Trimerization of a Divalent Silicon Species Bearing the 8-Dimethylamino-1-naphthyl Group Accompanied by the Migration of Methyl and Dimethylamino Groups

Kohei Tamao,* Masahiro Asahara, and Akio Toshimitsu*
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011

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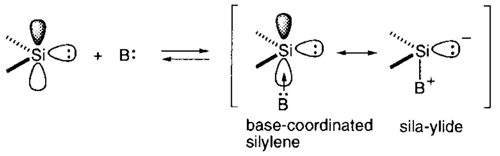
A divalent silicon species bearing the 8-(dimethylamino)-1-naphthyl group trimerizes to afford a 1,2-disilaacenaphthene framework incorporated in a trisilane chain and accompanied by the migration of the methyl and dimethylamino groups.

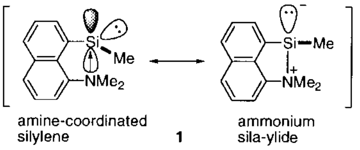
It has been well established that the ground state of a divalent silicon species, a silylene, is a singlet with an electron pair in a σ-orbital and a vacant orbital of π-symmetry.[1] During its reactions, the first step has been shown to have an electrophilic character. A Lewis base can thus coordinate to silicon through the vacant orbital to form a base-coordinated silylene,[2] resulting in the reduced electrophilic character of the silicon center. This species may also be represented as a zwitterionic species, a sila-ylide, through the formation of the base-to-silicon σ bond, in which the silicon center would have an increased nucleophilic character[3] (eq 1).



(1)

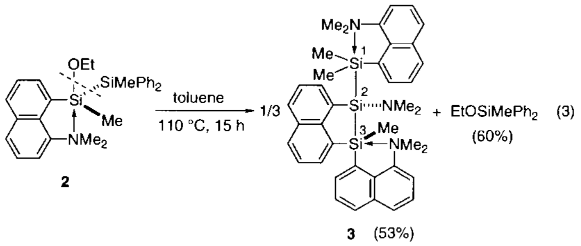
Such species, first proposed by Seyferth in 1978,[4] have been the subject of many investigations, which include the decreased reactivity as an electrophile,[5] spectroscopic observations,[6] theoretical studies,[7] and the first isolation as a kinetically stabilized species.[8] However, the sila-ylide character has rarely been reflected in the reaction products, presumably due to the ready dissociation of the coordinated base during the reaction. For this reason, some intramolecularly base-coordinated silylene species have been studied;[9-11] quite recently, Belzner and co-workers have clearly demonstrated the nucleophilic character of the silylene species containing two 2-(dimethylaminomethyl)phenyl groups based on the kinetic studies of the reaction with diarylacetylenes.[11] In the absence of a trapping agent, this amine-coordinated silylene undergoes trimerization to afford a cyclic trisilane; the silicon–silicon bond formation suggests that this amine-coordinated silylene species still functions as an electrophile.

We now report the trimerization reaction of the silylene species **1** bearing the 8-(dimethylamino)-1-naphthyl group affording a 1,2-disilaacenaphthene framework incorporated in a linear trisilane, accompanied by the migration of methyl and dimethylamino groups. The result will be explained in terms of the ambiphilic character of the amine-coordinated silylene **1**, especially the intervention of the ammonium sila-ylide as the nucleophilic species (eq 2).



(2)

As we reported in a previous paper,[10b] the thermal degradation of the pentacoordinate ethoxydisilane **2** bearing the 8-(dimethylamino)-1-naphthyl group generates the amine-coordinated silylene species **1**. The formation of **1** has been proven by a trapping experiment using 2,3-dimethyl-1,3-butadiene to afford the typical silylene adduct, the 1-silacyclopent-3-ene derivative. As also suggested in the paper, we observed oligomerization of the amine-coordinated silylene species **1** in the absence of any trapping agent. The structure of the oligomer has not yet been determined due to its highly unsymmetrical structure as observed by the ^{29}Si, ^{1}H, and ^{13}C NMR spectroscopies, which shows three kinds of silicon atoms, three kinds of methyl groups (bound to silicon), and three kinds of dimethylamino groups. We have now succeeded in growing single crystals suitable for an X-ray crystallographic analysis and determined the structure of the product to be a trimer, an unsymmetrical trisilane **3**, as shown in eq 3 and Figure 1. It should be noted that this trimerizaion reaction almost exclusively proceeded. Thus, after the thermal degradation of **2** at 110 °C for 15 h, all of the signals in the ^{1}H NMR spectrum were assigned as the α-eliminated ethoxysilane and the trisilane **3**, remaining very weak and broad signals. No stereoisomers of **3** were detected among the reaction products.



