

## Recent developments in silicon interelement linkage: the case of functionalized silyllithium, silylenoid and sila-ylide\*

Kohei Tamao†, Atsushi Kawachi, Masahiro Asahara and Akio Toshimitsu

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

*Abstract:* As one representative family of silicon interelement linkages, functionalized silyl anions and related species such as silylenoids and sila-ylides are described, focusing on the development of new synthetic methodologies and the effects of the heteroatom substituents on the bonding nature and the reactivity of these species.

### INTRODUCTION: SILICON INTERELEMENT LINKAGE?

'Interelement Linkage' was introduced as the new general term for the chemical bond between the heavy Main Group elements when our new research project started last year in Japan [1]. Bonds between the Main Group elements and alkali or alkali earth elements and those between the Main Group elements and transition metals are also included. It may be claimed by many chemists that all compounds have element-element bonds. This is true, but this terminology is based on the original Russian traditional term of 'elemento-organic compounds' for the organic compounds of the heavy Main Group elements; this term has been recently recognized world-wide. There are infinite possibilities for the interelement linkage, thus the number of just two-element combinations exceeds 1400, which may be compared with about 85 for the carbon-element linkage in traditional organic chemistry. In addition, there are possibilities for saturated, unsaturated, coordination, oxidation numbers, etc. Interelement linkage has some important characteristic features such as the high energy and high mobility of  $\sigma$  bonding electrons and the much more reactive  $\pi$  electrons of unsaturated bonds. A large number of studies have already been made in this field, but they have not necessarily been systematic enough in some cases. One main reason for this must reside in the large number of possibilities. Accumulation of basic concepts based on systematic studies is essential for the establishment of the chemistry of the interelement linkage. This is the reason why we have been interested in this field of chemistry.

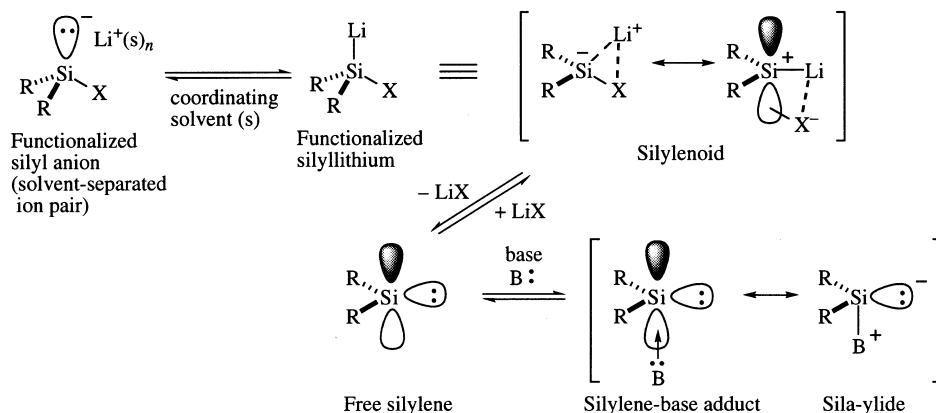
Described herein are our recent results on the silicon anionic species such as the functionalized silyllithium, silylenoid, and sila-ylide, as one representative family of silicon interelement linkages, which involve the Si–Li, Si–Si, Si–Sn, Si–N, Si–O, Si–F linkages and so on.

### FUNCTIONAL SILYLLITHIUM, SILYLENOID AND SILA-YLIDE

We have obtained several pieces of experimental evidence for these new silicon reactive intermediates. As summarized in Scheme 1, these species are formally correlated to each other via intervention of a free silylene. This is the silicon version of the well-studied carbanion chemistry [2], but the silicon analogs had rarely been studied [3] when we started this series of investigations several years ago [4]. We are now in a position where we can discuss these species as real reactive intermediates. Described herein are: (i) three methodologies for the preparation of functionalized silyllithiums, (ii) (aminosilyl)lithiums as the

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†Corresponding author.



