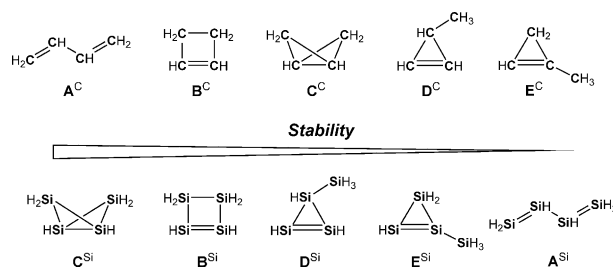**Valence Isomerism**

From a Si_3-Cyclopropene to a Si_3S-Bicyclo[1.1.0]butane to a Si_3S-Cyclopropene to a Si_3S_2-Bicyclo[1.1.0]butane: Back-and-Forth, and In-Between

Vladimir Ya. Lee,* Olga A. Gapurenko, Shogo Miyazaki, Akira Sekiguchi,* Ruslan M. Minyaev, Vladimir I. Minkin, and Heinz Gornitzka

Abstract: *Compact and highly reactive bicyclo[1.1.0]butanes constitute one of the most fascinating classes of organic compounds. Furthermore, interplay of bicyclo[1.1.0]butanes with their valence isomers, such as buta-1,3-dienes and cyclobutenes, is among the fundamental pericyclic transformations in organic chemistry. Herein we report the back-and-forth interconversion between the cyclotrisilenes and thiatrisilabicyclo[1.1.0]butanes, allowing for the synthesis of novel representatives of such classes of highly reactive organometallics. The peculiar structural and bonding features of the newly synthesized compounds, as well as the mechanism of their isomerization, were verified both experimentally and computationally.*

Structural isomerism is one of the most fundamental concepts in organic chemistry, being (at least in part) responsible for a colossal number of organic compounds. As a part of the structural isomerism phenomenon, valence isomerism is of paramount importance. Thus, for example, the valence interplay between the C_4R_6 structural isomers, including the widely known buta-1,3-diene $\mathbf{A^C}$ and cyclobutene $\mathbf{B^C}$ and less commonly encountered bicyclo-[1.1.0]butane $\mathbf{C^C}$ and 3-CH_3- (or 1-CH_3)-cyclopropenes $\mathbf{D^C}$ and $\mathbf{E^C}$ (Scheme 1), is among the most popular organic chemistry textbooks examples (electrocyclic cyclobutene-to-buta-1,3-diene ring opening).[1] From the computational viewpoint, the stability order for the series of C_4H_6 isomers is (in kcal mol^{-1}): $\mathbf{A^C}(0) > \mathbf{B^C}(+14.8) > \mathbf{C^C}(+31.1) > \mathbf{D^C}(+$

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Scheme 1. Relative stability of the E_4H_6 valence isomers (E = C, Si).

32.4) > $\mathbf{E^C}(+36.7)$, whereas for the silicon analogues Si_4H_6 the stability order is reversed with the tetrasilabicyclo-[1.1.0]butane $\mathbf{C^{Si}}(0)$ as the most favorable structure followed by the cyclotetrasilene $\mathbf{B^{Si}}(+3.0)$, 3-SiH_3- (or 1-SiH_3)-cyclotrisilenes $\mathbf{D^{Si}}$ and $\mathbf{E^{Si}}$ (+21.6 and +25.7), and tetrasilabuta-1,3-diene $\mathbf{A^{Si}}(+34.6)$ (Scheme 1: below).[2] Such a discrepancy in the stability within the carbon and silicon series of E_4H_6 (E = C, Si) structural isomers can be readily understood: for the carbon compounds the major destabilizing factor is the ring strain, whereas for the silicon derivatives the overall destabilization is mostly owing to the highly unfavorable presence of the weak Si=Si double bond.
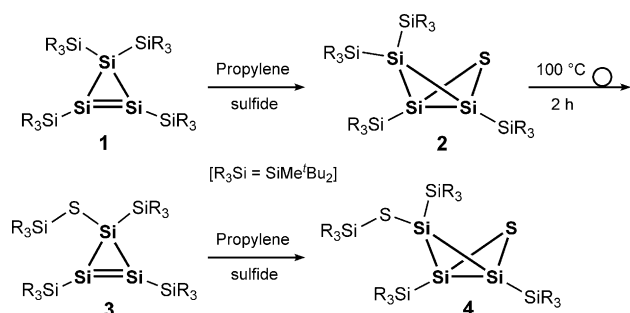
In contrast to the comprehensively studied interconversions of the C_4R_6 isomers, that of their heavy analogues E_4R_6 (E = Si-Pb) has scarcely been explored experimentally, being mostly represented by the thermal isomerization of the Si_4-bicyclo[1.1.0]butane to the Si_4-cyclobutene[3] and photochemical isomerization of the $Si_3(S/Se)$-bicyclo[1.1.0]butane to the $Si_3(S/Se)$-cyclobutene.[4] Herein, we report on the thermal isomerization of thiatrisilabicyclo[1.1.0]butane **2** that leads to a sulfur-substituted cyclotrisilene **3**, which was subsequently reacted with propylene sulfide forming the unprecedented trisilabicyclo[1.1.0]butane derivative **4** featuring two sulfur atoms: one endocyclic and the other one exocyclic. This repetitive {[1+2] cycloaddition–thermal isomerization–[1+2] cycloaddition} reaction sequence represents a unique back-and-forth transformation: from cyclotrisilene **1** to bicyclo-[1.1.0]butane **2**, and then to a new cyclotrisilene **3** and finally to a new bicyclo[1.1.0]butane **4** (Scheme 2).

