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Enhanced nucleophilicity of ambiphilic silylene and silylenoid bearing 8-(dimethylamino)-1-naphthyl group

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Abstract

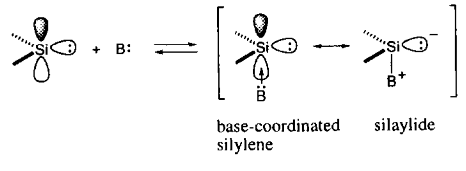
Some new aspects of intramolecularly amine-coordinated silylenes, ammonium silaylide, and amine-coordinated magnesium (chloro)silylenoids are summarized. The divalent silicon species bearing the 8-(dimethylamino)-1-naphthyl group, generated by the thermal degradation of a pseudo-pentacoordinated ethoxy- or fluoro-disilane, behaves as a nucleophilic ammonium silaylide as well as the amine-coordinated silylene, whose electrophilic character is weakened in comparison with that of free silylenes in some reactions in the presence of trapping agents such as 1,3-diene, diphenyl acetylene (in the absence or presence of water), and phenylacetylene, and in the absence of any trapping agent. The amine-coordinated silylenoid also behaves as an ambiphile, but the reaction courses are different from those observed with the amine-coordinated silylene and silaylide. A novel amino-group migration from naphthyl carbon to silicon has been observed in both species. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Silylene; Silaylide; Silylenoid; Base-coordinated silylene; 8-(Dimethylamino)-1-naphthyl group; 1-Silaphenalene; 1,2-Disilaacenaphthene

1. Introduction

It has been well established that a free silylene is a ground-state singlet with an electron pair in a σ-orbital and a vacant orbital of π-symmetry and thus behaves as both an electrophile and a nucleophile [1], the former character generally predominating in its reactions. A Lewis base can coordinate to silicon through the vacant orbital to form a base-coordinated silylene [2], as shown in Scheme 1. The base-coordinated species may also be represented as a zwitterionic species, a silaylide, as a resonance canonical form, through the formation of the base-to-silicon σ-bond, in which the silicon center should have a nucleophilic character rather than electrophilic character [3]. Such species, first proposed by Seyferth and Lim in 1978 [4], have been the main subject of many papers [5], but the silaylide character has rarely been reflected in the reaction products. This may be due to the ready dissociation of the coordinated base during the reaction. For this reason, some intramolecularly amine-coordinated silylene species have also been studied. Corriu et al. have thus observed the intramolecular migration of the coordinated amino group from carbon to silicon in a reaction of a divalent silicon species containing an 8-(dimethylaminomethyl)-1-naphthyl group [6]. Belzner has clearly demonstrated the nucleophilic character of the bis[2-(dimethylaminomethyl)phenyl]silylene in its reaction with acetylenes [7].

We have recently observed some strong evidence for the ammonium silaylide character of a divalent silicon species **1** containing the 8-(dimethylamino)-1-naphthyl group [8] during the course of our study on pentacoordinated oligosilanes [9]. In connection with this, some unprecedented reactions of amine-coordinated silylenoid species **2** containing the same aminonaphthyl group have also been studied [10]. We summarize the novel reactions of such species in this account.



Scheme 1.

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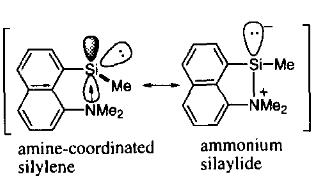

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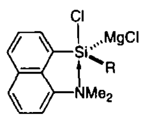

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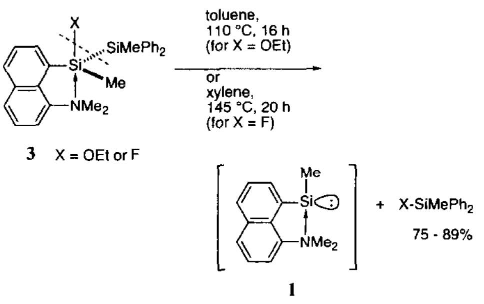
2. Results and discussion

