Remarkably Facile Thermal Generation of Silylene from a Pentacoordinate Alkoxydisilane and Its Trapping as a Pentacoordinate 1,2-Disilacyclobut-3-ene

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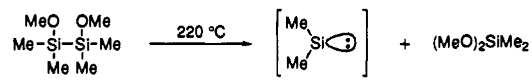
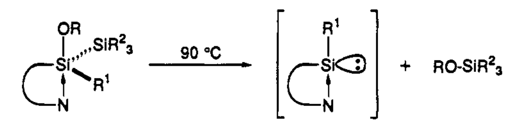
Received August 14, 1995

In 1966, Atwell and Weyenberg reported the first example of pyrolytic generation of a silylene (silanediyl) species from alkoxydisilanes such as 1,2-dimethoxytetramethyldisilane.[1] The reaction, however, occurs only at high temperatures around 220−250 °C (eq 1). We now report a remarkably enhanced reactivity of a "pentacoordinate" alkoxydisilane, which undergoes a similar thermal silylene formation at 90 °C (eq 2). The silylene species has been trapped with an acetylene as a 1,2-disilacyclobut-3-ene containing a pentacoordinate silicon atom.



(1)



(2)

Pentacoordinate ethoxydisilane **1**, which contains the 8-(dimethylamino)-1-naphthyl group and the ethoxy group on the same silicon atom, and the tetracoordinate counterpart **2** were prepared in high yields, as shown in Scheme 1.[2,3]

The X-ray structure and selected interatomic distances and angles of **1** are shown in Figure 1. The geometry of Si1 is deformed considerably from tetrahedral to pseudotrigonal bipyramidal (TBP), with the ethoxy group and the amino group at the two pseudoapical positions, having the N1···Si1 distance 2.969(3) Å and the N1···Si1−O1 angle 171.36(9)°.[4] The N···Si distance is somewhat larger than the normal "coordination distances" of ≤2.8 Å,[5] but the nearly linear N···Si−O arrangement and the deformation angles around silicon imply attractive interaction between nitrogen and silicon, making the silicon center slightly pentacoordinated: the sum of the three pseudoequatorial angles is 347.0°. The naphthalene ring is, however, highly deformed from planarity. While the Si1−Si2 distance, 2.368(1) Å, is normal,[6] the Si1−O1 length, 1.665(2) Å, is among the longest so far observed for ordinary tetracoordinate alkoxysilanes.[7] This slightly elongated Si−O bond and the unusually small O−Si−Si bond angle (~97°) may be partly responsible for the high thermolability of **1**, which will be discussed below.

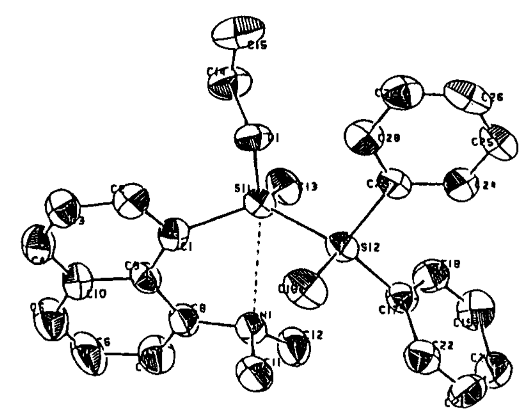
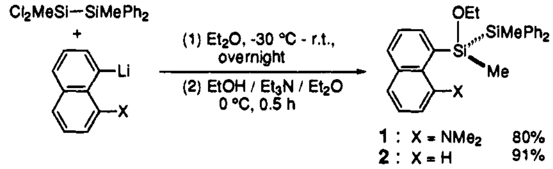


Figure 1. X-ray structure of **1**. Selected distances (Å) and angles (deg): N1···Si1, 2.969(3); O1−Si1, 1.665(2); Si1−Si2, 2.368(1); N1···Si1−O1, 171.36(9); O1−Si1−Si2, 97.35(8); O1−Si1−C1(Np), 103.1(1); O1−Si1−C13(Me), 106.4(1); Si1−C1−C8/N1−C1−C8, 31.32; C1−C2−C3/C6−C7−C8, 9.78.

Scheme 1



Coordination of the amino group to silicon in solution has been supported by the NMR spectroscopy. Thus, at room temperature in C_6D_6, the two aminomethyl groups in **1** appear as diastereotopic two separate signals at δ 2.21 and 2.26 in ^{1}H and δ 46.77 and 47.70 in ^{13}C NMR spectroscopy. The data indicate that the coordination of the amino group to silicon is strong enough to prevent equilibration of the two methyl groups via rotation about the amino−naphthyl bond on the NMR time scales. In the ^{29}Si NMR spectra, the aminonaphthyl-containing silicon atom in **1** (−7.32 ppm) resonates ~13 ppm upfield in comparison with the naphthyl-containing silicon atom in the tetracoordinate counterpart **2** (+6.08 ppm). The upfield shift strongly supports the pentacoordination of the particular silicon atom.[8]