The overall procedure started with the [1+2] cycloaddition of the cyclotrisilene $\mathbf{1}$[5,6] with the propylene sulfide (as the sulfur atom source) forming thiatrisilabicyclo-[1.1.0]butane **2**.[4] Thermal isomerization of **2** (toluene, 100 °C, 2 h) cleanly produced the cyclotrisilene **3** featuring a (tBu_2MeSi-S)-substituent at the skeletal sp^3-Si atom and

Scheme 2. Synthesis of the thiatrisilabicyclo[1.1.0]butane **2**, (*t*Bu₂MeSi-S)-substituted cyclotrisilene **3**, and (*t*Bu₂MeSi-S)-substituted thiatrisilabicyclo[1.1.0]butane **4**.

representing the first cyclotrisilene with a heteroatom substituent (Scheme 2).[7]

Reaction progress can be readily monitored by ^{29}Si NMR spectroscopy as the diagnostic high-field resonance of the bridgehead silicon atoms at −119.9 ppm in the starting **2** is gradually replaced with the characteristic resonances of the sp²-Si atoms in **3** observed at +137.1 ppm (compared to +97.7 ppm in the cyclotrisilene **1**[5]). To clarify which one of the *t*Bu₂MeSi groups was involved in the migration from Si to S atoms upon the isomerization of **2** to **3**, we at first performed thermolysis of the deuterium-labeled **2-d_6** (with the two *t*Bu₂(CD₃)Si groups at the bridging Si atom). However, that was of a little help because it resulted in a mixture of several isomers of **3-d_6**, in which the labeled *t*Bu₂(CD₃)Si substituents were scrambled over the cyclic sp³-Si, two cyclic sp²-Si and S-atoms.[8] Such nonselective distribution of the deuterium label in **3-d_6** is apparently indicative of competing pathways operating in the isomerization process. One such pathway may involve the initial bicyclo[1.1.0]butane **2** (0 kcal mol⁻¹, for the H-substituted model)[9] ring opening with the formation of intermediate 1-thia-2,3,4-trisilabuta-1,3-diene D₂Si1= Si3(H)-Si2(H)= S1 (**Int1**, +5 kcal mol⁻¹),[10] followed by its ring closure forming the final cyclopropene **3** (+15 kcal

