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New Isolable Dialkylsilylene and Its Isolable Dimer That Equilibrate in Solution

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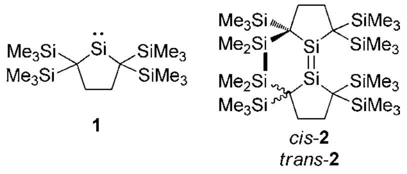
Ⓢ *Supporting Information*

ABSTRACT: The new isolable dialkylsilylene **3** bearing a bidentate alkyl substituent was synthesized. Recrystallization of silylene **3** gave yellow crystals of **3** and orange-red crystals of tetraalkyldisilene **4**, a dimer of **3**. In the solid state, **3** exists as a monomer with a closest distance of 6.745 Å between dicoordinate silicon atoms, while disilene **4** has a remarkably long Si═Si double bond distance of 2.252 Å. An equilibrium between **3** and **4** in solution was observed by NMR and UV−vis spectroscopies, and the thermodynamic parameters of the equilibrium were estimated to be $\Delta H = -36 \pm 3$ kJ mol^{-1} and $\Delta S = -170 \pm 15$ J mol^{-1} K^{-1}. Analysis of the percent buried volume, a measure of the steric demand around the divalent silicon, showed that the flexible steric bulkiness of the alkyl substituent of **3** and **4** allows the reversible dimerization of silylene **3** to disilene **4** and the isolation of both species.

Divalent silicon compounds (silylenes, R_2Si) are among the most important intermediates in silicon chemistry. Although various isolable silylenes stabilized by bulky and/or heteroatom substituents have been synthesized and their structures and reactivities have been extensively studied in recent years,[1,2] isolable donor-free silylenes are still quite rare.[3] We previously synthesized dialkylsilylene **1** bearing a cyclic bidentate alkyl substituent, 1,1,4,4-tetrakis(trimethylsilyl)-butane-1,4-diyl, as a sole example of an isolable dialkylsilylene (Chart 1).[3] While silylene **1** does not dimerize into the corresponding disilene either in solution or in the solid state, we recently found that fused tricyclic tetraalkyldisilenes in which the bidentate alkyl substituents are connected by a Si−Si bond (*cis*-**2** and *trans*-**2**; Chart 1) do not dissociate to give the corresponding bis(dialkylsilylene),[4] suggesting that small modifications of the bidentate alkyl substituent can remarkably affect the stability and properties of the dialkylsilylene. Here we report the new isolable dialkylsilylene **3**, which bears a new bidentate alkyl substituent with 1,3-disilaindane moieties, that equilibrates with its dimer, tetraalkyldisilene **4**, in solution (Scheme 1). Although silylene−disilene equilibria[5] have been evidenced by dimerization of the silylene to give the corresponding disilene and its reverse process,[6−11] we directly observed both silylene **3** and disilene **4** that equilibrate in solution via NMR and UV−vis spectroscopies and determined the thermodynamic parameters for the equilibrium experimentally. In addition, we successfully determined molecular structures of both **3** and **4** by single-crystal X-ray diffraction (XRD) as the first example of X-ray analysis of both a silylene and the corresponding disilene.

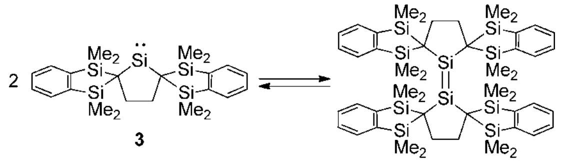
Chart 1



1

cis-**2**
trans-**2**

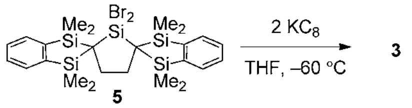
Scheme 1



3

4

Dialkylsilylene **3** was synthesized by the reduction of dibromosilane **5**[12] with potassium graphite in tetrahydrofuran (THF) at −60 °C (eq 1) and isolated in 93% yield as air- and moisture-sensitive yellow crystals. In contrast to dialkylsilylene **1**, which gradually isomerizes to a silene in solution via 1,2-trimethylsilyl migration,[3,13] dialkylsilylene **3** does not isomerize to the corresponding silene either in solution or in the solid state.[14]



5

(1)

Recrystallization of **3** from hexane at −30 °C gave yellow crystals of **3** together with a trace amount of orange-red crystals of disilene **4**. Both structures were confirmed by single-crystal XRD. The molecular structure and packing diagram of **3** are displayed in Figure 1. The divalent silicon is well-protected by two spirocyclic 1,3-disilaindane moieties with different conformations: one of the 1,3-disilaindanes is nearly flat, with an interplane angle (θ) of 13.6° between the Si2−C1−Si3 and Si2−C5−C10−Si3 planes, and the other adopts an envelope conformation with θ = 33.0° (Si4−C4−Si5 and Si4−C11−C16−Si5) to occupy the space in front of the divalent silicon.