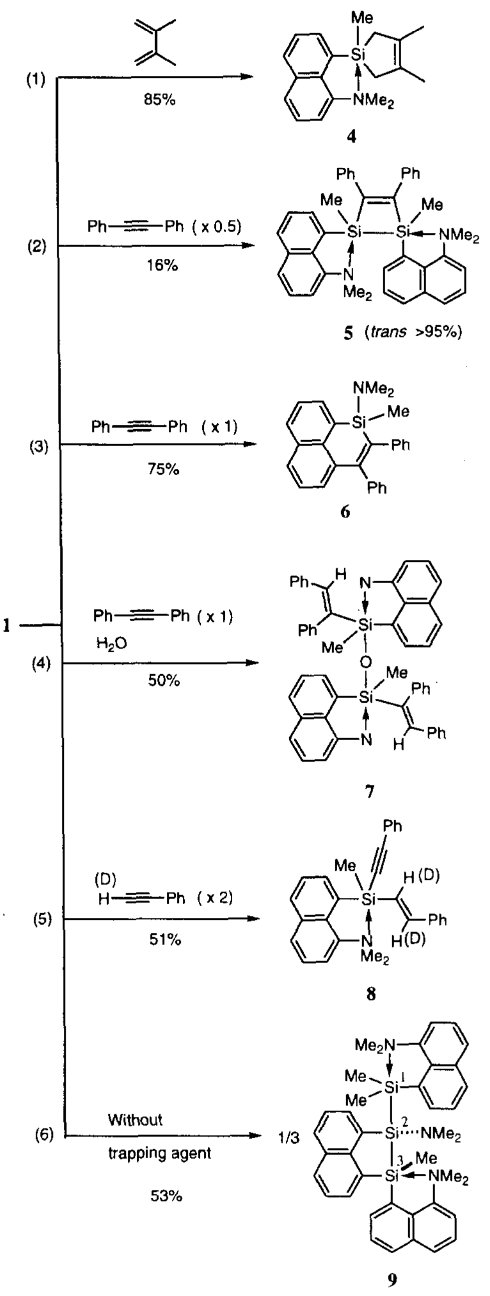
2.1. Generation and reactions of 1

The amine-coordinated silylene species **1** can be readily generated by the thermal degradation of a pseudo-pentacoordinated ethoxy- or fluoro-disilane **3** bearing the 8-(dimethylamino)-1-naphthyl group, as shown in Scheme 2 [8]. It is noted that the pentacoordiantion remarkably enhances the thermo-lability of the disilanes and thus the α-elimination of the alkoxy- or fluorosilane takes place around 100–145°C to form the corresponding silylene species, while traditional tetracoordinated alkoxy- and fluoro-disilanes undergo thermal α-elimination only at high temperatures in the range 200–700°C [11].

The reaction products of the amine-coordinated silylene in the absence and in the presence of trapping agents such as diene and acetylene are summarized in Scheme 3. The significant features are summarized as follows. (1) In the presence of 2,3-dimethyl-1,3-diene, the typical silylene adduct **4** is formed in high yield [8a], providing evidence for the formation of the divalent silicon species [12]. (2) In the presence of a 0.5 M amount of diphenylacetylene, a silylene/acetylene 2:1 adduct, the 1,2-disilacylcobut-3-ene derivative **5**, is formed as the characterizable product [8a]. (3) In contrast, in the presence of a 1 M amount of diphenylacetylene, the 1-dimethylamino-1-silaphenalene derivative **6** is formed in a nearly quantitative yield [8b]. This is quite an unexpected result in which the amino group has migrated from the naphthyl carbon atom to silicon and the diphenylacetylene is incorporated between the silicon atom and the naphthalene carbon atom which originally bore the amino group. (4) If water co-exists together with a 1 M amount of diphenylacetylene, a totally different product, disiloxane **7**, is obtained as the major product in which the aminonaphthyl group has survived and the proton from water has been introduced onto the acetylene carbon atom [8b]. (5) In the presence of 2 M amounts of a terminal acetylene, phenylacetylene, two acetylene groups are introduced onto the silicon atom to give an alkenyl–alkynyl–silicon compound **8**, keeping the aminonaphthyl group intact [8b]. The deuterium on the acetylene carbon has been introduced on the alkenyl moiety. (6) In the absence of any trapping agent, the silylene undergoes trimerization to form a trisilane derivative **9** of a quite unexpected structure [8c]. Thus, in the central silylene (Si2), the amino group migrates from the naphthyl carbon to its own silicon atom Si2,