mol⁻¹) with the overall migration of the *D*-substituent from the bridging position Si1 in **2** to the sulfur atom S1 in **3** (Figure 1: pathway A). To get more insight into the mechanistic pathways, we next performed a kinetic analysis of the thermal isomerization of **2** to **3**. ¹H NMR monitoring of the reaction progress in [D₈]toluene allowed for the estimation of activation parameters as follows: activation energy E_a = 22.6 ± 0.5 kcal mol⁻¹, activation enthalpy $\Delta H^{\ddagger}$ = 21.9 ± 0.9 kcal mol⁻¹, and activation entropy $\Delta S^{\ddagger}$ = −15.2 ± 2.5 cal mol⁻¹ K. The notably negative value of the activation entropy suggests that the isomerization of **2** is more likely to proceed through the rigidly fixed transition state (TS) rather than a stepwise process, involving bonds breaking at the rate-determining step. This may point to the operation of an alternative isomerization pathway of **2** (0 kcal mol⁻¹, for the H-substituted model) that involves initial 1,2-migration of one of its bridgehead *H*-substituents from Si2 in **2** to the sulfur atom S1 in **Int4** through the rigid TS giving the (disilenyl)silylene intermediate D₂Si1=Si3(H)-Si2-S1(H) (**Int4**, +13 kcal mol⁻¹). The latter may then undergo intramolecular cyclization to cyclotrisilene with the (*H*-S1)-substituent attached to the sp²-Si atom Si2 (**Int5**, +17 kcal mol⁻¹). This process can be considered as a version of the vinyl carbene-to-cyclopropene isomerization,[11] the silicon variant of which was recently exemplified by an equilibrium between a cyclotrisilene and *N*-heterocyclic carbene (NHC) with NHC-coordinated (disilenyl)silylene by the proposed cyclic NHC-adduct intermediate.[12] The final 1,2-*D*-migration from Si1 in **Int5** to Si2 in **Int6** results in the overall formation of cyclotrisilene **3** (+15 kcal mol⁻¹; Figure 2, pathway B).

It is interesting to note that the cyclotrisilene **3** underwent quantitative photochemical isomerization into the previously reported thiatrisilacyclobutene[4] (λ > 300 nm, r.t., benzene), which upon thermolysis reverted back to **3** (130 °C, toluene).

