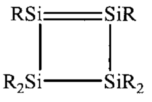
Chalcogenatetrasilacyclopentenes: Five-Membered Rings with Endocyclic Si–Si Double Bonds[**]

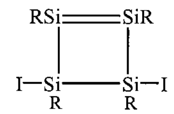
Andreas Grybat, Sven Boomgaarden, Wolfgang Saak, Heinrich Marsmann, and Manfred Weidenbruch*

Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

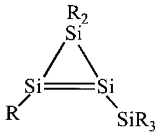
Acyclic disilenes are now well-established molecules, and their properties have been summarized in several review articles.[1] However, molecules containing an endocyclic Si–Si double bond were virtually unknown until recently. The first compound containing this structural element, the cyclotetrasilene **1**, was obtained by Kira et al. by the coupling reaction of two oligosilanes in very low yield (1.5%).[2] In contrast, Wiberg et al. were able to isolate the cyclotetrasilene **2** in high yield from the reaction of a *tetrahedro*-tetrasilane with iodine.[3] Very recently the formation of the cyclotrisilene **3** was described, whose constitution was indicated by spectroscopic data.[4] We now report on the synthesis, properties, and structures of the first five-membered rings containing Si–Si double bonds.



1 R = *t*BuMe$_2$Si



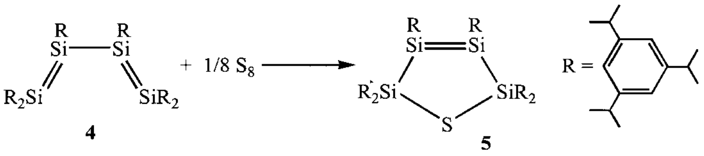
2 R = *t*Bu$_3$Si

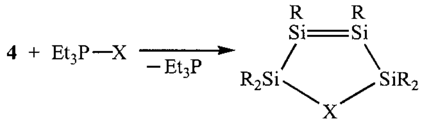


3 R = *t*BuMe$_2$Si

After the successful synthesis of the tetrasilabutadiene **4**[5] we presumed that this molecule should be ideally suited for [4 + 2] cycloadditions, since it adopts the s-*cis* form in the solid state as well as in solution.[6] However, all attempted reactions of **4** with either electron-poor and electron-rich olefins or with acetylenes have remained unsuccessful so far. The reason might be the steric overcrowding of **4** as well as the large 1,4-separation of the silicon atoms of 540 pm.

Thus, it was even more surprising that treatment of **4** with sulfur afforded the five-membered ring **5** in a formal [4 + 1] cycloaddition. Under addition of a small amount of triethylphosphane, selenium and tellurium reacted with **4** to give the analogous rings **6** and **7** in high yield. As opposed to the reactions of disilenes with sulfur,[7] selenium, and tellurium,[8] from which the chalcogenadisilacyclopropanes can be obtained at room temperature, the additions to the tetrasilabutadiene **4** demanded heating in toluene. The reaction time increased appreciably from sulfur to tellurium.





6 X = Se
7 X = Te

First indications on the constitution of **5**–**7** were provided by the ^{29}Si NMR spectra (Table 1), in which only two singlets were detected. The low-field signals are found in the characteristic region for 1,2-diaryl-1,2-disilyldisilenes,[1] while the high-field signals are consistent with the decreasing electronegativity from sulfur to tellurium. A similar tendency was observed in three-membered rings containing two silicon atoms and a chalcogen atom.[7b] The electron spectra of **5**–**7** show an analogous trend, with a bathochromic shift of the longest wavelength absorption from sulfur to tellurium.

Compounds **5**–**7** crystallize isotypically, each with two molecules of toluene. Figure 1 depicts the framework of the sulfur compound, and Figure 2 reflects the steric crowding of

Table 1. Selected data of the ring compounds **5**–**7**.

Compd.	M.p. [°C]	$\delta(^{29}\mathrm{Si})$[a]	$\lambda_{\max}$ [nm] (ε)[b]
5	> 300 (decomp)	86.0, −19.3	423 (16240)
6	279–281	90.3, −27.7	431 (10140)
7	228–229 (decomp)	97.8, −53.5	459 (11440)

[a] ^{29}Si NMR in [D$_6$]benzene. [b] UV/Vis in *n*-hexane.

