Silaselenones

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A Bis(silaselenone) with Two Donor-Stabilized Si=Se Bonds from an Unexpected Stereoconvergent Hydrolysis of a Diselenadisiletane**

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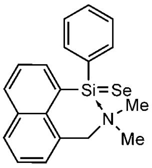
Dedicated to Professor Josef Michl on the occasion of his 70th birthday

Only a few reports of molecular compounds containing Si=Se bonds have appeared. The first such compound, **1**, reported in 1989,[1] was prepared by addition of elemental selenium to a silane. Recent examples, such as **2** (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dipp = 2,6-diisopropylphenyl),[2] **3**,[3] and **4** (Ar = Dipp),[4] were prepared by reaction of selenium with either a silylene or a siloxysilylene. To our knowledge, crystal structure determinations of compounds containing Si=Se double bonds have only been reported for **3** and **4**.



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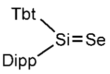

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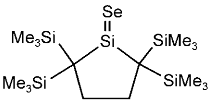

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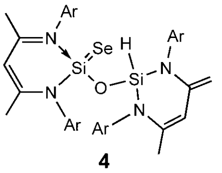

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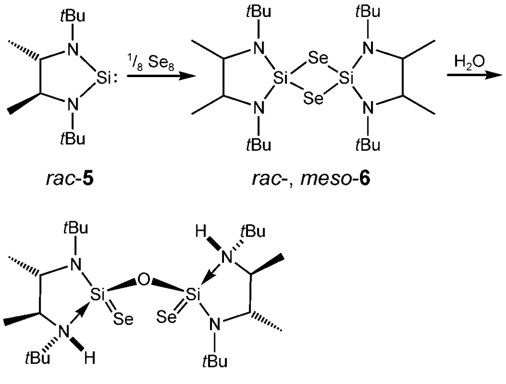
We recently reported the synthesis of the racemic silylene **5**.[5] Herein we present the reaction of **5** with elemental selenium to form both the racemic and *meso* forms of diselenadisiletane **6**, and the unexpected stereoconvergent hydrolysis of **6** with one equivalent of water to produce only the racemic form of the dimeric bis(silaselenone) **7** (Scheme 1). A proposed pathway that accounts for this stereoconvergent hydrolysis and affords only *rac*-**7** is presented. It involves an initial hydrolysis-induced dissociation of both diastereomers (*rac*/*meso*) of **6** to give common OH/SeH-ligated silicon monomers, followed by 1,3-hydrogen transfer from the selenium atom to a nitrogen center, followed by reassembly of the two monomers by condensation of their hydroxy ligands to give oxygen-bridged **7**. This reaction is the first example for the formation of a bis(silaselenone) and is a rare example of induced stereoconvergence.



Scheme 1. Formation of diselenadisiletane **6** and of bis(silaselenone) **7**.

Diselenadisiletane **6** was prepared in good yield (73 %) as a pale yellow solid by combination of equimolar amounts of elemental selenium with the silylene **5** in hexane. Multinuclear NMR (^{1}H, ^{29}Si, ^{77}Se) spectra all have two sets of signals at room temperature, which is consistent with the isolation of **6** as a solid consisting of a mixture of both the *meso* and racemic forms. The ^{1}H NMR spectrum has two sets of *tert*-butyl, backbone methyl, and backbone methine protons, as expected for a mixture of two diastereomers. Similarly, the ^{29}Si NMR spectrum also has two signals at $\delta = -73.8$ and -73.9 ppm. These shifts compare well with the ^{29}Si NMR shift for the similar Si_2Se_2 four-membered-ring-containing compound obtained from the reaction of elemental selenium with an unsaturated silylene ($\delta = -68.2$ ppm).[6] The ^{77}Se NMR spectrum of compound **6** shows two signals at $\delta = 311$ and 314 ppm.

