

# Chemical and photochemical approaches to amino(aryl)silylenes

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## Abstract

Generation by two different methods of silylenes stabilized by *o*-amino(aryl) groups is reported. The halodemetalation of difluoro- or dichloro-silanes with Li metal or lithium-naphthalene gave the same product, a stabilized sila-ylide (hypercoordinated silylene). Intramolecular Lewis base stabilization is not sufficient to isolate a monomeric species. The silylenes, however, have been trapped with 2,3-dimethylbutadiene. An unexpected intramolecular rearrangement to silaacenaphthene has been observed in the case of a six-membered ring amino(aryl) coordinated silylene. Photolysis of *o*-1-[(*N,N*-dimethylamino)methyl]-2-[tris(trimethylsilyl)silyl]benzene produced, among other products, Me<sub>3</sub>SiSiMe<sub>3</sub> and the sila-ylide, which has been trapped with Et<sub>3</sub>SiH and dimethylbutadiene. Our mechanistic interpretation is supported by spectral observation of the photochemically generated reaction intermediates in a 3-methylpentane glass at low temperature.

**Key words:** Silylene; Sila-ylide; Amino-aryl; Alkali metals; Stabilization; Photochemistry

## 1. Introduction

Silylenes are critically important species in many reactions involving silicon [1], but they have not been isolated as such, except in the case of decamethylsilicocene. Consequently, their role as intermediates in reactions has been inferred from a variety of techniques. Among these techniques are kinetic and product studies as well as spectral observation in inert matrices. One possible way to stabilize such reactive entities would be to prepare stable complexes with suitable donors [2]. An intriguing question is, would such stabilization so alter the electron distribution of the silylene that it no longer displays the chemical reactivity that is characteristic of a divalent silicon atom.

Intramolecular coordination of Lewis bases could facilitate stabilization for entropic reasons. The idea

has been successfully applied [3] to the isolation of doubly bonded silicon species  $D \rightarrow Si=X$ , as well as silanediyl-transition metal complexes [4]. Recently, a cyclotrisilane has been obtained by chlorodemetalation of dichlorosilane **1** with magnesium, in THF [5]. Trapping experiments gave those products expected of the formal silylene addition reactions.

We report our efforts to prepare intramolecularly Lewis-base stabilized silylenes. Both  $\alpha$ -halodemetalation of dihalogeno(aminoaryl)silanes and photochemical decomposition of trisilanes have been investigated.

## 2. Results

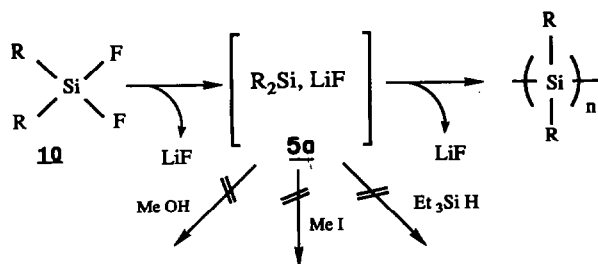
### 2.1. Reactivity of dichlorosilanes

#### 2.1.1. Reductive chlorine elimination of $R_2SiCl_2$ ( $R = o-C_6H_4CH_2NMe_2$ ) with lithium naphthalene

The reaction of **1** with lithium-naphthalene at  $-78^\circ C$  afforded after sublimation of naphthalene, a mixture of

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Scheme 7.

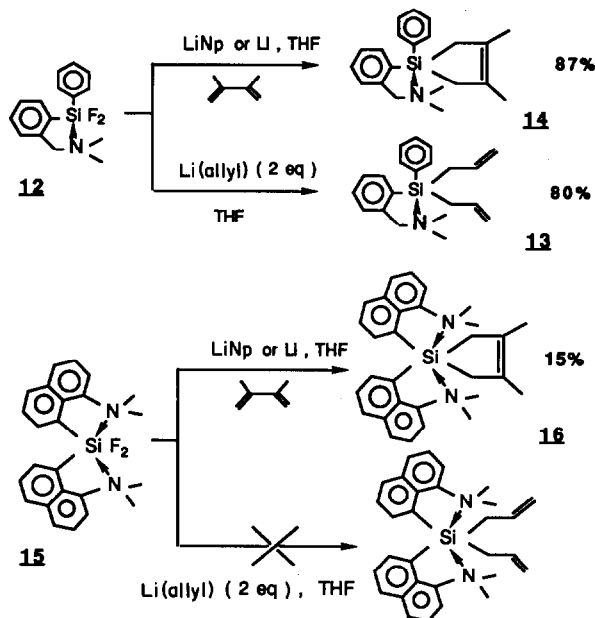
trapping product was obtained (Scheme 8). The <sup>1</sup>H NMR spectra show that the two dimethylaminomethylphenyl substituents of the bis[2-(*N,N*-dimethylamino)methylphenyl]-silyl derivatives described in this paper are equivalent at room temperature; by analogy with the known structure of the non-associated dichloro-compound **1** [4b], we describe these products as pentacoordinated silanes.

### 2.2.3. Other pentacoordinated difluorosilanes

Metal-promoted fluorine elimination was extended to other systems **12**, **15**. Higher yields were obtained when the trapping diene was added during the lithiation, and using only a small excess (Scheme 9).

In order to eliminate the possibility that the reaction was occurring through the transient formation of an organolithium reactant, we investigated the synthesis of analogous allylic derivatives. Diallylsilane **13** was easily obtained in the coupling reaction of allyllithium (from tetraallyltin) with **12**. On the other hand, allyllithium was unreactive with the sterically crowded **15**, [7] confirming a preliminary study which showed the absence of reactivity of the hexacoordinate compound **15** with RLi or RMgX. Fluorodemetalation of **12** with Li in the presence of 2,3-dimethylbutadiene gave **14** (87%), whereas the fluorodemetalation of **15** in the presence of 2,3-dimethylbutadiene afforded 15% of the hexacoordinate silacyclopentene **16** (Scheme 9).

Compound **17** has typical behaviour (Scheme 10). Halodemetalation, performed with LiNp or Li, metal initially gave a red solution, which turned yellow after 12 h. After work-up, a single product, dimethylaminosilaacacenaphthene (**18**) was isolated upon distillation under dinitrogen. Oxidation of **18** afforded the disiloxane **19a,b**, as a 52/48 isomeric mixture, and elimination of

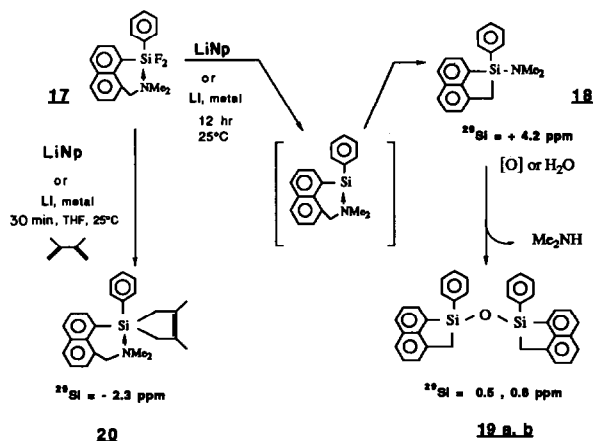


Scheme 9.

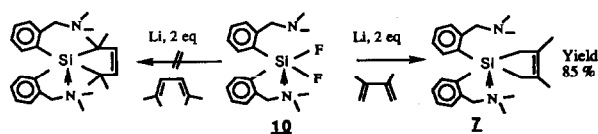
dimethylamine. Hydrolysis of **18** also afforded disiloxane **19a,b**, which was characterized by <sup>13</sup>C NMR and GC/MS. Attempts to trap the silylene with Et<sub>3</sub>SiH, MeOH or MeI failed, but 2,3-dimethylbutadiene gave the expected silacyclopentene **20** (27% yield).

### 2.3. Photochemical reactions of 1-[(*N,N*-dimethylamino)-methyl]-2-[tris(trimethylsilyl)silyl]benzene, **21**

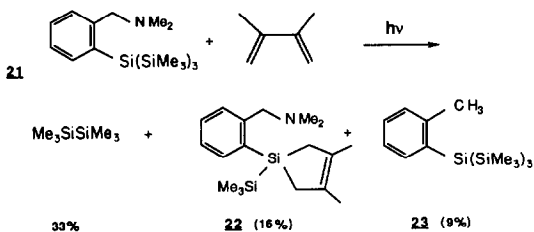
Linear trisilanes, R<sub>2</sub>Si(SiMe<sub>3</sub>)<sub>2</sub>, are frequently used as sources of free silylenes upon UV irradiation with laser flash or medium-pressure mercury lamps [1,2]. One driving force for the reaction is the formation of hexamethyldisilane. 1-[(*N,N*-dimethylamino)methyl]-2-[tris(trimethylsilyl)silyl]benzene **21** was obtained from the coupling reaction of *o*-lithiobenzyl dimethylamine



Scheme 10.