(3)

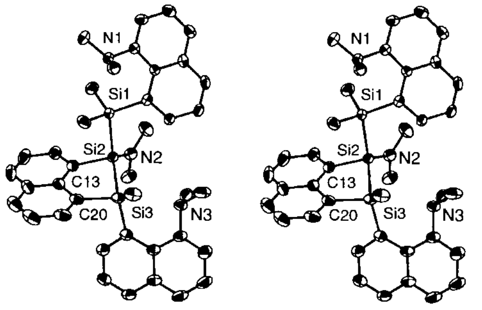
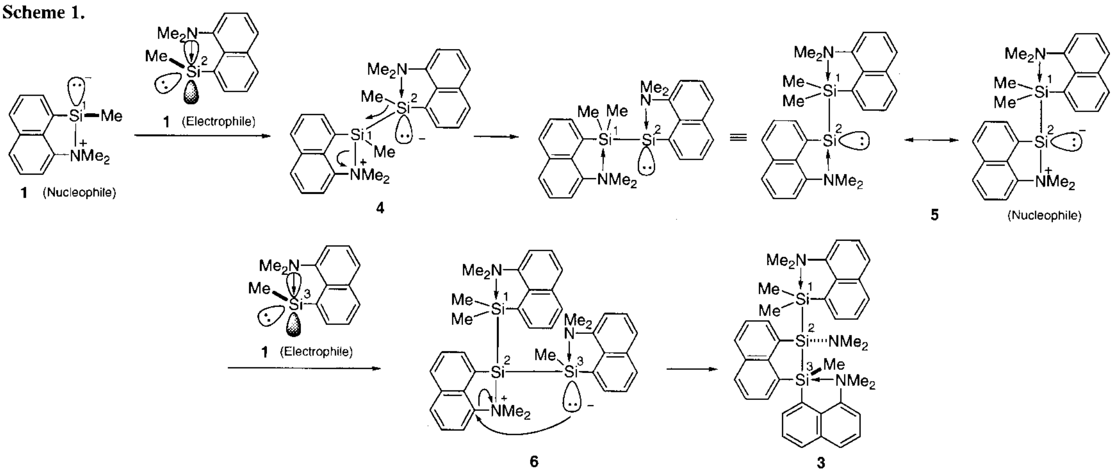


Figure 1. X-Ray structure of **3** drawn in stereoview at 50% probability level. All hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Si1—Si2, 2.371(1); Si2—Si3, 2.366(1); Si1···N1, 2.979(3); Si2···N2, 1.715(3); Si3···N3, 2.919(3); Si2—Si1—N1, 176.65(6); N2—Si2—C13, 110.5(1); N3···Si3—C20, 171.7(1).

Scheme 1.



The most striking feature in the structure of **3** is that one methyl group has migrated from the central silicon atom (Si^2) to the terminal one (Si^1), accompanied by the migration of the dimethylamino group from the naphthyl carbon to Si^2 which resulted in tetracoordinate. One of the terminal silicon atoms (Si^3) of **3** has been incorporated between the Si^2 and the naphthyl carbon atom to afford the 1,2-disilaacenaphthene skeleton.

A plausible mechanism is shown in Scheme 1. The intramolecularly amine-coordinated silylene species **1** (shown by the canonical form of the sila-ylide) undergo dimerization by nucleophilic attack on another **1** which functions as an electrophile to afford the zwitterionic silyl anion **4**, in which the Si^1 atom may be regarded as a silicocation coordinated with the nitrogen atom, while the Si^2 atom is an electron-rich anion. The methyl group on the Si^2 atom may thus migrate to the electron-deficient Si^1 atom to form a new amine-coordinated silylene species **5**, which has the electropositive silyl substituent and becomes more nucleophilic than the original **1**. Thus, nucleophilic attack of **5** on the third **1** produces the zwitterionic silyl anion **6**. The methyl group migration described above does not repeat here,[12] but instead, the anionic silicon seems to attack the naphthyl carbon atom[13] followed by cleavage of the carbon–nitrogen bond to afford the 1,2-disilaacenaphthene framework.

Although this mechanism clearly explains the selective formation of **3**, we cannot rule out other mechanisms such as rearrangement of a cyclic trimer of silylene **1** or nucleophilic attack of silylene **1** on the starting disilane **2**.[14] Further investigation on the mechanism of this reaction is under progress in our laboratory.

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References and Notes

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12 The reason why the silyl anion preferentially attacks the naphthyl carbon in species **6** over the methyl migration as observed in the first species **4** is not clear, but may reside in the electronic and steric effects such that the Si^2 atom in **6** may become less electron-deficient and more sterically crowded by the silyl substituent in comparison to that in **4**.

13 It is expected that the naphthyl carbon atom has become susceptible to nucleophilic attack due to the presence of the positive ammonium moiety. An addition-elimination mechanism and an electron transfer mechanism may be envisioned for the "nucleophilic substitution" of the ammonium moiety from the naphthyl carbon by the silicon anionic center in **6**, but further study is necessary for clarification of the mechanism.

14 We are grateful to both referees for the suggestion of this point.