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Diselenadisiletane **6** is stable towards oxygen, and even to an excess of O_2 in refluxing hexane. However, addition of a stoichiometric amount of water to a toluene solution of **6** at −78 °C, which was stirred and allowed to warm up to room temperature over a 20 h period, led to a color change of the solution from pale yellow to deep orange. Surprisingly, the ^{29}Si NMR spectrum of the reaction mixture showed complete disappearance of the two peaks corresponding to **6** and appearance of one new peak at $\delta = -30.3$ ppm. Similarly, only one peak was observed at $\delta = -344$ ppm in the ^{77}Se NMR spectrum. After concentration of the solution by removal of most of the solvent and storage at −25 °C for several days, orange-yellow crystals of **7** formed. The molecular structure of **7** was unambiguously established from a CCD X-ray diffractometry study at 105 K, in which all the hydrogen atoms were clearly resolved. The fact that **7** crystallizes with four symmetry-equivalent molecules ($Z = 4$) in a monoclinic unit cell of centrosymmetric $P2_1/c$ space group symmetry necessitates a racemic mixture of one crystallographically independent chiral molecule. Figure 1 shows the molecular configuration that ideally conforms to C_2 symmetry, with the twofold axis passing through atom O1. The Si=Se bond lengths are 215.3(1) and 215.6(1) pm, which compare favorably with those in **3** (209.6(1) pm) and **4** (211.7(1) pm),[3,4] and are distinctly shorter than the average Si−Se single bond length (227 pm). Salient structural features are that the two pseudo-equivalent silicon atoms are connected by a symmetrical bridging oxygen atom with Si−O distances of 162.0(2) and 163.9(2) pm and that one hydrogen atom from water is now attached to one of the two nitrogen atoms coordinated to each silicon atom. These two tetrahedrally coordinated nitrogen atoms N2 and N3 form N−Si dative bonds (190.7(2), 191.1(3) pm) that are 20 pm longer than the other two N−Si bonds (170.6(2), 171.7(2) pm) formed from the two trigonal planar nitrogen atoms N1 and N4. Each of the Si=Se double bonds is thereby stabilized by the electron-pair donor coordination of the tetrahedral nitrogen atom to each silicon atom, which gives rise to $N^+ \rightarrow Si{-}Se^-$ charge polarization (that is, a zwitterion).

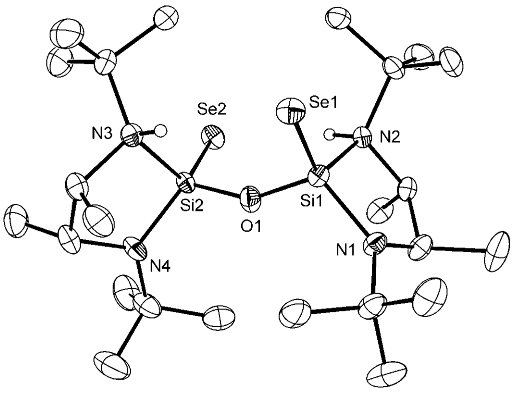
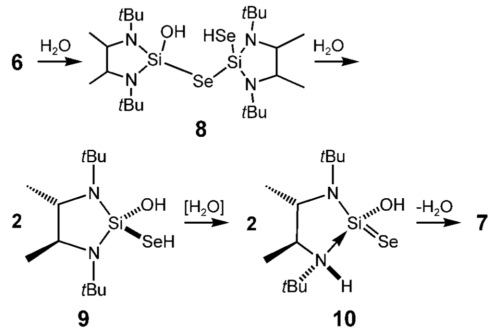


Figure 1. Pseudo-C_2-symmetric molecular structure of **7**. Ellipsoids are set at 50% probability. Hydrogen atoms attached to carbon atoms are omitted for clarity.

The ^{1}H NMR spectrum of **7** agrees well with the solid-state structure obtained from X-ray crystallography. The two non-equivalent *tert*-butyl groups in each unit lead to signals at $\delta = 1.61$ and 1.63 ppm. There are also two sets of chemical shifts for backbone methyl and methine protons of the ligand. The NH protons appear as a broad peak at $\delta = 6.11$ ppm. The ^{29}Si chemical shift $\delta = -30.3$ ppm and the ^{77}Se chemical shift $\delta = -344$ ppm are similar to that for the selenoester **4** (δ^{29}Si: −38.4, −39.1 ppm; δ^{77}Se: −384.8, −401.3 ppm). A UV/Vis spectrum of **7** in heptane has maxima at $\lambda = 210$ (3817), 261 (1333), 331 (564), and 456 (98) nm (ε values in brackets given in L mol^{-1} cm^{-1}).

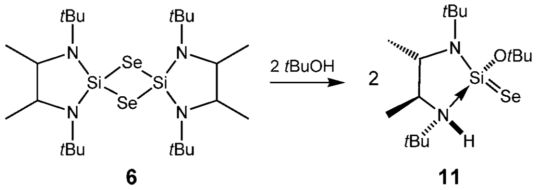
The most striking result of the hydrolysis reaction that affords **7** is that only the racemic mixture is formed instead of an expected mixture of both *meso* and racemic compounds. The hydrolysis reaction is therefore a rare example of spontaneous stereoconvergence. This conclusion is supported by the presence of only a single ^{29}Si and a single ^{77}Se NMR signal in the spectrum of the reaction mixture.

