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Disilenyl silylene reactivity of a cyclotrisilene

Hui Zhao, Kinga Leszczyńska, Lukas Klemmer, Volker Huch, Michael Zimmer, David Scheschkewitz*

Abstract: The highly reactive silicon congeners of cyclopropene, cyclotrisilenes (c-Si₃R₄), typically undergo either π -addition to the Si=Si double bond or σ -insertion into the Si-Si single bond. In contrast, treatment of c-Si₃Tip₄ (Tip = 2,4,6-^{*i*}Pr₃C₆H₂) with styrene and benzil results in ring opening of the three-membered ring to formally yield the [1+2] and [1+4] cycloaddition product of the isomeric disilenyl silylene to the C=C bond and the 1,2-diketone π system, respectively. At elevated temperature, styrene is released from the [1+2] addition product leading to the thermodynamically favored housane species after [2+2] cycloaddition of styrene and c-Si₃Tip₄.

The heavier congers of cyclopropenes $(c-C_3R_4)$, namely cyclotrisilene (c-Si₃H₄), continue to attract interest from theory^[1] and experiment alike due to their unique structure and reactivity. A significant number of stable cyclotrisilenes I have been isolated taking advantage of kinetic stabilization by sterically demanding silvl and aryl substituents.^[2] The extensive investigations into the reactivity of strained, unsaturated silacycles revealed two main generic reaction pathways (Scheme 1): (1) The π -addition to the Si=Si double bond leading to products of type $II^{[3,4]}$ and (2) the σ -insertion into one of the endocyclic Si-Si single bonds effectively resulting in ring expansion products of type III.^[4] In addition, a few reactions under (3) formal insertion into an exocyclic σ -bond of one of the substituents have been reported,^[5] for example the insertion of sulfur into one of the bonds to the silyl-substituents.^[5b] Ringopening reactions of cyclotrisilenes were notably absent, although well-studied in the cases of carbon-based cyclopropenes and even applied for the synthesis of polymers.^[6] Recently, we reported the first example of (4) the reversible ringopening of a cyclotrisilene: the equilibrium reaction of arylsubstituted cyclotrisilene with an N-heterocyclic carbene (NHC).^[7] Disilenyl silylenes such as the resulting NHCcoordinated example V (Scheme 1) have also been proposed as transient intermediates.^[1a,2f] Clear-cut preparative manifestations of disilenyl silylene reactivity of cyclotrisilenes, however, remain elusive. We now report the reactions of homoleptic cyclotrisilene c-Si₃Tip₄ (1, Tip = 2,4,6-^{*i*}Pr₃C₆H₂, Scheme 2) with substrates containing C=C or C=O double bond(s) that allow for the detection and - in two cases - even isolation and full characterization of the assumed kinetic product of disilenyl silylene-like reactivity of 1.

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Scheme 1. Generic reactivity pathways of cyclotrisilenes I.

One of the most investigated Si=Si reactivities in general is the [2+2] cycloaddition of carbonyl species to afford disiloxetanes.^[8] In the case of cyclotrimetallenes of heavier Group 14 elements, however, just a limited number of reactions with carbonyl compounds is known.^[3a,b,9] As the only example in the case of cyclotrisilenes, a [1+2] cycloaddition with carbon monoxide itself was reported.[3b] While the reaction of a 1disilagermirene with benzaldehyde affords the [2+2] cycloaddition product,^[3a] the same species gives rise to a 1,2-OH addition product with the enolizable ketone, acetophenone.^[9] Building on the divergent reactivity of cyclotrisilenes towards isonitriles ([1+2] cycloaddition leading to the kinetic and $\boldsymbol{\sigma}$ insertion to the thermodynamic product), $\ensuremath{^{[3b]}}$ we investigated the behavior of 1 towards carbonyl compounds with a view to possible disilenyl silylene-like reactivity.



