Synthesis, structure and isomerization of A₂Si=SiB₂-type tetrakis(trialkylsilyl)disilenes

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Abstract

Two novel A₂Si=SiB₂-type tetrakis(trialkylsilyl)disilenes: **3**(A = t-BuMe₂Si, B = i-Pr₂MeSi) and **4** (A = t-BuMe₂Si, B = i-Pr₃Si) were synthesized in good yields. X-ray structural analysis revealed that both **3** and **4** have a twisted Si=Si double bond with a planar arrangement around each of the unsaturated silicon atoms. The twist angle around the Si=Si double bond is remarkably dependent on the substituents and amounts to 27.95(3)° for highly congested disilene **4**. Disilene **3** underwent gradually a formal dyotropic rearrangement of trialkylsilyl substituents to give an equilibrium mixture of **3** and (E)- and (Z)-isomers of the corresponding ABSi=SiAB-type disilenes (**2E** and **2Z**). The activation energy for the isomerization of **3** to **2Z** and/or **2E** was found to be much smaller than that for the corresponding isomerization of a tetraaryldisilene system.
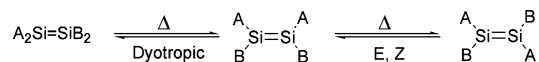© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Tetrasilyldisilenes; X-ray structural analysis; Dyotropic rearrangement; ²⁹SiNMR

1. Introduction

Stable disilenes (silicon–silicon doubly-bonded compounds) have been extensively studied since the first isolation of tetramesityldisilene in 1981 [1]. Now, various types of acyclic and cyclic disilenes such as simple disilenes with bulky aryl, alkyl, and trialkylsilyl substituents [1–3], tetrasila-1,3-dienes [4], cyclic and bicyclic disilenes [5], and a trisilaallene having a formally sp-hybridized silicon atom [6] are known as stable compounds. Although simple disilenes with two different substituents have attracted less attention than those with four identical substituents, West et al. have first demonstrated interesting rearrangements among a set of isomeric disilenes, (E)- and (Z)-ABSi=SiAB and A₂Si=SiB₂ [7]. In addition to the E,Z-isomerization, a formal dyotropic rearrangement was found, which was unprecedented among Group 14 metal–metal double bond systems (Scheme 1).

Following our studies of stable tetrakis(trialkylsilyl)disilenes (**1a**–**1c**) (Chart 1) [8a], we have recently reported the isomerization of (E)- and (Z)-1,2-bis(t-butyldimethylsilyl)-1,2-bis(diisopropylmethylsilyl)disilenes (**2E** and **2Z**) [8b]; the activation free energies for E,Z-isomerization between **2E** and **2Z** were found to be 10 kcal mol^{-1} lower than those for the corresponding isomerization in tetraaryldisilenes [7b]. Although a formal dyotropic rearrangement of **2E** and/or **2Z** to 1,1-bis(t-butyldimethylsilyl)-1,1-bis(diisopropylmethylsilyl)disilenes (**3**) was evidenced, disilene **3** has not been isolated or well characterized. We wish herein to report the successful synthesis and X-ray structures of disilene **3** and a novel A₂Si=SiB₂-type disilene **4** and a formal dyotropic rearrangement of **3** to **2Z** (or **2E**). While novel A₂Si=SiB₂-type disilenes (A = i-Pr₃Si, t-Bu₂MeSi; B = mesityl, 2,4,6-triisopropylphenyl) were recently synthesized using a new route, no formal dyotropic rearrangement was observed in these disilenes [9].

$$A_2Si=SiB_2 \underset{\text{Dyotropic}}{\overset{\Delta}{\rightleftharpoons}} \overset{A}{\underset{B}{\text{Si}}}=\overset{A}{\underset{B}{\text{Si}}} \underset{E, Z}{\overset{\Delta}{\rightleftharpoons}} \overset{A}{\underset{B}{\text{Si}}}=\overset{B}{\underset{A}{\text{Si}}}$$

