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Skeletal isomerism within 1,3-disilabicyclo[1.1.0]butane and 2,3-disilabuta-1,3-diene derivatives

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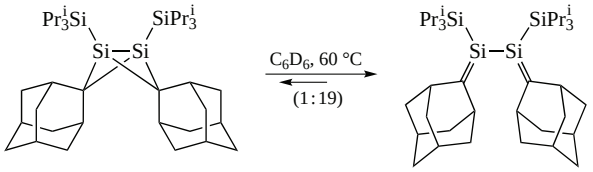
A bis-adamantane-spiro-fused 1,3-bis(triisopropylsilyl)-1,3-disilabicyclo[1.1.0]butane equilibrates with the corresponding 2,3-bis(triisopropylsilyl)-1,3-disilabuta-1,3-diene with a ratio of 1 : 19. The 1,3-disilabuta-1,3-diene was fully characterized by a combination of multinuclear NMR and UV-VIS spectroscopies, elemental analysis, and single-crystal X-ray diffraction analysis.



Keywords: skeletal isomerization, bicyclo[1.1.0]butanes, 1,3-disilabicyclo[1.1.0]butanes, 2,3-disilabuta-1,3-dienes, organosilicon compounds, tetrasilanes.

Skeletal isomerization of compounds with formula C_4R_6 (Figure 1, E = C), has been examined both experimentally and theoretically.[1] Among the C_4R_6 isomers, buta-1,3-diene **A** is substantially stable compared to other skeletal isomers such as cyclobutene **B**, bicyclo[1.1.0]butane **C**, and methylcyclopropenes **D/D′**.Thermal skeletal isomerization of C_4R_6 derivatives usually leads to the corresponding buta-1,3-dienes **A**.[1–5] Interestingly, the corresponding silicon analogues of buta-1,3-diene ($C_{4-n}Si_nR_6$, n = 1–4) are predicted theoretically to be relatively unstable compared to other skeletal isomers[6–9] due to the instability of multiple bonds to silicon and the relative stabilities among the skeletal isomers are substantially dependent on the substituent nature.[10,11] Although various isolable $C_{4-n}Si_nR_6$ derivatives of **A**–**D** stabilized with bulky substituents have been synthesized and their skeletal isomerization has been reported,[12–21] skeletal isomerization that involves thermally stable silabuta-1,3-dienes of type **A** still remains quite rare.[22–32]

Previously, we have reported the synthesis of 2,3-disilabuta-1,3-diene **1a** (Scheme 1) *via* a double sila-Peterson reaction of tetrasilyl-1,2-dilithiodisilane with 2-adamantanone.[33] Compound **1a** was stable below 0 °C, but it gradually isomerized above 0 °C to the corresponding 1,3-disilabicyclo[1.1.0]butane **2a**.[34] Very recently, we successfully synthesized a 1,3-disilabicyclobutane **2b** with more bulky triisopropylsilyl substituents at the bridgehead silicon atoms from **2a** *via* the substitution reaction of the bridgehead silyl groups.[35] Herein, we report the thermal isomerization of compound **2b** to 2,3-disilabuta-1,3-diene **1b**, which is an unprecedented isomerization route [**C** to **A** (E = Si), see Figure 1] among $C_{4-n}Si_nR_6$ species.

While compound **2b** is isolable as yellow crystals and is stable at room temperature, its heating in benzene-d_6 at 60 °C for 8 h caused its skeletal isomerization into 2,3-disilabuta-1,3-diene **1b** (see Scheme 1). This thermal reaction can be monitored by UV-VIS spectroscopy. In the UV-VIS spectrum in hexane, the longest-wavelength absorption band of **2b** at 384 nm arisen from a σ(Si–Si)→σ*(Si–Si) transition[35] is decreased, and a new absorption band at 327 nm appeared with isosbestic points at 271 and 353 nm (see Online Supplementary Materials, Figure S5), which indicates the direct conversions of **2b** to **1b** without the involvement of intermediates. Finally, an equilibrium mixture of **2b** and **1b** with a ratio of ~1 : 19 was obtained (Figure S6). Compound **1b** was estimated to be lower in Gibbs energy by ~8 kJ mol^{-1} than **2b** at 60 °C. Recrystallization from hexane provided analytically pure sample **1b**. The structure of **1b** was characterized by NMR spectroscopy, MS spectrometry, and single-crystal X-ray diffraction (XRD) analysis (*vide infra*). The direct conversion of **2b** to **1b** is opposite to that of the isomerization of Bu^{t}Me$_2$Si-substituted 2,3-disilabuta-1,3-diene **1a** to 1,3-disilabicyclo[1.1.0]butane **2a**. To the best of our knowledge, a skeletal isomerization to a stable silabutadiene from its skeletal isomers as observed in