The pentacoordinate ethoxydisilane **1** undergoes thermal degradation readily, as shown in Scheme 2. Thus, when a solution of **1** in toluene was heated at 110 °C for 16 h under nitrogen, ethoxymethyldiphenylsilane **3** was obtained as the sole volatile product in 79% yield. The thermal decomposition was complete within 20 h at 90 °C in DMF. In contrast, the tetracoordinate analogue **2** was stable under similar conditions: even under forced conditions at 200 °C in toluene or DMF in a sealed tube for 48 h, only 20% yield decomposition of **2** was observed. Addition of triethylamine to **2** showed no effect on the thermal stability, indicative of the importance of the intramolecular coordination in **1**.

The silylene species **4**, which should be formed in the thermolysis, appeared to have ended up as an oligomeric mixture as judged by the NMR spectra; we have been trying to isolate

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(1) Atwell, W. H.; Weyenberg, D. R. *J. Organomet. Chem.* **1966**, *5*, 594; *J. Am. Chem. Soc.* **1968**, *90*, 3438; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 469 (review).
(2) Pertinent references for 8-amino-1-naphthyl-lithium and -silicon compounds are available. Li: (a) Jastrzebski, J. T. B. M.; Knapp, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287. Si: (b) Chuit, C.; Corriu, R. J. P.; Rey, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (c) Lannear, G. F. *Main Group Chem. News* **1993**, *1* (3), 16.
(3) All new compounds exhibited satisfactory spectral and analytical data.
(4) These numbers may be compared with 3.16 Å and 155.95°, respectively, observed in a trisilane containing the same amino group at the central silicon atom: Tamao, K.; Tarao, Y.; Nakagawa, Y.; Nagata, K.; Ito, Y. *Organometallics* **1993**, *12*, 1113.
(5) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; p 1241.
(6) Sheldrick, W. S. In ref 5, p 227.
(7) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697.
(8) Tandura, St. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99.

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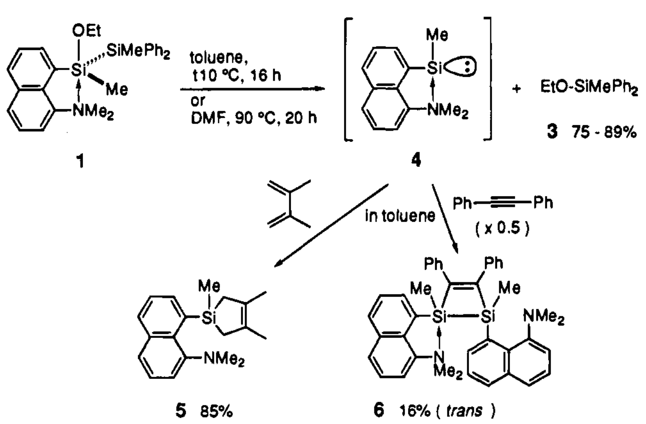
Scheme 2



any characterizable oligomer but without success so far, unfortunately. However, in the presence of a 1,3-diene or an acetylene, the silylene **4** was trapped efficiently, as shown in Scheme 2. Thus, reaction of **1** in the presence of 5 equiv of 2,3-dimethyl-1,3-butadiene in toluene at 110 °C for 15 h gave the expected adduct **5** in 85% yield,[3] together with **3** in 89% yield. In the presence of 0.5 equiv of diphenylacetylene, a silylene/acetylene 2:1 adduct, 1,2-disilacyclobut-3-ene **6**, was isolated as a crystalline trans isomer in 16% yield by workup and recrystallization under argon.[9]

The X-ray structure of **6** is shown in Figure 2.[10] In the solid state, **6** involves two different conformations of the amino-naphthyl groups on silicon atoms. Thus, the geometry of Si1 is pseudo-TBP, with N1 and the ring carbon atom C1 at the two apical positions and the short N1···Si1 distance, 2.789(3) Å, within the normal "coordination distance" of ≤2.8 Å,[5] the large N1···Si1—C1 angle 167.7(1)°, and the high planarity of the equatorial groups, the sum of the equatorial angles being 356.8°. Deformation of the naphthalene ring is relatively small. All the data demonstrate that the geometry of the Si1 is highly pentacoordinate. This is quite unusual for a tetraorganosilicon center without an electronegative group on silicon and might be ascribed to the release of the endocyclic angle strain of the four-membered ring.[11] In contrast, on Si2, the amino group interacts very weakly with the Si2 atom from the region anti to the Si1 atom with a rather long N2···Si2 distance, 3.039(3) Å, the N2···Si2—Si1 angle 170.42(7)°, the sum of pseudoequatorial angles 348.4°, and the highly distorted naphthalene ring. The unsymmetrical nitrogen coordination (interaction) makes the 1,2-disilacyclobut-3-ene ring also unsymmetical, having a longer apical Si1—C1 bond, 1.932(3) Å, than the normal Si2—C2 bond, 1.891(3) Å, together with the normal Si1—Si2 and C1=C2 bonds.