A = 2,4,6-trimethylphenyl, B = 2,6-dimethylphenyl
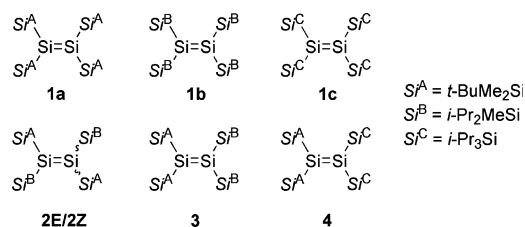A = 2,4,6-trimethylphenyl, B = 4-t-butyl-2,6-dimethylphenyl

Scheme 1.

Chart 1.

2. Results and discussion

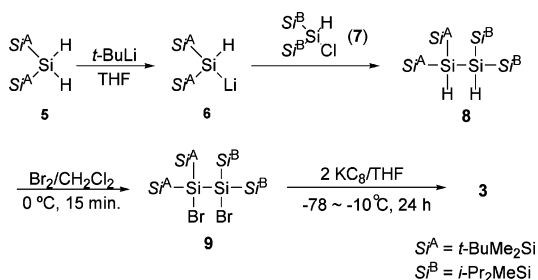### 2.1. Synthesis of $A_2Si=SiB_2$-type disilenes 3 and 4

As a precursor for disilene **3**, the corresponding 1,2-dibromodisilane **9** was synthesized as shown in Scheme 2 via a silametallation developed recently by us [10]. The reaction of bis(*t*-butyldimethylsilyl)hydridosilyllithium (**6**), which was obtained by the silametallation of the corresponding dihydridosilane (**5**) with *t*-butyllithium, with bis(diisopropylmethylsilyl)chlorosilane (**7**) afforded 1,1-bis(*t*-butyldimethylsilyl)-2,2-bis(diisopropylmethyl-silyl)disilane (**8**) in 71% yield based on **5**. Bromination of 1,2-dihydridodisilane **8** with bromine at 0 °C afforded the corresponding 1,2-dibromodisilane **9** in 76% yield. Reduction of **9** with potassium graphite in THF at low temperatures gave the corresponding disilene **3** as air- and moisture sensitive orange crystals in 92% yield. Neither **2E** nor **2Z** was detected in the product.

Disilene **4** was synthesized using a similar silametallation route in 33% yield based on bissilylsilane **5** (Eq. (1)). Disilenes **3** and **4** were characterized by ^{1}H, ^{13}C, and ^{29}Si-NMR spectroscopies, and X-ray crystallography.

(1) *t*-BuLi/THF, (2) (Si^C)$_2$SiHCl
(3) Br$_2$/CH$_2$Cl$_2$, (4)KC$_8$/THF

$$\mathbf{5} \xrightarrow{\hspace{4cm}} \mathbf{4} \qquad (1)$$

As an alternative synthesis of **3**, we have previously investigated the reduction of **9** with lithium naphthalenide [8b]. Although the NMR analysis of a product mixture showed the major formation of **3**, isolation of pure **3** failed because of the contamination of small amounts of disilenes **2E** and **2Z**. The spectroscopic data for **3** obtained by the present synthesis are in good accord with those assigned to **3** in the previous study.

Scheme 2.

2.2. X-ray structural analysis of 3 and 4

Although a number of stable $A_2Si=SiB_2$-type disilenes have been synthesized, no X-ray analysis of these disilenes have been reported so far. Recrystallization of **3** and **4** from hexane and diethyl ether, respectively, below −10 °C afforded single crystals suitable for X-ray diffraction studies. The molecular structures of **3** and **4** are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles. In a crystal of **3**, there are crystallographically independent two molecules with almost the same structural parameters to each other. Structural parameters for disilenes **3** and **4** are compared with those for related tetrakis(trialkylsilyl)disilenes in Table 1. The geometry around Si=Si bond of **3** and **4** is similar to that of $A_2Si=SiA_2$-type disilene **1a** but different from disilene **1b**. Disilenes **3**, **4** and **1a** have a twisted Si=Si double bond with a planar arrangement around each of the unsaturated silicon atoms, while **1b** has a bent Si=Si double bond. The twist angle around Si=Si double bond is considerably dependent on the substituents and amounts to 27.95(3)° for highly congested disilene **4**. Since the Si=Si double bonds in tetrakis(trialkylsilyl)disilenes are soft as suggested in a previous paper [8a], the geometry is determined by delicate balance of the steric effects of the substituents.