Scheme 2.



Scheme 3.

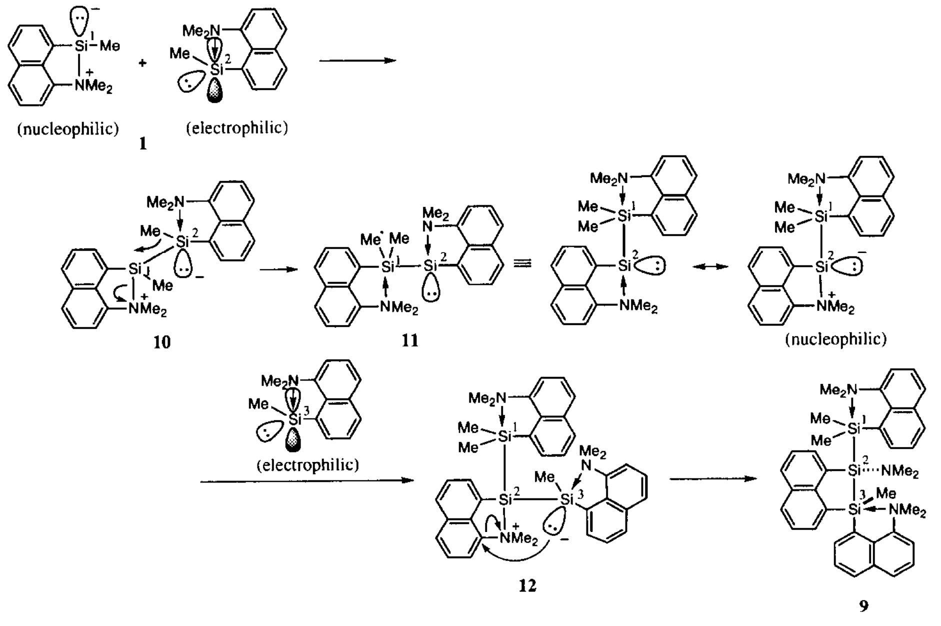
and the methyl group on the Si2 migrates to the terminal silicon atom Si1, while the third silylene species (Si3) has been incorporated between the Si2 and the naphthyl carbon atom without any structural change. The structures of all products except for **4** have been determined by X-ray crystallography.

Results (3) and (6) clearly demonstrate that the divalent silicon species **1** behaves as an ammonium silaylide during the reactions, because the silicon–nitrogen bond must be formed while the naphthalene carbon–nitrogen bond is cleaved. Plausible mechanisms for the formation of all products are explained in terms of the intermediacy of the ammonium silaylide as follows.

