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Stable Cyclic Silenes from Reaction of Disilenides with Carboxylic Acid Chlorides**

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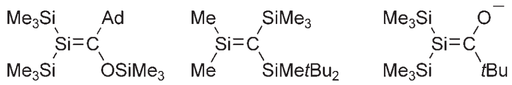
Dedicated to Professor Armin Berndt on the occasion of his 70th birthday

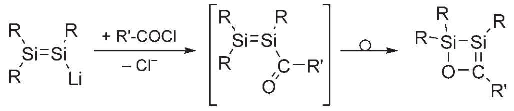
Since first evidenced as intermediates by Gusel'nikow and Flowers 40 years ago,[1] silenes, that is, compounds with Si=C bonds, have attracted continuous interest.[2] The stable silene **1** (Scheme 1) reported by Brook et al. gave further impetus to the field.[3] Its unexpectedly long Si=C bond prompted an intense discussion, which was resolved by calculations.[4] The term "reversed polarity" was coined: the π-donating siloxy group in **1** reduces the polarity of the Si=C bond significantly, thereby enhancing its stability and increasing the bond length.


1 **2** **3**

Scheme 1. Open-chained silenes **1**–**3** (Ad = 1-adamantyl).

Shortly thereafter Wiberg et al. reported silene **2**, which is free of π-donating substituents and accordingly exhibited the expected shorter Si=C bond.[5] Other isolable donor-free silenes were subsequently reported by the groups of Apeloig and Kira.[6] Recent studies by Ottosson et al. focusing on silenolate **3** and other silenes bearing substituents with stronger π-donating ability than that of the siloxy group in **1** revealed a decreasing bond order for Si=C accompanied by increased pyramidalization of the silicon center.[7]

Silenes of type **1** had been prepared by thermal and photochemical rearrangement of suitable acyl silanes, easily accessible from reactions of acid chlorides with silyl anions.[8] In the last years a few disilenides, that is, disila analogues of vinyl anions became available by efforts of both of our groups.[9] In light of a number of successful applications of **4a** as an unsaturated, nucleophilic reagent,[10] we attempted the preparation of acyl disilenes by reaction of **4a,b** (Scheme 2) with acid chlorides.



4a,b **5a-c** **6a-c**

Scheme 2. **4a**: R = Tip = 2,4,6-iPr$_3$C$_6$H$_2$; **5a**, **6a**: R = Tip, R′ = tBu; **5b**, **6b**: R = Tip = 2,4,6-iPr$_3$C$_6$H$_2$, R′ = 1-adamantyl; **4b**, **5c**, **6c**: R = SiMetBu$_2$, R′ = 1-adamantyl.

In reactions of **4a** with 1-adamantoyl and pivaloyl chloride, however, the expected (and likely intermediate) acyl disilenes **5a,b** were not detected even at 193 K. This instability is in marked contrast to the carbon analogues, α,β-unsaturated ketones. Instead, the four-membered cyclic silenes **6a,b** were formed quantitatively as indicated by NMR and UV/Vis spectroscopic data (Scheme 2, see the Supporting information).[11]

The reaction of disilenides with acid chlorides turns out to be quite general. Thus, **4b** readily reacts with 1-adamantoyl chloride to yield the cyclic silene derivative **6c**.

^{29}Si NMR spectroscopy reveals almost identical chemical shifts for the tri- and the tetracoordinated silicon nuclei of both **6a** and **6b**. Curiously, in the case of **6a** the signal at higher field ($\delta = 17.5$ ppm) is assigned to the Si atom of the double bond. It is considerably shielded compared to the corresponding signal of **1** ($\delta = 41.4$ ppm).[3c,12] The ring carbon atoms exhibit chemical shifts (**6a**: $\delta = 213.4$ ppm, **6b**: $\delta = 214.6$ ppm) that are very similar to that found for **1** ($\delta = 214.2$ ppm[3c]). The Si–C coupling of the double bond in **6b** is distinctly smaller than that in **1** (**6b**: ^1J(C,Si) = 67.3 Hz), **1**: ^1J(C,Si) = 84.4 Hz[3c]). These observations can be rationalized by the increase in p character of the endocyclic bonds due to ring strain. As a consequence the orbitals hosting the remaining electron density at silicon should get higher

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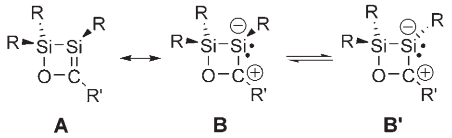
s character and thereby favor the reversed polarity of the Si=C bond of **6a**,**b**.

