# 16 Kautsky-Siloxene Analogous Monomers and Oligomers

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## 16.1 Introduction

Because of its indirect band structure, crystalline silicon does not show visible light emission at room temperature. Low-dimensional silicon polymers such as polysilanes, or silicon polymers with sheet-like structures, however, have a direct band structure. They attract considerable attention in solid-state physics mainly because of their outstanding luminescence properties.[1–3] Especially the two-dimensional sheet polymers such as siloxene $(Si_6O_3H_6)_n$ or polysilyne $(SiH)_n$ are promising candidates for technological application because of their higher mechanical stability and higher conductivity. Since $(SiH)_n$, accessible from $(SiBr)_n$ and $LiAlH_4$ or, more recently, from $CaSi_2$ and HCl,[4,5] is highly unstable and shows luminescence only in the UV part of the spectrum, siloxene with its strong room temperature photoluminescence in the green or yellow has been most thoroughly investigated. Research on siloxene has been further intensified by the recent suggestion that the efficient visible luminescence observed in porous silicon, a phenomenon of considerable current interest, is mainly due to the presence of siloxene species on the surface of the porous silicon particles.[6]

A prerequisite for an understanding of the luminescence properties of siloxene is to understand its solid-state structure. In the following section, the present knowledge about the structure of siloxene is briefly reviewed, and this is followed by a short summary of current studies aimed at rebuilding siloxene-like structures from well-defined molecular precursors to obtain structurally well defined sub-elements of the siloxene lattice. Particular attention will be devoted to the question as to whether the fluorescence properties of siloxene can be matched by selectively prepared siloxene sub-units or substituted cyclopolysilanes.

## 16.2 Synthesis and Structure of Siloxene

When $CaSi_2$ is reacted with HCl in a topochemical reaction, insoluble solid

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siloxene is obtained (Eq. 1).

$$3\ CaSi_2 + 6\ HCl + 3\ H_2O \rightarrow Si_6O_3H_6 + 3\ CaCl_2 + 3\ H_2 \qquad (1)$$

Two different experimental methods are available yielding siloxenes with different properties. The original Wöhler method,[7] later optimized by Hönle et al.,[5] affords a crystalline yellow product with green luminescence ($\lambda_{max,em}$ = 560 nm), while siloxene prepared according to Kautsky [8] is a grayish-green, X-ray amorphous solid showing blue luminescence ($\lambda_{max,em}$ = 500 nm). It was frequently argued that different structures might be responsible for this different behavior.

There are three commonly proposed structures for siloxene (Figure 16.1): (A) the planar modification, resembling the 111-double layers in crystalline silicon, consists of two-dimensional corrugated silicon layers with three Si-Si bonds per silicon and alternating OH or H substituents; (B) the ring structure consisting of $Si_6$ rings, which are linked by oxygen bridges to form planes, and (C) the chain structure containing Si chains interconnected by oxygen bridges.[9] In structures (B) and (C) the fourth valence of the silicon atoms is passivated by a hydrogen atom.