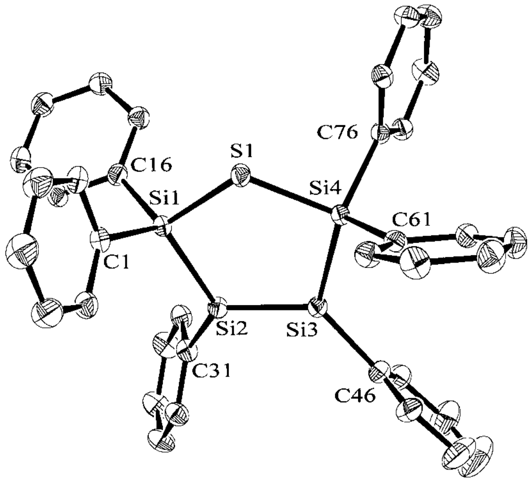


Figure 1. Structure of **5** in the crystal (hydrogen atoms and isopropyl groups omitted, ellipsoids represent the 50% probability level). Selected bond lengths [pm] and angles [°]: Si2–Si3 217.0(1), Si1–Si2 235.5(1), Si3–Si4 235.6(1), Si1–S 217.3(1), Si4–S 217.8(1); Si1-Si2-Si3 108.34(4), Si2-Si3-Si4 109.44(4), Si3-Si4-S 101.96(4), Si4-S-Si1 116.93(4), S-Si1-Si2 102.80(4).

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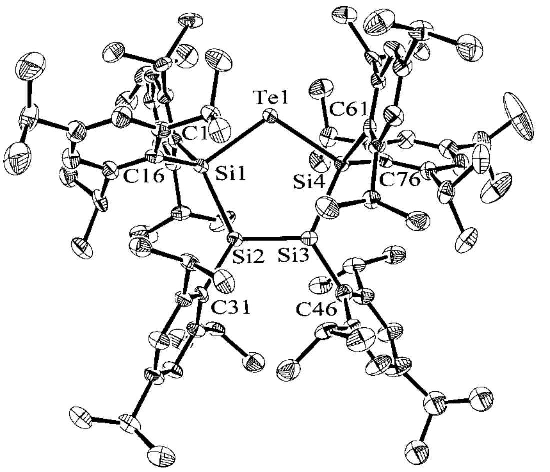

Figure 2. Structure of **7** in the crystal (hydrogen atoms omitted, ellipsoids represent the 50% probability level). Selected bond lengths [pm] and angles [°] for **6** and **7**. **6:** Si2–Si3 218.1(1), Si1–Si2 235.5(1), Si3–Si4 235.9(1), Si1–Se 230.77(9), Si4–Se 231.47(8); Si1-Si2-Si3 110.45(4), Si2-Si3-Si4 111.51(4), Si3-Si4-Se 101.37(4), Si4-Se-Si1 113.99(4), Se-Si1-Si2 102.27(4). **7**: Si2–Si3 219.8(2), Si1–Si2 236.1(2), Si3–Si4 236.4(2), Si1–Te 254.2(1), Si4–Te 254.9(1); Si1-Si2-Si3 114.71(7), Si2-Si3-Si4 114.74(7), Si3-Si4-Te 99.73(5), Si4-Te-Si1 110.40(4), Te-Si1-Si2 100.04(5).

these compounds represented by **7**. The five-membered rings are nearly planar (sum of angles 539.5°) with a slight deviation from planarity towards the twist form. A slight increase is observed in the Si–Si double bond lengths from the sulfur compound **5** to the tellurium compound **7**; all data are consistent with acyclic disilenes of a similar substitution pattern.[1] The highest ring strain should be present in compound **5**, since the large 1,4-separation of the silicon atoms leads to a lengthening of the S–Si bond and a notable widening of the Si-S-Si angle. Because of the larger Si–Se and Si–Te bond lengths the corresponding angles Si-X-Si are significantly smaller and at the same time allow larger Si–Si=Si angles than those observed in **5**.

The new ring compounds are thermally very stable and chemically inert, for example towards air. However, the tellurium compound shows the expected light sensitivity and deposition of tellurium occurs in daylight.

Although the mechanism of formation of **5**–**7** cannot be proven experimentally, the following proposal seems to be reasonable. In analogy to the reaction of disilenes,[7] the reaction sequence could be initiated by a [2 + 1] cycloaddition of a chalcogen atom to one of the Si–Si double bonds, followed by rearrangement of these intermediates into the presumably less strained five-membered rings **5**–**7**. All attempts to isolate **5** or its possible precursors by reaction of **4** with thiiranes remained unsuccessful, since no reaction occurred.