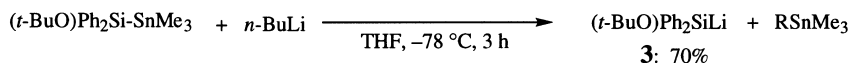
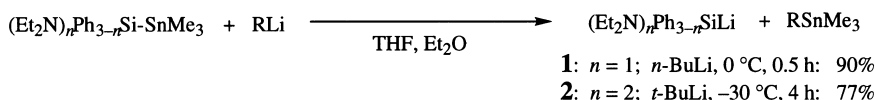
Scheme 1

first stable functionalized silyllithium, and their solution and solid state structures, (iii) the low stability of (monoalkoxysilyl)lithiums, behaving as silylenoid species, (iv) the first examples of the [2,3]-sila-Wittig rearrangement, and (v) generation and reactions of the intramolecularly amine-coordinated silylene behaving as an ammonium sila-ylide.

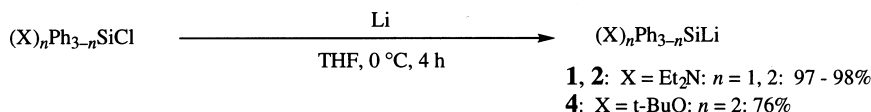
### THREE METHODOLOGIES FOR PREPARATION OF FUNCTIONALIZED SILYLLITHIUMS

We have developed the following three methodologies for the preparation of functionalized silyllithiums which contain amino and alkoxy group(s) on silicon. These results are summarized in Scheme 2. The yields are all based on the trapping products after treatment with  $\text{Me}_3\text{SiCl}$ .

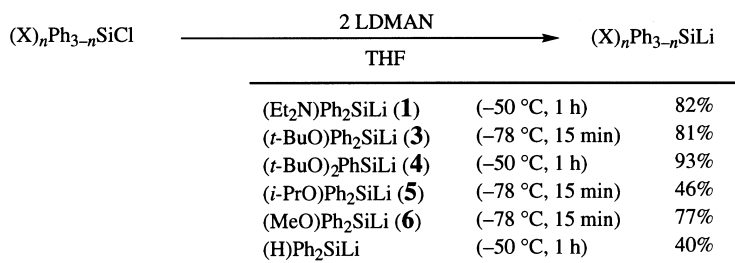
#### (1) Sn / Li Exchange Reaction



#### (2) Reductive Lithiation of Chlorosilane



#### (3) Low-Temperature Reduction of Chlorosilane with LDMAN



Scheme 2

Method (i): The tin-lithium exchange reaction smoothly proceeds to afford the (aminosilyl)lithiums **1** and **2** [4], and (*t*-butoxysilyl)lithium **3** [5] in high yields. While the former are highly stable species in THF at  $0^\circ\text{C}$  for several days, the latter is extremely unstable and readily undergoes a bimolecular

self-condensation reaction, as will be described below. This method, however, cannot be applied to silylstannanes which have small substituents such as methoxy group on the silicon, because the butyllithium may attack the silicon atom to give a stannyllithium instead of the desired silyllithium. Method (ii): (Aminosilyl)lithiums can also be prepared by the direct reaction of the corresponding aminosilyl chlorides with lithium in THF at 0 °C in quantitative yields [4]. This is the most practical procedure for the preparation of such stable (aminosilyl)lithiums. This method is also applicable to [di(*t*-butoxy)silyl]lithium **4** [6], but not to the monoalkoxy analog **3** because of its high reactivity. We thus sought a low-temperature method for the preparation of such reactive silyllithiums and found the third method. Method (iii): A variety of amino- and alkoxy-silyl chlorides are reduced at low temperatures with lithium (dimethylamino)naphthalenide (LDMAN) to afford the corresponding silyllithiums, which include highly reactive [(monoalkoxy)silyl]lithiums such as (isopropoxysilyl)lithium (**5**) and (methoxysilyl)lithium (**6**) as well as **3** [7].