A proposed reaction pathway that accounts for the hydrolysis of **6** and the formation of **7** is presented in Scheme 2. The hydrolysis of both the racemic and the *meso* forms of **6** involves an initial ring opening of the central Si/Se heterocycle by protonation of the selenium atom and nucleophilic attack at the second silicon atom to give compound **8**. A second hydrolysis step affords the monomeric OH/SeH-ligated silicon-containing heterocycle **9**, followed by 1,3-hydrogen transfer from the selenium atom to one nitrogen atom to give the selenosilacarbamic acid **10**.[7] In the final step, condensation of two molecules of **10** affords the oxygen-bridged compound **7**.



Scheme 2. Reaction of diselenadisilaetane **6** with water.

To provide evidence that compound **10** is an intermediate during the hydrolysis of **6** to give **7**, compound **6** and *t*BuOH were reacted in hexane in a 1:2 ratio (Scheme 3). The



Scheme 3. Reaction of diselenadisilaetane **6** with *t*BuOH.

resulting selenosilacarbamic ester **11** was isolated, and its entire molecular geometry was ascertained from a CCD X-ray diffraction determination at 100 K. The molecular structure of **11** (Figure 2) is analogous to that of the two pseudo-symmetry-equivalent halves of **7**, with the notable exception that it shows a *trans* relation between the *tert*-butyl group at N2 and the selenium atom Se1 at the silicon atom Si1. The presence of the *tert*-butoxy substituent attached to the silicon atom in compound **11**, instead of the hydroxy group in selenosilacarbamic acid **10**, prevents a subsequent condensation reaction. The Si=Se bond length (215.3(1) pm) and two markedly dissimilar Si−N bonds (172.1(2) pm) and 192.0(2) pm) in **11** are analogous to those in **7**, as expected. The formation of **11** thus provides compelling evidence for the proposed pathway for **7**, which involves a 1,3-hydrogen transfer from each selenium atom to one nitrogen atom (Scheme 2).

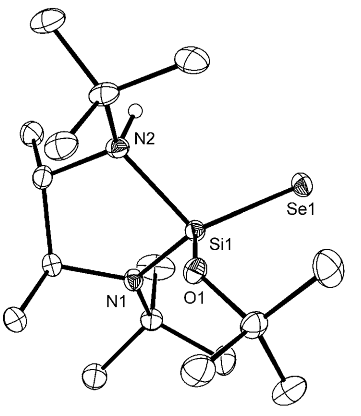
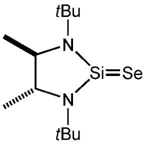


Figure 2. Molecular structure of **11**. Ellipsoids are set at 50% probability. Hydrogen atoms attached to carbon atoms are omitted for clarity.

Quantum mechanical computations[8] at the B3LYP/6-311+G(d,p) and at the MP2/6-311+G(d,p) level are consistent with the proposed pathway for the formation of compound **7**. The hydrolysis of **6** to give **7** is strongly exothermic (−170.6 kJ mol^{-1}; B3LYP/6-311+G(d,p)). The formation of silaselenone **12** as a short-lived intermediate is less likely in view of the unfavorable thermodynamics of the cycloreversion reaction (the formation of **12** from **6** is endothermic by 64.0 kJ mol^{-1}). In contrast, each step of the hydrolysis of compound **6** (Scheme 2) to give two equivalents of silaselenol **9** is predicted to be exothermic (formation of **8** by −29.5 kJ mol^{-1}, and formation of **9** by −39.8 kJ mol^{-1}; B3LYP/6-311+G(d,p)).[9] The 1,3-hydrogen transfer is central to the pathway proposed in Scheme 2 in two respects: 1) it accounts for the formation of the unusual intermediate **10**, and 2) it is the first reaction step in which one stereoisomer is formed selectively and, as a result, it will decisively influence the stereochemistry of the complete hydrolysis/condensation reaction sequence. Therefore, we studied this reaction in more detail using the model compounds **13** and **14** (see the Supporting Information for more details). The model reaction **13a**→**14a** is predicted to be exothermic by −22.0 kJ mol^{-1} (MP2/6-311+G(d,p)) and in the presence of water the formal 1,3-hydrogen shift has a barrier of only 3.8 kJ mol^{-1} (Supporting Information, Figure S2). This small activation energy is in agreement with the fact that the reaction **6**→**7** proceeds even at low temperatures.