Experimental Section

5: Sulfur (1 g, large excess) was added to a solution of **4** (0.45 g, 0.34 mmol) in toluene (50 mL) and the mixture was heated for 3 h under reflux. Sulfur was removed by cooling to –70 °C and filtration, and the solution was concentrated. Cooling at 4 °C provided yellow needles of **5** (0.40 g, 86% yield). ^{1}H NMR (Bruker ARX 500, [D$_6$]benzene, 60 °C): $\delta=0.35$ (d, 6H, $J=6.5$ Hz), 0.40 (d, 6H, $J=6.2$ Hz), 0.49 (d, 6H, $J=6.3$ Hz), 0.53 (d, 6H, $J=6.3$ Hz), 0.61 (d, 6H, $J=6.6$ Hz), 1.08 (d, 6H, $J=6.3$ Hz), 1.12 (d, 6H, $J=6.7$ Hz), 1.13 (d, 6H, $J=6.9$ Hz), 1.15 (d, 6H, $J=6.0$ Hz), 1.16 (d, 6H, $J=7$ Hz), 1.26 (d, 6H, $J=6.7$ Hz), 1.28 (d, 6H, $J=6.8$ Hz), 1.30 (d, 6H, $J=7$ Hz), 1.36 (d, 6H, $J=6.5$ Hz), 1.42 (d, 6H, $J=6.5$ Hz), 1.46 (d, 6H, $J=6.5$ Hz), 1.51 (d, 6H, $J=6.5$ Hz), 1.87 (d, 6H, $J=6.6$ Hz), 2.69 (sept, 4H), 2.83 (sept, 2H), 3.10 (sept, 2H), 3.66 (sept, 4H), 3.73 (sept, 2H), 4.05 (sept, 2H), 4.52 (sept, 2H), 7.08 (m, 12H); ^{13}C NMR (125 MHz, [D$_6$]benzene, 60 °C): $\delta=21.29$, 21.90, 23.83, 23.92, 24.07, 24.27, 24.50, 24.59, 25.36, 26.27, 26.44, 26.50, 27.34, 28.67, 29.30, 31.72, 34.57,35.09, 35.43, 37.43, 38.06, 38.29, 122.02, 122.26, 122.90, 122.97, 123.62, 123.96, 128.28, 128.49, 129.27, 129.79, 135.15, 142.05, 149.13, 149.98, 150.52, 151.34, 154.74, 154.87, 155.26, 156.29, 156.89; elemental analysis (%): calcd. for $C_{90}H_{138}SSi_4$: C 79.20, H 10.19, S 2.35; found: C 78.98, H 10.02, S 2.31.

6: To a solution of **4** (0.35 g, 0.26 mmol) in toluene (30 mL), an excess of selenium (1.0 g) and a few drops Et$_3$P were added, and the mixture was heated for 4 h under reflux. Toluene was replaced by *n*-pentane, excess selenium filtered off, and *n*-pentane was removed. Crystallization of the residue from a minimum amount of toluene at 4 °C afforded yellow crystals of **6** (0.30 g, 81% yield). ^{1}H NMR (Bruker ARX 500, ([D$_6$]benzene, 25 °C): $\delta=0.38$ (d, 6H, $J=6.3$ Hz), 0.43 (d, 6H, $J=6.3$ Hz), 0.50 (d, 6H, $J=6.4$ Hz), 0.51 (d, 6H, $J=6.4$ Hz), 0.62 (d, 6H, $J=6.6$ Hz), 1.11 (d, 6H, $J=6.5$ Hz), 1.14 (d, 6H, $J=6.6$ Hz), 1.15 (d, 12H, $J=6.9$ Hz), 1.18 (d, 6H, $J=6.9$ Hz), 1.28 (d, 6H, $J=6.9$ Hz), 1.29 (d, 6H, $J=6.7$ Hz), 1.35 (d, 6H, $J=6.7$ Hz), 1.40 (d, 6H, $J=6.5$ Hz), 1.46 (d, 6H, $J=6.4$ Hz), 1.47 (d, 6H, $J=6.5$ Hz), 1.55 (d, 6H, $J=6.6$ Hz), 1.88 (d, 6H, $J=6.6$ Hz), 2.68 (sept, 4H), 2.82 (sept, 2H), 3.15 (sept, 2H), 3.66 (sept, 4H), 3.79 (sept, 2H), 3.99 (sept, 2H), 4.74 (sept, 2H), 6.83 (d, 2H), 7.00 (d, 2H), 7.03 (d, 2H), 7.06 (d, 2H), 7.17 (d, 2H), 7.18 (d, 2H), $^4J=1.5$ Hz); ^{13}C NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta=21.80$, 23.73, 23.94, 23.98, 24.04, 24.13, 24.30, 24.47, 24.65, 25.26, 26.23, 26.36, 26.67, 27.15, 28.59, 34.51, 34.54, 34.59, 37.99, 121.96, 122.05, 122.76, 122.94, 123.47, 124.07, 127.81, 130.27, 134.30, 142.34, 148.93, 149.78, 149.99, 151.16, 154.69, 154.91, 154.97, 156.15, 156.52; elemental analysis (%): calcd. for $C_{90}H_{138}SeSi_4$: C 76.59, H 9.85, Se 5.59; found: C 76.47, H 9.72, Se 5.68.