Scheme 8.



Scheme 11.

with tris(trimethylsilyl)chlorosilane. **21** was photolyzed in cyclohexane with a medium pressure mercury lamp, in the presence of trapping agents. The mixtures were analyzed by GC/MS and NMR spectroscopy.

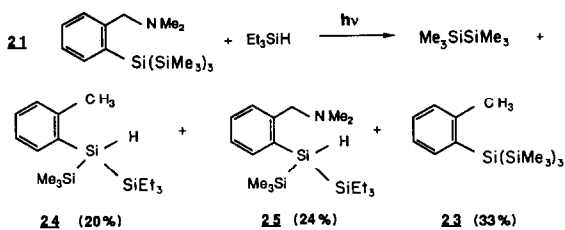
### 2.3.1. 2,3-dimethyl-1,3-butadiene

When the photolysis was carried out for 4.5 h in a solution of 2,3-dimethyl-1,3-butadiene (50 fold excess), three products: HMDS, *o*-tolyltris(trimethylsilyl)silane **23** and 1-[2-(*N,N*-dimethylamino)methylphenyl]-1-trimethylsilyl-3,4-dimethylsilacyclopentene (**22**) were formed in 33%, 9%, and 16% yields, respectively. The percentage of HMDS was determined using mesitylene as internal standard (Scheme 11).

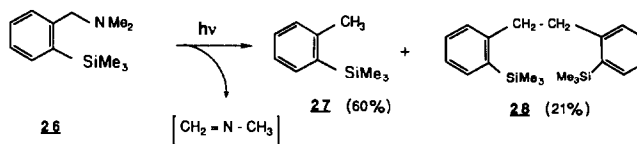
### 2.3.2. $\text{Et}_3\text{SiH}$

The photolysis in cyclohexane for 100 min with a ten-fold excess of triethylsilane, gave HMDS, plus 2-*o*-tolyl-1,1,1-triethyl-3,3,3-trimethyltrisilane (**24**) (20%), *o*-tolyltris(trimethylsilyl)silane (**23**) (33%) and the expected silylene insertion product, 2-[2-[(*N,N*-dimethylamino)methyl]phenyl]-1,1,1-triethyl-3,3,3-trimethyltrisilane (**25**) (24%). Attempts to separate HMDS and  $\text{Et}_3\text{SiH}$  by gas chromatography on several different columns were unsuccessful and, thus, prevented an absolute measure of the percentage of **21** transferred to  $\text{Et}_3\text{SiH}$ . Product yields therefore are relative. On the basis of the product yields, however,  $\text{Et}_3\text{SiH}$  was a better trapping agent than DMBD in this case (Scheme 12).

In order to show that the photodeamination pathway of **21** does not depend on the tetrasilane chromophore, the corresponding monosilane, [*o*-(*N,N*-di-



Scheme 12.



Scheme 13.

methylamino)methylphenyl]trimethylsilane (**26**) was photolyzed. We note that precedent for such a reaction is the photochemical decomposition of tribenzylamine which provides phenylbenzylimine and toluene [8]. Photolysis of **26** in the presence of *t*-butanol (10 equiv) in cyclohexane yielded no trapping products. Instead, (*o*-tolyl)trimethylsilane (**27**) and the dimer **28** were isolated in 60% and 21% yields, respectively (Scheme 13).

### 2.4. UV spectroscopic characterization of matrix-generated [2-(*N,N*-dimethylamino)methylphenyl]trimethylsilylsilylene

In a 3-methylpentane (3MP) glass at 77 K, photolysis of 1-[(*N,N*-dimethylamino)-methyl]-2-[tris(trimethylsilyl)silyl]benzene (**21**) produced three absorption bands with  $\lambda_{\text{max}}$  at = 272, 328 and 478 nm. The absorption band at  $\lambda_{\text{max}} = 478$  nm increased with longer irradiation, while the absorption bands at  $\lambda_{\text{max}} = 272$  nm and 328 nm increased rapidly, reached a maximum when irradiated after 11 min, and decreased as photolysis time continued thereafter (Fig. 1). When the photolysis was carried out in a soft matrix, isopentane/3MP (4:1), absorption bands with  $\lambda_{\text{max}} = 478$  and 326 nm appeared and their change with time were almost the same as in 3MP. A new absorption band with  $\lambda_{\text{max}} = 386$  nm was recognized after 20 min.

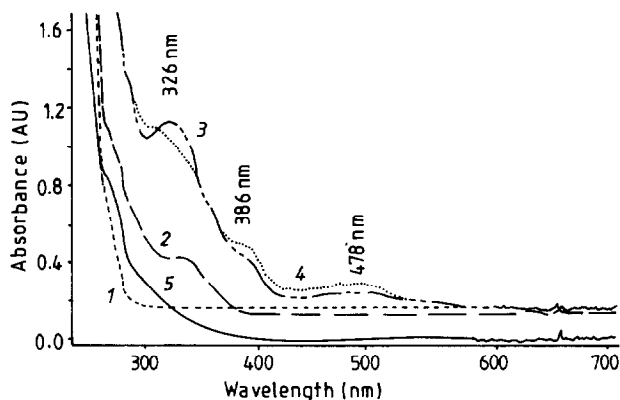


Fig. 1. The time course of the UV spectrum observed in the photolysis of **21** in a isopentane/3-methylpentane (4:1) soft matrix at 77 K: 1 (before photolysis); 2 (after 1 min); 3 (after 20 min); 4 (after 75 min); 5 (matrix melt).

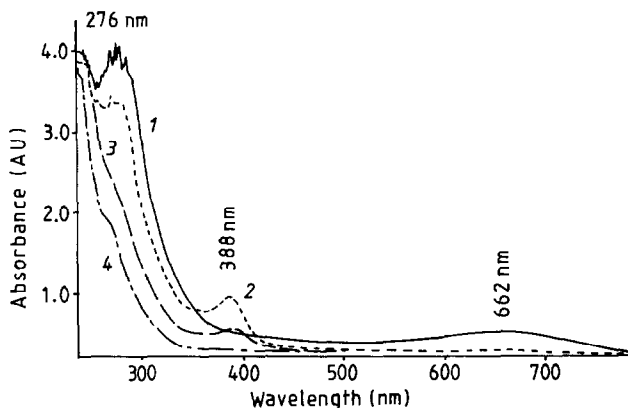
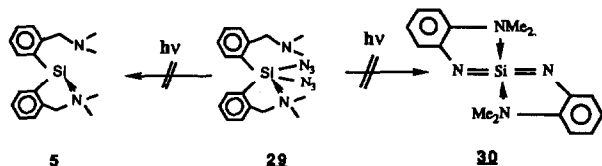


Fig. 2. The time course of the UV spectrum observed in the photolysis of compound **23** in an isopentane/3-methylpentane (4:1) soft matrix at 77 K: 1 (start of annealing); 2 (annealing 6 min); 3 (at 8 min); 4 (at 36 min).



Scheme 14.

Under the same conditions as for the photolysis of **21** in 3MP, *o*-tolyltris(trimethylsilyl)-silane (**23**) the photodeamination product, showed two absorption bands with  $\lambda_{\max} = 276$  and 662 nm (Fig. 2).

When the matrix was annealed, the band at  $\lambda_{\max} = 662$  nm disappeared immediately, with the appearance of a new band at  $\lambda_{\max} = 388$  nm, a band that also disappeared after *ca.* 8 min after slowly reaching room temperature (Fig. 2). The band with  $\lambda_{\max} = 276$  nm also disappeared slowly upon annealing.

Another reaction path leading to silylenes is the photolysis of diazidosilanes  $R_2Si(N_3)_2$  [9]. The diazide **29**, where ( $R = 2-C_6H_4CH_2NMe_2$ ) was prepared by the reaction of **1** with  $NaN_3$  and catalytic amounts of  $AlCl_3$  in THF solution. The photolysis (254 nm) of **29** in pentane or ether did not release  $N_2$  even at higher temperatures (hexane) indicating the surprising stability of **29**. The expected product **30**, resulting from nitrogen release and a subsequent 1,2-shift of the aryl ligands from silicon to nitrogen, was not detected (Scheme 14).

### 3. Discussion

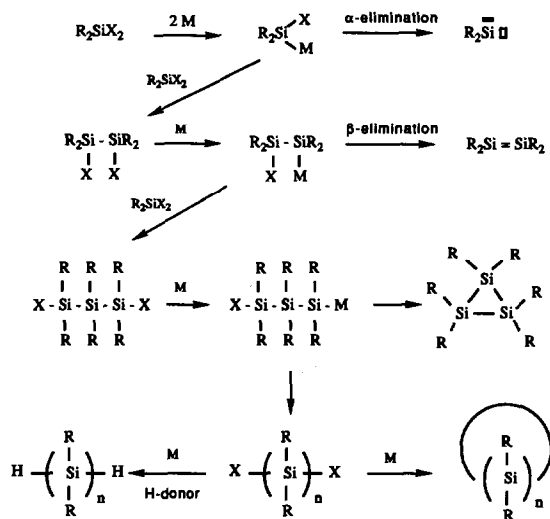
Before a discussion of our experiments, we comment briefly on previously reported results concerning the stability of silylenes and silylenoid species [1,10].