Homologous to compound **1**, cyclotrisilene **3** possesses a highly reactive endocyclic Si=Si bond, that is the subject for further [1+2] cycloaddition with sulfur forming a novel trisilabicyclo[1.1.0]butane derivative. This was indeed the
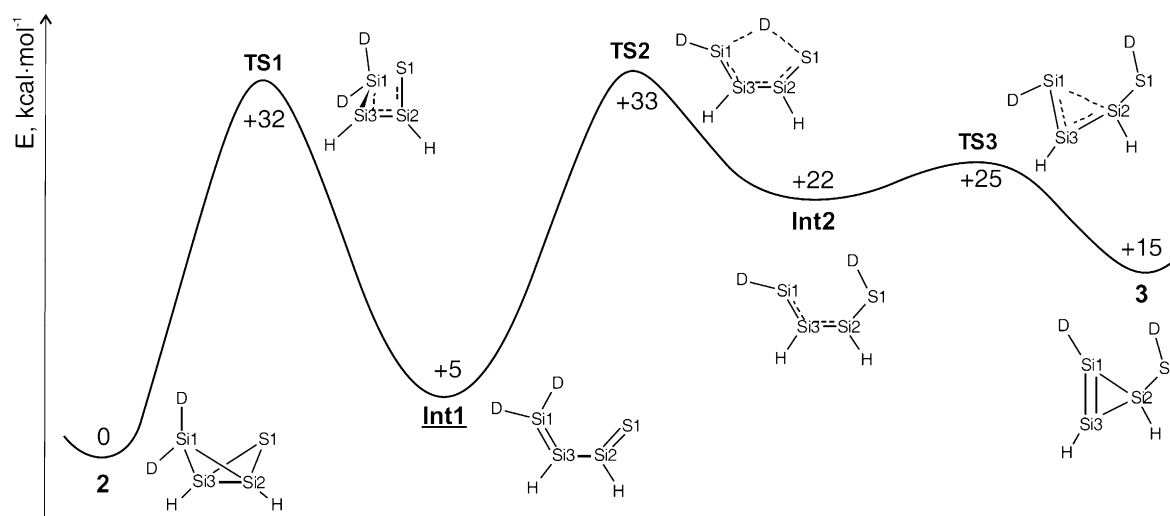
Figure 1. Potential energy surface (PES) for the isomerization of **2** to **3**: pathway A (although computations were performed using H-substituted model, D atoms (instead of H) were placed on the bridging Si1 to visualize the migration path of the substituent from silicon to sulfur).
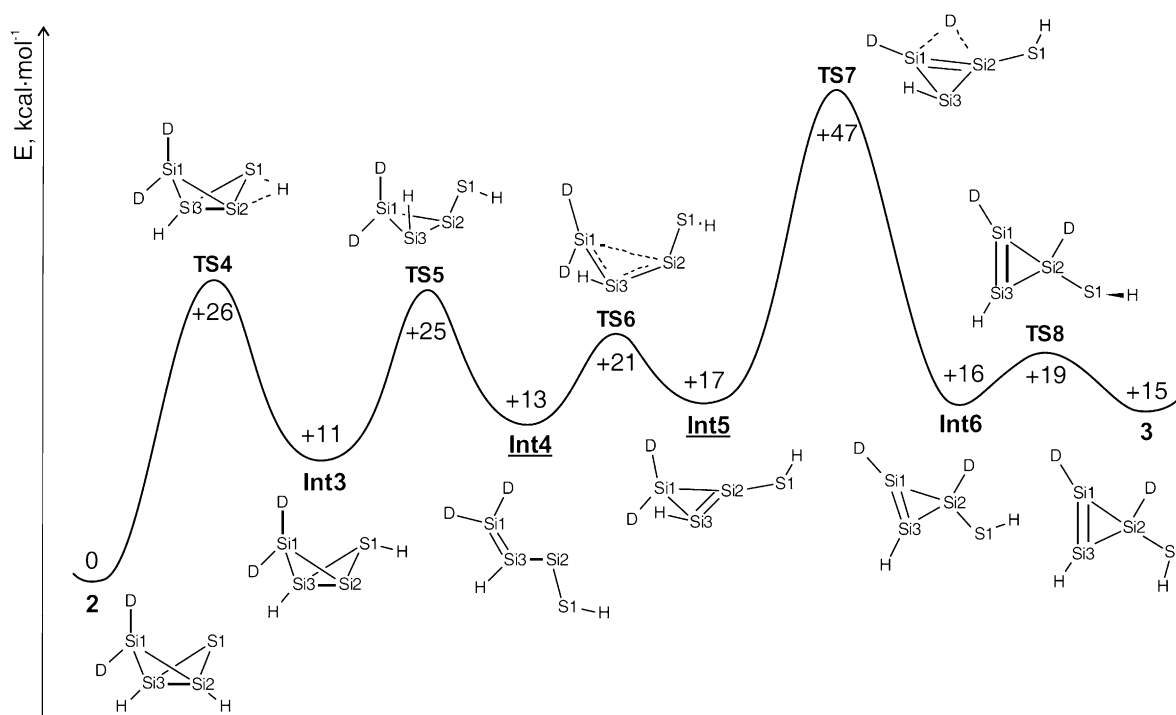
Figure 2. PES for the isomerization of **2** to **3**: pathway B (although computations were performed using H-substituted model, D atoms (instead of H) were placed on the bridging Si1 to visualize the migration path of the substituent from silicon to sulfur).

case when **3** was treated with an excess of propylene sulfide, quickly forming thiatrisilabicyclo[1.1.0]butane **4** with (*t*Bu$_2$MeSi-S)-substituent at the bridging Si atom, as a rather unusual structure with one endocyclic and one exocyclic sulfur atom (Scheme 2).[7] Compound **4** showed characteristic high-field signals for the bridgehead (Si2 and Si3) and bridging (Si1) silicon atoms observed at −123.1 ppm and −27.8 ppm, respectively (compared to −119.9 ppm and −22.0 ppm for the thiatrisilabicyclo[1.1.0]butane **2**[4]).