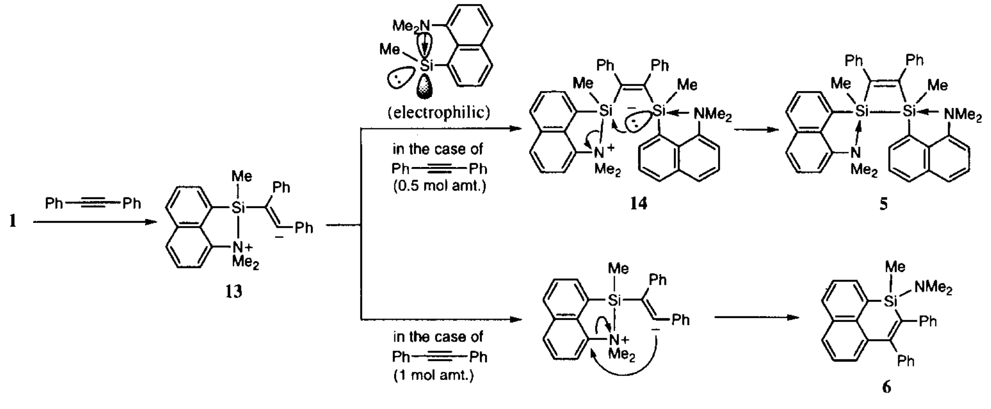
Result (6) is first explained for the sake of easy understanding. A plausible mechanism is visualized in Scheme 4. Thus, in the absence of any trapping agent, species **1** nucleophilically attacks the second species to form a zwitterionic ammonium silyl anion **10**, in which the Si1 atom may be regarded as a silicocation coordinated with the nitrogen atom, while the Si2 atom is an electron-rich anion. The methyl group on the Si2 atom may thus migrate to the electron-deficient Si1 atom to form a new amine-coordinated silylene species **11**, which has the electropositive silyl substituent and thus becomes more nucleophilic than the original species. This species can thus attack the third silylene species **1** to form another zwitterionic ammonium silyl anion **12**. This silyl anion subsequently attacks the naphthalene carbon atom, which has become susceptible to nucleophilic attack due to the presence of the positive ammonium moiety followed by cleavage of the carbon–nitrogen bond [13] to form the observed trisilane derivative **9** containing the disilaacenaphthene skeleton. The reason why the silyl anion preferentially attacks the naphthyl carbon in the species **12** over the methyl migration as observed in the first species **10** is not clear, but may reside in the electronic and steric effects such that the Si2 atom may become less electon-deficient and more sterically crowded by the silyl substituent in comparison with **10**.

Results (2) and (3) are next explained, with possible mechanisms being shown in Scheme 5. In the presence of diphenylacetylene, species **1** first nucleophilically attacks the acetylene to form the zwitterionic ammonium alkenyl anion **13** [14]. In the case of a deficiency in the acetylene (0.5 M amount), the alkenyl anion attacks another silylene species **1** to form a new ammonium silyl anion **14**, which may form the four-membered cyclic product **5** via nucleophilic attack on the first electron-deficient silicon atom by the second silicon anionic center. In the presence of a 1 M amount of acetylene, the alkenyl anion **14** may undergo intramolecular nucleophilic attack on the naphthyl carbon atom followed by cleavage of the carbon–nitrogen bond [13] to form the observed 1-amino-1-silaphenalene derivative **6**.

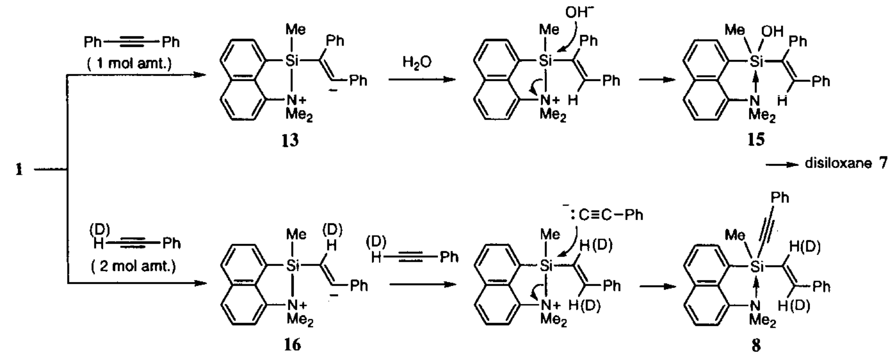
Results (4) and (5) provide strong evidence for the intermediacy of the carbanionic species, as shown in Scheme 6. Thus, if water is present in addition to acetylene (result 4), the alkenyl anion intermediate **13** is quenched by water to be protonated and the thus formed hydroxide ion preferentially attacks the silicon atom to form an alkenyl–silanol **15** via cleavage of the silicon–nitrogen bond, which may undergo dimerization to form the observed disiloxane. However, the silanol **15** most likely serves as a proton source for a second carbanionic species **13** due to the more acidic proton in



Scheme 4.