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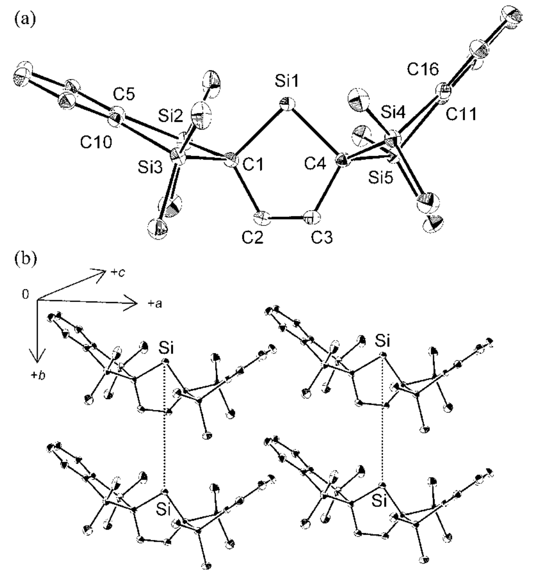

Figure 1. (a) Molecular structure of **3**. Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−C1, 1.904(2); Si1−C4, 1.899(2); Si2−C1, 1.902(2); Si3−C1, 1.915(2); Si4−C4, 1.895(2); Si5−C4, 1.911(2); C1−C2, 1.563(3); C2−C3, 1.533(3); C3−C4, 1.551(3); C1−Si1−C4, 92.56(8). (b) Packing diagram for **3**. The shortest distance between divalent silicon atoms (shown by the dotted lines) is 6.745 Å.

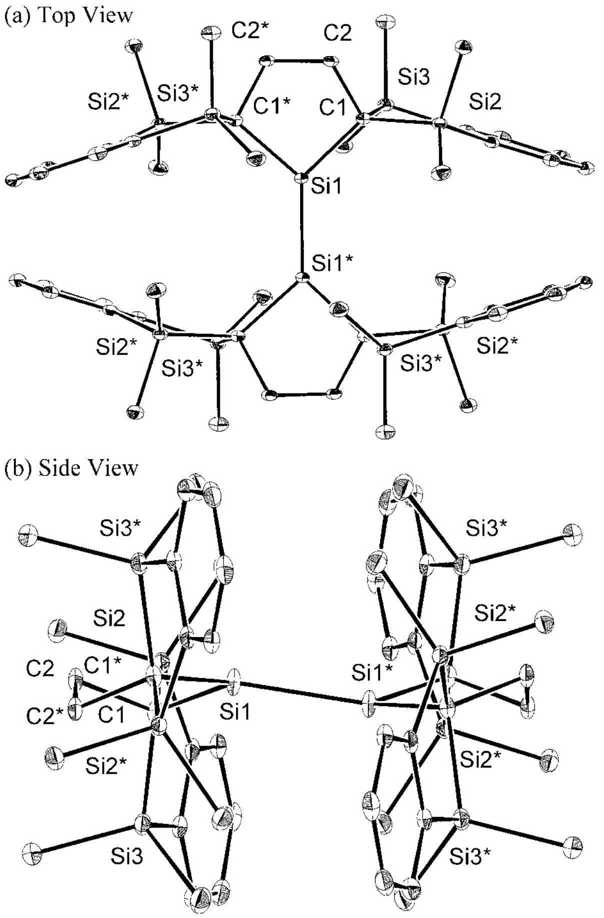

Figure 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Si1*, 2.252(3); Si1−C1, 1.952(9); Si1−C1*, 1.954(9); Si2−C1, 1.918(2); Si3−C1, 1.899(2); C1−C2, 1.569(2); C2−C2*, 1.509(4); C1−Si1−C1*, 95.5(1); C1−Si1−Si1*, 131.6(2); C1*−Si1−Si1*, 128.2(3).

