Nucleophilic Addition of a Divalent Silicon Species Bearing the 8-Dimethylamino-1-naphthyl Group to Diphenylacetylenes to Form the 1-Amino-1-silaphenalene Skeleton

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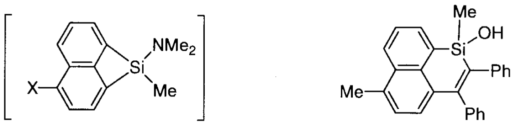
A 1-amino-1-silaphenalene skeleton is formed by the reaction of a divalent silicon species bearing the 8-(dimethylamino)-1-naphthyl group with diphenylacetylene *via* an alkenyl anion intermediate.

In the preceding paper, we reported the enhanced nucleophilicity and reduced electrophilicity of the ambiphilic divalent silicon species, a silylene, bearing the 8-(dimethylamino)-1-naphthyl group.[1] It is expected that in the presence of electrophilic trapping agents such intramolecularly base-coordinated silylenes would behave as nucleophiles. Recently, Beltzner and co-workers have clarified the nucleophilic character of the silylene species containing two 2-(dimethylaminomethyl)phenyl groups based on the kinetic studies of the reaction with diarylacetylenes.[2] The products of this reaction, silacyclopropenes, are similar to those derived from traditional (non-coordinated) silylenes[3] and do not afford direct evidence for the alkenyl anion intermediates during the reaction.

We now report that a strikingly different product, the 1-silaphenalene derivative, is formed by the reaction of the silylene species bearing the 8-(dimethylamino)-1-naphthyl group with diphenylacetylene. We also report that the alkenyl anion intermediates can be trapped by electrophiles such as acidic hydrogens.

The thermal degradation of a pentacoordinate fluorodisilane[4] **1a** in the presence of a 1 molar amount of diphenylacetylene afforded, in addition to the α-eliminated fluorosilane, 1-dimethylamino-1-silaphenalene **4a**[9] in a nearly quantitative yield based on a ^{1}H NMR analysis (Scheme 1). The structure of this unexpected product was confirmed by X-ray crystallography (Figure 1a).[10] It should be noted that during this reaction (1) the alkenyl group has been incorporated between the silicon center and the naphthyl ring and (2) the amino group has migrated from the naphthyl carbon to the silicon center. The first step in this reaction seems to be the nucleophilic attack of the amine-coordinated silylene **2a** on the diphenylacetylene to afford the alkenyl anion intermediate **3a**. Analogous to the silyl anion described in the preceding paper,[1] the alkenyl anion attacks the naphthalene C8 atom followed by cleavage of the carbon-nitrogen bond to afford the 1-silaphenalene skeleton.

As an alternative mechanism, a four-membered intermediate **5a**[11] would be formed by the intramolecular insertion of the silylene center in **2a** into the naphthalene C8–N, followed by insertion of acetylene into the strained naphthyl carbon-to-silicon bonds to afford **4a**. However, this possibility has readily been ruled out using the methyl-substituted analog **1b**. Thus, if **5b** were formed, acetylene would insert into both silicon–naphthyl carbon bonds to afford a mixture of regioisomers of the 1-silaphenalene derivatives, but only a single regioisomer **4b** was experimentally obtained. The structure of **4b** was confirmed by X-ray crystallography of the hydrolyzed silanol **6**. This result clearly indicates that **5** is not the intermediate in the present reaction.



5 **a**: X = H
b: X = Me

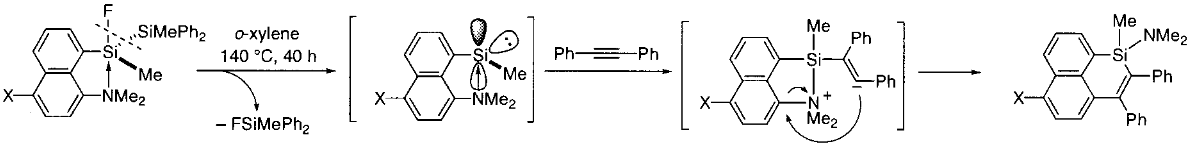
6

Chart 1.

The alkenyl anion intermediate **3** was actually quenched by acidic hydrogens; thus, when the reaction of **1a** with diphenylacetylene was carried out in the presence of water, pentacoordinate disiloxane **8** bearing the alkenyl groups and keeping the aminonaphthyl group intact was produced as a mixture of *meso*- and *dl*-isomers (Scheme 2). The structure of *meso*-**8** was also confirmed by X-ray crystallography (Figure 1b).[12] It is likely that after the protonation of the alkenyl anion intermediate **3a** by water, the formed hydroxide ion preferentially attacks the electron-deficient silicon center bearing the ammonium moiety to afford the silanol **7**, which may undergo dimerization to produce the observed disiloxane **8**.

When phenylacetylene was used in place of diphenylacetylene, pentacoordinate monosilane **10** bearing alkenyl and alkynyl groups was exclusively formed (Scheme 2 and Figure 1c). In the case of the deuterated phenylacetylene, the two deuterium atoms were incorporated in the alkenyl group. The result is also consistent with the formation of the alkenyl anion intermediate **9**, which is quenched with the acetylenic proton, followed by the nucleophilic attack of the resulting alkynyl anion on the silicon atom

Scheme 1.