2.3. ^{29}Si-NMR of disilenes 3 and 4

The ^{29}Si resonances due to unsaturated silicon nuclei appeared at 132 and 157 ppm for **3** and 142 and 152 ppm for **4**. Differences of the ^{29}Si resonances between two differently substituted unsaturated silicon nuclei in **3** and **4** are remarkably large, in spite of small differences in electronic effects of the two substituents. Although we have suggested in a previous paper [8b] that the large separation of the ^{29}Si resonances observed for **3** resulted from a difference of the geometry around two unsaturated silicon atoms, in fact the geometry is quite similar for the two silicon atoms in these compounds. The chemical shift differences in **3** and **4** may be a reflection of small but significant polar nature of the unsymmetrically substituted Si=Si double bond.

2.4. Formal dyotropic isomerization of 3 to 2

A formal dyotropic rearrangement of tetraaryldisilenes was first observed by West et al. as shown in Scheme 3. On the basis of a kinetic study for a set of disilenes (A = mesityl, B = 2,6-xylyl), a concerted dyotropic rearrangement [11] in Scheme 1 was proposed as a favorable pathway for the intramolecular rearrangement rather than a disilene–silylsilylene rearrangement. Equilibrium among three isomeric disilenes was attained after 70 days at 25 °C; the activation parameters were
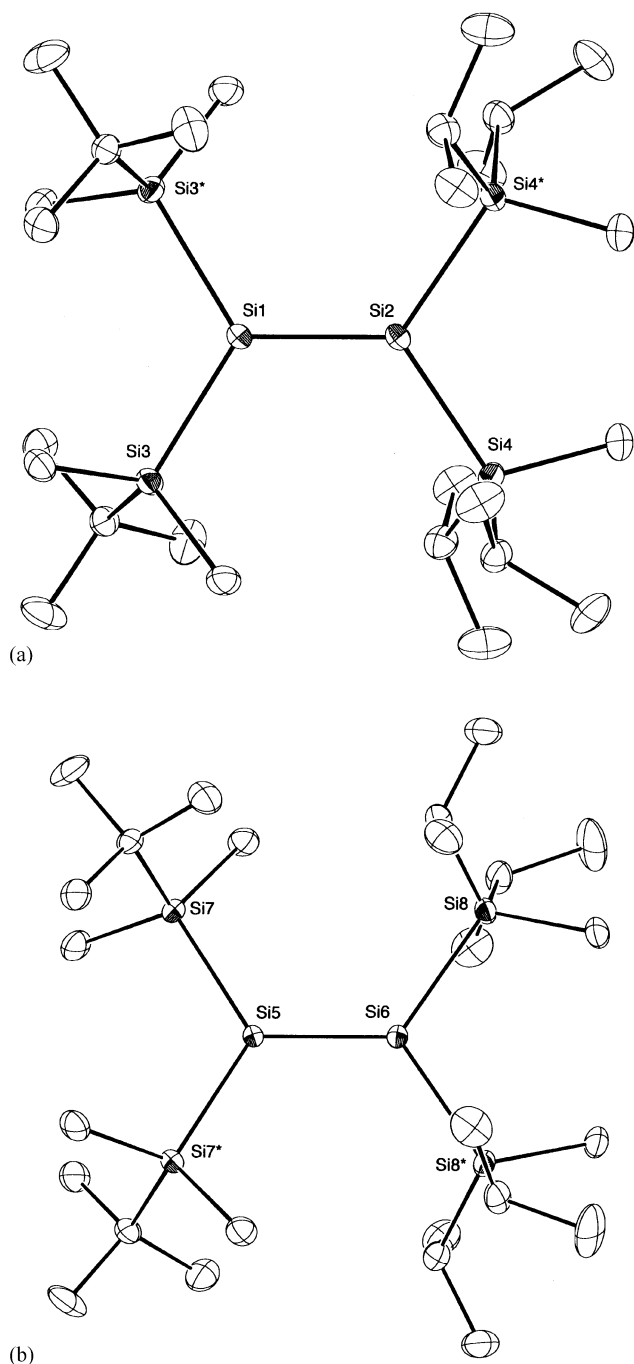
(a)