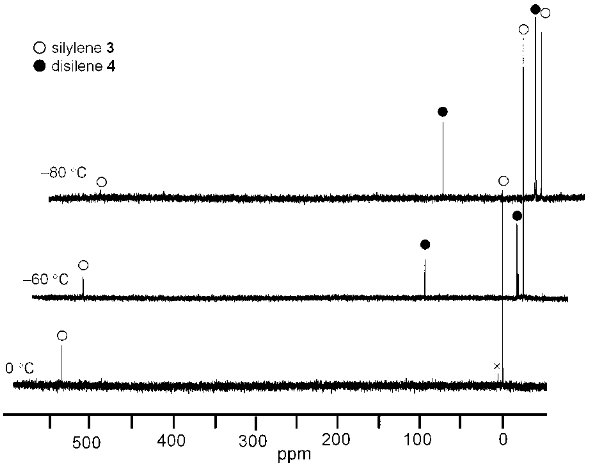

Figure 3. ^{29}Si NMR spectra of **3** in C_7D_8 solution at various temperatures. The open and solid circles indicate ^{29}Si resonances of **3** and **4**, respectively (× : trace amount of **5**).

Neighboring divalent silicon atoms do not face each other, and the shortest distance between divalent silicon atoms is 6.745 Å (Figure 1b), showing that silylene **3** is monomeric in the solid state.[15]

The molecular structure of disilene **4** is shown in Figure 2.[16] Notable structural characteristics of **4** include the long Si=Si distance of 2.252(3) Å and the twist angle of 22.6°. The Si=Si distance is near the longer end of the reported[10,17] range (2.132[17d]–2.289[10] Å) but shorter than that in the structurally similar tetraalkyldisilene *trans*-**2** [2.2687(7) Å].[4] The Si1−C1 and Si1−C1* bonds in **4**, with lengths of 1.952(9) and 1.954(9) Å, are also considerably long; the lengths of the corresponding bonds in **3** are 1.904(2) and 1.899(2) Å. The tricoordinate silicons adopt a slightly pyramidalized geometry in which the sum of the bond angles is 355.3(2)° and the trans-bent angle is 17.5°. These structural features can be rationalized by the severe steric repulsion between the silylene moieties.

The formation of crystals of silylene **3** and disilene **4** clearly indicates the existence of the equilibrium between **3** and **4** in solution. In fact, the equilibrium could be observed spectroscopically, as the ^{29}Si NMR spectrum of silylene **3** in toluene-d_8 changed reversibly with the temperature (Figure 3). At 273 K, only a set of ^{29}Si resonances due to **3** were observed at 539.0 and 5.8 ppm; the extraordinarily low-field-shifted signal at 539.0 ppm is characteristic of the dicoordinate silicon nuclei of dialkylsilylenes [$\delta_{\mathrm{Si(silylene)}}$ = 567.4 for silylene **1**],[3] while the signal at 5.8 ppm is due to the 1,3-disilaindane moiety. As the temperature was lowered, a new set of ^{29}Si resonances appeared at 12.6, 13.3, and 123.3 ppm. On the basis of the chemical shifts of structurally similar tetraalkyldisilenes [$\delta_{\mathrm{Si(disilene)}}$ = 128.1 and 135.9 ppm for *cis*-**2** and *trans*-**2**, respectively],[4] the signals that appeared at low temperature can be assigned to the tricoordinate silicon nuclei of disilene **4**. The two resonances at 12.6 and 13.3 ppm due to the silicon nuclei of the silyl substituents would be attributed to its twisted structure as found in the solid state. From the **3** $\rightleftarrows$ **4** equilibrium constants at various temperatures determined by ^{1}H NMR spectroscopy, the thermodynamic parameters for the dimerization of silylene

3 to give disilene 4 were estimated to be $\Delta H = -36 \pm 3$ kJ mol^{-1} and $\Delta S = -170 \pm 15$ J mol^{-1} K^{-1}.[18,19] The bond dissociation enthalpy of 4 is much smaller than that of the parent disilene $H_2Si{=}SiH_2$ [239.7 kJ mol^{-1} calculated at the MP3/6-31G(d) level],[20] indicating that the silicon−silicon double bond in 4 is quite weak. The significantly large negative value of $\Delta S = -170 \pm 15$ J mol^{-1} K^{-1} is close to that for the dimerization of a divalent germanium compound (germylene) reported by Tokitoh et al.,[11a] who found the thermodynamic parameters $\Delta H = -61.6 \pm 0.8$ kJ mol^{-1} and $\Delta S = -177.7 \pm 3.4$ J mol^{-1} K^{-1} for the equilibrium between the diarylgermylene TbtMesGe and its dimer TbtMesGe═GeTbtMes {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl}, although TbtMesGe was not isolated.