7: To a solution of **4** (0.31 g, 0.23 mmol) in toluene (30 mL), an excess of tellurium (1.0 g) and a few drops of Et$_3$P were added, and the mixture was heated for 16 h under reflux. Toluene was replaced by *n*-pentane, excess tellurium filtered off, and *n*-pentane was removed. Crystallization of the residue from a minimum amount of toluene at 4 °C yielded orange crystals of **7** (0.28 g, 82% yield). ^{1}H NMR (Bruker ARX 500, ([D$_6$]benzene, 25 °C): $\delta=0.31$ (d, 6H, $J=6.4$ Hz), 0.36 (d, 6H, $J=6.3$ Hz), 0.42 (d, 6H, $J=6.4$ Hz), 0.45 (d, 6H, $J=6.3$ Hz), 0.53 (d, 6H, $J=6.6$ Hz), 1.10 (d, 6H, $J=6.8$ Hz), 1.12 (d, 6H, $J=7$ Hz), 1.14 (d, 6H, $J=7$ Hz), 1.15 (d, 6H, $J=6.8$ Hz), 1.17 (d, 12H, $J=6.7$ Hz), 1.29 (d, 6H, $J=6.4$ Hz), 1.42 (d, d, 6H, $J=6.5$ Hz), 1.44 (d, 6H, $J=6.7$ Hz), 1.46 (d, 6H, $J=6.6$ Hz), 1.53 (d, 6H, $J=6.3$ Hz), 1.55 (d, 6H, $J=6.6$ Hz), 1.90 (d, 6H, $J=6.6$ Hz), 2.66 (sept, 2H), 2.67 (sept, 2H), 2.77 (sept, 2H), 3.14 (sept, 2H), 3.59 (sept, 4H), 3.81 (sept, 2H), 3.99 (sept, 2H), 5.07 (sept, 2H), 6.79 (d, 2H), 6.97 (d, 2H), 6.98 (d, 2H), 7.03 (d, 2H), 7.17 (d, 2H), 7.18 (d, 2H), $^4J=1.5$ Hz; ^{13}C NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta=22.21$, 23.86, 24.03, 24.83, 25.42, 25.71, 26.28, 26.71, 27.37, 28.58, 29.43, 33.36, 34.36, 34.50, 34.58, 35.97, 36.24, 37.51, 37.81, 38.29, 121.52, 122.28, 122.97, 123.29, 123.52, 124.32, 127.81, 131.78, 133.46, 143.19, 148.93, 149.34, 149.91, 150.87, 154.46, 155.29, 156.10, 156.25. On account of the light sensitivity of **7** no satisfactory elemental analysis could be obtained.