Scheme 2. Reactions of cyclotrisilene **1** with benzaldehyde, benzophenone and benzil to give housanes **2a,b** and disilenyl-substituted 2,5-dioxasilol **3** (R' = H (**2a**), Ph (**2b**); R = Tip = 2,4,6- ${}^{t}\text{Pr}_3\text{C}_6\text{H}_2$).

Treatment of **1** with one equivalent of benzaldehyde or benzophenone in benzene at room temperature, however, leads to rapid conversion to the [2+2] cycloaddition products, housane derivatives **2a,b** (Scheme 2). Three sharp ²⁹Si NMR signals each (**2a**: δ 43.87, 7.87 and -65.83 ppm; **2b**: δ 27.61, -1.66 and -67.14 ppm) are comparable to those of the aforementioned imino trisilabicyclo[1.1.0]butane (δ 45.0, 27.9 and -78.7 ppm).^[3b] On the basis of ¹H/²⁹Si HMBC spectrum, the two low-field ²⁹Si NMR signals are assigned to the bridgehead silicon atoms, while the high-field signal is due to the SiTip₂ bridge. In the ¹H NMR spectrum of **2a**, the benzylic hydrogen atom gives rise to a singlet at δ 6.34 ppm, very similar to that of *trans*-

disilagermabicyclo[2.1.0]pentane (δ 6.01 ppm).^[3a] Both, **2a** and **2b** show diagnostic ¹³C NMR resonances (**2a**: δ 77.38; **2b**: δ 92.31 ppm) in the typical range for the ring carbon atoms in disilaoxetanes.^[3a]

Housanes **2a,b**, were isolated as single crystals suitable for X-ray diffraction in acceptable yields (**2a**: 60%, yellow blocks, m.p. > 200°C; **2b**: 55%, colorless blocks, m.p. > 200°C). The solid state structures of **2a,b** were confirmed by X-ray crystallography (**2a**: Figure 1, **2b**: see SI).^[10] Housanes **2a,b** display a three- and four-membered ring fused skeleton with the angle between the two planes being 115.9(4)° in **2a** and 113.4(1)° in **2b**, which is slightly larger than that of the *trans*-disilagermabicyclo[2.1.0]pentane (107.8°),^[3a] but significantly smaller than the dihedral angle in imino-1,2,3-trisila-bicyclo[1.1.0]butane (134.2°).^[3b] The Si–Si bond lengths in the three-membered rings of **2a,b** (**2a**: 2.333(6), 2.347(6) and 2.364(7) Å, **2b**: 2.338(2), 2.349(3) and 2.403(3) Å) are within the typical range for Si–Si single bonds.

as an orange powder in acceptable yield (60%). In the ^{29}Si NMR, the two signals at low field are assigned to the formally sp² hybridized silicon atoms. The signal at δ 14.40 ppm corresponds to the tetracoordinate silicon atom of the dioxasilole ring. As typical for disilenes, the UV/vis spectrum of **3** in hexane shows a longest wavelength absorption at $\lambda_{max} = 437$ nm ($\epsilon = 14950$ $M^{-1}cm^{-1}$), which is assigned to the π - π^{*} transition.^[81]

Crystals of **3** suitable for X-ray crystallography were obtained from hexane solution (Figure 2).^[10] The Si=Si double bond length of 2.179(4) Å is within the typical range (2.138-2.289 Å).^[12] The twisted Si=Si double bond (twist angle $\tau = 23.5(4)^{\circ}$) is only moderately *trans*-bent ($\theta = 12.4(3)^{\circ}$ at SiTip₂, 6.7(2)° at Si(Tip)Si). The dioxasilole ring of **3** exhibits an envelope confirmation with an angle of 6.3(4)° between the planes of O1-C61-C62-O2 and O1-Si3-O2, slightly more than in the reported 1,3,2-dioxasilole (3.3°).^[11g] The two phenyl groups of the former benzil moiety twist from the dioxasilole ring by interplane angles of 39.9(4)° and 37.3(4)°.