Low-valent silicon species  $R_2Si$  are involved in many reactions, and their value in synthesis was more widely appreciated with the isolation of their dimers, disilenes  $R_2Si=SiR_2$ , and the higher homologues, cyclopolysilanes,  $(R_2Si)_n$ . Such compounds generally have bulky substituents, which suppress their intrinsic reactivity. Syntheses of these homologues,  $(R_2Si)_n$ , where  $n = 1, 2, 3$  etc., generally involve two types of reaction: 1) reductive coupling of dihalosilanes with lithium naphthalene [11] or alkali metal [12] and 2) photolysis of linear trisilanes [13] or cyclic polysilanes [14].

The ring size of the cyclopolysilanes obtained by halodemetalation varies with the bulkiness of the substituents (Scheme 15). From Me, <sup>n</sup>Pr, Bu or phenyl derivatives, cyclosilanes with  $n = 4, 5, 6$  and greater are generally obtained [15]. With 2,6-dimethylphenyl or 2,6-diethylphenyl groups on dichlorosilanes, trimers are isolated [16] and when the substituents on Si become larger, only disilenes are obtained [17]. Using the highly strained 2,4,6-tri-*t*-butylphenyl groups, formation of the disilene was suppressed and the results have been interpreted to indicate the formation of silylene via  $\alpha$ -elimination [18].

Some years ago, Boudjouk and co-workers described the synthesis of siliranes via metal-promoted  $\alpha$ -elimination of dihalosilanes [19]. Dehalogenation in the absence of silylene trapping agent gave different products depending on the halogen atom ( $X = Cl, Br$  or  $I$ ). Boudjouk concluded that "a silylenoid is the reactive intermediate in at least one of the three cases".

In 1981, Drahnak, Michl, and West described the first isolated dialkylsilylene,  $R_2Si$ , dimethylsilylene, obtained by photolysis of dodecamethylcyclohexasilane  $Me_{12}Si_6$  in a 3MP glassy matrix at 77 K ( $\lambda_{\max} = 454$



Scheme 15.

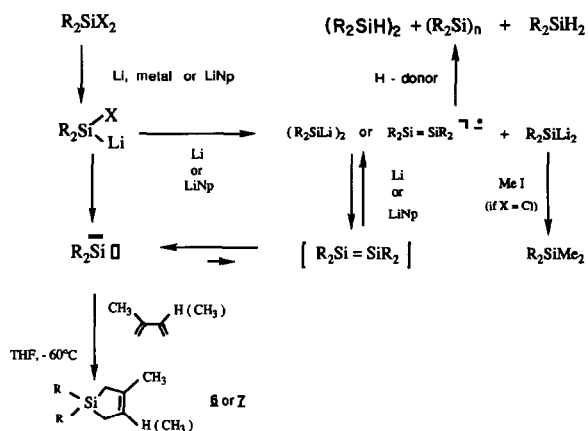
nm). [20]. Photolysis of polysilanes, linear or cyclic, has been developed over the last 20 years to produce a variety of silylenes. In the absence of trapping agents, most silylenes dimerize [21] upon annealing and many disilyenes have been now fully characterized, by methods including X-ray structure determination.

Silylene-ether complexes were initially studied by Weber in 1980 [22]. The complexes are less reactive and more selective than free dimethylsilylenes, and the facile generation of free silylenes has permitted study of their complexation with Lewis bases. Sila-ylides have been characterized in various glass matrices at low temperature [2] and also, kinetically, at ambient temperature [23].

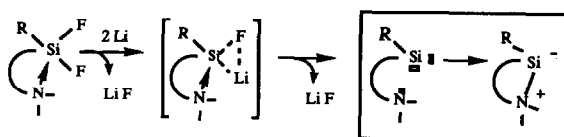
In 1989, preliminary studies [3] showed that intramolecular coordination with aminoaryl substituents could be a fruitful approach to stabilized low-coordinated silicon species. Stabilized doubly bonded silicon derivatives were isolated,  $R_2Si=X$  ( $X = S, Se, NR, \text{ or } PR$ ). These species possess zwitterionic character, and a characteristic feature is that they are unreactive with the usual trapping agents [4]. Silanediyltransition metal complexes are also stabilized by donor molecules [24,25]. Aminoarylsilanediyl-transition metal complexes were obtained through dehydrogenation or halodemetalation [4]. We had considered the possibility that intramolecularly stabilized silylenes might be also isolated.

The present results indicate that amino(aryl)silylenes were present at low concentrations with trapping agents. The halodemetalation of dichloro- and difluoro-silanes with  $LiNp$  afforded a mixture of hydrosilanes and hydropolysilanes in various ratios, after addition of methanol (Schemes 1, 5, 7). Methoxysilanes, which might be the products expected from addition of methanol to silylenes, were not formed. Only trapping experiments with dienes at low temperature, or with the trapping agent already present in the medium before the addition of  $LiNp$ , gave the expected bimolecular adducts (Schemes 2, 6). Further addition of 2,3-dimethylbutadiene after the complete disappearance of  $Li$  gave only traces of silacyclopentene, which implies that a silylene or silylenoid is no longer present to a significant extent in the medium (Scheme 8). Moreover, we have not been able to characterize the silylenes or silylenoids by  $^{29}Si$  NMR spectroscopy, even when the experiments were carried out in different conditions (solvents, temperature, NMR relaxation times, pulse sequences and measurements performed at different locations).

Our initial interpretation of these results is described below (Scheme 16): the reduction of **1** with  $LiNp$  or  $Li$  metal leads to silylenes or silylenoids at low temperature and they oligomerize or polymerize upon



Scheme 16.



Scheme 17.

warming. A side-reaction is the generation of an unknown species that reacts, probably with the solvent, to produce different  $Si-H$  compounds [25\*]. The formation of the stable  $R_2SiLi_2$  in the case of metallic  $Li$  is supported indirectly by trapping with  $MeI$  to give  $R_2SiMe_2$  (Scheme 4). Pertinent data have also been described by Weidenbruch [26].

Similarly, an unexpected rearrangement observed in the fluorodemetalation of aminoarylsilane (**17**) with  $LiNp$  or  $Li$  metal (Scheme 10), affording the silaacephthalene (**18**), is explained through the transient formation of a silylene or silylenoid. The competitive trapping experiment with 2,3-dimethylbutadiene supports this hypothesis. The reaction of highly strained bis[(8-dimethylamino)naphthyl]difluorosilane (**15**) with  $Li$  metal and 2,3-dimethylbutadiene yielding the silacyclopentene (**16**) (17%), also provides indirect evidence of the transient formation of silylene (Scheme 9). Even if an organolithium species were formed from  $Li$  and 2,3-dimethylbutadiene, it could not react with the hexacoordinated **15** as shown in an earlier study on the coupling of **15** with Grignard or organolithium reagents [7]. A possibly more reasonable mechanistic proposal is that the silylene is formed by the  $\alpha$ -elimination of the silylenoid species. Such a path is entropically favoured in this situation, and leads to the silylene-ylide (Scheme 17).

\* Reference number with asterisk indicates a note in the list of references.

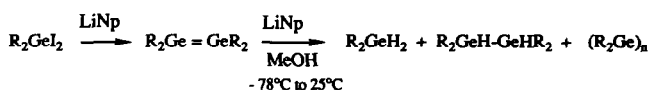
Yet, another possibility for the overall scheme would be initial intermolecular halodemetalation producing a dihalosilane, which is further metallated prior to oligomerization, as suggested by Masamune for the heavier Group 14 germanium compounds [27]. With an excess of LiNp digermenes might rearrange to germanes, digermenes and polygermanes during ethanolysis (Scheme 18).

Analogies with the present data are obvious (*i.e.* Schemes 1, 5). Disilenes would be formed through  $\beta$ -elimination, but the symmetry in the M = M double bond might prevent intramolecular stabilization with donors, and the disilenes could undergo redistribution to stabilized silylenes. The computed dissociation energies for the gas-phase process  $H_2M=MH_2 \rightarrow 2H_2M$  are *ca.* 30, 20, and 60 kcal mol<sup>-1</sup> for E = Ge, Sn, and Si, respectively [28]. Stabilization of the silylene as an ylide with a Lewis base could compensate for some of the energy of dissociation.