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[9] Crystal structure analyses: STOE-IPDS area detector, $Mo_{K\alpha}$ radiation, graphite monochromator, $T = 193(2)$ K, The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2.[10] Hydrogen atoms were placed in calculated positions and refined with anisotropic temperature factors; all other atoms were refined anisotropically. In all structures one of the *para*-isopropyl groups was disordered and was refined on two positions with the occupancy factors of 0.5 each. **5**: $C_{90}H_{138}SSi_4 \cdot 2\,C_7H_8$, triclinic, space group $P\bar{1}$, $a = 1421.59(6)$, $b = 1672.47(12)$, $c = 2291.20(15)$ pm, $\alpha = 69.142(8)$, $\beta = 72.451(7)$, $\gamma = 81.476(7)^\circ$, $Z = 2$, $V = 4848.5(5) \times 10^6$ pm^3, $\rho_{calcd} = 1.061$ g cm^{-3}, $2\theta_{max} = 52^\circ$; of 59638 measured reflections, 17716 were independent and 11548 observed with $I > 2\sigma(I)$, $R1 = 0.063$, w$R2$ (all data) = 0.1671 for 817 parameters. **6**: $C_{90}H_{138}SeSi_4 \cdot 2\,C_7H_8$, triclinic, space group $P\bar{1}$, $a = 1433.48(6)$, $b = 1674.36(10)$, $c = 2300.24(12)$ pm, $\alpha = 68.812(6)$, $\beta = 71.954(5)$, $\gamma = 81.111(6)^\circ$, $Z = 2$, $V = 4888.9(4) \times 10^6$ pm^3, $\rho_{calcd} = 1.084$ g cm^{-3}, $2\theta_{max} = 52^\circ$; of 60128 measured reflections, 17891 were independent and 12099 observed with $I > 2\sigma(I)$. $R1 = 0.0526$, w$R2$ (all data) = 0.1459 for 817 parameters. **7**: $C_{90}H_{138}Si_4Te \cdot 2\,C_7H_8$, triclinic, space group $P\bar{1}$ $a = 1453.30(8)$, $b = 1697.00(9)$, $c = 2029.62(15)$ pm, $\alpha = 95.390(8)$, $\beta = 90.089(8)$, $\gamma = 100.912(6)^\circ$, $Z = 2$, $V = 4892.4(5) \times 10^6$ pm^3, $\rho_{calcd} = 1.116$ g cm^{-3}, $2\theta_{max} = 52^\circ$; of 60004 measured reflections, 17885 were independent and 8548 observed with $I > 2\sigma(I)$. $R1 = 0.0548$, w$R2$ (all data) = 0.0985 for 879 parameters. Crystallogaphic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-116 227 (**5**), CCDC-116 228 (**6**), and CCDC-116 229 (**7**) Copies of the data can be obtained free of charge on application to CCDC, 12 Union Raod, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Regio- and Enantioselective Cyclization of Epoxy Alcohols Catalyzed by a [Co^{III}(salen)] Complex**

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The construction of substituted oxygen heterocycles stands as a significant target for synthetic methodology, mainly as a consequence of the abundance of interesting natural products that contain this structural unit.[1] One of the most important approaches to cyclic ether synthesis involves the intramolecular cyclization of epoxy alcohols, whereby stereospecific epoxide opening offers a stereocontrolled route to these targets.[2] An inherent challenge to this strategy is the control of the regioselectivity of the ring opening of epoxy alcohols. Our own interest in intermolecular asymmetric ring opening (ARO) reactions[3] led us to the question of whether chiral catalysts might influence the regiochemical outcome of intramolecular cyclizations of epoxy alcohol. Such regiocontrol would be rendered even more powerful if accompanied by enantiocontrol, so that racemic or prochiral substrates could be cyclized to produce enantioenriched oxygen heterocycles. Herein we disclose the first intramolecular ARO reaction catalyzed by a chiral [Co^{III}(salen)] complex, with the successful attainment of both regio- and stereochemical elements of control (H_2salen = bis(salicylidene)ethylenediamine).

To date, terminal epoxides represent the most successful substrate class identified in Co-catalyzed ARO reactions. While products arising from *exo* attack are favored under either acidic or basic conditions for epoxides such as 4,5-epoxypentanol (**2**)[4], we were quite surprised to observe that (*R*,*R*)-**1** catalyzed the *endo*-selective ring closure of **2** to afford the tetrahydropyranol **5** as the major cyclization product (12:1) in 46 % yield (by GC). Equally impressive was the remarkable enantiodiscrimination displayed in this reaction. Racemic **2** underwent efficient kinetic resolution to afford the *endo* product in 95 % *ee*,[5] which was isolated in 41 % yield following benzoylation of the crude reaction mixture and subsequent purification by flash chromatography (Table 1). The [Co^{III}(salen)] complex **1** also catalyzed the *endo*-selective kinetic resolution of racemic 5,6-epoxyhexan-1-ol (**3**) to afford the hydroxyoxepane **6** in 47 % yield (39 % yield of isolated product) and 94 % *ee*. A dramatic decrease in the reaction rate was observed with the homologous substrate **4** containing seven carbon atoms; no detectable cyclization products were observed after 48 hours. Nonetheless, the ability of (*R*,*R*)-**1** to override the inherent stereoelectronic preference for *exo* attack in the ring opening of epoxides **2** and

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