

Interplay of $E_nE'_{3-n}C$ Valence Isomers ($E, E' = \text{Si}, \text{Ge}$): Bicyclo[1.1.0]butanes with Very Short Bridging Bonds and Their Isomerization to Alkyl-Substituted Cyclopropenes

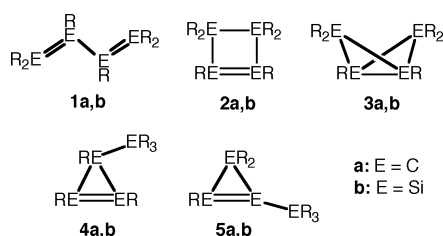
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The interplay and electrocyclic interconversion of the C_4H_6 valence isomers is one of the most intriguing of organic chemistry stories.¹ It is now well established, both experimentally and theoretically, that *trans*-buta-1,3-diene **1a** is much more stable than its valence isomers, representing a global minimum on the C_4H_6 potential-energy surface (Chart 1, $R = \text{H}$).²

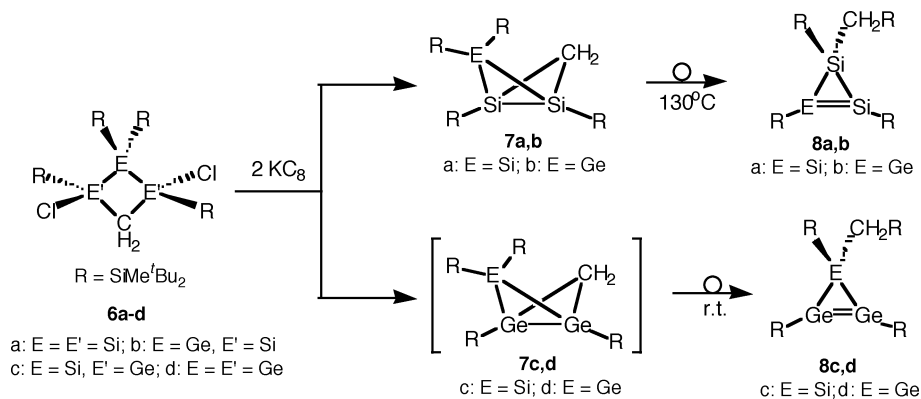
Chart 1



The cyclic versions of C_4H_6 isomers, that is, cyclobutene **2a**, bicyclo[1.1.0]butane **3a**, and 1- and 3- CH_3 -cyclopropenes **4a** and **5a** are significantly destabilized compared with **1a** by 14.8, 31.1, 32.4, and 36.7 kcal/mol, respectively (Chart 1, $R = \text{H}$).² However, among the Si_4H_6 valence isomers, the stability order is reversed with the most favorable structure represented by tetrasilabicyclo[1.1.0]butane **3b**, which is more stable than tetrasilacyclobutene **2b**, 1- and 3- SiH_3 -trisilirenes **4b** and **5b**, and *trans*-tetrasilabuta-1,3-diene **1b** by 3.0, 21.6, 25.7, and 33.3 kcal/mol (Chart 1, $R = \text{H}$).² In marked contrast to the currently well documented C_4R_6 chemistry, the experimental accomplishments in the field of their heavy analogues E_4R_6 ($E = \text{Si}, \text{Ge}$) are much more modest.³ In this paper, we describe the synthesis and unique structures of the novel representatives of heavy bicyclo[1.1.0]butanes, as well as their thermal isomerization to unprecedented alkyl-substituted heavy cyclopropenes.⁴

As suitable starting materials, the four-membered ring *trans*-1,3-dichloro derivatives **6a–d**, readily available by the reaction of

Scheme 1



heavy cyclopropenes^{5,6} with CH_2Cl_2 ,⁶ were selected. The formation of transannular Si–Si bonding was smoothly achieved by the dechlorinative reduction of **6a,b** with 2 equiv of KC_8 to produce the bicyclo[1.1.0]butane derivatives **7a,b** composed of different group 14 elements (C, Si, Ge) (Scheme 1).⁷ In the ^1H NMR spectrum of **7a,b** the three signals of the Me-protons were observed in the ratio 2:1:1, diagnostic of the nonplanar, folded structure of bicyclo[1.1.0]butanes in solution. The signals of the skeletal Si atoms were observed in the high-field range typical for the three-membered ring systems: -132.3 (bridgehead Si) and -81.5 (bridging Si) ppm for **7a** and -130.3 (bridgehead Si) ppm for **7b**. The longest wavelength absorptions in the UV spectra were observed at 352 (for **7a**, ϵ 3050) and 354 (for **7b**, ϵ 3640) nm, corresponding to the σ (bridging Si–Si bond)– σ^* (bridging Si–Si bond) electronic transitions.

The structure of **7a** was determined by X-ray analysis, which unambiguously confirmed its butterfly-type skeleton (Figure 1).⁷ There are two independent molecules in the unit cell of **7a**, which vary only slightly in their geometry; therefore the structural features of only one of them will be discussed below. Of particular importance are the structural peculiarities around the bridgehead Si atoms (Si8 and Si9). First of all, the bridging Si8–Si9 bond is exceedingly short, 2.2664(9) Å, which is much shorter than the average 2.34 Å for the Si–Si single bond, and 2.3540(9) (Si8–Si10) and 2.3769(9) Å (Si9–Si10) in the same molecule **7a**. In fact, such a value of 2.2664(9) Å lies within the upper limit of the Si=Si double bond range (2.138–2.289 Å)⁸ and very closely approaches the 2.2598(18) Å for Si=Si bond of $(\text{tBu}_2\text{MeSi})_2\text{Si}=\text{Si}(\text{SiMe}^t\text{Bu}_2)_2$.⁹ This value is also much shorter than those of two other bicyclo[1.1.0]butanes having bridging Si–Si bonds: 2.373(3)^{3j} and 2.412(1) Å.^{3k} In the framework of the well-established in bicyclo[1.1.0]butane chemistry “short- and long-bond isomers” concept,¹⁰ one should definitely recognize **7a** as the “very short bond isomer”, representing an opposite extreme to 1,3-