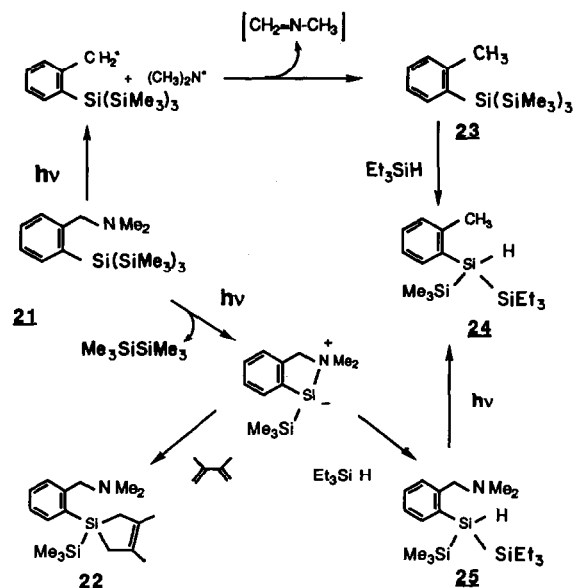
This process might explain the formation of trisilane ( $R_2Si$ )<sub>3</sub> observed by Beltzner in the case of halodemetalation with magnesium in THF [5]. Cyclosilanes could result from the addition of  $R_2Si$  to the  $R_2Si=SiR_2$   $\pi$  bond, but to our knowledge such reactions have not been observed unambiguously for silicon. Further experiments with pentacoordinated disilanes might provide an answer.

The hypothesis that silylenes are stabilized as silylene-ylides by intramolecular coordination with aminoaryl groups is strengthened in the photochemical study of 1-[(*N,N*-dimethylamino)methyl]-2-[tris(trimethylsilyl)silyl]benzene (**21**).

Photolysis of **21** at room temperature in a cyclohexane solution containing  $Et_3SiH$  produces the silylene-ylide, which was trapped to afford the 2-[2-[(*N,N*-dimethylamino)methyl]phenyl]-1,1,1-triethyl-3,3,3-trimethyltrisilane (**25**) (33% yield). A second decomposition pathway, photodeamination, produces *o*-tolyltris(trimethylsilyl)-silane (**23**) which under the photochemical conditions affords (*o*-tolyl)trimethylsilyl silylene, again trapped with triethylsilane, giving **24**. An independent synthesis and photochemical degradation of *o*-tolyltris(trimethylsilyl)silane (**23**) produced the same results. Trapping experiments with triethylsilane and 2,3-dimethylbutadiene have also been carried out for photolysis of **21**, supporting the transient formation of the silylene. The overall data are summarized in Scheme 19.



Scheme 18.



Scheme 19.

It has been reported that C–N cleavage is the major process in photolysis of tribenzylamine in solution, and the products were phenylbenzylimine and toluene [8]. Photolysis of 2-(trimethylsilyl)(*N,N*-dimethylamino)methyl)benzene (**26**) in the presence of *t*-butanol (Scheme 13) is consistent with the above report. Two compounds, *o*-tolyl-(trimethyl)silane (**27**) and the dimer **28** were obtained. No transients were trapped by the alcohol, suggesting that relatively polar intermediates were not involved, and it is likely that the photolysis proceeds by a mechanism similar to the photodeamination of tribenzylamine. Absence of a 'dimer' from photodeamination of **21** might be attributable to steric factors. We note the possibility that the silylene adduct **23** might also originate from photodeamination of trisilane **25**.

The isolation of silylenes in cold glassy matrices in recent years has contributed significantly to further understanding of these reactive species [1,2]. The UV spectrum of the silaammonium ylide formed in the photochemical degradation of **21** at 77 K in 3 MP, shows three absorption bands with values of  $\lambda_{max}$  at 272, 328 and 478 nm (Fig. 1). In a soft matrix (IP/3MP = 4:1), the same absorption bands appeared at the beginning of the photolysis ( $\lambda_{max} = 270, 326, 478$  nm). However, when the photolysis time was longer than 20 min, a new absorption band appeared at  $\lambda_{max} = 386$  nm.

The bands at  $\lambda_{max} = 270$  nm and 326 nm are attributed to  $(CH_3-N=CH_2)$  or related fragments arising from photocleavage of the aminoaryl group. The species with  $\lambda_{max} = 478$  nm is most likely the intramolecular ylide complex and the absorption band with  $\lambda_{max} = 386$

nm very likely corresponds to an unstable disilene, (Scheme 20). Mass spectral evidence supports the formation of the corresponding silylene adducts to *t*-BuOH: ( $M^+ = 351$ ;  $M^+ - 15 = 336$ ).

Consistent with this suggestion, *o*-tolyltris(trimethylsilyl)silane (**23**) was photolyzed in 3MP under the same conditions as photolysis of **21**. Two new absorption bands were observed, at  $\lambda_{\max} = 270$  and 662 nm [29] (Fig. 2). After compound **23** was photolyzed in 3 MP for 85 min at 77 K, it was annealed. An unstable compound with  $\lambda_{\max} = 388$  nm appeared after 6 min and disappeared after annealing for 8 min. The photolysis of compound **23** in a soft matrix (IP/3MP = 4:1) at 77 K directly produced an absorption band with  $\lambda_{\max} = 388$  nm, which is again assigned to an unstable disilene. Possibly, the disilene is directly formed from the ylide in the soft matrix.

In summary, these experiments show that under photolytic conditions, silylene-ylides can be generated at low temperature and their UV spectra are different from those of free silylenes. They rearrange to disilenes upon annealing, finally yielding oligomers. That the generation by reductive coupling of dihalogenosilanes with alkali or LiArH has also been demonstrated by trapping experiments. In the absence of such trapping agents, the decomposition process is complicated, but nevertheless disilenes or disilenoid radical anions appear to be involved.

#### 4. Experimental details

##### 4.1. General

$^{19}\text{F}$  NMR spectra were recorded on a Varian EM-390 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded either on a Bruker SY-200, and SY-250,

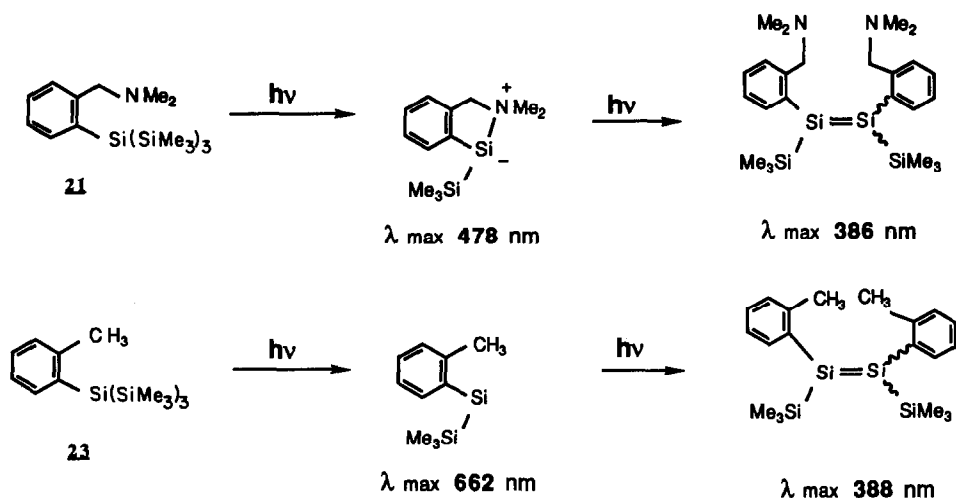
or on a Gemini-200 spectrometer with deuterated chloroform as lock solvent.  $^{29}\text{Si}$  NMR spectra were obtained on a Bruker SY-200, SY-250, or a Varian VXR-300 spectrometer, with deuterated chloroform as lock solvent. Experiments to detect silylene-ylides by  $^{29}\text{Si}$  NMR spectroscopy were performed directly on THF solutions, with  $\text{C}_6\text{D}_6$  as an external lock. All chemical shifts reported are downfield from tetramethylsilane.

Preparative gas chromatography was done on a Varian 920 gas chromatograph (thermal conductivity detector). Analytical gas chromatography was performed on a Hewlett Packard 5840A gas chromatograph (flame ionization detector). Products yields from photolysis were based on the percentage decomposition of starting material and determined chromatographically with cyclohexane or mesitylene as an internal standard for the organosilanes. Photolyses were carried out in a Rayonet Photochemical Reactor equipped with 16 lamps (254 nm).

UV spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Mass spectra were obtained on an Hewlett Packard 5970A gas chromatograph/mass spectrometer, or with a JEOL JMS D-100 instrument. High-resolution mass spectroscopy of disilanes was carried out at the Rice University facility for mass spectral analysis.

Organolithium reagents were prepared by published methods [30,31]. Melting points and boiling points are uncorrected. Elemental analyses were performed by the Centre de Microanalyse du CNRS (Vernaison).

