

Facile Rotation around Si=Si Double Bonds in Tetrakis(trialkylsilyl)disilenes

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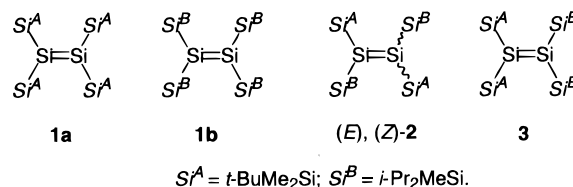
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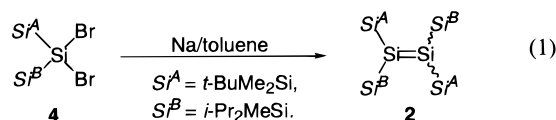
Summary: Stable disilenes having two different trialkylsilyl substituents [$\text{Si}^{\text{A}}\text{Si}^{\text{B}}\text{Si}^{\text{A}}\text{Si}^{\text{B}}$ (*(E)*-**2** and (*(Z)*-**2**) and $\text{Si}^{\text{A}}_2\text{Si}^{\text{B}}_2$ (**3**), where $\text{Si}^{\text{A}} = t\text{-BuMe}_2\text{Si}$ and $\text{Si}^{\text{B}} = i\text{-Pr}_2\text{MeSi}$] were prepared and characterized. Disilene (*(E)*-**2** was found by X-ray crystallography to have the highest planarity around the Si=Si bond among isolated tetrasilyl disilenes. Temperature-dependent ^{29}Si NMR spectra of a mixture of (*(E)*- and (*(Z)*-**2** revealed the facile intramolecular isomerization between (*(E)*-**2** and (*(Z)*-**2** with a free energy of activation less than 15 kcal/mol at 300 K; the value is ca. 10 kcal/mol smaller than those of *E,Z*-isomerization of other known stable disilenes with aryl or alkyl substituents. The origin of the low barrier for the silyl-substituted disilenes is ascribed to the effective $\sigma-\pi$ interaction at the transition state of the isomerization. In addition to the rotational isomerization, the isomerization of **2** to **3** was also observed at higher temperatures.

A number of isolable disilenes (silicon–silicon doubly bonded compounds) have been reported to date,¹ since the first isolation of tetramesityl disilene by West et al. in 1981.² However, substituent effects on structure, reactivities, and reaction mechanisms of disilenes have been discussed only sparsely.³ Such studies of substituent effects will be crucial to the systematic understanding of the characteristics of group-14 homopolar double bonds including C=C bonds. We have recently isolated three tetrakis(trialkylsilyl)disilenes (R_3Si)₂Si=Si(SiR₃)₂ (R_3Si ; *t*-BuMe₂Si (**1a**), *i*-Pr₂MeSi (**1b**), and *i*-Pr₃Si (**1c**)) and described their unusually long Si=Si bond distances, the remarkable dependence of their electronic spectra on the alkyl substituents, and very low-field ^{29}Si NMR resonances of the unsaturated silicon nuclei.⁴ Unique electronic effects of trialkylsilyl substituents would be responsible for these structural characteristics.

We report herein the synthesis, structure, and isomerization of disilenes that have two different trialkylsilyl substituents: (*(E)*-**2**, (*(Z)*-**2**, and **3**. Disilene (*(E)*-**2** was found by X-ray crystallography to have the highest planarity around the Si=Si bond among the tetrasilyl disilenes that have been investigated. The activation free energies for *E,Z*-isomerization of disilenes **2** were sufficient low to allow facile rotation around the Si=Si bonds even at room temperatures.



Reductive coupling of 1-*tert*-butyl-2,2-dibromo-3,3-diisopropyl-1,1,3-trimethyltrisilane (**4**) with sodium in toluene led to a mixture of tetrasilyl disilenes (*(E)*- and (*(Z)*-**2** (eq 1), as observed by NMR spectroscopy.⁵ The major isomer was tentatively assigned as (*(E)*-**2** on the basis of its NMR spectral features.