Scheme 5.



Scheme 6.

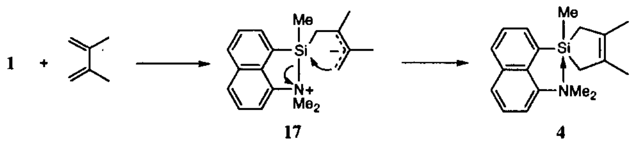
silanol than in water, and the silanolate anion thus formed attacks the second silicon atom to form the disiloxane. Result (5) can be accounted for by a mechanism similar to that for result (4). Thus, species **1** first nucleophilically attacks the terminal acetylene to form a zwitterionic ammonium alkenyl anion **16**. The alkenyl anion is immediately trapped by the acetylenic proton of another molecule of the terminal acetylene followed by nucleophilic attack on the silicon atom by the acetylide anion thus formed to form the observed alkenyl–alkynyl–silicon compound **8**.

Finally, result (1) is explained as follows. As shown in Scheme 7, in the presence of the 1,3-diene, the reactive species **1** nucleophilically attacks the terminal carbon atom of the 1,3-diene to afford a zwitterionic allyl anion species **17** [15]. The terminal carbanionic center subsequently attacks the silicon atom to preferentially form the five-membered cyclic product **4**, resulting in the cleavage of the nitrogen–silicon bond.

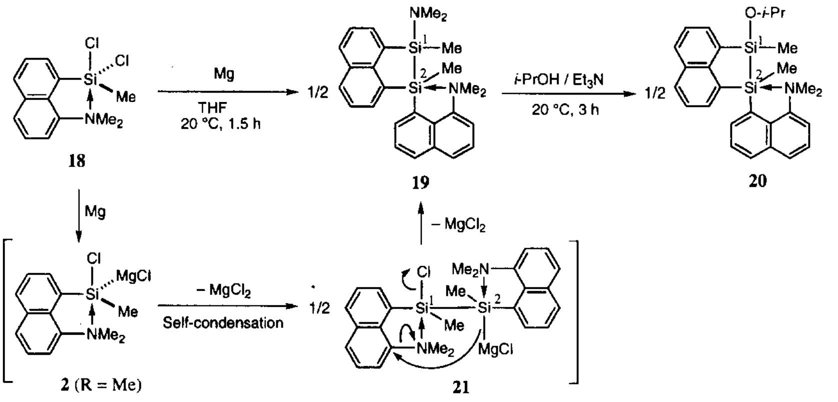
2.2. Generation and reactions of amine-coordinated silylenoids 2

In the hope of obtaining polysilanes containing the 8-(dimethylamino)-1-naphthyl group on each silicon atom [16], we have treated a dichlorosilane **18** with magnesium in THF followed by treatment with isopropyl alcohol to unexpectedly obtain not polymer but the dimerized product, 1-isopropoxy-1,2-disilaacenaphthene derivative **20**, obviously derived from the amino group migration product **19**, as shown in Scheme 8 [10].