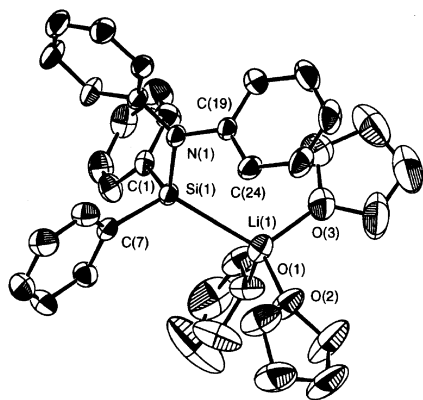
### (AMINOSILYL)LITHIUMS AS THE FIRST STABLE FUNCTIONALIZED SILYLLITHIUM: STRUCTURAL ASPECTS

The (aminosilyl)lithiums were the first stable functionalized silyllithiums. Their structures can thus be examined by multinuclear NMR spectroscopy for solution structures and by X-ray crystallography for the solid state structure [8].

In solution (aminosilyl)lithiums **1** and **2** exist as monomers as observed using  $^{29}\text{Si}$  NMR spectroscopy. For example, **1** in THF- $d_8$  exhibits the silicon resonance at  $\delta$  19.3 p.p.m. as a triplet due to the coupling with  $^6\text{Li}$  ( $I = 1$ ) with  $J = 18$  Hz (at 173 K) or a quartet due to the coupling with  $^7\text{Li}$  ( $I = 3/2$ ) with  $J = 48$  Hz (at 163 K).

It is also noted that the chemical shift is nearly 40 p.p.m. downfield than  $\delta -20.5$  for  $\text{MePh}_2\text{SiLi}$  [9]; the downfield shift may be due to the  $\sigma$ -inductive electron-withdrawing effect of the amino group.

An X-ray structure determination was done for the diphenylamino analog  $(\text{Ph}_2\text{N})\text{Ph}_2\text{SiLi}(\text{thf})_3$  which was obtained by the previously mentioned tin-lithium exchange reaction. This structure is shown in Fig. 1, which clearly indicates that there is no  $\text{N}\cdots\text{Li}$  interaction. It may also be mentioned that the Si–Li bond length (2.732(7) Å) is longer than that of  $\text{Ph}_3\text{SiLi}(\text{thf})_3$  (2.672(9) Å) [10] and among the longest for the previously reported monomeric silyllithiums (2.54–2.72 Å).

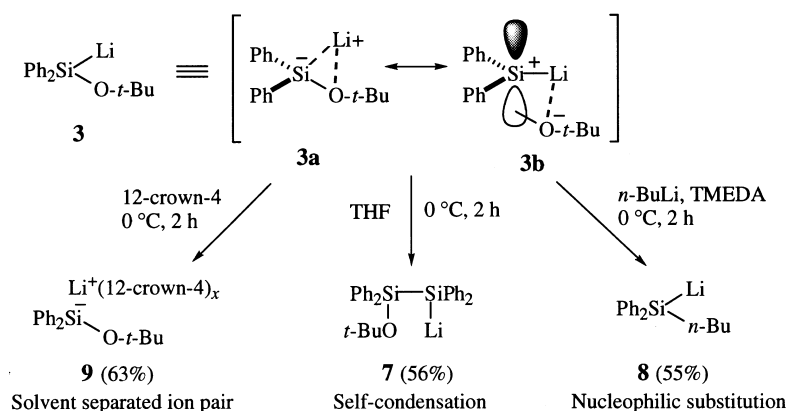


**Fig. 1** Crystal structure of  $(\text{Ph}_2\text{N})\text{Ph}_2\text{SiLi}(\text{thf})_3$  at 30% probability level. H atoms are omitted for clarity.