Recrystallization from hexane at low temperature gave (*(E)*-**2** as air-sensitive orange crystals. The molecular structure as determined by X-ray crystallography is shown in Figure 1 with selected bond lengths and angles.⁶ Among isolated tetrakis(trialkylsilyl)disilenes (**1a–c** and (*(E)*-**2**), disilene (*(E)*-**2** has the highest planarity around silicon–silicon double bond with a bent angle of 0.65° and no twisting. The Si–Si double-bond distance

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(5) Treatment of 2,2-dibromotrisilane **4** (1.00 g, 2.34 mmol) with sodium dispersion (0.16 g, 7.0 mmol) in toluene at room temperature overnight afforded a dark red solution. Filtration of the resulting salt and then removal of solvent in vacuo gave orange crystals. Recrystallization from hexane provided (*(E)*-**2** (179 mg, 0.33 mmol, 29%) as oxygen- and moisture-sensitive orange crystals: HRMS calcd for $\text{C}_{26}\text{H}_{64}\text{Si}_6$, 544.3625; found, 544.3620. The structure was determined by X-ray crystallography. When the crystals were dissolved in toluene, the resulting solution was found to contain (*(E)*-**2** and (*(Z)*-**2** in a ratio of 2:1 (or 1:2) by NMR spectroscopy. (*(E)*-**2**: ^1H NMR (C_7D_8 , 273 K, δ) 0.34 (s, 6 H), 0.44 (s, 12 H), 1.10 (s, 18 H), 1.15 (d, $J = 7.2$ Hz, 12 H), 1.22 (d, $J = 7.2$ Hz, 12 H), 1.30–1.55 (m, 2 H); ^{29}Si NMR (C_7D_8 , 273 K, δ) 6.7, 10.4, 141.8. (*(Z)*-**2**: ^1H NMR (C_7D_8 , 273 K, δ) 0.33 (s, 6 H), 0.47 (s, 12 H), 1.09 (s, 18 H), 1.15 (d, $J = 7.2$ Hz, 12 H), 1.22 (d, $J = 7.2$ Hz, 12 H), 1.30–1.55 (m, 2 H); ^{29}Si NMR (C_7D_8 , 273 K, δ) 6.0, 10.8, 141.9.

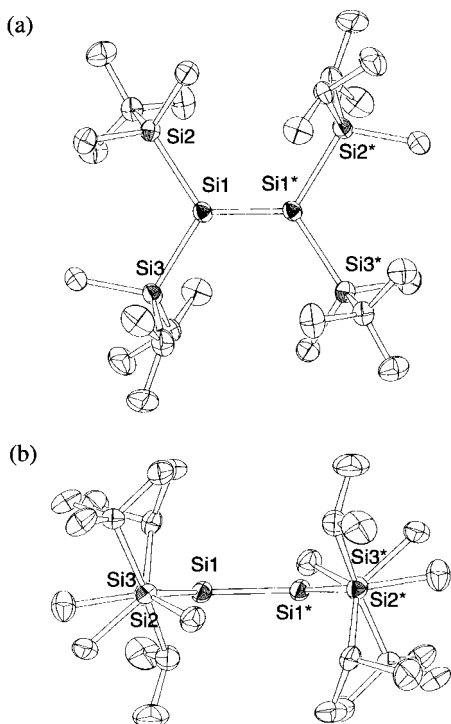


Figure 1. ORTEP drawing of (*E*)-**2**: (a) top view and (b) side view. The thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and bond angles (deg) are Si(1)–Si(1)* 2.196(3); Si(1)–Si(2) 2.369(2); Si(1)–Si(3) 2.379(2); Si(2)–Si(1)–Si(3) 115.73(7); Si(1)*–Si(1)–Si(2) 121.7(1); Si(1)*–Si(1)–Si(3) 122.6(1).

of (*E*)-**2** [2.196(3) Å] is the shortest among the known tetrasilyldisilenes. These results are indicative of a smaller steric repulsion between the vicinal trialkylsilyl substituents Si^A and Si^B than those between two vicinal Si^A in **1a** and between two vicinal Si^B in **1b**.

Dissolving the crystals of (*E*)-**2** in toluene- d_8 afforded again a mixture of (*E*)- and (*Z*)-**2** even at 273 K with an isomer ratio of ca. 2:1, as determined by ^{29}Si NMR spectroscopy using an inverse-gated pulse sequence; the energy difference between (*E*)- and (*Z*)-**2** is estimated to be 0.4 kcal/mol.

The ^{29}Si NMR spectrum of a mixture of (*E*)-**2** and (*Z*)-**2** was remarkably dependent on the temperature. Aside from signals due to another isomer of **2** (**3**, vide infra), two pairs of signals due to *t*-BuMe $_2$ Si (Si^A) and *i*-Pr $_2$ MeSi (Si^B) groups were observed independently at 273 K, as shown in Figure 2. Both pairs coalesced at 303 K (for Si^A) and 308 K (for Si^B) to give two pairs of sharp singlets at temperatures higher than 330 K, indicating that facile isomerization between (*E*)- and (*Z*)-**2** occurs even at room temperature.