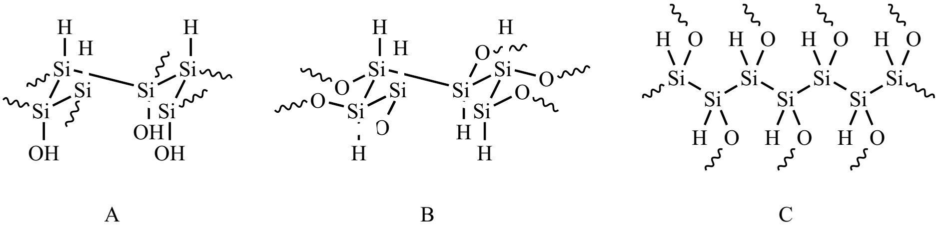


**Figure 16.1.** Structural models for siloxene.

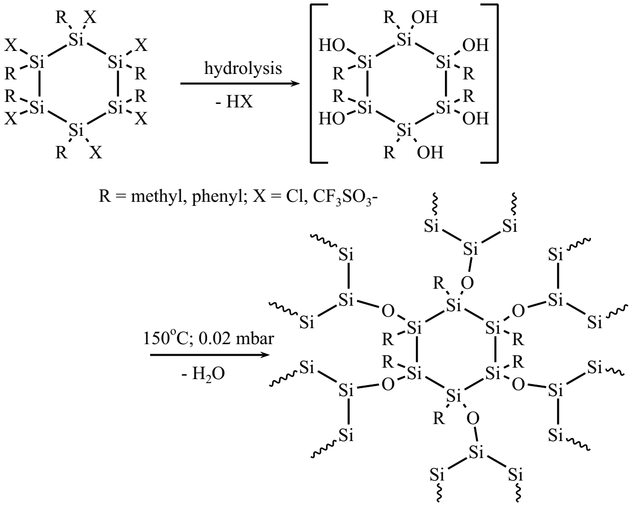
Single crystals of Wöhler siloxene can be obtained either by growing epitaxial $CaSi_2$ on Si and transforming the layer to siloxene by treatment with HCl [2] or from $CaSi_2$ single crystals and HCl.[5, 10] As a consequence, it is now well established from X-ray diffraction studies that siloxene freshly prepared by the Wöhler method predominately consists of the planar modification (A).[4, 5, 10] This assignment is also supported by $^{29}Si$ NMR [11] and vibrational spectroscopy.[12] There is no experimental proof for the existence of the ring (B) or chain structure (C). However, it has been argued that siloxene may undergo structural transformations upon heat treatment[13] or further oxidation,[14] and that polymers with structures related to the modifications (B) and (C) might be generated due to the stepwise insertion of oxygen into the $Si_6$

rings, although experimental evidence for this interpretation is very limeted.

The exact structure of Kautsky siloxene has not been determined so far, mainly because of its X-ray amorphous character and the inhomogeneous composition of the material. X-ray emission and infrared spectra confirm that *Kautsky*-siloxene samples are mixtures of several modifications with a predominant contribution of the ring structure (B).[12, 15] An idealized structure according to model (B) is therefore not unlikely, as has already been proposed by Kautsky mainly on the basis of the substitution chemistry of the material.[16]

## 16.3 Siloxene-like Polymers from Molecular Precursors

One of the basic properties of siloxenes is their general insolubility in organic solvents, a fact that strongly impedes physical and structural characterization. As a result, the question arose as to whether structurally better defined siloxene-like polymers with improved solubility can be assembled in a stepwise manner starting from appropriate molecular precursors, and whether the properties of siloxene, such as the intense photoluminescence, can be matched. We thus attempted to rebuild the proposed structure of *Kautsky*-siloxene by the controlled hydrolysis of cyclic or linear oligosilanes bearing hydrolytically labile substituents followed by the thermal condensation to polymeric siloxanes.[17] The general route is outlined in Scheme 16.1.



R = methyl, phenyl; X = Cl, $CF_3SO_3$-

**Scheme 16.1.** General reaction scheme for the synthesis of polymers with siloxene-like structures.

The resulting polymers exhibit properties closely resembling those of siloxene. The materials are insoluble in organic solvents, their IR spectra exhibit characteristic bands near 3400 cm$^{-1}$ [ν (O-H)] and 1050 cm$^{-1}$ [$\nu_{as}$ (Si-O-Si)], and in some cases intense photoluminescence is observed. Depending on the starting materials the fluorescence maxima of the obtained products range from 400 to 550 nm. The fluorescence spectra of selected examples are shown in Figure 16.2.