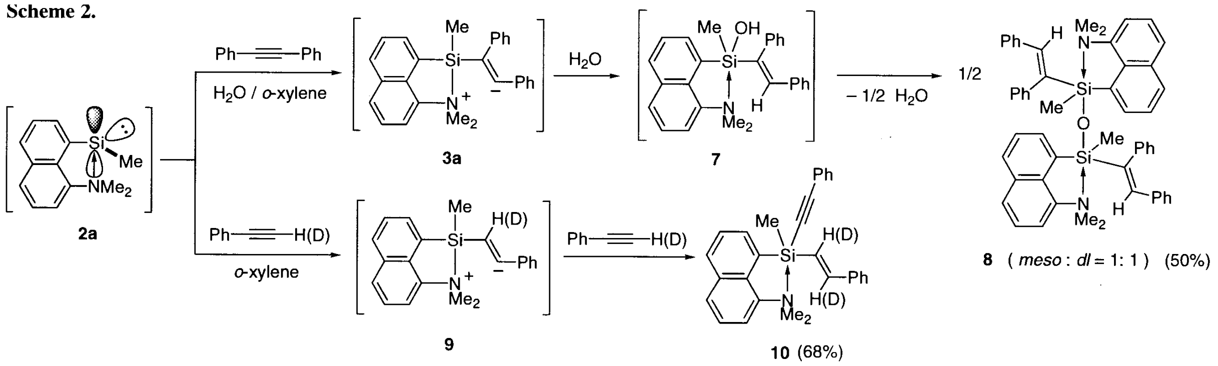
1 **a**: X = H
b: X = Me

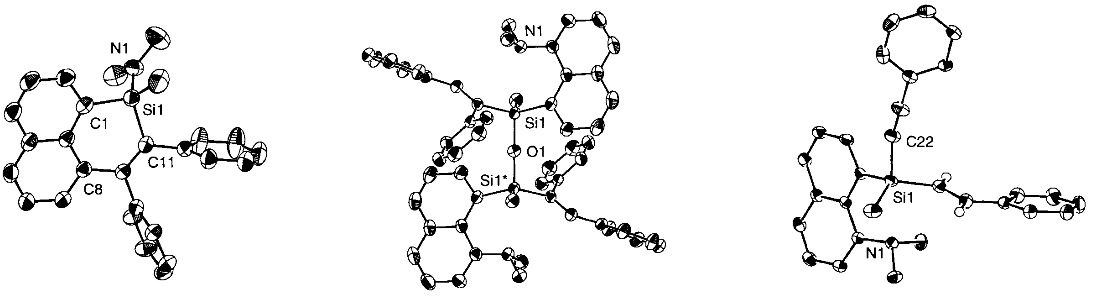
2 **a**: X = H
b: X = Me

3 **a**: X = H
b: X = Me

4 **a**: X = H (70%)
b: X = Me (75%)

Scheme 2.





a (**4a**) **b** (*meso*-**8**) **c** (**10**)

Figure 1. X-Ray structure of **4a** (**a**) (at 30% probability level), *meso*-**8** (**b**) (at 50% probability level), and **10** (**c**) (at 50% probability level). All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): **4a**: Si1–N1, 1.699(4); Si1–C11, 1.871(3); N1–Si1–C11, 111.3(2); N1–Si1–C1, 110.4(2). *meso*-**8** : Si1···N1, 2.921(2); Si1–O1, 1.6323(6); N1···Si1–O1, 172.48(5); Si1–O1–Si1*, 180.0. **10**: Si1···N1, 2.771(2); Si1–C22, 1.871(2); N1···Si1–C22, 173.70(8).

bearing the ammonium moiety to afford **10**.

We have clarified that the silylene species bearing the 8-(dimethylamino)-1-naphthyl group nucleophilically attack acetylenes to afford alkenyl anion intermediates which can be utilized in various transformations.

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References and Notes

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4 Pentacoordinate[5] fluorodisilane **1a** and its triphenylsilyl analog **1a’** (SiPh$_3$ instead of SiMePh$_2$ in **1a**) were prepared from the corresponding 1,1-difluorodisilane by treatment with 8-(dimethylamino)-1-naphthyllithium. Coordination of the amino group to the silicon atom in the fluorodisilanes has been confirmed by X-ray crystal structure analysis of **1a’** and by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies. The characteristic features of the solid state structure are the small F–Si–Si angle 95.59(7)° and the slightly elongated Si–F bond 1.637(2) Å, as in the case of a similar alkoxydisilane which we have previously reported.[6] The high thermo-lability of the pentacoordinate flurodisilane **1** with respect to the formation of a divalent silicon species should be noted, due to the extremely high thermostability of ordinary fluorodisilanes.[7]
5 In view of the weak coordination of the nitrogen atom of the 8-(dimethylamino)-1-naphthyl group, it may be better to describe the resulting structures as [4+1]-coordinate.[8] However, we prefer to refer to them as “pentacoordinate” for the sake of simplicity.
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10 Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101077 (**1a’**), 101095 (**4a**), 141148 (**6**), 101095 (*meso*-**8**), and 141147 (**10**). Copies of the data cab be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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12 It should be noted that the pentacoordinate disiloxane *meso*-**8** has a completely linear Si–O–Si skeleton.[13] The Si–O bond length 1.6323(6) Å is rather long compared with that in other linear disiloxanes containing an ordinary tetracoordinte silicon atom but is comparable to that of the pentacoordinate oxygen-bridged bis(tricarbasilatrane) [N(CH$_2$CH$_2$CH$_2$)$_3$Si]$_2$O.[13a]
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