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1,2-Disilacyclobut-2-enes: Donor-Free Four-Membered Cyclic Silenes from Reaction of Disilenides with Vinylbromides

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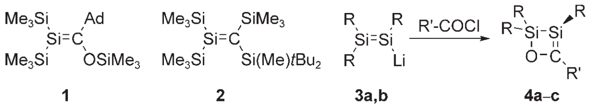
In 1981 the report by Brook et al. on the first stable silene **1**,[1] that is, a compound with a Si=C double bond, contributed to the change of the paradigm that silicon as a heavier main group element would not engage in multiple bonding.[2] The unexpectedly long Si=C bond of **1** was attributed to the influence of the electron-releasing siloxy group (Scheme 1). The subsequent synthesis of donor-free **2** with a considerably shorter Si–C distance[3] further supported a strong dependency of the electronic and topological character of the Si=C π bond on the nature of the substituents, which was later put on a firm theoretical basis.[2c,4] As Ottosson and Steel pointed out recently,[2a] the application of the resulting versatile reactivity of the numerous stable and transient silenes reported to date is still limited due to the particular (sometimes forcing) conditions for their generation: high temperatures or irradiation,[1,5] use of strong bases,[3,6] or formation of nucleophilic secondary products.[7]



Scheme 1. Ad = 1-adamantyl, **3a**, **4a**: R = Tip = 2,4,6-iPrC_6H_2, R′ = Ad; **4b**: R = Tip, R′ = tBu; **3b**, **4c**: R = Si(Me)tBu$_2$, R′ = Ad.

We recently reported the quantitative conversion of disilenides **3a**,**b**, disila analogues of vinyl anions,[8] into cyclic silenes **4a–c** featuring an endocyclic oxygen atom by reaction with carboxylic acid chlorides under very mild conditions (Scheme 1).[9] On grounds of DFT calculations we demonstrated that the unprecedented significant pyramidalisation of the silicon atom of the double bond was not entirely due to the presence of the electron-releasing oxygen atom next to the carbon atom of the double bond, but also to the incorporation of the Si=C moiety into a four-membered ring. Early theoretical calculations, however, predicted a planar topology in case of the related 1,4-dihydro-1,2-disiletes, in which the endocyclic oxygen atom of the hydrogen substituted parent of **4** is formally replaced by a CH_2 moiety.[10] These 1,2-disilacyclobutenes are particularly interesting synthetic targets in view of the rich cycloreversion chemistry of their saturated congeners, that is, 1,2- and 1,3-disilacyclobutanes, which under photolytic or thermal conditions fragment into transient silenes and were therefore pivotal for the development of Si=C double bond chemistry as a whole.[11]

The recent successful transfer of Si=Si moieties to aromatic substrates by reaction of disilenide **3a** with the weakly electrophilic aryl iodides[12] encouraged us to investigate the reactivity of **3a**,**b** towards vinyl bromides. We speculated that intermediately formed vinyl substituted disilenes would likely not be stable and therefore rearrange to the desired cyclic derivatives.

Indeed, upon treatment of vinyl bromides $H_2C{=}C(R')Br$ with disilenides **3a**,**b** in benzene or toluene at room temperature affords 1,4-dihydro-1,2-disiletes **5a–d** in good to excellent yields (Scheme 2). Moreover, reaction of **3b** with the parent vinyl bromide (R′ = H) yielded **5e**, the first stable compound with a hydrogen atom directly attached to the carbon atom of the Si=C double bond.[13,14] All compounds are thermally stable in the absence of oxygen and moisture

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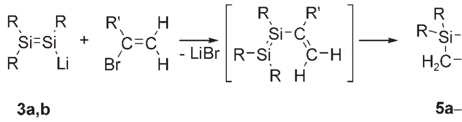


Scheme 2. **5a**: R = Tip, R′ = Ph; **5b**: R = Si(Me)*t*Bu$_2$, R′ = Ph; **5c**: R = Tip, R′ = SiMe$_3$; **5d**: R = SiMe*t*Bu$_2$, R′ = SiMe$_3$; **5e**: R = SiMe*t*Bu$_2$, R′ = H.

and were characterized by multinuclear NMR and UV/Vis spectroscopy. Additionally, the structure of phenyl substituted derivative **5a** in the solid state was confirmed by single crystal X-ray diffraction (Figure 1).[15]