All solvents were dried and distilled before used. Ether, THF and cyclohexane were dried over  $\text{CaH}_2$  and freshly distilled. 3-Methylpentane and isopentane were dried over sodium/potassium alloy and freshly distilled. *t*-Butanol was dried and purified by passage



Scheme 20.



through an alumina column. 2,3-Dimethyl-1,3-butadiene was dried over  $\text{LiAlH}_4$  and freshly distilled. Triethylsilane was dried over molecular sieves. All samples were degassed on a Hg-free vacuum line by three freeze/thaw cycles or purged of dioxygen by passing argon through the solution.

#### 4.2. Reaction of $\text{R}_2\text{SiCl}_2$ with $\text{LiNp}$ in THF

$\text{R}_2\text{SiCl}_2$  (**1**) was dissolved in THF and cooled to  $-78^\circ\text{C}$ . The solution was stirred for 3 h, after addition of  $\text{LiNp}$  and then warmed to room temperature. After addition of pentane, the white precipitate was filtered off. The remaining naphthalene was sublimed under reduced pressure ( $10^{-1}$  Torr) at  $70^\circ\text{C}$ . A viscous product mixture was obtained. The identity of the different compounds containing Si-H bonds was confirmed by independent syntheses.

##### 4.2.1. $\text{R}_2\text{SiH}_2$ (**2**) [5]

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.16 (s, 12H,  $\text{NCH}_3$ ); 3.7 (s, 4H,  $\text{NCH}_2$ ); 4.98 (s, 2H,  $\text{SiH}_2$ ); 7.14–7.44 (m, 8H, ArH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  140.9, 136.5, 137.3, 129.5, 129.0 (CH=), 61.3 ( $\text{NCH}_2$ ), 43.1 ( $\text{NCH}_3$ ).  $^{29}\text{Si}$  ( $\text{CDCl}_3$ ):  $\delta$  -49.2. IR (THF-Diff.  $\text{cm}^{-1}$ ):  $\nu$  (SiH) 2154vs, 2098.5vs. MS(EI)  $m/e$  (relative intensity): 298 ( $\text{M}^+$ , 15), 254 ( $\text{M}^+ - 44$ , 55), 240 ( $\text{M}^+ - 58$ , 67), 164 ( $\text{M}^+ - 134$ , 100), 58(60).

##### 4.2.2. $\text{R}_3\text{SiH}$ (**4**) [6]

$\text{Mp}$ :  $124^\circ\text{C}$  (recrystallized from benzene).  $^1\text{H}$  NMR( $\text{C}_6\text{D}_6$ ):  $\delta$  1.9 (s, 18H,  $\text{NCH}_3$ ); 3.6 (s, 6H,  $\text{NCH}_2$ ); 5.8 (s, 1H, SiH); 7.1–7.8 (m, 12H, ArH).  $^{13}\text{C}$  NMR( $\text{C}_6\text{D}_6$ ):  $\delta$  145.3, 138.6, 137.2, 128.4, 128.2, 126.2; (CH=), 64.9 ( $\text{NCH}_2$ ), 44.5 ( $\text{NCH}_3$ ).  $^{29}\text{Si}$ ( $\text{C}_6\text{D}_6$ ):  $\delta$  -34.9 (d,  $^1J(\text{SiH}) = 226.4$  Hz). IR (Nujol,  $\text{cm}^{-1}$ )  $\nu$  (SiH) 2189.5s, 2173.3s. MS(Cl):  $m/e$  (relative intensity): 430 ( $\text{R}_3\text{Si}^+$ , 28); 387(11); 328(18); 297 ( $\text{M}^+ - \text{R}$ , 100).

##### 4.2.3. $(\text{R}_2\text{SiH})_2$ (**3**) [5]

$^1\text{H}$  NMR( $d_8$ -THF):  $\delta$  2.1 (s, 24H,  $\text{NCH}_3$ ); 3.5, 3.7 (AB-coupling system, 8H,  $J = 12.7$  Hz,  $\text{NCH}_2$ ); 5.6 (s, 2H, SiH); 7.18 (t, 4H,  $J = 7.32$  Hz), 7.35 (t,  $J = 7.3$  Hz, CH=).  $^{13}\text{C}$  NMR (THF- $d_8$ ):  $\delta$  45.3 ( $\text{NCH}_3$ ); 65.7 ( $\text{NCH}_2$ ); 126.4, 128.8, 129.2, 138.5, 138.1, 146.1,  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -41.9,  $^1J(\text{SiH}) = 203$  Hz; (THF- $d_8$ ):  $\delta$  -43. IR (THF-Diff.  $\text{cm}^{-1}$ )  $\nu$  (SiH) = 2146w. MS(Cl)  $m/e$  (relative intensity): 593, ( $\text{M}^+ - 44$ , 1); 430 ( $\text{R}_3\text{Si}$ , 18); 297 ( $\text{R}_2\text{SiH}$ , 100); 238(5); 164 ( $\text{RSiH}_2$ , 4).

#### 4.3. Reduction of $\text{R}_2\text{SiCl}_2$ (**1**) with magnesium anthracene ( $\text{MgAn}$ )

$\text{MgAn}$  (5.3 g, 12.5 mmol) was added to 250 ml THF and cooled to  $-78^\circ\text{C}$ .  $\text{R}_2\text{SiCl}_2$  (**1**) was dissolved in 100 ml THF and added slowly to the reaction mixture.

After warming to room temperature and addition of 50 ml pentane, the white precipitate ( $\text{MgCl}_2$ , anthracene) was filtered off. The filtrate was taken to dryness *in vacuo*, leaving: 3.5 g of a pale yellow solid.  $^{29}\text{Si}$ ( $\text{CDCl}_3$ ):  $\delta$  -59.8, +1.8, +39.5, +45, and several weak resonances in the range  $-44$  to  $-20$   $\delta$ . MS(Cl):  $m/e$ : 474, ( $\text{M}^+$ , 12); 430, ( $\text{M}^+ - 44$ , 2); 340 ( $\text{M}^+ - 134$ , 2). The mass spectral pattern is due to a cycloaddition product **8** of  $\text{R}_2\text{Si}$  and anthracene ( $m/e = 474$ ).

#### 4.4. Reduction of $\text{R}_2\text{SiCl}_2$ (**1**) with elemental lithium

A solution of 3.66 g of  $\text{R}_2\text{SiCl}_2$  **1** (10 mmol) was dissolved in 100 ml THF and cooled to  $0^\circ\text{C}$ . After addition of Li, the solution turned to deep red. The mixture was warmed to RT and stirred for an additional 12 h. The white precipitate was removed, 50 ml of ether added and 2.8 g of a red-brown solid was isolated. The  $^{29}\text{Si}$  NMR spectrum indicated the signals for  $(\text{R}_2\text{SiH})_2$  (**3**) and  $\text{R}_2\text{SiH}_2$  (**2**) ( $\delta$  (-41 and -49), respectively). After addition of MeI the red THF solution turned colourless.  $\text{R}_2\text{SiMe}_2$  (**9**) was proved by GC/MS analysis.  $\text{R}_2\text{SiMe}_2$  (retention time = 6.9 min):  $m/e$ : 327 ( $\text{M}^+ - 15$ , 8); 282 ( $\text{M}^+ - 44$ , 40); 192, ( $\text{M}^+ - 134$ , 100); 134 ( $\text{R}^+$ , 6).

#### 4.5. Bis(2-dimethylaminomethylphenyl)bis(azido)silane (**29**)

3.66 g **1** (10 mmol), 3.9 g  $\text{NaN}_3$  (60 mmol, dried over  $\text{P}_2\text{O}_{10}$ ) and 0.1 g  $\text{AlCl}_3$  were added to 200 ml THF. After heating the mixture for 3 h under reflux and additional stirring at RT for 12 h, the white precipitate was filtered off. Solvent was removed from the filtrate *in vacuo*, leaving 3.7 g of a colourless oil (97%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.1 (s, 12H,  $\text{NCH}_3$ ); 3.6 (s, 4H,  $\text{NCH}_2$ ); 7.4–7.6 (s, 6H); 7.9–8.2 (d, 2H, CH=).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  143.3, 131.52 (Cq); 130.0, 127.4, 126.5, 134.8 (CH=); 63.4 ( $\text{NCH}_2$ ); 45.0 ( $\text{NCH}_3$ ).  $^{29}\text{Si}$  ( $\text{CDCl}_3$ ):  $\delta$  -59.46; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  ( $\text{N}_3$ ) 2147vs, 2118vs, 2030m. UV-VIS: absorbance  $\lambda_{\text{max}}$ : 231 nm (conc.  $11.4 \times 10^{-3}$  M). MS(Cl)  $m/e$  (relative intensity): 379 ( $\text{M}^+ - 1$ , 3); 338 ( $\text{M}^+ - 42$ , 62), 58(100).