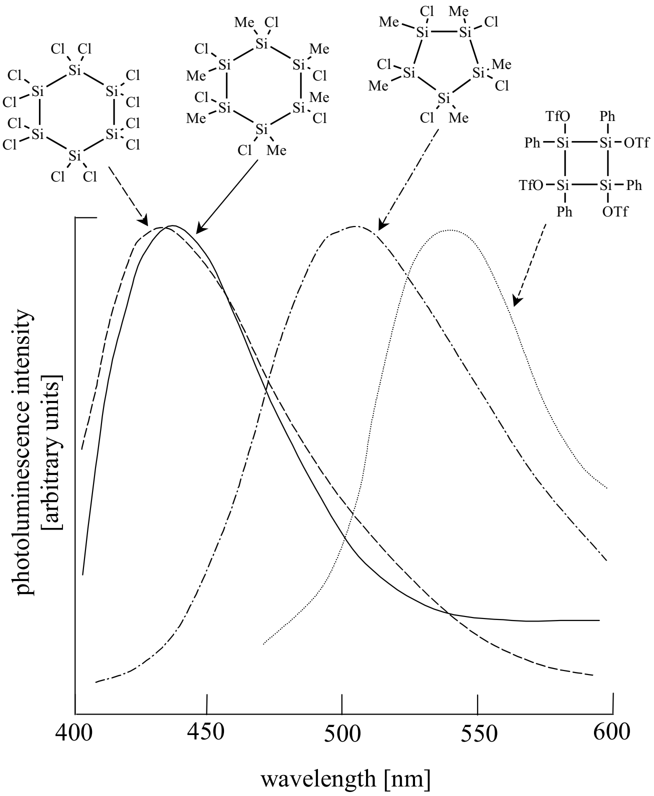
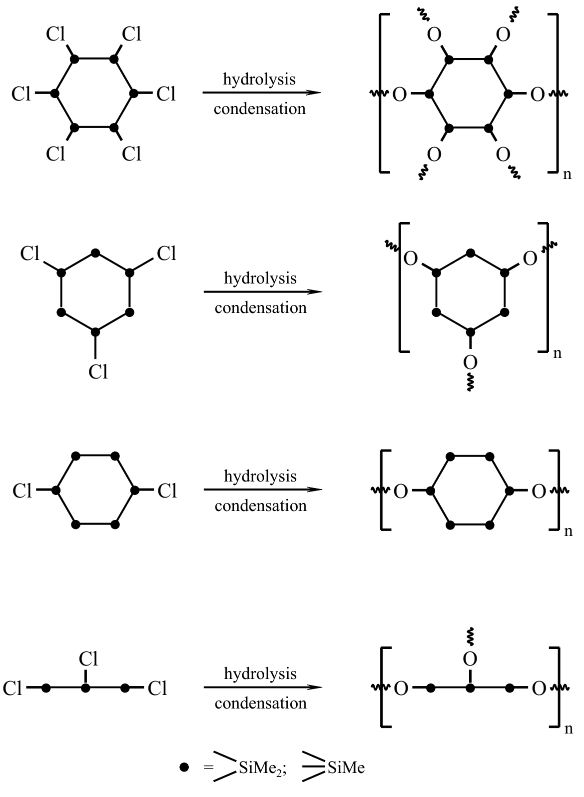


**Figure 16.2.** Normalized fluorescence spectra of selected siloxene-like polymers (the molecular precursors used for polymer preparation are indicated above the spectra).

Criteria for fluorescence are the presence of cyclosilanyl sub-units and polymeric multidimensional structures,[18] as clearly indicated by the diminishing fluorescence on going from polymer **1** to **4** in Scheme 16.2. While the precursor of polymer **1** has six Si-Cl functionalities per cyclohexasilanyl unit, which is likely to result in the formation of highly cross-linked materials upon hydrolysis and condensation, the degree of cross-linking in polymer **2** is strongly reduced, because only three hydrolytically labile substituents per precursor molecule are present. Polymer **3** most probably has a linear structure, and polymer **4**, derived from an open-chained precursor, does not exhibit fluorescence at all.

Since only polymers derived from cyclic starting materials, which are likely to have siloxene-like structures, exhibit color and fluorescence, the polysilane ring seems to be essential for the exceptional optical properties. This is in agreement with the original idea assuming the cyclosilane ring to be the chromophore responsible for the photoluminescence of siloxenes.