The crystal structure of **4** was determined by X-ray diffraction analysis, and several of its structural features are of particular importance (Figure 3).[7] First of all, the bridging Si2−Si3 bond is remarkably short, 2.2664(7) Å, which is significantly shorter than the sum of two silicon atoms single-bond covalent radii of 2.32 Å[13] (compared to 2.3541(7) Å for the cyclic Si1−Si2 and 2.3544(7) Å for Si1−Si3 bonds in **4**), being at the upper limit for the Si=Si double bond range of 2.132–2.289 Å.[14]

The Si2−Si3 bond is also notably squeezed compared to other known bicyclo[1.1.0]butanes **5** featuring Si–Si bridges (2.373(3) Å,[15a] 2.367(1) Å,[15b] and 2.412(1) Å),[15c] being on the other hand very close to the values of 2.2664(9) Å and 2.2616(19) Å, recently reported for trisilabicyclo-[1.1.0]butane[8] and selenatrisilabicyclo[1.1.0]butane,[4] respectively. Other striking peculiarities of **4** involve: 1) rather acute interplanar angle ϕ (Si1-Si2-Si3/S2-Si2-Si3) of 106.33° (compared to 115.5(2)° in trisilabicyclo-[1.1.0]butane[8] and 110.34(6)° in selenatrisilabicyclo-[1.1.0]butane[4]); 2) remarkable co-planarity of the bridgehead silyl substituents Si4 and Si5 with the Si$_3$[Si1Si2Si3]-ring (the sum of the bond angles around the bridgehead Si2 and Si3
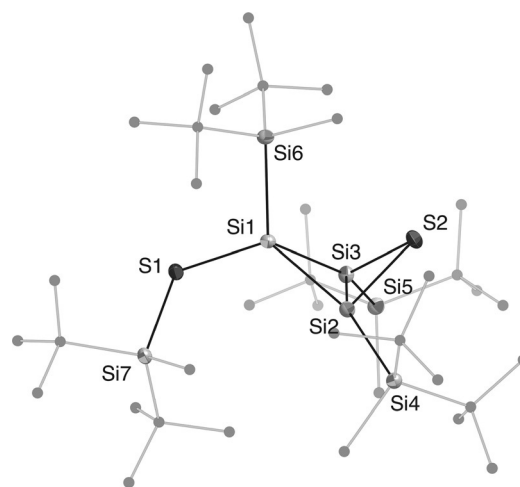
Figure 3. Crystal structure of the (*t*Bu$_2$MeSi-S)-substituted thiatrisilabicyclo[1.1.0]butane **4** (ORTEP view; thermal ellipsoids are given at the 30% probability; H atoms and co-crystallized hexane solvent molecule are not shown; Si6-substituent is positionally disordered and only major contribution (85%) is shown). Selected bond lengths (Å) and bond angles (°): Si2-Si3 = 2.2664(7), Si1-Si2 = 2.3541-(7), Si1-Si3 = 2.3544(7), Si2-S2 = 2.2092(7), Si3-S2 = 2.1925(7), Si1-S1 = 2.1715(7); Si2-Si1-Si3 = 57.55(2), Si1-Si2-Si3 = 61.23(2), Si1-Si3-Si2 = 61.22(2), Si2-S2-Si3 = 61.98(2), S2-Si2-Si3 = 58.65(2), S2-Si3-Si2 = 59.37(2), Si1-Si2-Si4 = 153.70(3), Si3-Si2-Si4 = 144.12(3), Si1-Si3-Si5 = 149.04(3), Si2-Si3-Si5 = 139.97(3), Si6-Si1-S1 = 110.52(4), Si1-S1-Si7 = 115.19(3). Interplanar angle ϕ [Si1-Si2-Si3/S2-Si2-Si3] = 106.33(3).

atoms, ignoring the S2 atom, are 359.15° and 350.23°, respectively).

How one can interpret such peculiar structural features of **4**? One of the superficial explanations is based on the contribution of a Dewar–Chatt–Duncanson-type[16] cyclotrisilene-sulfur π-complex (Supporting Information, Figure S2), similar to the one originally proposed for disilacyclopropanes having an electronegative heteroatom in the ring, namely, oxa-, thia-, and selenadisiliranes, in which the cyclic Si–Si bonds were remarkably short (2.227–2.303 Å).[17,18] Inspection of the fragment molecular orbital interactions of **4** (H-substituted model) revealed a remarkable overlap integral value for the π-donation from the occupied p_S-orbital to the vacant $\pi^*_{Si=Si}$-orbital (HOMO-4) (Supporting Information, Figure S3), that corresponds to a metallacycle structure (Supporting Information, Figure S2), whereas σ-donation of the type $\pi_{Si=Si} \rightarrow p_S$, responsible for the π-complex contribution, was not found.[9] Thus, one should acknowledge a minor (if any) contribution of the π-complex structure to the overall composition of bicyclo[1.1.0]butane **4**. This conclusion is in agreement with the observation of the remarkably high-field resonance of the bridgehead Si atoms in **4** at −123.1 ppm, which does not support notable importance of the π-complex contribution.