The unsymmetrical nature of the structure of **6** can also be observed by solid state CP/MAS ^{29}Si NMR spectroscopy, which shows two singlets at δ +5.349 and −9.558 at room temperature. In solution, however, the structure is symmetrical, as observed by NMR at room temperature: a ^{29}Si singlet is observed for two silicon atoms at δ −3.456, being around the middle of the two signals observed in the solid state, as well as a singlet for Si—Me (^{1}H, δ 0.95) and two singlets for the diastereomeric NMe_2 (^{1}H, δ 2.169, 2.185).

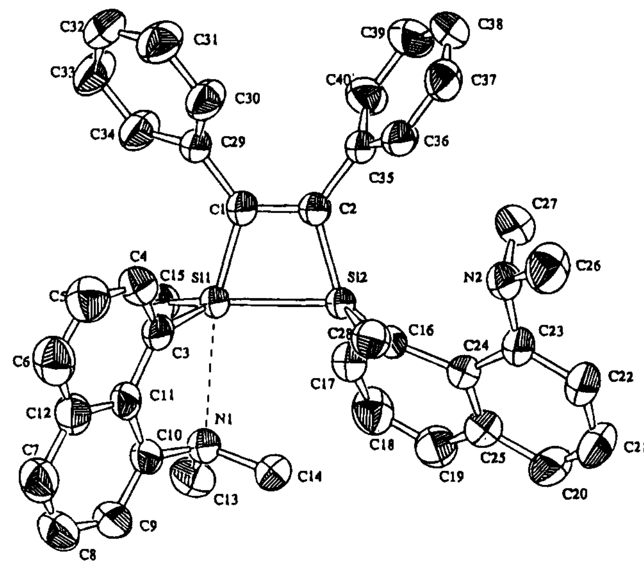


Figure 2. X-ray structure of **6**. Selected distances (Å) and angles (deg): N1···Si1, 2.789(3); N2···Si2, 3.039(3); Si1—Si2, 2.344(1); C1—C2, 1.356(4); C1—Si1, 1.932(3); C2—Si2, 1.891(3); N1···Si1—C1, 167.7(1); N2···Si2—Si1, 170.42(7); Si1—C3—C10/N1—C3—C10, 14.30; C3—C4—C5/C8—C9—C10, 6.41; Si2—C16—C23/N2—C16—C23, 39.80; C16—C17—C18/C21—C22—C23, 14.67.

Compound **6** is the first 1,2-disilacyclobut-3-ene containing a pentacoordinate silicon atom, which may exhibit interesting reactivities different from those of its ordinary tetracoordinate counterparts. The purified **6** was quite stable to O_2 oxidation in C_6D_6 at room temperature for 6 h, whereas it was readily converted into the corresponding five-membered cyclic disiloxane[9] upon stirring with silica gel in the air for 2 h. Other reactivities are now under investigation in our laboratory.

All the results described herein demonstrate that the intramolecular coordination by the amino group enhances the thermolability of the alkoxydisilane with respect to the α-elimination,[12] suggesting new designs for readily degradable polysilanes under thermal conditions[13] and a new access to "pentacoordinate" oligosilanes.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for the Grants-in-Aid (Nos. 055453137, 07405043, and 06303002).

Supporting Information Available: Experimental details for the preparation of **1** and **2** and their reactions, including tables of crystal data, atomic coordinates, anisotropic displacement parameters, bond distances and angles for **1** and **6** (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) Workup and column chromatographic isolation in air afforded the corresponding five-membered cyclic disiloxane 1-oxo-2,5-disilacyclopent-3-ene[4] in 77% yield.

(10) The first X-ray structure analysis for 1,2-disilacyclobut-3-ene has recently been reported on a 1,1,2,2-tetrakis[2-[(dimethylamino)methyl]-phenyl] derivative, which reveals no N···Si interaction: Belzner, J.; Ilmels, H.; Kneisel, B. O.; Herbst-Irmer, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1989.

(11) High Lewis acidity of a silacyclobutane: (a) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480. (b) Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, *114*, 7922. (c) Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026. (d) Matsumoto, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 7152.

(12) Disproportionation of alkoxydisilanes induced by metal alkoxides may involve penta- and hexacoordinate silicon intermediates, but no evidence for generation of silylene species has been obtained. Watanabe, H.; Higuchi, K.; Goto, T.; Muraoka, T.; Inose, J.; Kageyama, M.; Iizuka, Y.; Nozaki, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *218*, 27 and references therein.

(13) Ready degradation of a cyclotrisilane containing two 2-[(dimethyl-amino)methyl]phenyl groups on each silicon atom has recently been reported: (a) Belzner, J. *J. Organomet. Chem.* **1992**, *430*, C51. (b) Belzner, J.; Ihmels, H. *Tetrahedron Lett.* **1993**, *34*, 6541.