### (MONOALKOXSILYL)LITHIUM AS SILYLENOID: SELF-CONDENSATION

(*t*-Butoxysilyl)lithium **3** has been found to behave as a silylenoid, i.e. the species has ambiphilic character due to the contribution of two electronic structures: a nucleophilic silyl anion structure and an electrophilic silyl cationic structure. The entire chemistry of **3** is summarized in Scheme 3 [5]. This is just a silicon analog of the classical carbenoid chemistry reported by Wittig 40 years ago [11].

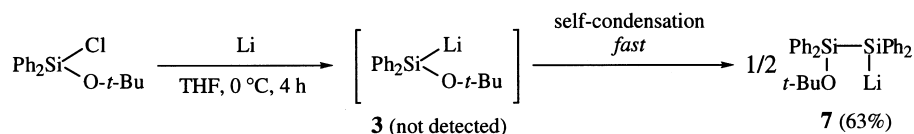
As described above, **3** is stable at  $-78$  °C for several hours, but it completely decomposes at 0 °C within 2 h. The decomposition product is [2-(*t*-butoxy)disilanyl]lithium **7**. The formation of **7** may be explained



**Scheme 3** (Yields are all based on the trapping product with  $\text{Me}_3\text{SiCl}$ ).

by the self-condensation of **3**, in which one molecule behaves as a nucleophile and the other as an electrophile. It should be noted that in the latter, the lithium atom bound to the silicon atom ionizes and activates the silicon-oxygen bond, so that the silicon center becomes more electrophilic than in the neutral alkoxy-silane counterparts. The enhanced electrophilicity of silicon in **3** has been demonstrated by rapid nucleophilic alkylation when treated with *n*-butyllithium in the presence of TMEDA to afford **8**. In contrast, the electrophilicity completely disappears by the addition of a crown ether which is expected to convert **3** into a 'solvent-separated ion pair' **9**, which is stable even at 0 °C for 2 h and undergoes neither self-condensation nor butylation, but only behaves as a nucleophilic silyl anion.

Several additional points deserve comment. First, the (alkoxysilyl)lithium **3** undergoes no  $\alpha$ -elimination to form the silylene; thus no trapping products have been obtained in the presence of silylene-trapping agents such as hydrosilane and diene. Second, the high stability of [2-(*t*-butoxy)disilanyl]lithium **7** should be noted. It never undergoes  $\beta$ -elimination of lithium alkoxide to form the silicon-silicon double bond species, in contrast to the carbon analog which readily undergoes  $\beta$ -elimination to form the corresponding olefin [11]. Third, in contrast to the [(monoalkoxy)silyl]lithium **3**, the [(dialkoxy)silyl]lithium **4** exhibits no ambiphilic character; thus, **4** is stable at 0 °C for at least 2 h and undergoes no self-condensation, most probably due to the steric hindrance around the silicon center. This high stability is the reason why **4** can be prepared by the direct reaction of the corresponding silyl chloride with lithium under the condition of method 2, as mentioned above, while **3** cannot survive this reaction condition, resulting in the formation of the self-condensation product **7**, as shown by Scheme 4 [6].