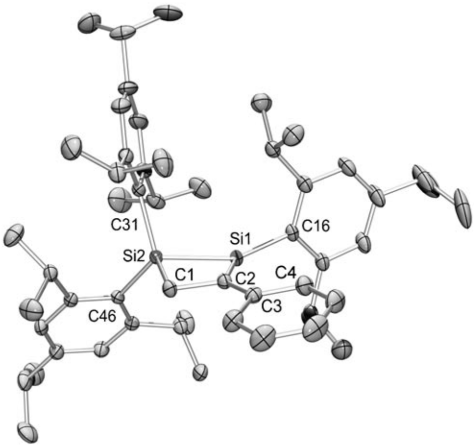


Figure 1. Structure of **5a** in the solid state. All hydrogen atoms and disordered isopropyl groups removed for clarity. Ellipsoids at 30% probability. Selected bond lengths [Å] and angles [°]: Si1–C2 1.7459(15), Si1–Si2 2.3154(5), Si2–C1 1.9191(16), C1–C2 1.536(2), C2–C3 1.457(2), Si1–C16 1.8729(15), Si2–C31 1.9111(15), Si2–C46 1.9056(14); C2-Si1-C16 127.43(7), C2-Si1-Si2 80.74(5), C16-Si1-Si2 148.06(5), C1-Si2-Si1 74.45(5), C3-C2-C1 121.45(13), C3-C2-Si1 134.99(12), C1-C2-Si1 103.53(10), C2-C1-Si2 100.43(9).

As expected, the NMR data of **5a**–**e** suggest a significant influence of the substituents on the electronic structure of the Si=C bond. Trisilyl-substituted disilacyclobutenes **5b**,**d** show strongly deshielded tricoordinate Si and C atoms compared to those of **5a**,**c** with triaryl substitution of the Si$_2$ moiety (Table 1). Within these two subsets the most shielded double bond silicon atoms are those of **5a** and **5b**, respectively, with a phenyl group attached to the Si=C carbon atom, which may be explained in terms of a reduced polarity of the double bond due to π conjugation with the substituent. A comparison of the longest-wavelength absorption maxima in the UV/Vis spectra of **5a**,**b** shows that the influence of the substituents at silicon on the HOMO–LUMO gap is negligible (λ_{max}, **5a**: 385, **5b**: 389 nm). Conversely, the effect of the phenyl substituent at the Si=C carbon atom is much more pronounced and responsible for a significant red-shift (λ_{max}, **5d**: 330, **5e**: 322 nm), which is widely appreciated as evidence for conjugation.

Table 1. Comparison of selected NMR and structural data of 1,2-disilacyclobut-2-enes **5a**–**e** (exptl) and **6a**–**f** (calcd).

	Si=C [Å]	Si–Si [Å]	ΣSi [°]	δ ^{29}Si (*Si*=C)[c]	δ ^{13}C (Si=*C*)[c]
5a	1.746(2)	2.3154(5)	356.2(1)	75.0	155.2
5b	–	–	–	98.6	185.4
5c	–	–	–	112.5	159.6
5d	–	–	–	139.1	195.6
5e	–	–	–	112.5	175.1
6a[a]	1.762	2.305	360.0	85.5	171.5
6b[b]	1.775	2.326	360.0	118.8	201.9
6c[a]	1.748	2.314	359.9	124.8	179.5
6d[b]	1.760	2.338	360.0	166.0	224.2
6e[b]	1.750	2.345	360.0	127.0	193.6
6f[a]	1.738	2.318	360.0	99.6	153.9

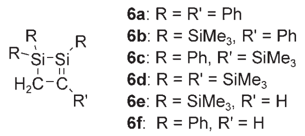
[a] B3LYP/6-31 g(d,p). [b] B3LYP/6-31 g(d). [c] GIAO/B3LYP/6-311 g-(2df,p).

It is important to note that the half-parent system **5e** offers the unprecedented possibility to study the spectroscopic features of a hydrogen directly attached to the carbon atom of the Si=C bond. While a recently reported hydrosilene exhibited a ^{1}H NMR shift at δ 6.06 ppm for the hydrogen bonded to the silicon atom of the Si=C moiety;[13] in the case of **5e** a signal at much lower field (7.47 ppm) is observed probably due to the different electronegativities of silicon and carbon. This resonance can indeed be unambiguously assigned to the hydrogen at the carbon atom of the Si–C double bond on grounds of its triplet splitting due to coupling with the adjacent protons of the methylene group ($^3J = 4.8$ Hz). This coupling is significantly higher than that reported for carbon based cyclobutenes ($^3J = 0.9$ to 1.4 Hz).[16] Conversely, the ^1J coupling constant of the "vinylic" proton to the Si=C carbon atom is somewhat smaller in case of **5e** (153.4 Hz) than the corresponding value of parent cyclobutene (168.5 Hz).[16c] This observation can be rationalized in terms of the larger covalent radii of the silicon atoms in the ring as compared to carbon allowing for larger inner angles at the endocyclic carbon atoms, which by consequence should raise the s character of the C–C bond in the four-membered ring and hence the spin couplings through that bond.