#### 4.6. Preparation of $\text{R}_2\text{SiF}_2$ (**10**)

A solution of  $^n\text{BuLi}$  (45.7 mmol, 2.5 M in hexane) was added to a solution of *N,N*-dimethylbenzylamine (6.16 g, 45.7 mmol) in  $\text{Et}_2\text{O}$  (100 ml) at  $0^\circ\text{C}$ . After stirring at room temperature for 48 h, the mixture was added slowly at  $0^\circ\text{C}$  to a solution of [2-[(*N,N*-dimethylamino)methyl]phenyl]trifluorosilane (10 g, 45.7 mmol) [31]. The mixture was stirred at room temperature for 48 h, then concentrated *in vacuo*. Pentane (100 ml) was added, and the solution filtered. After removal of the solvent and distillation (b.p.  $150^\circ\text{C}/10^{-2}$  mmHg),

bis[2-[(*N,N*-dimethylamino)methyl]phenyl]difluorosilane (**10**) was isolated. (12.6 g, 83% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.89 (s, 12H,  $\text{NCH}_3$ ); 3.41 (s, 4H,  $\text{NCH}_2$ ); 7.1–8.05 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  142, 134.5, 130.0, 126.5, (Ar); 64.5 (t,  $\text{NCH}_2$ ); 45.7 (q,  $\text{NCH}_3$ ).  $^{29}\text{Si}$  ( $\text{CDCl}_3$ ):  $\delta$  -53.9 (t,  $J(\text{SiF}) = 270$  Hz);  $^{19}\text{F}$  ( $\text{CDCl}_3$ ):  $\delta$  23 (reference  $\text{C}_6\text{F}_6$ ). Anal. Found: C, 63.38; H, 7.05; F, 11.64; N, 8.06; Si, 8.49.  $\text{C}_{18}\text{H}_{24}\text{F}_2\text{N}_2\text{Si}$  calc. C, 64.63; H, 7.23; F, 11.35; N, 8.37; Si, 8.39%.

#### 4.7. Reduction of $\text{R}_2\text{SiF}_2$ (**10**) with LiNp in THF

A solution of **10** (2.4 g, 72 mmol) in THF (15 ml) was added at  $0^\circ\text{C}$ , to lithium naphthalene (14.5 mmol). The blue colour disappeared immediately, and the red/brown solution was stirred overnight at  $25^\circ\text{C}$ , turning yellow-brown. Pentane (20 ml) was added, and the white precipitate of LiF was separated by filtration. After removal of the solvent, the mixture was analyzed by  $^{29}\text{Si}$  NMR spectroscopy and resonances assigned to compounds **3,4** and to polysilanes were observed.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ) **4**:  $\delta$  -34.7 (d,  $^1J(\text{Si-H}) = 230$  Hz); **3**:  $\delta$  -42.2 (d,  $^1J(\text{Si-H}) = 199$  Hz); ( $\text{R}_2\text{Si}$ ) $_n$ :  $\delta$  -20 to -35 (broad signals). MS (EI):  $m/e$  (relative percent): 564, 430, 386, 371, 328, 297. When methanol was added in the THF solution mixture and followed by work-up, the resulting viscous oil had an unchanged  $^{29}\text{Si}$  NMR spectrum.

#### 4.8. Reaction of **10** with Li metal

The silane **10** (2 g, 6 mmol) was dissolved in 30 ml of THF, and 0.084 g of lithium wire was added (small pieces, washed in pentane). A Schlenk tube containing the reaction mixture was immersed in an ultrasonic bath and maintained at  $20^\circ\text{C}$ . The solution became red-brown and then changed to yellow-orange. After stirring overnight, the solution was checked by  $^{29}\text{Si}$  NMR spectroscopy and displayed broad signals at  $\delta$  -36 and -45 (THF/ $\text{C}_6\text{D}_6$ ). After addition of 3 ml of methanol there was no change in the  $^{29}\text{Si}$  NMR spectrum (no Si-H signal by the DEPTC technique). The reaction was repeated and again monitored by  $^{29}\text{Si}$  NMR spectroscopy. This time instead of adding methanol, the solution was separated into three fractions on which the operations A, B, and C were carried out.

A. After addition of an excess of MeI (1.4 g) and the usual work-up, the  $^{29}\text{Si}$  NMR spectrum ( $\text{CDCl}_3$ ) was recorded. No new signal corresponding to  $\text{R}_2\text{SiMe}_2$  appeared.

B. An excess of  $\text{Et}_3\text{SiH}$  (1.2 g) did not react with the silicon species present in the reaction mixture, nor were any additional signals observed in the  $^{29}\text{Si}$  NMR spectrum (THF/ $\text{C}_6\text{D}_6$ ).

C. An excess of 2,3-dimethylbutadiene was added to the mixture. Evaporation of the solvent left an oil which was analyzed by  $^{29}\text{Si}$  NMR spectroscopy ( $\text{CDCl}_3$ ). No signal corresponding to **7** was observed.

#### 4.9. Trapping experiments with dienes

##### 4.9.1. Reaction of **1** with LiNp and 2-methylbutadiene

The reaction was carried out under the conditions described above.  $\text{R}_2\text{SiCl}_2$  (**1**) was dissolved in THF and cooled to  $-78^\circ\text{C}$ . After addition of LiNp the solution was stirred for 3 h. 2-Methylbutadiene was then added at  $-60^\circ\text{C}$ , and the mixture warmed to room temperature. After separation of LiCl and LiNp from the reaction mixture, the cycloadduct **6** was isolated by liquid chromatography. Nevertheless, the compound could not be obtained pure (only the  $^{13}\text{C}$  NMR data were assigned to **6**).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $\text{C}^1$ : 145.2;  $\text{C}^2$ : 136.42;  $\text{C}^3$ : 128.68;  $\text{C}^4$ : 128.3;  $\text{C}^5$ : 126.11,  $\text{C}^6$ : 135.57;  $\text{C}^7$ : 139.68;  $\text{C}^8$ : 124.63;  $\text{C}^9$ : 23.0;  $\text{C}^{10}$ : 18.82;  $\text{C}^{11}$ : 22.59;  $\text{NCH}_2$ : 64.5;  $\text{NCH}_3$ : 44.9. GC/MS(EI):  $m/e$  (relative intensity): 364 ( $\text{M}^+ - 15$ , 20); 320 ( $\text{M}^+ - 44$ , 35); 306 ( $\text{M}^+ - 58$ , 100); 230 ( $\text{M}^+ - 134$ , 10); 134 ( $\text{R}^+$ , 5).

##### 4.9.2. Reaction of **10** with LiNp and 2,3-dimethylbutadiene

2 g of **10** (6 mmol) and 7 ml of dimethylbutadiene (20 equiv) were cooled at  $0^\circ\text{C}$  in THF (20 ml). Lithium-naphthalene, freshly prepared from 84 mg of lithium wire and 1.53 g (6 mmol) of naphthalene, was added dropwise. The blue solution changed immediately to red-brown. After 12 h, the solution turned to brown-yellow. After addition of pentane (20 ml), LiF was separated by filtration. Evaporation of the solvents, and bulb-to-bulb distillation gave 0.8 g (2.1 mmol) of bis[[2-(*N,N*-dimethylamino)methyl]phenyl]-3,4-dimethylsilacyclopent-3-ene (**7**) (yield 65%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.5–1.6 (2s, 6H,  $2\text{CH}_3$ ); 1.7 (s, 12H,  $2\text{N}(\text{CH}_3)_2$ ); 1.9–2.2 (m, 8H,  $2\text{CH}_2\text{N}$  and  $2\text{CH}_2\text{C}=\text{C}$ ).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -2.44 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  19.63 (q,  $\text{CH}_3$ ); 25.9 (t,  $\text{CH}_2$ ); 45.45 (q,  $\text{N}(\text{CH}_3)_2$ ); 64.89 (t,  $\text{CH}_2\text{N}$ ); 126.6–145.6 (m, Ar +  $\text{C}=\text{C}$ ); MS (EI):  $m/e$  (relative intensity) 377 ( $\text{M}^+$ , 16); 334(5); 296(11); 281(100); 244(76).

##### 4.9.3. Reaction of **10** with Li and 2,3-dimethylbutadiene (2,3-DMB)

$\text{R}_2\text{SiF}_2$  (**10**) (1.97 g, 5.9 mmol) was dissolved in THF (20 ml) with 2,3-DMB (0.5 g, 6.1 mmol). After 30 min, the lithium was added in small pieces (0.038 g, 11.9 mmol). The red-brown solution changed to yellow after stirring for 5 h. The solvent was evaporated and bulb-to-bulb distillation afforded 1.89 g (85%) of an oily

product. b.p. 152–190°C (0.05 mmHg), identified as **7** by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopies ( $\text{CDCl}_3$ ).