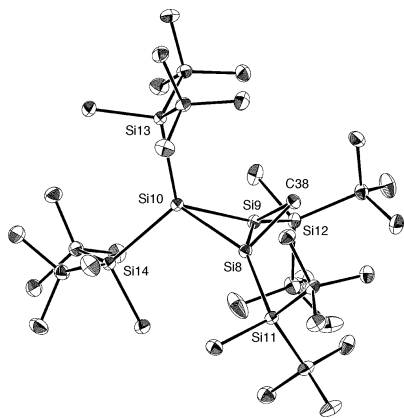


Figure 1. ORTEP drawing of **7a** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Si8–Si9 = 2.2664(9), Si8–Si10 = 2.3540(9), Si9–Si10 = 2.3769(9), Si8–C38 = 1.906(3), Si9–C38 = 1.920(3), Si8–Si11 = 2.3592(9), Si9–Si12 = 2.3769(9), Si10–Si13 = 2.4204(9), Si10–Si14 = 2.4095(9). Selected bond angles (deg): Si9–Si8–Si10 = 61.89(3), Si8–Si10–Si9 = 57.25(3), Si8–Si9–Si10 = 60.87(3), Si8–Si9–C38 = 53.39(8), Si8–C38–Si9 = 72.66(9), Si9–Si8–C38 = 53.95(8). Torsion angle (deg): Si10–Si8–Si9–C38 = 115.5(2).

disilabicyclo[1.1.0]butane with the very long bridging Si–Si bond.^{3k} Consequently, as one can expect for the short-bond isomer, the interplanar angle between the Si8–Si9–Si10 and Si8–Si9–C38 planes is acute (115.5(2)°), whereas the bond angles Si11–Si8–Si9 and Si12–Si9–Si8 are wide (141.72(4) and 152.51(4)°). On the other hand, the short Si–Si bridging bond in **7a** is very similar to that of the only other reported compound with a cyclo-R₄Si₂CH₂ fragment, 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilirane, (2.272(2) Å).¹¹ Similarly, the particular Si₂C bonding situation in **7a** might be realized in view of the crucial importance of the presence of a highly electronegative (relative to Si) bridging carbon atom, which plays the role of an electron acceptor with respect to both bridgehead Si atoms.¹² This would attribute some degree of π -bonding to the Si–Si bridging bond, thus making it rather short.^{13,14} The partial rehybridization of the bridgehead Si atoms was further supported by the essential alignment of the Si11 and Si12 atoms along the Si₃ ring: the sum of the bond angles around the Si8 and Si9 atoms (ignoring the CH₂ fragment) being 351.3 and 358.5°, respectively. The Si8–Si11 (2.3592(9) Å) and Si9–Si12 (2.3769(9) Å) bonds are shorter than Si10–Si13 (2.4204(9) Å) and Si10–Si14 (2.4095(9) Å) bonds because of the smaller steric congestion around the Si8 and Si9 atoms, and also because of the partial π -bond character of the Si8–Si9 bond. Another important reason, contributing to the overall geometry and, in particular, to the shortening of the bridging Si–Si bond, is the small size of the CH₂ bridge, which excludes the possibility of overcrowding typically leading to the elongation of the bridging bond.

Remarkably, when a similar reduction with KC₈ was carried out with **6c,d**, the initially formed bicyclo[1.1.0]butanes **7c,d** were unstable and underwent room temperature isomerization to the more stable heavy cyclopropenes **8c,d** (Scheme 1).^{7,15} The corresponding Si versions **8a,b** were also prepared by the thermolysis of bicyclo[1.1.0]butanes **7a,b** at 130 °C in toluene (Scheme 1). The structures of **8** were confirmed by their crystal (for **8a**) and spectral data (Scheme 1).⁷ Thus, **8a** (**8b**) characteristically exhibited both upfield, sp³-Si, and downfield, sp²-Si, signals for the skeletal Si atoms at –71.7 (–62.5) and 122.8 (126.6) ppm. The mechanism of such a

rather unusual isomerization is not clear in detail at the moment; however, our preliminary study with the deuterium-labeled **7a-d**₆ (with the two ¹Bu₂(CD₃)Si groups at the bridging Si atom) clearly indicate that the migration of one of the ¹Bu₂MeSi groups from the Si to the C atom occurred from the bridgehead, but not from the bridging, position. Interestingly, all of the heavy cyclopropenes **8a–d** represent the nearest homologues of the parent heavy cyclopropenes (¹Bu₂MeSi)₄EE′₂ (E, E′ = Si, Ge),^{5,6} distinguishing from them by only a CH₂ unit. More importantly, **8a–d** represent previously unknown novel E₄ valence isomers of type **4** and also unprecedented alkyl-substituted heavy cyclopropenes (Chart 1).⁵

Supporting Information Available: Experimental procedures and spectral data for **7** and **8**, tables of crystallographic data including atomic positional and thermal parameters for **7a** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) The HOMO of **7a** is represented by the bonding combination of the highly bent orbitals of the bridgehead Si atoms, directed approximately midway between the horizontal (σ -type) and vertical (π -type) overlap (GAUSSIAN 98 at the B3LYP/6-31G(d) level).
- (14) The detailed description of the nature of Si–Si bridging bond in **7a,b**, as well as the mechanism of thermal isomerization of **7** to **8** (kinetics, trapping reactions) will be discussed in the forthcoming full paper.
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