(b)

Fig. 1. Molecular structure of disilene **3**. (a) Molecule A. (b) Molecule B. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1–Si2 2.198(1), Si1–Si3 2.3807(6), Si2–Si4 2.3727(6), Si5–Si6 2.1940(8), Si5–Si7 2.3706(6), Si6–Si8 2.3692(6), Si2–Si1–Si3 121.04(2), Si1–Si2–Si4 123.22(2), Si3–Si1–Si3* 117.92(4), Si4–Si2–Si4* 113.56(4); Si6–Si5–Si7 121.00(2), Si5–Si6–Si8 124.19(2), Si7–Si5–Si7* 118.00(3), Si8–Si6–Si8* 111.63(3), Si3–Si1–Si2–Si4 8.96(2), Si7–Si5–Si6–Si8 11.73(2).

determined to be $\Delta H^{\ddagger} = 15 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -36$ cal mol^{-1} s^{-1} for the forward reaction.
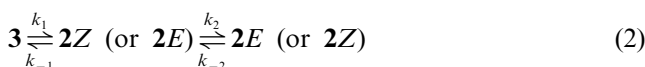
We have previously reported that during the facile reversible isomerization between **2E** and **2Z**, a rearran-

Table 1
Structural parameters for **3**, **4** and related disilenes

| Disilene	d(Si=Si) (Å)	θ (°)	γ (°)	Ref.
3 (molecule A)	2.198(1)	0	8.97(2)	This work
3 (molecule B)	2.1942(8)	0	11.73(2)	This work
4	2.2011(9)	0	27.95(3)	This work
1a	2.202(1)	0	8.9	[3b]
1b	2.228(2)	5.4	0	[3b]
2E	2.196(3)	0.65	0	[8]

gement of **2E** and/or **2Z** to **3** was observed; when a mixture of **2E** and **2Z** 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 **2E**:**2Z**:**3** = 1:0.5:0.5 [8b].

To obtain more detailed information of the formal dyotropic rearrangement, we investigated the isomerization of **3** to a mixture of **2E** and **2Z**. The equilibrium was established after 7 days at 283 K with the **2E**:**2Z**:**3** ratio of 1:0.47:0.67. By pursuing the time course of the signal intensities of these isomers by ^{1}H-NMR spectroscopy, the rate constants k_1 and k_{-1} in Eq. (2) were determined at 283 K as 2.6×10^{-6} s^{-1} and 3.7×10^{-6} s^{-1}, respectively. The activation free energy for the rearrangement from **3** to **2Z** (or **2E**) at 283 K was calculated to be 17.4 kcal mol^{-1}, which was ca. 1.7 kcal mol^{-1} larger than that for the E,Z-isomerization and 7.7 kcal mol^{-1} smaller than those for the dyotropic rearrangement of tetraaryldisilenes reported by West et al. [7b].

$$3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Z \text{ (or } 2E) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2E \text{ (or } 2Z) \qquad (2)$$