Figure 1. Molecular structure of **2a** in the solid state. Hydrogen atoms are omitted for clarity (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (°): Si1-Si2 2.347(6), Si2-Si3 2.333(6), Si1-Si3 2.364(7), Si1-O1 1.675(1), Si2-C1 1.975(2), C1-O1 1.453(2), C1-C2 1.505(2), C1-H1 0.964(2); Si1-Si3-Si2 59.95(2), Si3-Si1-O1 109.14(5), Si3-Si2-C1 98.99(5), Si1-O1-C1 104.76(8), Si2-C1-O1 102.85(9), C2-C1-H1 106.40(1).

Si3

Si

Si2

H1

As the [2+2] cycloaddition of an isolated C=O moiety prevails over the targeted [1+2] cycloaddition with the postulated transient disilenyl silylene **6** (Scheme 4), we speculated that the [1+4] cycloaddition of the silylene moiety with a 1,2-diketone might be sufficiently favored compared to any reaction of the Si=Si fragment. Reactions of isolated silylenes with 1,2diketones were previously reported to give dioxasilole derivatives.^[11] Indeed, an equimolar mixture of benzil and **1** dissolved in C₆D₆ or toluene afforded an intensely bright red solution almost instantly, as opposed to the pale yellow to colorless reaction mixtures of **2a,b**. Three new signals in ²⁹Si NMR spectrum at δ 99.69, 36.01 and 14.40 ppm served as first indication for the formation of 1,3,2-dioxasilole **3** with an exocyclic Si=Si double bond and thus the desired disilenyl silylene reactivity of cyclotrisilene **1**. The product **3** was isolated

Figure 2. Molecular structure of disilenyl-substituted 2,5-dioxasilole $3 \cdot C_6 H_{14}$ in the solid state. Co-crystallized $C_6 H_{14}$ and hydrogen atoms are omitted for clarity (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (°): Si1-Si2 2.179(4), Si1-Si3 2.333(4), Si3-O1 1.679(8), Si3-O2 1.679(8), C61-O1 1.396(1), C62-O2 1.393(1), C61-C62 1.345(2); Si2-Si1-Si3 136.78(2), Si1-Si3-O1 122.40(3), O1-Si3-O2 94.17(4), Si3-O1-C61 109.06(6), O1-C61-C62 113.59(9).

It is well-established that polar substrates facilitate the [2+2] cycloaddition to Si=Si bonds.^[13] As the lower polarity of the C=O bonds in benzil might contribute to the prevalence of the [1+4] cycloaddition pathway, we extrapolated that a reaction of cyclotrisilene **1** with the inherently less polar C=C bond of alkenes might also result in disilenyl silylene reactivity. While a cis/trans isomeric mixture of stilbene (1,2-diphenyl ethene) did not react with **1** even at elevated temperatures, presumably due to steric hindrance, the treatment of cyclotrisilene **1** with one equivalent of styrene (phenyl ethene) at room temperature results in the uniform appearance of three new signals in the ²⁹Si NMR spectrum at δ 103.42, 36.16 and -94.15 ppm (Scheme 4). As in case of **3**, the two low-field signals are diagnostic of an acyclic Si=Si unit. The signal at high field falls well within the

typical region for the endocyclic silicon atom of three-membered C₂Si rings: for instance, siliranes obtained by the reaction of an acyclic iminosilylsilylene and a silylsilylene with ethylene were reported to show resonances at δ -100.90 and -80.76 ppm, respectively.^[14] With the help of a DEPT-135 spectrum (Figure S14-15), the ¹³C NMR signal at δ 10.84 ppm is assigned to the CH₂ moiety in the three-membered ring of 4, while the phenyl substituted ring carbon gives rise to a signal at δ 23.59 ppm. As in the case of 3, the longest wavelength absorption in the UV/Vis spectrum of **4** at $\lambda_{max} = 426$ nm ($\epsilon = 17430$ M⁻¹cm⁻¹) confirms the presence of an acyclic Si=Si unit as it is almost identical to that of a previously reported chlorosilyl disilene ($\lambda_{max} = 427 \text{ nm}$).^[15]



Scheme 3. Synthesis of disilenyl-substituted silirane 4 (kinetic product) and its conversion to housane 5 (thermodynamic product; $R = Tip = 2,4,6-Pr_3C_6H_2$).