#### 4.9.4. 2,5 dimethylhexadiene with Li and **10**

Under similar conditions, addition of Li metal in the presence of 2,5-dimethyl-2,4-hexadiene (5.3 g, 0.10 mol) gave only a mixture of polysilanes, and siloxanes.  $^{29}\text{Si}$  NMR:  $\delta$  – 20, – 38 (broad signals).

#### 4.9.5. Reaction of **1** with Li and 2,3-dimethylbutadiene

The same reaction as above was carried out with **1** (0.63 g, 1.72 mmol), lithium (3.44 mmol) and an excess of dimethylbutadiene (2 ml). Bulb-to-bulb distillation gave 0.2 g of a yellow oil.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  – 2.41, 7, ( $\text{R}_2\text{Si}$ ) $_n$   $\delta$  – 20 to – 35 (major peak at – 28.3).

#### 4.9.6. Reaction of **12** with Li and 2,3-dimethylbutadiene

To a solution, at 20°C, containing **12** (2 g, 7.7 mmol) and dimethylbutadiene (2 ml) were added two equivalents of lithium wire (0.1 g) with ultrasonic activation. After 5 h, the initially red solution turned yellow-brown. Bulb-to-bulb distillation gave 2.11 g of silacyclopentene (**14**) (yield 87%). b.p. 193°C/0.05 mmHg.

$^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  – 1.76.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  19.66 (q,  $\text{CH}_3$ ); 25.3 (t,  $\text{CH}_2$ ); 45.35 (q,  $\text{N}(\text{CH}_3)_2$ ); 65.2 (t,  $\text{CH}_2\text{N}$ ); 125.5–146.5 (Ar + C=C). MS (EI):  $m/e$  (relative intensity): 321(17), 306(12), 239(100), 224(47), 195(23). Anal. Found: C, 78.84; H, 8.48; N, 4.49; Si, 8.72.  $\text{C}_{21}\text{H}_{27}\text{NSi}$  calc: C, 78.49; H, 8.51; N, 4.38; Si, 8.71.

#### 4.9.7. Reaction of **12** with allyllithium

Allyllithium was prepared from tetraallyltin (1 g, 3.5 mmol) and 3.5 ml of  $^n\text{BuLi}$  (2.0 M in cyclohexane). The white solid was washed with pentane, then dissolved in THF. A solution of **12** (1 g, 3.5 mmol) was added. The yellow solution was stirred for 48 h under argon. Pentane was added (20 ml), and the product separated by filtration and removal of the solvents. Characteristics of **13**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.84 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 3.05 (s, 2H,  $\text{CH}_2\text{N}$ ); 2.25 (d, 4H,  $\text{CH}_2$ ); 4.5–4.9 (m, 6H, vinyl); 7.4–7.9 (m, 9H, Ar).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  – 14.1. MS (EI)  $m/e$  (relative intensity): 322(3), 277(26), 188(90).

#### 4.9.8. Reaction of **15** with Li and 2,3-dimethylbutadiene

1.73 g of **15** (4.26 mmol) was dissolved in 10 ml of THF, in the presence of 9 ml of dimethylbutadiene (20 equiv). The lithium in small pieces (0.06 g) was added. The solution became red-brown immediately, then changed to yellow after 12 h. Pentane was added, and the LiF precipitate removed by filtration. After con-

centration of the solution, the resulting oil solidified *in vacuo*: m.p. 115–160°C.  $^1\text{H}$  NMR spectrum of the mixture in  $\text{CDCl}_3$  showed that polymerized dimethylbutadiene was present, together with silane. Bulb-to-bulb distillation afforded **16** (235 mg, 15% yield).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  – 14.4;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21 (br q,  $\text{CH}_3$ ) 29 (br t,  $\text{CH}_2$ ); 48 (br q,  $\text{N}(\text{CH}_3)_2$ ); 125.5–146.5 (Ar + C=C). MS (EI):  $m/e$  (relative intensity): 450 ( $\text{M}^+$ , 15), 368 ( $\text{M} - 82$ , 100), 354(60), 280(40), 224(47), 169(23).

#### 4.9.9. Attempted reaction of **15** with allyllithium

In a similar procedure as for **12**, allyllithium (7 mmol) was mixed with **15** (1.43 g, 3.5 mmol) in THF.  $^{19}\text{F}$  NMR spectrum showed only one signal at  $\delta$  29, corresponding to reactant **15**. After 48 h no change was observed. Concentration of the solution left an oil shown to be **15** by  $^{29}\text{Si}$  NMR spectroscopy.

#### 4.10. Halodemethylations of **17**

##### 4.10.1. Reaction of **17** with Li metal

To 1.58 g (4.8 mmol) of (8-dimethylaminomethyl-naphthyl)phenyldifluorosilane [**4**] (**17**) in 20 ml of THF was added lithium wire (0.067 g, 9.6 mmol) at 25°C. After one h, the solution was red-brown, then turned to yellow after 3 h. THF was removed *in vacuo*, and the product **18** distilled with a Kugelrohr. (b.p. 190°C, 0.1 mmHg) 1-*N,N*-dimethylamino-1-phenyl-1-silaacenaphthene [**32**],  $m = 0.83$  g (yield 60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.35 (m, 2H,  $\text{CH}_2\text{Si}$ ), 2.54 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ) 7.1–7.9 (m, 11H, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  15.5 (t,  $\text{CH}_2\text{Si}$ ); 38.6 (q,  $\text{NMe}_2$ ); 124–140 (m, Ar).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  + 4.2 MS (EI):  $m/e$  (relative intensity): 289 ( $\text{M}^+$ , 34), 276(12), 264(38), 244(68), 215(50), 186(85), 167(12), 141(87), 115(59), 55(100).

##### 4.10.2. Reaction of **17** with LiNp

To 4.8 mmol of **17** (1.58 g) dissolved in 15 ml of THF were added dropwise at 0°C, 9.7 mmol of lithium naphthalene (prepared from 0.068 g of Li and 1.24 g of naphthalene). The brown solution changed to yellow after 12 h. To the solution were added 10 ml of pentane. The precipitate LiF was separated by filtration, and removal of the solvents left an oil which was analyzed by  $^{29}\text{Si}$  NMR spectroscopy  $\delta$  + 4.2 MS (EI)  $m/e$  289 ( $\text{M}^+$ ).

##### 4.10.3. Oxidation of the silaacenaphthene **18**

The silane **18** was dissolved in  $\text{CDCl}_3$  (3 ml) and exposed to air for 1 h. A white solid was deposited, then separated by filtration and characterized as a 52/48 mixture of isomeric disiloxanes, **19a** and **19b**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.32 (m, 4H,  $\text{CH}_2\text{Si}$ ), 6.9 – 8.0 (m, 22H, ArH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  18.37(a) and

18.44(b) (2s, CH<sub>2</sub>Si); 124.3 – 143.4(m, Ar). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ +0.5, +0.8 (2s) (obtained using the inverse Gate — INVGATE — NMR program).

#### 4.10.4. Reaction of 17 with Li and 2,3-dimethylbutadiene

The difluorosilane 17 (2.03 g, 6.2 mmol) was dissolved in THF (20 ml) with dimethylbutadiene (20 equiv, 14 ml). After 30 min, <sup>1</sup>H NMR spectrum of an aliquot showed that no reaction had occurred. Lithium wire (0.087 g, 2 equiv) was added in small pieces. The yellow solution was analyzed after stirring for 12 h. All the lithium was consumed. Evaporation of THF and bulb-to-bulb distillation left a mixture of two products, identified as 18 and silacyclopentene 20. Characteristics of 20: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.7 (s, 6H, CH<sub>3</sub>); 1.96 (s, 6H, NMe<sub>2</sub>); 2.22 and 2.36 (2s, 4H, CH<sub>2</sub>); 3.6 (s, 2H, CH<sub>2</sub>H); 7.0–8.3 (m, 11H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 20.7, 21.2 (2s, CH<sub>3</sub>); 34.4 (s, CH<sub>2</sub>); 45.3 (s, NMe<sub>2</sub>); 63.3 (s, CH<sub>2</sub>N); 124.2–140.6 (m, Ar) <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -2.3; MS (EI): *m/e* (relative intensity): 371 (M<sup>+</sup>, 18); 356(25); 308(27); 289(26); 274(100); 245(35); 215(19); 167(12); 141(13); 55(20).

#### 4.11. Synthesis of 1-(trimethylsilyl)-2-(dimethylaminomethyl)benzene (26)

63 mmol of 1-lithio-2-(dimethylaminomethyl)benzene were added to 10.3 g (95 mmol) of trimethylchlorosilane and stirred magnetically. The mixture rapidly changed from yellow to white, with evolution of heat. The remaining trimethylchlorosilane was removed *in vacuo* and the product was distilled under reduced pressure (*ca.* 10<sup>-3</sup> mmHg). The yield was 5 g of colourless oil. Samples for photolysis were purified by gas chromatography on a methylsilicone/phenylsilicone(1/1, OV-17) column.