It is interesting to note that the activation free energies for both E,Z-isomerization and formal dyotropic rearrangement for the tetrasilyldisilene system are remarkably lower than those for tetraaryldisilenes. A disilene–silylsilylene rearrangement may not be excluded for the rearrangement between **3** and **2Z** (or **2E**), because of the high 1,2-migratory aptitude of silyl
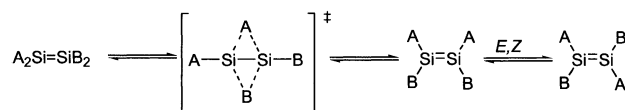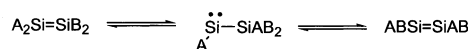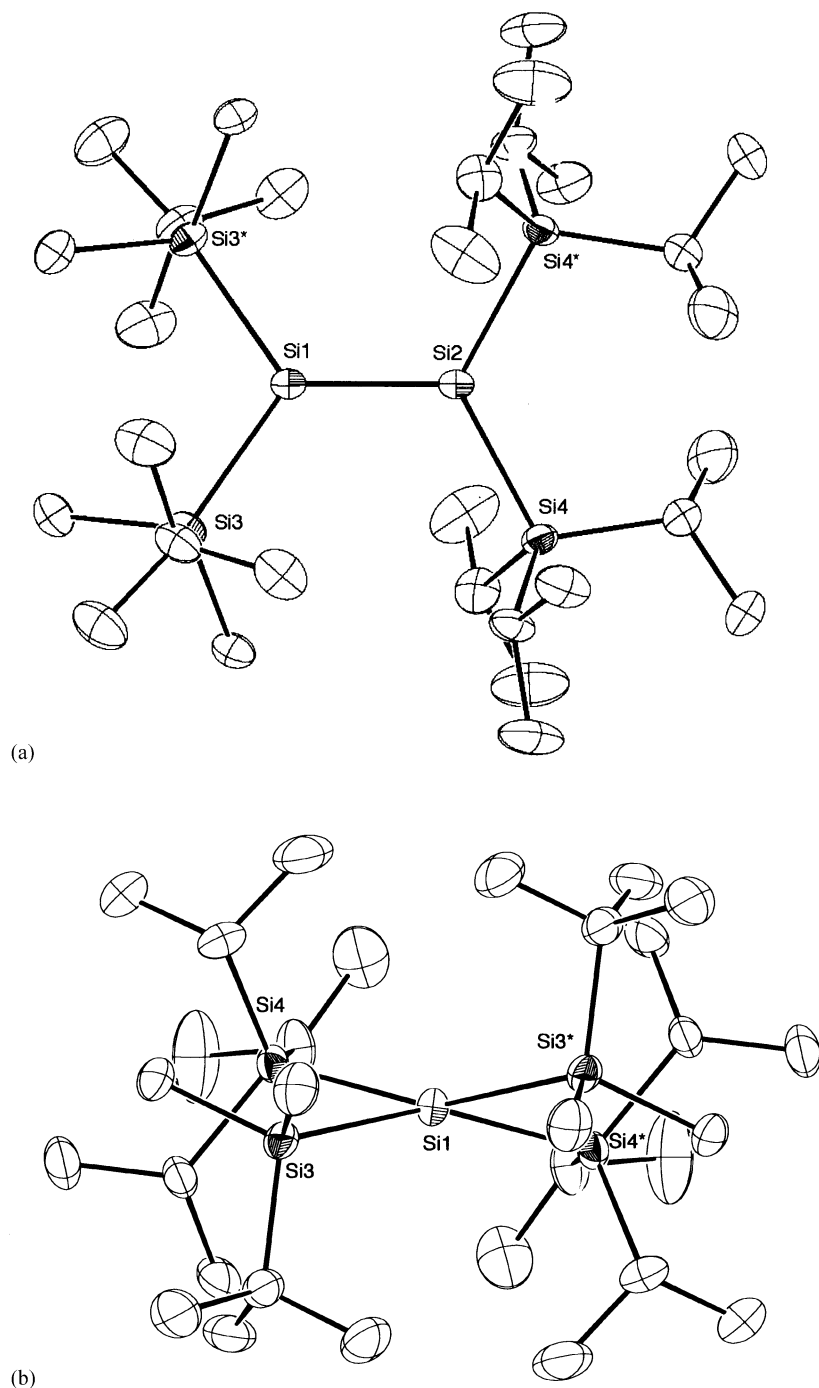

Scheme 3.