Polymer **1**:
yellow solid, highly fluorescent,
$\lambda_{\text{max, em}} = 436$ nm

Polymer **2**:
white solid, weak fluorescence,
$\lambda_{\text{max, em}} = 420$ nm

Polymer **3**:
white solid, non-fluorescent

Polymer **4**:
white solid, non-fluorescent

**Scheme 16.2.** Possible structures and properties of hydrolysis products derived from chloropermethylpolysilanes of different constitutions.[†]

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[†] In the following the common notation will be used in which a dot represents a Si atom with methyl groups attached to bring the total coordination number to four.

## 16.4 Synthesis and Fluorescence of Molecular Models

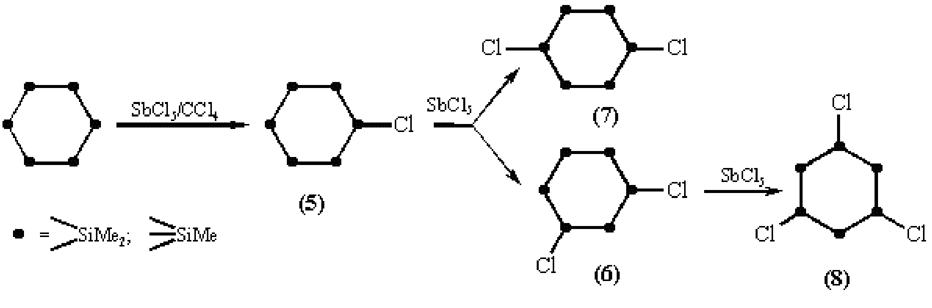
If the luminescence of siloxenes is a molecular rather than a solid-state property, as has been argued in an earlier study,[12] smaller sub-units of siloxene such as cyclohexasilane derivatives of the general formula $Si_6Me_n(OSiR_3)_{6-n}$ bearing siloxy groups attached to the polysilane ring should represent suitable models. While numerous cyclosilanes bearing organic side groups have been prepared in the past, synthetic routes to functional cyclopolysilanes are limited to a very few examples so far. The following section covers only selected aspects of cyclohexasilane chemistry relevant to the scope of this article. For a more general overview the interested reader is referred to several reviews on cyclopolysilanes.[19]

### 16.4.1 Synthesis of Methylsiloxycyclohexasilanes $Si_6Me_n(OSiR_3)_{6-n}$

$Si_6Me_{12}$ can be conveniently prepared from $Me_2SiCl_2$ with sodium/potassium alloy in THF in the presence of an equilibrating catalyst, which causes depolymerization of the initially formed permethylpolysilane (Eq. 2).[20]

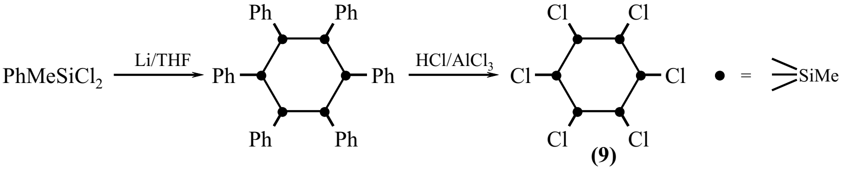
$$\begin{array}{lcccc} Me_2SiCl_2 & \xrightarrow{\text{Na/K, THF}} & (Me_2Si)_6 & + (Me_2Si)_5 & + (Me_2Si)_7 \\ & & >80\% & <10\% & \text{traces} \end{array} \quad (2)$$

The methyl groups in $Si_6Me_{12}$ can be substituted by halogen without destruction of the ring structure. With $SbCl_5$, either one, two or three of the methyl groups can be replaced by chlorine depending on the stoichiometric ratio of the reactants.[21] In the case of $Si_6Me_{10}Cl_2$, the 1,3- and 1,4-isomers are produced exclusively (Scheme 15.3).