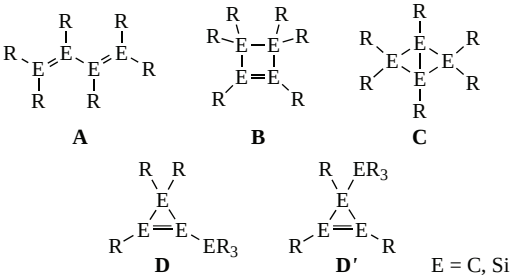
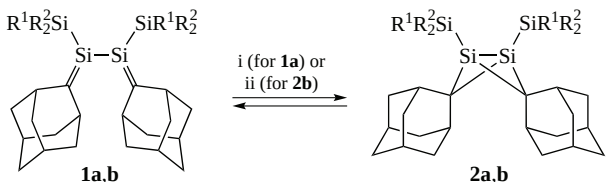


Figure 1 Examples of E_4R_6 skeletal isomers.



a R^1 = Bu^t, R^2 = Me (ref. 34)
b R^1 = R^2 = Pr^i (this work)

Scheme 1 *Reagents and conditions*: i, hexane, >0 °C, $t_{1/2}$ (**1a** → **2a**) 62 min at 32 °C, **1a**/**2a** ratio 0/1; ii, C_6D_6, 60 °C, 8 h, equilibrium **1b**/**2b** ratio ~19/1.

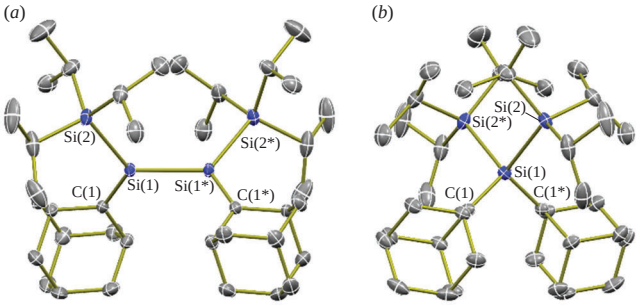


Figure 2 ORTEPs of **1b** (atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity): (*a*) a perspective view; (*b*) a view along the Si(1)–Si(1*) bond. Selected bond lengths (Å) and angles (°): Si(1)–Si(1*) 2.3263(7), Si(1)–Si(2) 2.3720(6), Si(1)–C(1) 1.7474(15), Si(1*)–Si(1)–C(1) 117.29(5), Si(2)–Si(1)–C(1) 119.45(5), Si(1*)–Si(1)–Si(2) 122.92((2), Si(1)–C(1)–C(2) 124.21(11), Si(1)–C(1)–C(3) 124.89(10), C(2)–C(1)–C(3) 110.85(12), C(1)–Si(1)–Si(1*)–C(1*) 90.30(8).

this study is unprecedented. When pure diene **1b** is dissolved in benzene-d_6, bicycle **2b** would gradually form thus indicating that the isomerization between **1b** and **2b** is reversible.

Single crystals of **1b** suitable for XRD analysis (Figure 2) were obtained by recrystallization from hexane.† Molecules of **1b** reside on a crystallographic 2-fold axis. Two Si=C moieties are almost perpendicular to each other, and the dihedral angle [C(1)=Si(1)–Si(1*)=C(1*) 90.30(8)°] is larger than that of less bulky 1,3-bis(*tert*-butyldimethylsilyl)-2,3-disilabuta-1,3-diene **1a** [76.8(1)°].[33] The larger dihedral angle is probably due to the severer steric demand of triisopropylsilyl groups, the environment in the crystals, and an inherent low rotational barrier of the central Si–Si bond in 2,3-disilabuta-1,3-diene: the rotational barrier for parent 2,3-disilabuta-1,3-diene was calculated to be very low (10.9 kJ mol^{-1} at the CCSD(T)/cc-pVTZ level of theory).[36] The Si(1)=C(1) distance [1.7474(15) Å] is comparable to that of **1a** [1.748(2) Å] and a structurally similar isolated silene $(Me_3Si)(Bu^tMe_2Si)Si{=}CR^{Ad}_2$ [CR^{Ad}_2 = 2-adamantylidene, 1.741(2) Å] reported by Apeloig.[37]