A reversible spectral change was also observed by UV−vis spectroscopy (Figure 4). The UV−vis spectrum of **3** in 3-methylpentane at 273 K showed a weak, broad absorption band at 429 nm (ε = 175 M^{-1} cm^{-1}) assignable to the n → 3p transition of silylene **3**, similar to that observed for **1** (440 nm).[3] As the measurement temperature was lowered, a set of broad absorption bands appeared at 441, 371, and 335 nm. The absorption band at 441 nm can be assigned to the $\pi_{(Si=Si)} \rightarrow \pi^*_{(Si=Si)}$ transition of **4** overlapped with the n → 3p transition of **3**. The two absorption bands at 371 and 335 nm are tentatively assigned as two $\pi_{(Si=Si)} \rightarrow \sigma^*_{(Si-C)}$ transitions or two $\sigma_{(Si-C)} \rightarrow \pi^*_{(Si=Si)}$ orbitals of **4** because structurally similar tetraalkyldisilenes showed similar absorption bands at ~350 nm[4,7f] and compound **4** has two different C−SiMe$_2$ units as a result of the twist geometry around the Si═Si double bond.

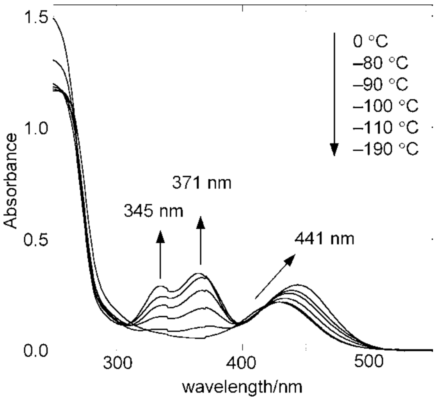

Figure 4. Temperature dependence of the UV−vis spectrum of **3** in 3-methylpentane.

Steric bulkiness around the divalent silicon should be responsible for the different behavior of dialkylsilylenes **1** and **3** toward dimerization. We employed percent buried volume (%V_{bur})[21,22] as a measure of the steric occupancy of the bulky alkyl groups around the divalent silicon atom. Interestingly, whereas the apparent substituent size of **3** is larger than that of **1**, the estimated %V_{bur} value of 40.5% for **3** is slightly smaller than that for **1** (42.3%). In addition, the %V_{bur} of **3** with the conformation fixed to that observed for one silylene unit in disilene **4** was significantly smaller (34.3%). The considerable reduction in %V_{bur} in going from **3** to **4** can be rationalized by the conformational change of the 1,3-disilaindane moieties in **3** upon dimerization. The flexible steric bulkiness of the 1,3-disilaindane moieties in **3** allows the reversible dimerization to give **4** and the isolation of both **3** and **4**.

In summary, the new isolable dialkylsilylene **3** was successfully synthesized and fully characterized. NMR and UV−vis spectroscopies clearly showed the equilibrium between **3** and the corresponding disilene **4** in solution, and the thermodynamic parameters for the equilibrium between silylene and disilene were determined experimentally. We accomplished for the first time the X-ray crystal structure analysis of both a silylene and a disilene that equilibrate with each other in solution using **3** and **4**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterizations of compounds **3** and **4**, details of theoretical calculations, and X-ray crystallographic data for **3** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Although neither dimerization nor isomerization of **3** in the solid state or in THF solution was observed, **3** gradually decomposed to give an unidentified white precipitate in hexane or benzene solution after several hours. Elemental analysis and solid-state ^{29}Si CP/MAS NMR spectroscopy of the insoluble precipitate indicated that intermolecular cycloaddition of **3** with an aromatic moiety may occur. Thermal and photochemical cycloaddition reactions of silylenes with aromatic compounds have been reported.[23]

(15) The shortest distance between the divalent silicon atoms is much longer than the sum of the van der Waals radii of two silicon atoms (4.20 Å). See: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(16) The position of the Si1 atom was disordered in the crystal of **4** because of the presence of two molecules in which the configurations around the unsaturated silicon atoms are opposite to each other. Because the structures of the disordered molecules were crystallographically identical to each other with the same site occupancy factors, one molecule is shown in Figure 4. For details, see the Supporting Information.

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(18) Only signals for silylene **3** were observed by ^{1}H NMR spectroscopy when a crystal of disilene **4** was dissolved in C_6D_6, indicating very fast dissociation of **4** to **3** in solution. Hence, we were not able to estimate the kinetic parameters for the dissociation of **4**.

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