**Scheme 3.** Partial chlorination of $Si_6Me_{12}$.

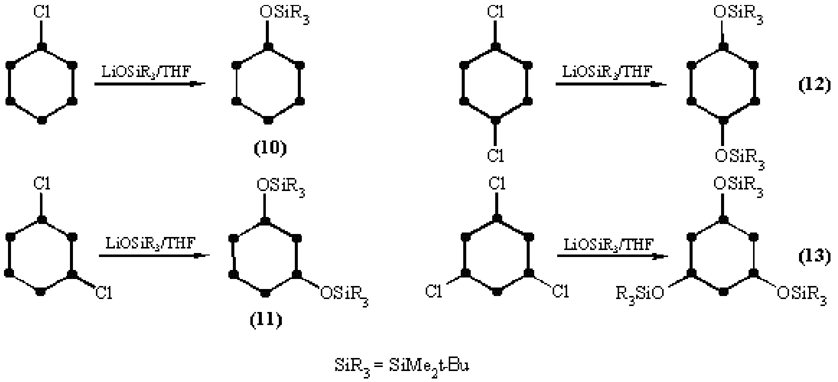
Separation of **6** and **7** can easily be accomplished by hydrolysis of the isomeric mixture, distillation of the hydrolysis products 1,3-dihydroxydecamethylcyclohexasilane and decamethyl-7-oxa-1,2,3,4,5,6-hexasilanorbornane, followed by rechlorination of the Si-O bonds with acetyl chloride.[22] 1,2-Dichlorodecamethylcyclohexasilane can be synthesized systematically from 1,2-diphenyltetramethyldisilane by several Si-Si bond-formation and selective substituent exchange steps.[23] 1,2,3,4,5,6-Hexachlorohexamethylcyclohexasilane (**9**) is prepared as shown in Eq. 3.[24]



(3)

Reactions of the partially chlorinated cyclohexasilanes **5–8** with various nucleophiles such as $H^-$, $[(CO)_2CpFe]^-$, $RS^-$ or $R^-$, afford the corresponding substitution products.[25] The siloxy-substituted cyclohexasilanes **10–13** can be prepared in a similar way by reacting **5–8** with lithium silanolates according to Scheme 15.4.[26]

The di- and trisubstituted derivatives **11–13** were obtained as statistical mixtures of *cis/trans* isomers. Isolation of the least soluble isomer was achieved by crystallization. Single-crystal X-ray diffraction studies of **11** and **12** [27] reveal that the cyclohexasilane ring adapts a slightly distorted chair conformation with the bulky $OSiMe_2{}^tBu$ groups in equatorial sites in order to minimize non-bonding interactions (Figure 16.3).[28]



$SiR_3 = SiMe_2t\text{-}Bu$

**Scheme 16.4.** Synthesis of siloxy-substituted cyclohexasilanes.

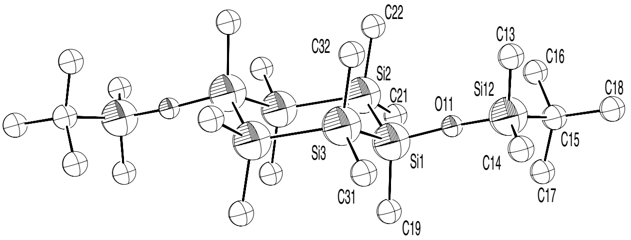


**Figure 16.3.** Crystal structure of compound **12**.

### 16.4.2 Absorption and Photoluminescence Spectra of Methylsiloxycyclohexasilanes

UV absorption and fluorescence emission spectra of compounds **10–13** are shown in Figure 15.4. All spectra show relatively weak absorption bands at the low energy side, which are not present in the spectrum of $Si_6Me_{12}$ and exhibit pronounced bathochromic shifts as the number of siloxy groups increases.

When isomerically pure samples of **10–13** are excited at the wavelength of the first UV maximum around 290 nm, distinct photoluminescence is observed. Several overlapping fluorescence bands appear at around 340 nm, the positions of which are not influenced markedly by the number of the siloxy groups attached to the cyclohexasilane ring (see Figure 16.4).