Ottosson et al. pointed out that strong reversed polarity is expressed in significant pyramidalization of the Si center[7] as depicted for **6** by resonance structure **B** (Scheme 3). In this case the *ipso*–C atoms bonded to the tetracoordinate Si atom should be chemically inequivalent. Indeed, for **6a** two signals ($\Delta\nu = 94$ Hz) were detected at 193 K, which collapse at $T_c = (218 \pm 5)$ K. The barrier for the corresponding process can be estimated with the Eyring equation to $\Delta G^{\neq} = (10.3 \pm 0.2)$ kcal mol^{-1}. Even though hindered rotation of the Tip substituents may without doubt be present in **6a**, "freezing" of the ring inversion between **B** and **B′** is a necessary condition for inequivalence of the *ipso*-C atoms in question. Therefore, the determined value can be attributed to the latter process.



Scheme 3. Ring inversion in cyclic silenes **6**.

As expected NMR data of **6c** differ significantly from those of **6a**,**b** due to the silyl groups. The ^{29}Si NMR spectrum of **6c** shows signals at $\delta = 56.7$ ppm for the tetra- and at 34.4 ppm for the tricoordinated Si nucleus. The tendency observed for **6a** that the higher field signal is due to the Si nucleus of the double bond is even more pronounced in **6c**. The influence of the substituents on the first long-wave UV/Vis absorptions of **6a**–**c** ($\lambda_{max} = 351$, 355, and 354 nm, respectively) is negligible. They are significantly red-shifted compared to that of **1** ($\lambda_{max} = 340$ nm), exhibiting typical extinction coefficients from 2700 to 6900 L mol^{-1} cm^{-1}.

The markedly pyramidal silicon atom Si1 is the most prominent feature of the molecular structure of **6b** in the solid state, as determined by single-crystal X-ray diffraction (Figure 1).[13] Whereas **1** is almost perfectly planar, the sum of angles of Si1 in **6b** amounts to 342.2°. Despite the pyramidal Si atom in **6b** the Si–C distance of 177.5(3) pm is very close to the corresponding distance in **1** (176.4 pm).[3b] C1 features a practically undistorted sp^2 coordination environment (sum of angles C1: 358.6°). The C–O distance of 141.6(3) pm in **6b** is slightly longer than that in **1** (140.0 pm). In Ottosson's silenolate **3** strong pyramidalization is accompanied by significant lengthening of the Si=C bond to 192.6(3) pm and shortening of the C–O bond length to 124.5 pm.[7b]

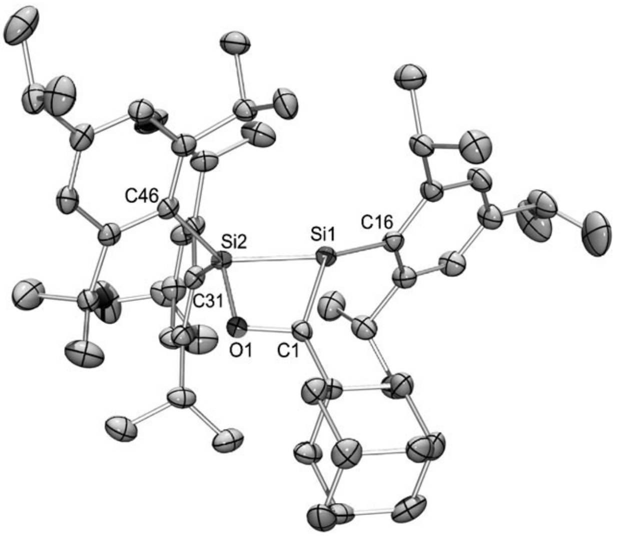


Figure 1. Structure of **6b** in the solid state; thermal ellipsoids at 50% probability; H atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Si1-C1 177.5(3), Si1-Si2 231.0(1), Si2-O1 171.3(2), C1-O1 141.6(3), Si1-C16 188.3(3), Si2-C31 190.3(3), Si2-C46 190.4(3); C1-Si1-Si2 71.88(9), O1-Si2-Si1 77.86(6), C1-O1-Si2 101.87(14), O1-C1-Si1 106.72(16), C1-Si1-C16 127.99(12), C16-Si1-Si2 142.29(9).

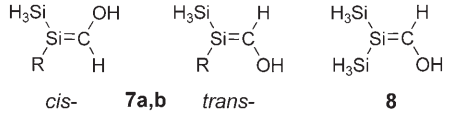
Table 1: Chemical shifts [ppm] and sum of angles angles Si [°] of **6a**–**g**.