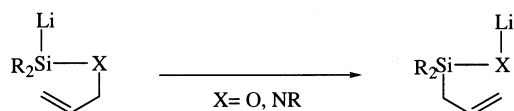
**Scheme 4**

Our recent *ab initio* calculations at the MP2//HF/6-31G\*\* level of theory using  $(\text{MeO})_2\text{SiLi}(\text{H}_2\text{O})_2$  **10** as a model of the doubly solvated species of **3** have shown that the self-condensation may smoothly proceed along an exothermic downhill energy profile by the approaching of two molecules of **10** [12]. After formation of an intermediate (relative energy  $-7.8$  kcal/mol), the transition state ( $-6.9$  kcal/mol) is attained at the Si-Si distance of 2.62 Å, and finally the [2-(alkoxy)disilanyl]lithium  $(\text{MeO})_2\text{Si}-\text{SiH}_2\text{Li}$  and LiOMe are formed, which are 24.8 kcal/mol more stable than the starting materials. In the transition state, one silicon center works as a nucleophile and the other as an electrophile. In the electrophilic part, the lithium-assisted ionization of the Si-O bond lowers the energy of the  $\sigma^*(\text{Si}-\text{O})$  orbital. The interaction between the lobe of the HOMO localized on the silicon atom in the nucleophilic part and the backside lobe of the  $\sigma^*(\text{Si}-\text{O})$  orbital in the electrophilic part leads to the formation of the Si-Si bond and the breaking of the Si-O bond. This reaction thus proceeds via an  $\text{S}_{\text{N}}2$  type displacement with retention of

configuration of the silicon in the nucleophilic part, but with inversion of configuration of the silicon in the electrophilic part.

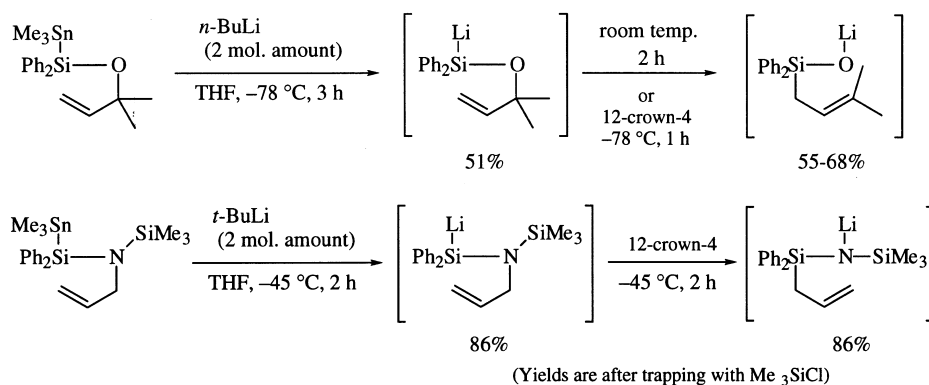
### [2,3]-SILA-WITTIG REARRANGEMENT

The Wittig rearrangement has been extensively studied as one of the most important reactions of  $\alpha$ -oxygen and  $\alpha$ -nitrogen substituted carbanions [13]. We have found the first examples of the silicon version of the [2,3]-Wittig rearrangement, i.e. [2,3]-sila-Wittig and [2,3]-aza-sila-Wittig rearrangements, which involve intramolecular migration of an allyl group from oxygen or nitrogen to silicon in the [(allyloxy)silyl]lithium or [(allylamino)silyl]lithium, as shown by Scheme 5 [14].



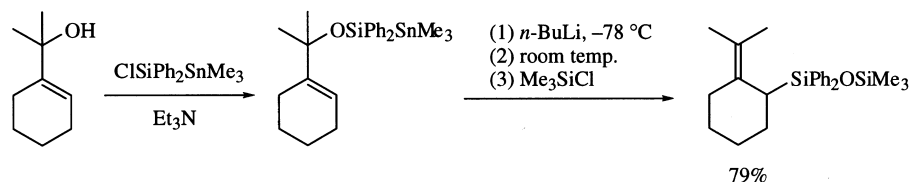
Scheme 5

Typical examples are shown in Scheme 6. It may be noted that both rearrangements are highly accelerated by the addition of 12-crown-4. In particular, the aza-sila-Wittig rearrangement hardly occurs without 12-crown-4, but the rearrangement smoothly proceeds even at low temperatures upon its addition.



Scheme 6 (Yields are after trapping with  $\text{Me}_3\text{SiCl}$ ).