Fig. 2. Molecular structure of disilene **4**. (a) Top view. (b) Side view. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.2011(9), Si1–Si3 2.3682(6), Si2–Si4 2.3773(8), Si2–Si1–Si3 123.80(2), Si3–Si1–Si3* 112.41(4), Si1–Si2–Si4 117.71(2), Si4–Si2–Si4* 124.58(4), Si3–Si1–Si2–Si4 27.95(3).

groups [12]. While no silylene insertion product was detected during the rearrangement in the presence of excess triethylsilane, a typical trapping reagent for silylenes, this fact may not provide evidence for the concerted dyotropic rearrangement. At higher theoretical levels, disilene ($H_2Si=SiH_2$) is calculated to be more stable than silylsilylene ($H(H_3Si)Si:$) with rather high activation energy for the forward rearrangement of

disilene to silylsilylene [13]; the relative energy is 7.9 kcal mol^{-1} at the G1 level [14] and the activation energy is 17.3 kcal mol^{-1} at the MP3/6-31G(d,p)//HF/6-31G(d) level [15], while these values depend considerably on the theoretical levels. If disilenes **3** as well as **2E** and **2Z** are more stable than the corresponding silylsilylenes and the activation energy for the rearrangement of **3** to the corresponding silylsilylene is a little lower than the

theoretical value, the disilene–silylsilylene rearrangement will be feasible and the insertion of the silylsilylene into a Si–H bond may not compete with the rapid backward rearrangement to the disilenes. Further works including theoretical calculations for tetrasilyldisilenes are required for the elucidation of the detailed mechanism for the formal dyotropic rearrangement.

3. Experimental

3.1. General methods

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.6 MHz)-NMR spectra were measured on a Bruker AC300P NMR spectrometer. EI mass spectra were recorded on a JEOL JMS-600W mass spectrometers.

3.2. 1,1-Di(t-butyldimethylsilyl)-2,2-di(diisopropylmethylsilyl)disilane (8)

A THF solution of 1,3-di-t-butyl-1,1,3,3-tetramethyl-2-lithio-trisilane (6), which was prepared by the reaction of 1,3-di-t-butyl-1,1,3,3-tetramethyltrisilane (5, 3.00 g, 11.5 mmol) and a pentane solution of t-butyllithium (1.45 mol l^{-1}, 11.9 ml, 17.3 mmol) in THF [11], was added to a solution 2-chloro-1,1,3,3-tetraisopropyl-1,3-dimethyltrisilane (7, 3.72 g, 11.5 mmol) in hexane (40 ml) at −78 °C. The mixture was stirred overnight, and then hydrolysed. After the mixture was extracted with diethyl ether, the organic layer was washed with brine and dried over sodium sulfate. Removal of solvent from the mixture gave a colorless oil. The pure title compound 8 (4.46 g, 8.15 mmol, 71% yield) was obtained by Kugelrohr distillation. 8: a colorless oil; b.p. 120–140 °C/0.003 Torr; ^{1}H-NMR (C$_6$D$_6$, δ) 0.29 (s, 6H), 0.30 (s, 6H), 0.34 (s, 6H), 1.07 (s, 18H), 1.16–1.18 (m, 24 H), 1.20–1.27 (m, 4H), 3.11 (s, 1H), 3.17 (s, 1H); ^{13}C-NMR (C$_6$D$_6$, δ) −4.8, −1.6, −1.4, 14.9, 15.0, 19.0, 19.3, 19.6, 19.87, 19.91, 27.7; ^{29}Si-NMR (C$_6$D$_6$, δ) −128.9, −125.9, 1.5, 5.0; MS (EI, 70 eV) m/z (%) 546 (19, M$^+$), 431 (83), 416 (61), 57 (100); Anal. Calc. for C$_{26}$H$_{66}$Si$_6$: C, 57.06; H, 12.15. Found: C, 56.81; H, 12.19%.