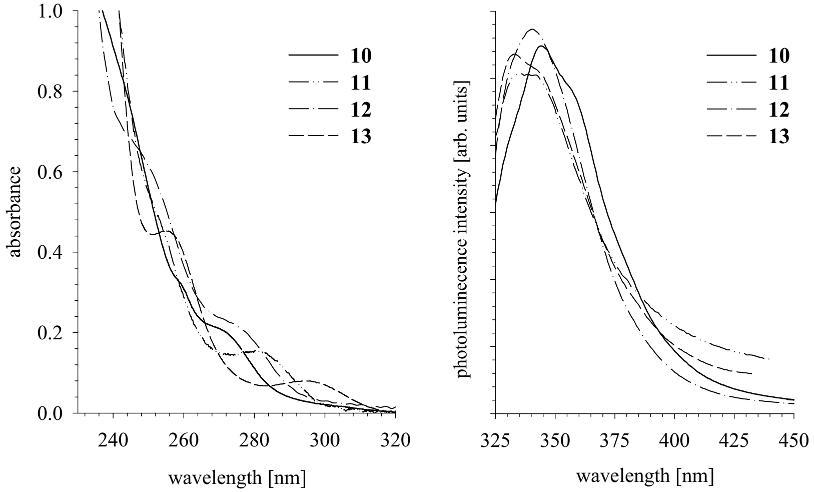


**Figure 16.4.** Absorption and photoemission spectra of **10–13** in cyclohexane ($c = 5\cdot10^{-4}$ mol/L, $\lambda_{ex} = 288$nm).

Although the trends appearing in the luminescence spectra of **5**–**8** and related compounds cannot yet be interpreted straightforwardly, the fluorescence intensity of siloxy-substituted cyclohexasilanes turns out to be considerably higher compared to that of the corresponding phenyl derivatives, while the fluorescence of $Si_6Me_{12}$ is rather weak (Figure 16.5). Intense photoluminescence, therefore, can be traced back to the smallest subunit of *Kautsky* siloxene, that is the cyclohexasilane ring linked to other silyl groups by oxygen bridges.

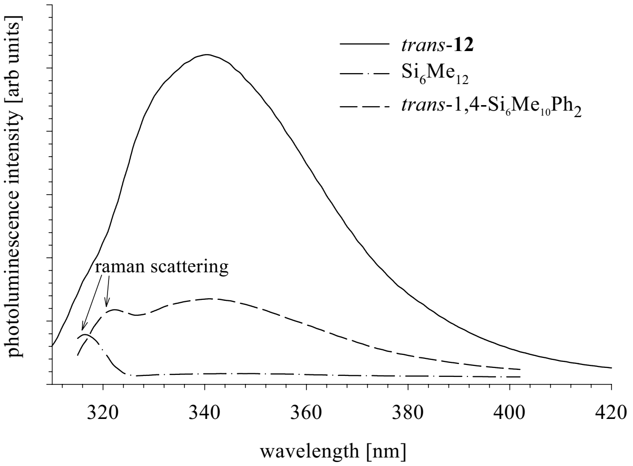
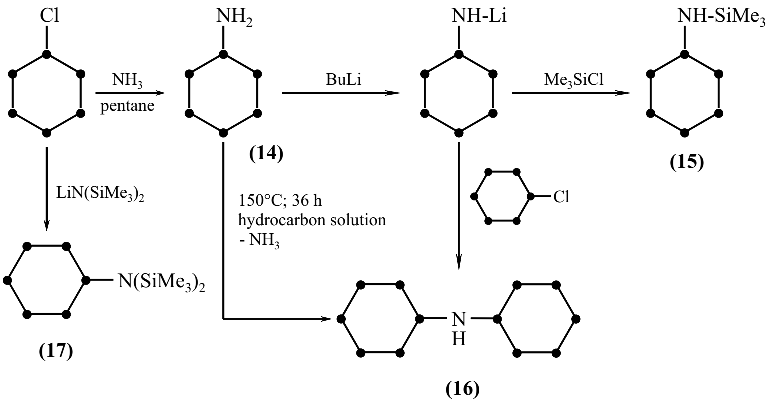


**Figure 16.5.** Normalized photoemission spectra of *trans*-**12**, $Si_6Me_{12}$ ($c = 5\cdot10^{-4}$ mol/L, $\lambda_{ex} = 288$nm) and *trans*-1,4-$Si_6Me_{10}Ph_2$ ($c = 1\cdot10^{-3}$ mol/L; $\lambda_{ex} = 291$nm)