There are two possible mechanisms for the *E,Z*-isomerization other than simple rotation around the central Si–Si bond (eq 2): (1) the dissociation–recombination mechanism between the disilene and the

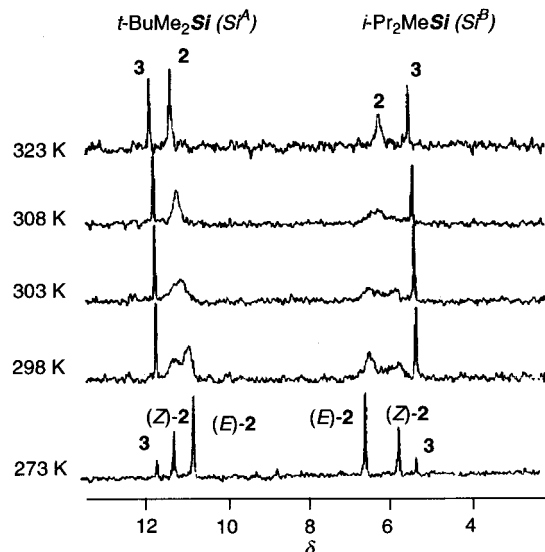
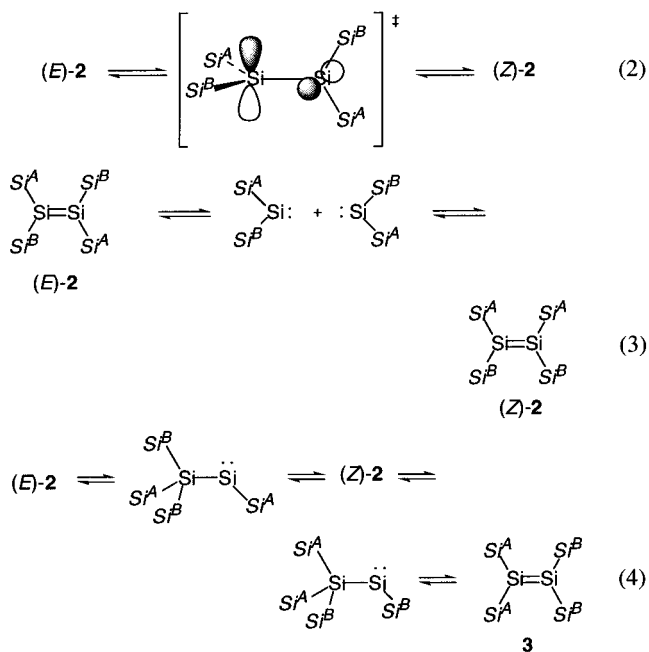


Figure 2. Temperature-dependent ^{29}Si NMR of **2** in the region of the saturated ^{29}Si resonances in toluene- d_8 .

corresponding silylenes (eq 3) and (2) the repeated disilene–disilanylsilylene rearrangement (eq 4).



The dissociation–recombination pathway is known for a tetraaryldisilene,⁷ but the process in the tetrakis-(trialkylsilyl)disilenes is eliminated by the cross-experiments; heating **3**⁸ or a mixture of **1a** and **1b** at 40 °C gave no cross-products. The disilene–disilanylsilylene rearrangement is also known to occur between the transient hexamethyltrisilene and the corresponding trisilane-1,1-diyl at 200 °C.⁹ Although during this process, it is expected to give **3**, our dynamic NMR experiment has shown that the isomerization occurs only between *E* and *Z* isomers of **2**; the signals due to **3** remain sharp between 0 and 50 °C, as shown in Figure

(6) X-ray analysis of (*E*)-**2**: $\text{C}_{26}\text{H}_{64}\text{Si}_6$; fw 545.30; yellow prism; monoclinic; space group $P2_1/c$ (No. 14); $a = 11.395(2)$ Å, $b = 10.339(2)$ Å, $c = 16.223(2)$ Å, $\beta = 109.94(1)^\circ$, $V = 1796.6(5)$ Å 3 ; $Z = 2$; $\rho_{\text{calc}} = 1.01$ g/cm 3 ; $\mu(\text{Cu K}\alpha) = 22.49$ cm $^{-1}$. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (40 kV, 180 mA) using graphite-monochromated Cu K α radiation ($\lambda = 1.54178$ Å) at 150 K. The structure was solved by direct methods, using SIR-92, and refined by full-matrix least-squares on F_o . A total of 3362 reflections were measured, and of these, 1820 reflections [$F_o > 3.0\sigma(F_o)$] were used in refinement: $R = 0.055$, $R_w = 0.057$.