3.3. 1,2-Dibromo-1,1-di(t-butyldimethylsilyl)-2,2-di(diisopropylmethylsilyl)disilane (9)

To a solution of 8 (1.10 g, 2.01 mmol) in dichloromethane (30 ml), bromine (321 mmol, 2.01 mmol) was added at 0 °C in the dark for 15 min. After the solvent was pumped out, pure 9 (1.07 g, 1.52 mmol, 76% yield) was obtained by Kugelrohr distillation. 9: a colorless oil; b.p. 120–140 °C/0.003 Torr; ^{1}H-NMR (C$_6$D$_6$, δ) 0.40 (s, 6H), 0.42 (s, 6H), 0.43 (s, 6H); 1.13 (s, 18H), 1.16–1.22 (m, 24H), 1.53–1.63 (m, 4H); ^{13}C-NMR (C$_6$D$_6$, δ) −

4.9, −1.4, −1,1, 14.8, 15.1, 19.9, 20.1, 20.69, 20.72, 20.8, 28.7; ^{29}Si-NMR (C$_6$D$_6$, δ) −8.0, −7.8, 2.4, 3.8.

3.4. 1,1-Di(t-butyldimethylsilyl)-2,2-di(diisopropylmethylsilyl)disilene (3)

In a Schlenk flask, a suspension of 9 (1.07 g, 1.52 mmol) and potassium graphite (0.452 g, 3.34 mmol) in dry THF (5 ml) was stirred at −78 °C with allowing the mixture to warm to −10 °C. After THF was pumped out, the residue was dissolved in hexane at −10 °C. The resulting salt and graphite was removed by decantation. Concentration of the hexane solution gave pure orange crystals of 3 (0.761 g, 1.40 mmol, 92% yield). 3: air-sensitive orange crystals; m.p. 110 °C (decomp.); ^{1}H-NMR (C$_6$D$_6$, δ) 0.29 (s, 6H), 0.40 (s, 12H), 1.08 (s, 18H), 1.14 (d, $J = 7.3$ Hz, 12H), 1.19 (d, $J = 7.3$ Hz, 12H), 1.40 (sept, $J = 7.3$ Hz, 4 H); ^{13}C-NMR (C$_6$D$_6$, δ) −6.9, 7.3, 16.7, 21.6, 28.8; ^{29}Si-NMR (C$_6$D$_6$, δ) 5.9 (t-BuMe$_2$Si), 11.7 (i-Pr$_2$MeSi), 132.4 ((t-BuMe$_2$Si)$_2$Si=), 156.6 ((i-Pr$_2$MeSi)$_2$Si=); UV–vis (3-methylpentane) λ_{max}/nm(ε) 413 (5000), 359 (2000); MS (EI, 70 eV) m/z (%) 544 (25, M$^+$), 73 (100); HRMS Calc. for C$_{26}$H$_{64}$Si$_6$: 544.3524. Found: 544.3629.

3.5. 1,1-Di(t-butyldimethylsilyl)-2,2-di(triisopropylsilyl)disilene (4)

