under inert atmosphere at room temperature for three months, whereas the corresponding lithium 2-silenolate decomposes within a few hours. Nonetheless, the potassium 2-silenolates degrade instantaneously when exposed to air. Further reaction with [18]crown-6, which enhances the crystallization of silyl anions,[14,15] leads to an orange compound. Crystals suitable for a structure determination can then be grown from solutions in toluene.



Scheme 2. Synthesis of the 2-silenolate **2**. TMS = trimethylsilyl.

The X-ray structure of **2** is shown in Figure 1.[16] This compound is described by resonance form **II** (see Scheme 1) since it has a SiC bond that is even longer than a normal Si–C single bond (1.926 versus 1.87 Å for reference Si–C bonds[10]), a C=O double bond (1.245 versus ≈1.20 Å for reference C=O bonds[17]), and a pyramidal Si atom (sum of valence angles ΣSi = 317.8°). Thus, **2** is strongly influenced by reversed polarization. The coordination to K$^+$ is distant, with the O atom showing a closer contact than the Si atom. In the B3LYP/6-31+G(d)-optimized structure[18–20] of the smaller [(H$_3$Si)$_2$SiC(O)Me]$^-$K$^+$(OMe$_2$)$_3$ complex (**3**, Figure 2), the K$^+$

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[*] Dr. H. Ottosson, T. Guliashvili, Dr. I. El-Sayed
Department of Organic Chemistry
Institute of Chemistry, Box 599
Uppsala University
751 24 Uppsala (Sweden)
Fax: (+46) 18-417-3818
E-mail: henrik.ottosson@kemi.uu.se
Dr. A. Fischer
Department of Chemistry (Inorganic Chemistry)
Royal Institute of Technology
100 44 Stockholm (Sweden)

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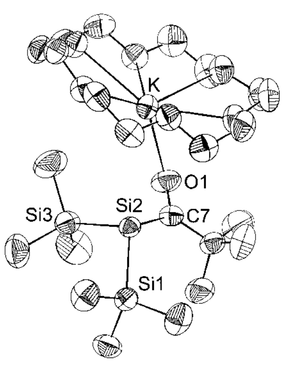

Figure 1. Structure of **2** (ORTEP drawing). The hydrogen atoms have been omitted for clarity, and the thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]: Si1-Si2 2.350(1), Si2-Si3 2.333(1), Si2-C7 1.926(3), C7-O1 1.245(3), K1-O1 2.846(2), K1-Si2 3.714(1); Si1-Si2-Si3 103.21(3), Si1-Si2-C7 117.95(8), Si3-Si2-C7 96.61(8), C7-O1-K1 113.2(2), Si2-C7-O1 116.6(2), C8-C7-O1 117.2(2), C8-C7-Si2 125.9(2); O1-C7-Si2-Si1 15.1(3), O1-C7-Si2-Si3 56.7(2).

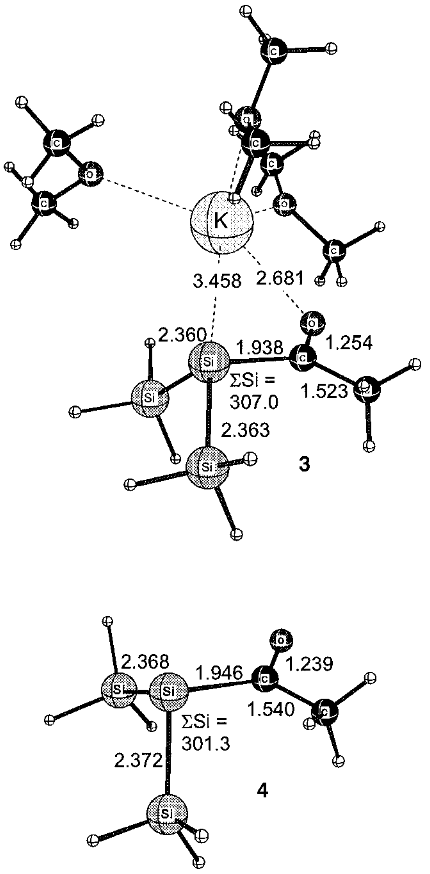

Figure 2. The optimized geometries of **3** and **4** calculated at the B3LYP/6-31+G(d) level, with selected bond lengths [Å] and angles [°].

ion is also closer to O than to Si. However, computations of the corresponding bare 2-silenolate **4** reveal that the presence of the solvated K^+ ion only alters the structure of the 2-silenolate a little. Potassium 2-silenolates should essentially correspond to unperturbed 2-silenolates, even in absence of crown ethers. The smaller degree of pyramidalization of the Si atom in **2** than in **3** is most likely due to the larger steric repulsion between the TMS groups in **2** than between the SiH_3 groups in **3**.

The ^{29}Si and ^{13}C NMR chemical shifts of the Si and C atoms of the Si–C bond of **2** are $\delta = -78.7$ and 274.1 ppm in THF and $\delta = -93.8$ and 268.7 ppm when [18]crown-6 is present. The ^{29}Si NMR shift for the central Si atom of **2** is within the range measured for silyl anions,[11] indicating that resonance structure **II** dominates the electronic structure. Furthermore, the NPA charge calculated at the B3LYP/6-31+G(d) level for the silenolate Si atom of **4** (−0.120 e) resembles that of the $(H_3Si)_2SiMe^-$ silyl anion (−0.108 e), even though this comparison neglects the fact that methyl and acyl groups show different degrees of inductive electron-withdrawing ability. In complex **3** the negative charge at Si increases to −0.198 e. Trapping of **2** by MeI yields the Si-methylated product, in agreement with previous findings by Ishikawa, Ohshita, and co-workers.[4] In analogy with other reverse-polarized silenes, only the [4+2] adduct is found upon the reaction of **2** with 2,3-dimethyl-1,3-butadiene.

To conclude, the X-ray structural, NMR spectroscopic, and atomic charge data reveal that 2-silenolates are dominated by resonance structure **II**. They have pyramidal Si atoms, Si–C single bonds, and C=O double bonds. The much stronger C=O than Si=C double bond favors resonance structure **II** over **I**. Our results reveal that silenes that are strongly affected by reversed polarization ($Si^{\delta -}{=}C^{\delta +}$) have structures that are unconventional for Si=C double-bonded compounds. This also shows that 2-silenolates are structurally dissimilar to enolates.

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[16] Crystal structure determination of **2**: orthorhombic, space group $Pna2_1$, $a = 1981.1(1)$, $b = 1063.2(2)$, $c = 1574.4(3)$ pm. $V = 3319.49(7) \times 10^6$ pm^3. $\rho_{\text{calcd}} = 1.127$ g cm^{-3}; $2\theta_{\text{max}} = 52.74°$, $\text{Mo}_{K\alpha}$ radiation, $\lambda = 71.073$ pm, $T = 297$ K. The diffraction data were collected on a Bruker-Nonius Kappa CCD diffractometer. All non-hydrogen atoms were refined with anisotropic temperature parameters. The structure was solved with SHELXS97 and refined against F^2 using SHELXL97. Final R values: $R_1 = 0.0475$, $wR_2 = 0.0932$; GOF = 1.043 for 6668 unique reflections and 307 parameters; Flack parameter $x = 0.00(4)$; min./max. residual electron density 0.18/−0.14. CCDC-191717 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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