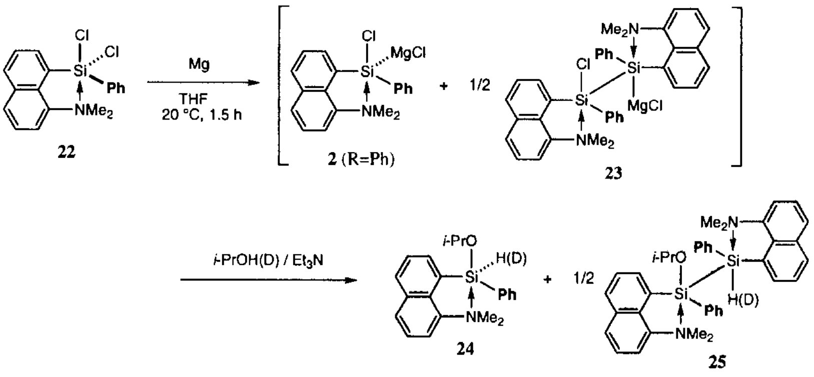
The product is regarded as a dimer of an amine-coordinated divalent silicon species. This is in a sharp contrast to the trimer **9** obtained from the amine-coordinated silylene species **1** (vide infra). This difference suggests that the real reactive species in this case is not a silylene species but a silylenoid **2** that contains a chlorine atom and a magnesium moiety on the silicon atom. The most plausible mechanism for the formation of **20** is also shown in Scheme 8. Thus, the dichlorosilane reacts with magnesium to form an amine-coordinated magnesium (chloro)silylenoid **2** (R = Me), which should behave as an ambiphile, as recently observed by us for a lithium (alkoxy)silylenoid [17]. The species thus undergoes dimerization by self-condensation to form a disilane species **21** together with elimination of the magnesium chloride. It should be mentioned that the



Scheme 7.



Scheme 8.



Scheme 9.

amine coordination may enhance the nucleophilicity of the silylenoid species to accelerate the self-condensation. In the disilane species **21** thus formed, one silicon atom has a chlorine atom and the other a magnesium moiety. It is noted that this is different from the intermediate **10** proposed for the first step of the reaction of the amine-coordinated silylene **1**, which has no such substituents on the silicon atoms and undergoes the methyl migration (cf. Scheme 4). In the present case, the methyl group on Si2 would not migrate to the Si1 atom due to the presence of the chlorine atom. Instead, the anionic Si2 center may attack the naphthalene carbon atom bearing the amino group to cause the amino-group migration from the carbon to the Si1 atom, the extrusion of the chloride ion from the Si1, and the formation of the silicon–carbon bond to form the observed disilaacenaphthene derivative **20**.

In a similar reaction of phenyl-substituted dichlorosilane **22** with magnesium, the magnesium (chloro)silylenoid species **2** (R = Ph) and the self-condensation product **23** has been trapped with *i*-PrOH(D) as **24** and **25**, respectively, as shown in Scheme 9 [10]. The previously mentioned results suggest that similar species may also be involved in the reaction of **18** with magnesium. However, it is noted that in the phenyl case, no disilaacenaphthene skeleton is formed. This may be ascribed to the anion-stabilizing effect and the steric effect exerted by the phenyl groups in the self-condensation species **23**.

3. Conclusions

The significant aspects of this study are summarized as follows:

1. Amino-group migration from carbon to silicon has been observed during some reactions of the intramolecularly amine-coordinated silylene species. The findings clearly indicate that during the reactions, the nitrogen to silicon σ bond should be formed while the carbon to nitrogen bond should be cleaved, indicative of the intervention of the silaylide species of nucleophilic character.
2. Despite the nucleophilic silaylide character, the intramolecularly amine-coordinated silylene still has an electrophilic character, behaving as an ambiphile, because it is found that such species do undergo dimerization to form the Si–Si bond, in which one species should behave as a nucleophile and the other as an electrophile.

3. The intramolecularly amine-coordinated silylenoid also behaves as an ambiphile, but the reaction courses are different from those observed for the amine-coordinated silylene.

4. Perspectives

We are convinced that these findings may shed new light on the chemistry of divalent silicon species. Our current researches are on the following two lines. One is a detailed mechanistic study on the dependency of the reactivity of silylenes on the coordinating heteroatom by changing from nitrogen to phosphorus, oxygen and sulfur, especially in hoping for isolation of a stable phosphonium silaylide. The other is the application of the present chemistry to materials science. The photophysical properties of some novel products such as 1-amino-1-silaphenalene [18] would be interesting as new silicon-containing π-electron systems. The results will be reported in due course.

Acknowledgements

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