After workup, disilenyl-substituted silirane 4 is isolated in 54% yield (m.p. 168-170°C) as an orange powder. Orange blocks suitable for X-ray structure analysis were obtained at -20°C from toluene solution. The molecular structure of 4 in the solid state confirmed the connectivity deduced from the spectroscopic data (Figure 3).^[10] The Si=Si double bond of 2.180(1) Å displays moderate twisting and trans-bending (twist angle $\tau = 17.9(9)^\circ$, trans-bent angle $\theta = 13.2(7)^\circ$ at SiTip₂, 18.4(6)° at Si(Tip)Si). Interestingly, the Si1-Si2 distance of 2.300(1) Å is rather short for the typical Si-Si single bond suggesting a certain degree of hyperconjugation^[16] with the adjacent Si=Si unit.

Given that the steric requirements of styrene

benzaldehyde are fairly comparable, we considered the

possibility of isomerization of the disilenyl-substituted silirane 4

to an isomeric saturated housane structure akin to 2a,b. Indeed,

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and

heating of solid 4 slightly above the melting point for 20 minutes under argon atmosphere affords trisilabicyclo[2.1.0]pentane 5 (Scheme 3) in 32% yield after crystallization from hexane. Colorless single crystals suitable for X-ray diffraction analysis (Figure 4) were obtained from hexane at 5°C confirming the constitution of a housane structure.^[10] The angle between the mean planes of the three- and four-membered rings is 119.0(9)°, which is slightly larger than that in 2a,b (2a: 115.9(4)°; 2b: 113.4(1)°). The Si-Si bond lengths vary between 2.311(2) Å and 2.392(2) Å. Curiously, in the ²⁹Si NMR spectrum of 5 in C₆D₆ solution at 25°C only one signal at δ 14.28 ppm is observed, while in the solid state CP-MAS ²⁹Si NMR revealed the expected three signals at δ 14.72, 8.39 and -88.75 ppm. Similarly, the ²⁹Si NMR spectrum in solution at -40°C displays three signals at δ 13.19, 9.28 and -84.22 ppm, which coalesce in a rather cepted Manusc undefined manner upon warming to room temperature. These findings suggest that the two signals at 9.28 and -84.22 ppm are involved in an unknown dynamic process. Despite the high probability that the high-field signal at -84.22 ppm belongs to the SiTip₂ molety on grounds of similarity with 2a, we confirmed the assignment by calculating the NMR shifts at the M06-2X/def2TZVPP level of theory. The predicted results (δ^{29} Si_{calc} -79.04 (SiTip₂), 29.43 (SiCPh), 20.90 (SiCH₂) ppm) are in qualitative agreement with the experiments. We tentatively explain the peculiar NMR behavior with hindered rotation at the two more congested silicon atoms.



Figure 3. Molecular structure of disilenyl-substituted silirane 4. Hydrogen atoms are omitted for clarity (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (°): Si1-Si2 2.300(1), Si2-Si3 2.180(1), C1-C2 1.533(4), Si1-C1 1.844(3), Si1-C2 1.890(2); Si1-Si2-Si3 125.37(4), C1-Si1-C2 48.44(1), Si1-C2-C1 64.21(2).