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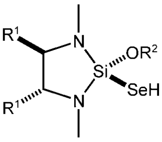

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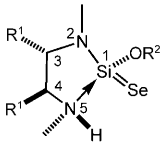
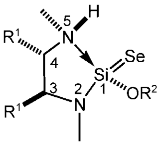


4,5-*trans*-**14**

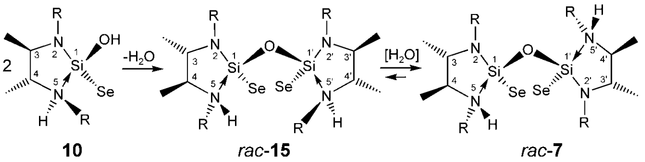


4,5-*cis*-**14**

a: $R^1 = R^2 = H$;
b: $R^1 = R^2 = Me$

To test the stereochemical consequences of the formal 1,3-hydrogen shift, the tautomeric equilibrium for the methoxysubstituted compounds **13b**/**14b** was investigated. In the presence of methanol, the formation of 4,5-*trans*-**14b** is favored over the generation of its 4,5-*cis* isomer by a lower activation barrier (difference in activation barriers: 7.2 kJ mol^{-1}; MP2/6-311+G(d,p); Supporting Information, Figure S4) and, in addition, 4,5-*trans*-**14b** was predicted to be more stable by 6.5 kJ mol^{-1}. Notably, the stereochemical arrangement of the substituents at the five-membered heterocycle in 4,5-*trans*-**14b** is identical to that found for the selenosilacarbamic ester **11** (Figure 2). The preference for the 4,5-*trans* configuration is expected to be even more pronounced for the experimentally investigated *N*-*tert*-butyl-substituted heterocycle **11**, and likewise for the putative intermediate **10**. Thus, the results of the computations provide a mechanism that rationalizes the stereoconvergent formation of the intramolecularly stabilized silaselenone derivatives **10** and **11**.

The stereoconvergent formation of **10** potentially determines the stereochemistry of the subsequent condensation reaction to form **7** (Scheme 4). Consideration of steric factors caused by the bulky *tert*-butyl groups suggests that formation of *rac*-**15** (3*R*,4*R*/3′*R*,4′*R* and 3*S*,4*S*/3′*S*,4′*S*), in which the configuration at Si1 is inverted, is favored over the formation of its *meso* isomer (3*R*,4*R*/3′*S*,4′*S*). The primary condensation product, *rac*-**15**, is then converted into the more stable tautomer *rac*-**7**. This scenario is supported by the results of computations for the relative energies of the tautomers *rac* **7** and *rac* **15**, which reveal that *rac* **7** is more stable by 31.4 kJ mol^{-1} (B3LYP/6-311+G(d,p)).



Scheme 4. Condensation reaction of carbamic acid **10**. R = *t*Bu.

In summary, we have prepared a structurally unprecedented bis(silaselenone) **7**, which contains two donor-stabilized silicon–selenium double bonds, through an unexpected stereoconvergent hydrolysis reaction. The findings are significant from several standpoints. First, this is a unique compound possessing two silicon–chalcogen double bonds. Second, this is the first example in which a direct hydrolysis reaction has been used to form any type of multiple bond between heavier main group elements. Although addition of water to multiple bonds with such elements has been previously studied in much detail, the opposite (i.e., formation of multiple bonds by the addition of water) is rare.[10] The example presented herein suggests the possibility of using analogous solvolysis reactions as a new tool to form donor–stabilized multiple bonds of heavier elements. Finally, it illustrates an intriguing case of spontaneous stereoconvergence. Further experimental/theoretical research currently in progress, including similar reactions with sulfur and tellurium compounds, will be published in due course.

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Keywords: density functional calculations · hydrolysis · silicon · selenium · stereoconvergent reactions

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[7] For related tautomeric shifts in silanoic acid, see: Q.-G. Li, C. Deng, Y. Ren, N.-B. Wong, S.-Y. Chu, X. Wang, *Int. J. Quantum Chem.* **2008**, *108*, 142.

[8] Computations were carried out using Gaussian03 (Revision D.01): M. J. Frisch et al. (see Supporting Information).

[9] The addition of water across a Si–N bond is not expected to give intramolecularly stabilized silicon compounds, as calculations at the B3LYP/6-311+G(d,p) level predict that the product of this water addition features a tetracoordinated silicon atom and that it is stabilized by a intramolecular Si–OH···NH hydrogen bridge. Details of this reaction will be published elsewhere.

[10] Recently a borane-stabilized Si=O complex was synthesized by addition of $H_2O{\cdot}B(C_6F_5)_3$; see: S. Yao, M. Brym, C. van Wüllen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159.