In the UV-VIS spectrum in hexane, compound **1b** exhibits two distinct absorption bands at 368 (ε = 2900) and 324 nm (ε = 33000) arising from π(Si=C)→π^*(Si=C) transitions, respectively (Figure 3). This spectral feature of **1b** resembles that observed for **1a** (371 and 322 nm), which exhibits a significant conjugation between two Si=C double bonds. The ^{29}Si and ^{13}C resonances due to the silicon and carbon nuclei (δ_{Si} and δ_C) in the Si=C double bond of **1b** in benzene-d_6 appeared at 41.3 and 196.1 ppm, respectively, which are close to those of **1a** (δ_{Si} = 41.2 and δ_C = 197.3) as well as structurally similar isolated silenes $(Me_3Si)_2Si{=}CR^{Ad}_2$ (CR^{Ad}_2 = 2-adamantylidene) (δ_{Si} = 51.7 and δ_C = 196.6) and $(Bu^tMe_2Si)_2Si{=}CR^{Ad}_2$ (δ_{Si} = 49.7 and δ_C = 198.2) reported by Apeloig.[37]

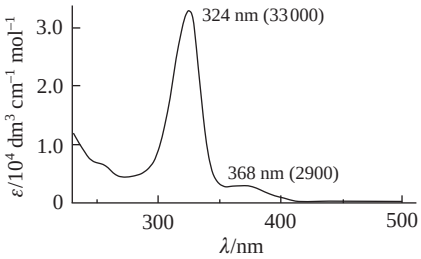


Figure 3 UV-VIS spectrum of **1b** in hexane at room temperature.

The structure and electronic structure of **1b** were further examined by DFT calculations. The structural feature of **1b** optimized at the B3LYP-D3/6-311G(d) level of theory [Si(1)=C(1) distance 1.7484 Å; Si(1)–Si(1*) distance 2.3334 Å; Si(1)–Si(2) distance 2.3737 Å; C(1)=Si(1)–Si(1)=C(1) dihedral angle 83.8°] is close to that obtained from the XRD analysis. Compound **1b** is lower in Gibbs energy (333.15 K) than **2b** (24.4 kJ mol^{-1}) which is consistent with the observed stability of **1b** relative to **2b**. Considering the results of our previous calculations that a model 2,3-disilabuta-1,3-diene with 2-adamantylidene units and two Me_3Si substituents in place of bulky silyl group was higher in energy than the corresponding 1,3-disilabicyclo[1.1.0]butane [73.2 kJ mol^{-1} at the M06-2X/6-311G(d) level of theory],[33] the steric demand of triisopropylsilyl groups would substantially destabilize a 1,3-disilabicyclo[1.1.0]-butane compared to a 2,3-disilabuta-1,3-diene, which should be responsible for the observed relative stability of **1b** and **2b**. This result indicates that relative energies among $C_{4-n}Si_nR_6$ (n = 1–4) isomers including silabuta-1,3-dienes should be controllable using a careful design of the substituents.

In conclusion, we successfully observed an unprecedented isomerization route of a 1,3-disilabicyclo[1.1.0]butane to a 2,3-disilabuta-1,3-diene and characterized the resulting 2,3-disilabuta-1,3-diene.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.012.

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† *Crystal data for* **2b**. $C_{38}H_{70}Si_4$ (M = 639.30), monoclinic, space group $C2/c$ (#15) at 100 K, a = 14.4409(14), b = 15.7090(16) and c = 17.0745(17) Å, β = 96.9760(10)°, V = 3844.7(7) Å^3, Z = 4, d_{calc} = 1.104 Mg m^{-3}, μ(MoKα) = 0.179 mm^{-1}, F(000) = 1416. Total of 19097 reflections were corrected (3.846° ⩽ 2θ ⩽ 50.994°, 3577 independent reflections, R_{int} = 0.0180, R_{sigma} = 0.0113) and used in the refinement, which converged to wR_2 = 0.0911, GOF = 1.038 for all independent reflections [R_1 = 0.0356 for 3577 reflections with $I > 2\sigma(I)$].

The X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer (MoKα radiation, λ = 0.71073 Å). An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS[38] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2018/3).[39] Molecular structure was analyzed by Yadokari-XG software.[40]

CCDC 2100625 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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