Figure 4. Molecular structure of housane 5. Hydrogen atoms are omitted for clarity (thermal ellipsoids at 50%). Selected bond lengths (Å) and angles (°): Si1-Si2 2.392(2), Si1-Si3 2.311(2), Si2-Si3 2.371(1), Si1-C1 1.905(4), Si2-C2 1.916(4), C1-C2 1.546(7), C1-H1 1.05(4), 0.92(5), C2-H2 0.97(3); Si3-Si1-Si2 60.54(5), Si1-Si3-Si2 61.41(5); C1-Si1-Si2 75.38(2), Si1-C1-C2 106.0(3), Si2-C2-C1 99.6(3).

Si3

H1 Si1

Si2 H2

Finally, we pondered the question whether the formation of 5 proceeds (i) as an intramolecular isomerization or (ii) through the dissociation of styrene from the kinetic product 4. A few

reversible [1+2] cycloadditions involving silylenes and ethylene have indeed been reported, e.g. the reaction of ethylene with a phosphonium silaylide^[17] and with acyclic silylenes.^[14b,18] Melting of **4** was therefore repeated under dynamic vacuum in order to remove any liberated styrene rapidly. The melt residue of **4** after having been kept in vacuum at 170°C for two minutes showed the characteristic ²⁹Si NMR signals of cyclotrisilene **1** at δ 42.82, -22.98 ppm. From the ¹H NMR spectrum the yield of regenerated **1** was estimated to about 78% (Figure S15-16), accompanied by small quantities of π addition product **5** and other by-products.

On this basis, we propose the following mechanistic scenario for the formation of 5: the kinetic product of [1+2] addition 4 redissociates to give free styrene and the transient disilenyl silvlene 6, which should rapidly isomerize to cyclotrisilene 1 even at elevated temperature. Under thermodynamic control, [2+2] cycloaddition of 1 with styrene affords housane 5 (Scheme 4). DFT calculations at the dispersion-corrected M062X/def2-SVP level of theory indeed reveal 4 to be about 16.8 kcal mol higher in ΔG_{298} than 5 (Scheme 4). While this difference is only slightly lowered at 443 K, dissociation of 4 to free disilenyl silylene 6 is thermodynamically significantly more feasible $(\Delta \Delta G_{298} = +28.2 \text{ kcal mol}^{-1} \text{ vs. } \Delta \Delta G_{443} = +21.4 \text{ kcal mol}^{-1}).$ According to Hammond's postulate, the kinetics of an equilibrium between 1 and 4 under these conditions ($\Delta\Delta G_{443}$ = +5.7 kcal mol⁻¹) can be approximated by the energy of the transient intermediate 6.



Scheme 4. Mechanism proposed for the formation of housane **5** from the kinetic product disilenyl-substituted silirane **4** (R = Tip = 2,4,6- $Pr_3C_6H_{21}$; Gibb's enthalpies at the M062X/def2-SVP level of theory are given in kcal mol⁻¹).

In conclusion, with species with one isolated carbonyl group cyclotrisilene 1 undergoes formal [2+2] cycloaddition to give housanes 2a,b. In contrast, the reaction with less polar double bonds of benzil and styrene at room temperature likely proceeds via ring-opening to transient disilenyl silylene 6 to give [1+4] and [1+2] addition products 3 and 4, respectively, which represent the first examples of disilenyl silylene reactivity of any cyclotrisilene. Under thermodynamic control, however, 1 and

styrene react through the usual [2+2] cycloaddition pattern to give the housane product **5**. Thermolysis of **4** under vacuum strongly supports the dissociative nature of the transformation to **5**.

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Keywords: Group 14 elements • silicon • low-valent species • ring-opening • cycloaddition

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Layout 2:

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Speed is of the essence in order to ring-open the peraryl-substituted cyclotrisilene $(R = 2,4,6^{-i}Pr_3C_6H_2)$ and coax disilenyl silylene reactivity towards benzil and styrene from it. In case of styrene, the kinetic product with a residual $R_2Si=SiR$ - substituent is transformed into the saturated thermodynamic product via the re-detachment of the styrene reagent at elevated temperature as proven by a control experiment under vacuum.

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