	R	R′	$\delta(^{29}Si)$ (Si=C)	$\delta(^{29}Si)$ (SiR_2)	$\delta(^{13}C)$ (Si=C)	Σ angles Si [°]
6a[a]	Tip	*t*Bu	+17.5	+22.6	+213.4	–
6b[a]	Tip	Ad	+21.9	+18.8	+214.6	342.2
6c[a]	SiMe*t*Bu$_2$	Ad	+34.4	+56.7	+231.6	–
6d[b]	H	H	–	–	–	316.1
6d[c]	H	H	–	–	–	293.7
6e[b]	Me	Me	+15.4	+38.6	+209.1	323.8
6e[c]	Me	Me	+22.2	+37.2	+271.1	311.4
6f[c]	Ph	*t*Bu	+22.9	+18.1	+288.2	309.9
6g[c]	SiMe$_3$	Me	+11.2	+63.7	+279.6	316.9

[a] Experimentally determined. [b] MP2/6-31g(d,p)//GIAO/MP2/6-31g-(d,p). [c] B3LYP/6-31G(d,p)//GIAO/B3LYP/6-311+G(2df,p).

To rule out the possibility that pyramidalization in silenes **6** is due to substituents, we examined the proton- and methyl-substituted models **6d**,**e** (**6d**: R = R′ = H, **6e**: R = R′ = Me) by ab initio and DFT methods (Table 1, details in the Supporting Information).[14] The MP2/6-31g(d,p) level of theory reproduces the experimental geometry fairly well, considering the simplicity of the models. On the other hand, the B3LYP functional not only overestimates bond lengths (which is a well known tendency) but also the pyramidalization at the Si atoms. However, these structural differences seem to have only little effect on the NMR chemical shifts as shown by comparison of the results for **6e** (Table 1). Accordingly the more realistic models **6f** (R = Ph, R′ = *t*Bu) and **6g** (R = SiMe$_3$, R′ = Me) reasonably reproduce the experimental trends.

Unlike cyclic silenes **6** the open-chained models *cis*- and *trans*-**7a**,**b** (Scheme 4) reveal only little pyramidalization (see the Supporting Information). Whereas again B3LYP overestimates it largely, the replacement of the Si-bonded proton in **7a** by the phenyl group in **7b** does not have much effect.

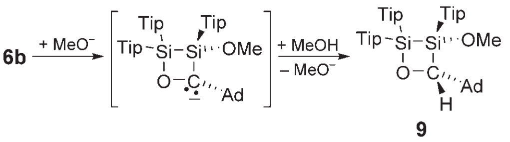


Scheme 4. Open-chained models **7a**,**b** (**a**: R = H, **b**: R = Ph) and **8**.

The cyclic constitution of silenes **6** seems to be a determining factor for the degree of pyramidalization. Electronegative substituents at silicon are, however, not as important as silyl-substituted **6g** demonstrates again. A suitable open-chained counterpart for cyclic **6g** has been calculated by Ottosson,[15] (**8**; Scheme 4) which shows a nearly planar Si center, thus corroborating the above statements.

Another interesting feature of cyclic silenes **6a**,**b** is their insensitivity. Both melt without any detectable decomposition (**6a**: 95–97 °C, **6b**: 165–167 °C). In the solid state they react only slowly with air and moisture, whereas Brook's silene **1** "on exposure to air immediately reacts exothermically producing white smoke, melts, and some evaporates".[3a] Solutions of **6a**,**b**, however, are quickly oxidized to mixtures of unidentified products.

Addition of MeOH to the Si=C double bond of silenes generally proceeds rapidly and smoothly even at low temperatures.[2,16] The regioselectivity of this reaction has been used as an indicator for the degree of reverse polarization.[6b] The cyclic silenes **6a**,**b**, however, do not react with MeOH at any appreciable rate. After two weeks at room temperature **6a**,**b** were recovered quantitatively from MeOH/toluene (50:50) solution. Only the presence of an excess of NaOMe accelerates the reaction of **6b** to such an extent that conversion is complete after 12 h yielding the *trans*-adduct **9** (see the Supporting Information). The inertness of **6a**,**b** towards pure MeOH and the *trans*-selectivity of the base-catalyzed reaction are a clear indication for a stepwise mechanism (Scheme 5). It should be noted that despite the reverse-polarity of **6b** the nucleophilic attack occurs at the silicon center.



Scheme 5. Base-catalyzed addition of MeOH to **6b**.

Interestingly, the ^{29}Si NMR data of **9** ($\delta = 29.5$ and 21.4 ppm), which does not contain a Si=C double bond, are shifted downfield with respect to those of **6b**, which does contain a Si=C double bond. The regioselectivity of the reaction is easily derived from the gated decoupled ^{13}C NMR spectrum, in which a doublet at $\delta = 92.98$ ppm (^{1}J(C,H) = 135.6 Hz) in the typical region for 2,3-disilaoxetane ring carbon atoms proves the presence of a CH moiety within the ring of **9**.[17]

The facile formation of stable cyclic silenes from readily available nucleophilic, low-valent silicon reagents raises a broad variety of possibilities, which are currently being explored in our laboratories.

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