26 <sup>1</sup>H NMR (neat): δ 0.4 (9H, s, Si-CH<sub>3</sub>); 2.2 (6H, s, N-CH<sub>3</sub>); 3.5 (2H, s, N-CH<sub>2</sub>-Ar); 7.3 (4H, m, Ar-H) MS(EI): *m/e* (relative intensity) 207 (M<sup>+</sup>, 9); 206(3); 203(2); 192 (M - 15, 30); 310(15); 149(17); 73(21); 58(100).

#### 4.12. Synthesis of [2-(*N,N*-dimethylamino)methylphenyl]tris(trimethylsilyl)silane, 21

Tris(trimethylsilyl)chlorosilane (9 g, 27.5 mmol) was added to 42 mmol of 1-lithio-2-(dimethylaminomethyl)benzene with a syringe during 8 min. The mixture was stirred and heated under reflux (*ca.* 100°C) for 80 h. Analytical GC showed that the reaction was complete. The reaction mixture was quenched with 10 ml of water and extracted three times with 50 ml of ether. The organic phases were combined and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed to yield 12 g of a crude brown

product. Repeated crystallization from toluene gave 3.0 g of product (26%). Final purification was achieved by preparative gas chromatography (1/4 in × 10 ft, 20% OV-17 on Chromosorb W) to provide a clear semi-solid, m.p. room temperature.

21 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.24 (27H, s, Si-CH<sub>3</sub>); 2.33 (6H, s, N-CH<sub>3</sub>); 3.60 (2H, s, N-CH<sub>2</sub>-Ar); 7.10 (1H, m, Ar-H); 7.30 (1H, m, Ar-H); 7.56 (2H, m, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 2.15 (q); 45.31 (q); 65.50 (t); 125.37 (d); 127.07 (d); 128.22 (d); 138.64 (d). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -76.82, -12.60. MS(EI) *m/e* (relative intensity): 366 (M-15, 10); 310(15); 309(33); 308(100); 73(20).

#### 4.13. Photolysis of 21 in 2,3 dimethyl-1,3-butadiene

A solution containing 200 mg of 21 (0.52 mmol), and 2,3-dimethyl-1,3-butadiene (3 ml, 26.5 mmol) was placed in a 12 mm quartz tube. After three freeze/thaw cycles, the solution was irradiated for 4.5 h by 16 medium-pressure mercury lamps. Two new products formed in a 2:1 ratio, as well as hexamethyldisilane. These were isolated by preparative GC and subsequently identified as *o*-tolyltris(trimethylsilyl)silane (23) (66% yield) and 1-[2-(*N,N*-dimethylaminomethyl)phenyl]-1-trimethylsilyl-3,4-dimethylsilacyclopent-3-ene (22) (33%). 22 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.012 (9H, s, Si-CH<sub>3</sub>); 1.72 (6H, s, =C-CH<sub>3</sub>); 1.62–1.91 (4H, dd but coupling is partially hidden by the signal at 1.72, SiCH<sub>a</sub>H<sub>b</sub>-); 2.19 (6H, s, N-CH<sub>3</sub>); 3.42 (2H, s, N-CH<sub>2</sub>-); 7.30 (4H, m, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.66; 19.05; 23.64; 45.62; 65.26; 126.34; 128.48; 128.57; 130.88; 135.68; 137.94; 145.10. <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -18.19; -13.42. MS(EI) *m/e* (relative intensity): 303 (M-15, 9); 245(16); 244(70); 235(100); 221(20); 220(86); 162(53); 161(11); 159(10); 146(15); 119(19); 73(17). High-resolution mass spectrum: calc. for Si<sub>2</sub>C<sub>17</sub>H<sub>28</sub>N, *m/e* 302.1760; found 302.1756.

#### 4.14. Photolysis of 21 with triethylsilane

A solution containing 130 mg of 21 (0.34 mmol), 0.54 ml of triethylsilane (0.40 g, 3.4 mmol) and 2 ml of cyclohexane was placed in a 12 mm quartz tube. After degassing, the solution, it was irradiated for 100 min. Three products (A, B and C) were formed in 20/33/24 ratio and were isolated by preparative GC.

##### 4.14.1. 24 2-(*o*-tolyl)-1,1,1-triethyl-3,3,3-trimethyltrisilane

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.13 (9H, s, Si-CH<sub>3</sub>); 0.68 (6H, q, Si-CH<sub>2</sub>-); 0.91 (9H, t, -CH<sub>3</sub>); 2.36 (3H, s, Ar-CH<sub>3</sub>); 3.91 (1H, s, Si-H); 7.10 (3H, m, Ar-H); 7.38 (1H, d, *J* = 8.0 Hz, Ar-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 0.09 (q); 4.67 (t); 8.00 (q); 24.18(q); 124.85 (d); 128.34 (d); 129.51 (d); 137.21 (s); the two substi-

tuted aromatic C atoms were not observed.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.81; -14.17; -71.86. MS  $m/e$  (relative intensity): 309(13); 308(35); 293, [M-15], (6); 235(18); 234(71); 206(25); 205(56); 192(13); 179(17); 178(37); 177(100); 163(15); 149(31); 145(12); 121(18); 119(22); 115(15); 87(31); 73(20); 59(32); 45(13); 43(11).

#### 4.14.2. 23 *o*-tolyltris(trimethylsilyl)silane

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.21 (27H, s, Si- $\text{CH}_3$ ); 2.41 (3H, s, Ar- $\text{CH}_3$ ); 7.10 (3H, m, Ar-H); 7.53 (1H, d,  $J = 7.1$  Hz, ArH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.91 (q); 25.56 (d); 8.00 (q); 124.72 (d); 128.01 (d); 129.66 (d); 135 (d); 138.36 (s); 144.2 (s).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -75.66, -12.40. MS:  $m/e$  (relative intensity) 339(10), 338(26), 323(14), 265(22), 264(26), 250(21), 249(23), 205(26), 192(14), 191(64), 176(38), 175(29), 174(78), 161(11), 159(9), 149(44), 145(15), 131(13), 121(18), 73(100), 45(36), 43(12).

#### 4.14.3. 25 2-[2-(*N,N*-dimethylamino)methylphenyl]-1,1,1-triethyl-3,3,3-trimethyltrisilane

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.15 (9H, s, Si- $\text{CH}_3$ ); 0.70 (6H, q,  $J = 8.0$  Hz, Si- $\text{CH}_2$ ); 0.93 (9H, t,  $J = 7.5$  Hz, - $\text{CH}_3$ ); 2.23 (6H, s, N- $\text{CH}_3$ ); 3.49 (2H, s, Ar- $\text{CH}_2$ -N); 4.03 (1H, s, Si-H); 7.2 (3H, m, Ar-H); 7.39 (1H, d,  $J = 7.1$  Hz, Ar-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.45 (q); 5.00 (t); 8.40 (t); 45.34 (t); 65.14 (q); 126.30 (d); 128.43 (d); 129.72 (d); 135.20 (d); 137.48 (s).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -14.06. MS(EI):  $m/e$  (relative intensity) 339(10); 338(26); 336(M-15, 6); 279(16); 278(57); 237(21); 236(83); 220(14); 163(20); 162(100); 149(12); 146(17); 119(27); 87(13); 73(17); 59(33); 45(13); 43(10).

#### 4.15. 27 *o*-tolyltrimethylsilane

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.35 (9H, s, Si- $\text{CH}_3$ ); 2.48 (3H, s, Ar- $\text{CH}_3$ ); 7.2 (3H, m, Ar-H); 7.48 (1H, d,  $J = 6.2$  Hz, Ar-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.39 (q); 22.77 (q); 125.00 (d); 129.28 (d); 129.83 (d); 134.41 (d); the resonances of the two substituted aromatic C atoms were not observed.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -4.34. MS(EI):  $m/e$  (relative intensity) 165(3); 164(M, 13); 150(21); 149(M-15, 100); 121(15); 73(4); 43(19).

#### 4.16. 28 1,2-bis(2-trimethylsilylphenyl)ethane

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.35 (18H, s, Si- $\text{CH}_3$ ); 3.11 (4H, s, Ar- $\text{CH}_2$ ); 7.3 (6H, m, Ar-H); 7.53 (2H, d,  $J = 60$  Hz, Ar-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.67 (q); 37.70 (t); 125.85 (d); 128.56 (d); 129.87 (d); 135.20 (d); 138.91 (s); 148.06 (s).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -4.53. MS(EI):  $m/e$  (relative intensity) 328(5); 327(13); 326 (M, 21); 313(24); 312(65); 311(M-15, 100); 163(36); 148(29); 133(11); 105(19); 73(35).

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