### 16.4.3 Studies Concerning Methylaminocyclohexasilanes $Si_6Me_n(NR_2)_{6-n}$

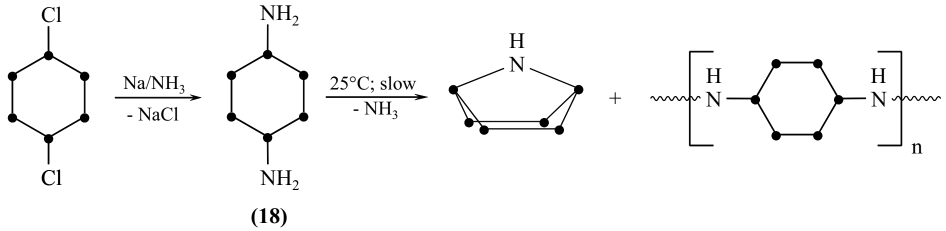
In order to clarify whether the presence of oxygen is a prerequisite for the pronounced fluorescence of the cyclopolysilane derivatives **10**–**13**, the photoluminescence behavior of aminocyclohexasilanes $Si_6Me_{6-n}(NR_2)_n$ was also studied. Aminosilanes are most commonly prepared from chlorosilanes and amines or alkali metal amides.[28] When chloropermethylcyclohexasilanes are reacted with $NH_3$, the corresponding amino derivatives are obtained. As shown in Scheme 15.5, the reaction of **5** with ammonia cleanly affords $Si_6Me_{11}(NH_2)$ (**14**), which can be further silylated yielding the silazanes **15** and **16** after lithiation with *n*-BuLi. **16** is also easily accessible directly from **14** by thermal condensation. The air-stable compound **17** is obtained in good yield from the reaction of **10** with $LiN(SiMe_3)_2$.



**Scheme 16.5.** Synthesis of aminocyclohexasilanes **14**–**17**.

The crystal structure of **14** again exhibits the cyclohexasilanyl ring in a chair conformation. Unlike the bulky hetero substituents in the structures of **6** and **7**, however, the small $NH_2$ group occupies an axial position with an unusually long Si-N bond distance of 183.4 pm. This extraordinarily long Si-N bond length implies a relatively weak Si-N bond, what is manifested by the sensitivity of **14** towards thermal condensation.

1,4-Diaminodecamethylcyclohexasilane **18**, which can be prepared from **7** and $Na/NH_3$ according to Scheme 16.6, undergoes inter- and intramolecular condensation even at room temperature when stored for several days. As a consequence, silazane polymers with sheet-like structures similar to the polymers **1** and **2** depicted in Scheme 16.2 might be accessible from **8** or **9** under very mild and controlled conditions.



**Scheme 16.6.** Synthesis and condensation of 1,4- $Si_6Me_{10}(NH_2)_2$.

Remarkably, the UV absorption and emission spectra of **15**–**17** do not show any photoluminescence above 300 nm. The absorption spectra of **16** and **17** also lack the weak, low-energy absorption band near 270 nm present in the absorption spectrum of the corresponding siloxy derivative **10**.

## 16.5 Summary

It has been demonstrated that polymeric materials with siloxene-like properties, including intense photoluminescence, can be synthesized by the hydrolysis and thermal condensation of partially functionalized oligosilanes bearing hydrolytically labile substituents. However, only polymers obtained from cyclic starting materials exhibit color and fluorescence. Well-defined monomeric model substances $Si_6R_{6-n}(OSiR_3)_n$ bearing siloxy groups on the cyclohexasilane ring were also found to exhibit significantly increased luminescence intensities, while the corresponding aminocyclohexasilane $Si_6R_{6-n}(NR_2)_n$ do not show any photoluminescence at all. Cyclosilanyl subunits in the polymer lattice and the presence of oxygen-containing substituents are therefore the essential criteria for the observed photoluminescence behavior of the molecular and polymeric materials investigated in this study.

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