The rearrangements afford a new synthetic methodology for the preparation of silicon-functionalized allylsilanes from allyl alcohols or allylamines in a regio-controlled fashion, as exemplified by the following transformation. Advantageously, the requisite reagent,  $\text{ClPh}_2\text{SiSnMe}_3$ , can be readily prepared using our (aminosilyl)lithium **1**, by successive treatment with  $\text{ClSnMe}_3$  and acetyl chloride (Scheme 7).

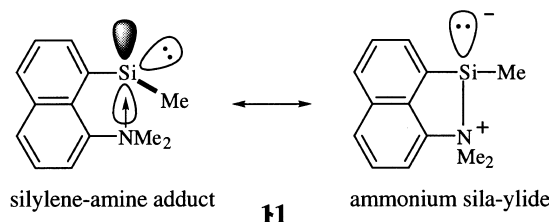


Scheme 7

### AMMONIUM SILA-YLIDES

It has been well established that silylene is a ground state singlet with an electron pair in a  $\sigma$ -orbital and a vacant orbital of  $\pi$ -symmetry [15]. A Lewis base can thus coordinate to silicon through the vacant orbital to form a silylene-base adduct, as shown in Scheme 1. This species may also be represented as a zwitterionic species, a sila-ylide, through the formation of the base-to-silicon  $\sigma$ -bond, in which the silicon

center would no longer have electrophilic character but nucleophilic character. Such species, first proposed by Seyferth in 1978 [16], have been the main subject of many papers [17], but the sila-ylide character has rarely been reflected in the reaction products. This may be due to a slight charge separation in the silylene-base adduct, as predicted by theoretical studies [18]. We have recently observed the first strong evidence for the intervention of the ammonium sila-ylide species during the main course of reaction of a divalent silicon species **11** containing the 8-(dimethylamino)-1-naphthyl group (Scheme 8) [19].



**Scheme 8**

Our observations and plausible mechanism are summarized in Scheme 9. Thus, the thermal degradation of a *pseudo*-pentacoordinate fluorodisilane **12** bearing the 8-(dimethylamino)-1-naphthyl group in the presence of a 1 molar amount of diphenylacetylene affords, in addition to the  $\alpha$ -eliminated fluorosilane, 1-dimethylamino-1-silaphenylene **13** in a nearly quantitative yield, which contains the amino group on the silicon instead of the naphthyl group. If water is present in the reaction mixture, a totally different product **14** is obtained as the major product, in which the aminonaphthyl group has survived.