Single crystals suitable for an X-ray diffraction study were obtained in case of phenyl substituted **5a** (Figure 1) confirming the constitution of a 1,2-disilacyclobut-2-ene. The Si1–C2 distance of 1.7459(15) Å is within the typical range of Si=C double bonds[2] Even though the four-membered ring is slightly twisted (Si2-Si1-C2-C1 7.17(9)°; Si2-C1-C2-Si1 −8.69(10)°) the Si=C double bond is essentially planar (sum of angles Si1 356.2(1), C2 360.0(1)°) in sharp contrast to the strongly pyramidalized Si=C silicon atom of oxygen containing **4a**–**c**.[9] The π conjugation of the phenyl group of **5a** suggested by the spectroscopic data becomes readily apparent from the co-planar arrangement of the phenyl substituent with the Si$_2$C$_2$ ring (dihedral angle Si1-C2-C3-C4 5.4(2)°) and the relatively short bond to the *ipso*-carbon atom (C2–C3 1.457(2) Å). The larger covalent radius of silicon compared with carbon indeed imposes small inner angles at Si1 and Si2 and larger ones at C1 and C2 (Si2-Si1-C2 80.74(5), C1-Si2-Si1 74.45(5), Si1-C2-C1 103.53(10), C2-

C1-Si2 100.43(9)°) corroborating the above assumption that was used to explain the observed NMR couplings of **5e**.

In order to clarify the electronic nature of **5a–e**, we carried out DFT calculations[17] on model compounds **6a–f** (Scheme 3). In previous work on cyclic silenes **4a–c** we concluded that B3LYP compared to MP2 overestimates the pyramidalization of the double bond's silicon atom. Given that **5b** exhibited an almost planar coordination environment at silicon we opted for B3LYP in the present case to avoid unnecessary simplification of the models, which would have been mandatory with the more costly MP2 level of theory. The agreement of calculated and experimental parameters (Table 1) is indeed good given the still rough approximation of the experimental substitution patterns. Irrespectively of the nature of substituents, the Si=C bonds of all calculated 1,2-disilacyclobut-2-enes **6a–f** feature a strictly planar geometry. The carbon bonded phenyl groups of **6a,b** are almost co-planar to the double bonds as it had been observed experimentally in the solid state structure of **5a**. The HOMO of **6a** is dominated by the Si–C π bond, but nonetheless highly delocalized across the phenyl substituent with a little hyperconjugative admixture of σ electron density from the endocyclic methylene group's C–H bonds (Figure 2). The main contribution to the LUMO is procured from the antibonding Si-C π*-orbital, which participates in bonding interactions to both pending phenyl groups.



6a: R = R' = Ph
6b: R = $SiMe_3$, R' = Ph
6c: R = Ph, R' = $SiMe_3$
6d: R = R' = $SiMe_3$
6e: R = $SiMe_3$, R' = H
6f: R = Ph, R' = H

Scheme 3.

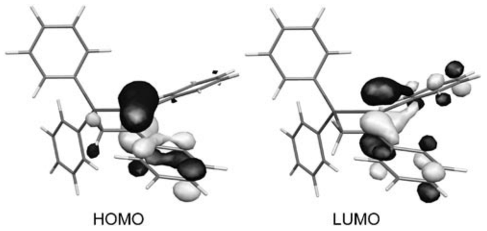


Figure 2. Contour plots of the frontier orbitals of **6a** at 0.05 cut-off level (Molekel).[18]

Additionally, an NBO analysis[19] of **6a** according to second-order perturbation theory provides further support for an effective π conjugation: the Si=C π orbital strongly donates into antibonding π orbitals of the phenyl group (π Si1–C2→π* C3–C4: 19.31 kcal mol^{-1}). The reverse donation is somewhat less pronounced (π C3–C4→π* Si1–C2: 13.53 kcal mol^{-1}) reflecting the electron withdrawing nature of the phenyl substituent.

To conclude, we have synthesized a number of donor-free 1,2-disilacyclobut-2-enes with planar Si–C double bonds from disilenides and vinyl bromides. Derivatives **5a,b** show pronounced π conjugation of the Si=C moiety with the phenyl substituent. The vast number of readily available vinyl bromides offers a broad basis for future exploitation of this new synthetic approach to Si–C double bond containing compounds. The chemistry of the new silenes, particularly under photochemical conditions, is currently being investigated.

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Keywords: density functional calculations · multiple bonds · silenes · small rings · synthesis

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