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2, while the isomerization of **2** to **3** occurs at much slower rates (vide infra). The *E,Z*-isomerization of **2** observed by the dynamic ^{29}Si NMR then must occur through the rotation around the Si=Si bond.

The barrier to isomerization from (*E*)-**2** to (*Z*)-**2** was estimated to be ca. 15 kcal/mol at the coalescence temperature (303 K). The barrier height is about 10 kcal/mol smaller than those of *E,Z*-isomerization of other known stable disilenes with aryl or alkyl substituents.¹⁰ The major reason for the low barrier for the silyl-substituted disilenes may be ascribed to the effective σ - π conjugation in the transition state of the isomerization as invoked in the relatively low rotational barrier in tetrasilylethylenes.¹¹ Thus, in the twisted transition structure (eq 2), the $p\pi$ orbital on an unsaturated silicon can interact with the σ and σ^* orbitals of the neighboring unsaturated silicon with the substituent silicons, which leads to the stabilization of the transition structure. The stabilization energy will be much larger than those expected for tetraaryldisilenes, where σ and σ^* orbitals of an Si-C_{Ar} type are involved in the σ - π conjugation; the energy levels of $\sigma(\text{Si-Si})$ and $\sigma^*(\text{Si-Si})$ orbitals are known to be higher and lower than those

of $\sigma(\text{Si-C})$ and $\sigma^*(\text{Si-C})$ orbitals, respectively and, hence, closer to the energy level of the 3p orbital of silicon.¹²

The temperature dependence of the ^{29}Si NMR spectrum was reversible, but significant increase of the signals due to **3** was observed during repeated NMR experiments, suggesting another isomerization pathway of **2** in addition to the *E,Z*-isomerization (eq 2). When a mixture of (*E*)-**2** and (*Z*)-**2** in toluene-*d*₈ was kept for 10 days at 278 K, structural isomer **3** was formed and an equilibrium was established among these three isomers with the ratio of (*E*)-**2**:(*Z*)-**2**:**3** = 2:1:1 (eq 5; see Supporting Information). The structure of **3** was confirmed by comparing the NMR spectra with those of the authentic disilene, which was prepared by reduction of $\text{Si}^{\text{A}}_2\text{SiBrSiBrSi}^{\text{B}}_2$.⁸ Although similar isomerization has been known for dimesityl(dixylyl)disilene, 70 days are needed at 298 K to attain equilibrium.¹³ Interestingly, the ^{29}Si resonances due to unsaturated silicon nuclei of **3** appeared at 131.3 and 156.2 ppm, which are remarkably up- and downfield shifted from that of **2** (δ_{Si} 142). The large separation of the ^{29}Si resonances observed for **3** may imply a significant difference of the geometries around two tricoordinate silicons.



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Supporting Information Available: X-ray structural information on (*E*)-**2** and time course of thermal isomerization of **2** to **3** monitored by ^{29}Si NMR (PDF). An X-ray crystallographic file is also available (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. OM990982K

(8) An alternative synthesis of **3** was performed as follows: To a toluene solution of $\text{Si}^{\text{A}}_2\text{SiBrSiBrSi}^{\text{B}}_2$ (0.36 g, 0.5 mmol), which was prepared by the coupling of $\text{Si}^{\text{A}}_2\text{SiHLi}$ and $\text{Si}^{\text{B}}_2\text{SiHCl}$ followed by the bromination with bromoform at 95 °C, was added a dark green solution of lithium naphthalenide in THF (1.0 M, 1.31 mL, 1.0 mmol) at -73 °C. After the mixture was allowed to warm to 0 °C, the solvent and naphthalene were removed in vacuo at 0 °C. The NMR analysis of the resulting orange oil showed the major formation of **3**. Several attempts to isolate **3** as pure crystals failed because of the easy isomerization to **2** at room temperature. The NMR data of **3** were good in agreement with those observed as a major side product of the *E,Z*-isomerization of **2**. The NMR data of **3**: ^1H NMR (C_7D_8 , 273 K, δ) 0.32 (s, 6 H), 0.46 (s, 12 H), 1.09 (s, 18 H), 1.15 (d, $J = 7.2$ Hz, 12 H), 1.23 (d, $J = 7.2$ Hz, 12 H), 1.30–1.55 (m, 2 H); ^{29}Si NMR (C_7D_8 , 273 K, δ) 5.6, 11.3, 131.3, 156.2.

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