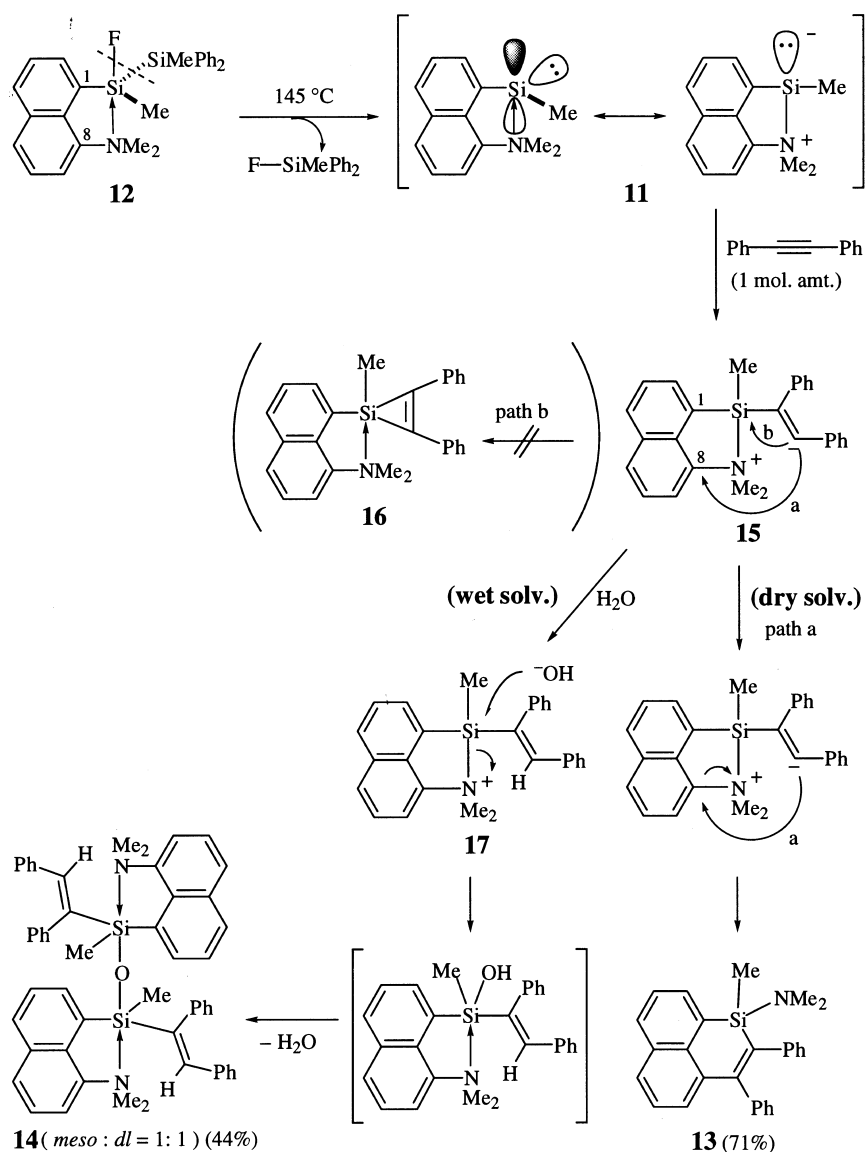
Most remarkably, the coordinated amino group is incorporated in the final product **13** in such a fashion that it has migrated from the naphthalene carbon atom to the silicon atom, and the diphenylacetylene is incorporated between the silicon atom and the naphthalene carbon atom which has originally borne the amino group. These results reveal that the divalent silicon species **11** behaves as the ammonium sila-ylide, because during the reaction, the silicon-nitrogen bond must be formed while the naphthalene carbon-nitrogen bond is cleaved.

The following are plausible mechanisms. The reactive species **11** nucleophilically attacks the acetylene carbon atom to afford the zwitterionic alkenyl anion **15**. This carbanion subsequently attacks the naphthalene C8 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, probably via the Meisenheimer-type complex, to give the 1-amino-1-silaphenylene **13** (path a in Scheme 9). It should be noted here that, if the carbanion attacks the silicon atom by taking path b in Scheme 9, silacyclopentene **16** would be formed via cleavage of the silicon-nitrogen bond, as the typical classical reaction pathway of silylene-base adducts, but this is not the case. This may be ascribed to the presence of the more favored cyclization course to the six-membered ring in this substrate.

If water is present, the carbanion center in **15** may be quenched with water to give the silyl-ammonium salt **17**. Subsequent attack by the hydroxide ion selectively occurs on the silicon atom in accordance with the standard mechanism for the nucleophilic substitution reactions of organosilicon compounds to cause cleavage of the silicon-nitrogen bond, resulting in the eventual formation of **14**.

## CONCLUDING REMARKS

We have developed several new species of anionic silicons containing heteroatom substituents on silicon. The (aminosilyl)lithiums and related anionic silicon species have already been recognized as new standard reagents not only for the synthesis of polyfunctionalized oligosilanes and polysilanes in organosilicon chemistry [20], but also for modern synthetic organic chemistry [21]. It should be noted, however, that these anionic silicon chemistries are roughly 40–50 years behind in comparison with the corresponding carbanion chemistries. Obviously, we must continue the systematic and basic research in the chemistry of the silicon interelement linkage in order to find new species.



Scheme 9

## ACKNOWLEDGEMENTS

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