Accordingly, instead of relying on the π-complex character of **4**, one can provide an alternative explanation of its structural peculiarities based on the assumption that the decrease in the interplanar angle ϕ and flattening at the bridgehead Si2 and Si3 are both caused by the remarkable steric repulsion between the bulky silyl substituents at the bridging and bridgehead positions (see the Supporting Information for details).[19]

On the other hand, the observed shortening of the bridging Si2−Si3 bond to 2.2664(7) Å can be viewed in terms of the optimal MO interaction. To realize this, it is instructive to compare thiatrisilabicyclo[1.1.0]butane **4** with the tetrasilabicyclo[1.1.0]butanes **5** that have usual Si−Si bridging bonds (for example, 2.373(3) Å[15a] and 2.367-(1) Å[15b]; Figure 4). Replacing one bridging Si atom in **5** with the lone pair heteroatom (sulfur) to form **6** causes less effective Si−S bonding orbital overlap in the latter. To overcome this unfavorable trend, one should rotate the bridgehead silicons around their inversion centers to gain a better overlap and stronger Si−S bonds in **7**. This, however, occurs at the expense of the bridging Si−Si bond, whose bonding begins to suffer from the poor orbital overlap. Finally, to remedy this situation, the bridgehead silicons in **7** are forced to approach each other to the unusually short distance, thus making the highly bent and ultrashort Si−Si bond in the final **4**.

It is interesting that the tBu$_2$MeSi-S-substituent in **4** exclusively occupies a pseudoequatorial position at the bridging Si1 atom (in respect to the bicyclo[1.1.0]butane skeleton; Figure 3). Geometry optimization gave us two energy minima, **4**^{eq} (with the pseudoequatorial S-substituent) that correspond to the experimental structure **4**, and the **4**^{ax} (with the tBu$_2$MeSi-S-group at the pseudoaxial position). Of these two stereoisomers, despite the negligible energy difference between them (ca. 1 kcal mol^{-1} in favor of **4**^{eq} or **4**^{ax}, depending on the orientation of the substituents),[9] only **4**^{eq} was experimentally realized. This can be understood in terms of a substantial steric repulsion hindering the approach of a second S2 atom towards the cyclic Si=Si bond of **3** from the side of the (tBu$_2$MeSi-S)-substituent on the cyclic sp^3-Si atom rather than from the side of the tBu$_2$MeSi-substituent, which can be seen in the side view of the final **4** (Figure S5).

In summary, we reported the synthesis and structural characterization of novel members of highly strained cyclotrisilenes and thiatrisilabicyclo[1.1.0]butanes, which offer a unique blend of room temperature stability and high reactivity. Mechanistic pathways for the thermal isomerization of the thiatrisilabicyclo[1.1.0]butane into the S-substituted cyclotrisilene were investigated both experimentally and computationally. The peculiar structural features of the final S-substituted thiatrisilabicyclo[1.1.0]butane were explained based on the remarkable repulsive interaction between the bulky silyl substituents at the bridging and bridgehead positions.
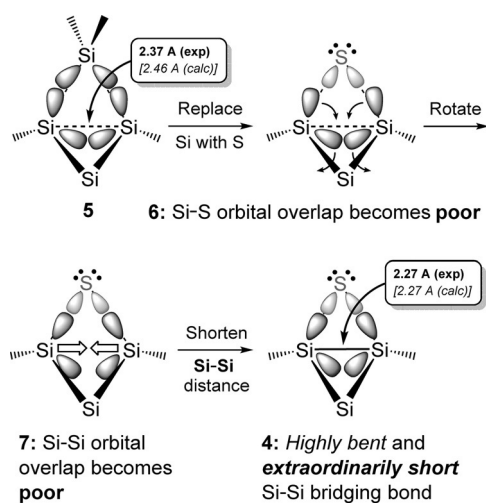
Figure 4. Orbitals matching on going from Si$_4$-bicyclo[1.1.0]butane **5** to Si$_3$S-bicyclo[1.1.0]butane **4**.

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