Prerequisite 1,1-di(t-butyldimethylsilyl)-2,2-di(triisopropylsilyl)disilene (10) and 1,2-dibromo-1,1-di(*tert*-butyldimethylsilyl)-2,2-di(triisopropylsilyl)disilene (11) were prepared in a similar manner to the syntheses of 8 and 9 in 36 and 94% yields, respectively. To a suspension of potassium graphite (92 mg, 0.68 mmol) in THF (2 ml), a solution of 11 (237 mg, 0.311 mmol) in THF (5 ml) was added at −78 °C. After the mixture was stirred with warming up to −10 °C, brown–orange suspension was obtained. The solvent was exchanged from THF to hexane, and then the resulting salt was filtered off. Removal of hexane gave pure disilene 4 (179 mg, 0.298 mmol, 96% yield). 10: a colorless solid; ^{1}H-NMR (C$_6$D$_6$, δ) 0.31 (s, 6H). 0.40 (s, 6H), 0.80 (s, 36H). 1.25 (d, $J = 7.0$ Hz, 36H), 1.38–1.48 (m. 6H); ^{13}C-NMR (C$_6$D$_6$, δ) −3.4, −1.3, 13.0, 14.9, 20.6, 20.8, 28.0; ^{29}Si-NMR (C$_6$D$_6$, δ) −135.4, −122.7, 2.1, 13.2. 11: a colorless solid; ^{1}H-NMR (C$_6$D$_6$, δ) 0.46 (s, 6H), 0.48 (s, 6H), 1.11 (s, 18H), 1.33 (d, $J = 7.5$ Hz, 36H), 1.77 (sept, 6H); ^{13}C-NMR (C$_6$D$_6$, δ) −0.7, −0.4, 15.9, 21.6, 21.7, 21.8, 28.9; ^{29}Si-NMR (C$_6$D$_6$, δ) −1.2, 3.6, 11.5. 4: a bloody red solid; ^{1}H-NMR (toluene-d_8, 293 K, δ) 0.38 (s, 12H, SiMe), 1.02 (s, 18H, t-Bu), 1.27 (d, $J = 7.3$ Hz, 36H), 1.54 (sept, $J = 7.3$ Hz, 6H); ^{13}C-NMR (toluene-d_8, 258 K, δ) 0.5, 17.0, 20.4, 21.2, 28.3; ^{29}Si-NMR (toluene-d_8, 258 K, δ) 5.6 (t-BuMe$_2$Si), 15.8 (i-Pr$_3$Si), 142.0, 152.7 (Si=Si).

3.6. Isomerization of tetrasilyldisilene 3 to 2Z and 2E

A solution of disilene **3** (15 mg, 2.8×10^{-5} mol) in toluene-d_8 (0.50 ml, 5.5×10^{-2} mol 1^{-1}) was sealed in a NMR tube and the tube was kept at 283 K with a cooling bath during isomerizaiton. The rate constant of isomerization of **3** to **2Z** (or **2E**) at 283 K was determined by the time course of the concentrations of the disilenes **3** monitored by ^{1}H-NMR spectroscopy.

3.7. X-ray crystallography of disilenes 3 and 4

Single crystals of disilenes **3** and **4** suitable for X-ray diffraction study were obtained by recrystallization from hexane and diethyl ether, respectively. X-Ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo−K$_\alpha$ radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using all data [16]. Crystallographic data for disilene **3**: $C_{26}H_{64}Si_6$, m_w 545.30, monoclinic, $a = 17.885(2)$, $b = 11.678(1)$, $c = 18.169(2)$ Å, $\beta = 109.6407(8)^\circ$, $V = 3573.9(6)$ Å^3, $T = 150$ K, space group $P2/n$ (no. 13), $Z = 4$, $D_{calc} = 1.013$ g cm^{-3}; μ(Mo−K$_\alpha$) = 2.46 cm^{-1}; 31 930 reflections measured, 9235 unique ($R_{int} = 0.034$). The ?nal $R1$ and $wR2$ values were 0.041 [$I > 2\sigma(I)$] and 0.116 (for all data), respectively. Crystallographic data for disilene **4**: $C_{30}H_{72}Si_6$, m_w 601.41, monoclinic, $a = 18.906(7)$, $b = 12.740(4)$, $c = 18.132(7)$ Å, $\beta = 110.505(4)^\circ$, $V = 4090(2)$ Å^3, $T = 223$ K, space group $C2/c$ (no. 15), $Z = 4$, $D_{calc} = 0.977$ g cm^{-3}; μ(Mo−K$_\alpha$) = 2.20 cm^{-1}; 22 217 reflections measured, 6462 unique ($R_{int} = 0.034$). The final $R1$ and $wR2$ values were 0.047 [$I > 2\sigma(I)$] and 0.142 (for all data), respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207190 and 207191 for compounds **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.ca-m.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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