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Lithiosilanes and their application to the synthesis of polysilane dendrimers

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Abstract

An account is given of the preparation and structural investigations of silyllithium compounds, including X-ray and NMR data. This review covers the chemistry of lithiosilanes with alkyl, aryl, functional substituents and lithiooligosilanes with Si–Si bonds. Application of lithiosilanes for the synthesis of polysilane dendritic molecules is also described.

Keywords: Silicon derivatives; Silyllithium compounds; Group I metals; Dendrimer; Polysilane

1. Introduction

After the discovery of organomagnesium compounds (Grignard reagents), the most important organometallic compounds were probably organolithium compounds, which quickly became very powerful synthetic tools in organic chemistry [1–3]. Now it is almost impossible to imagine the work of a modern research laboratory without the use of organolithium reagents. Many of these compounds are among the most common and frequently used synthetic reagents, some of them (such as MeLi, ^{n}BuLi and ^{t}BuLi, PhLi and others) now being commercially available. It is therefore understandable why the chemistry of organolithium compounds is well established and still attracts great interest among researchers.

In contrast, the chemistry of the heavier Group 14 elements — lithium compounds, first of all — silyllithiums, is less well studied due to high reactivity and the difficulty in their preparation, in comparison with organolithium derivatives. However, the obvious importance of silyllithium compounds caused an increasing interest among organosilicon chemists and great progress has been made in recent years in synthesis and structural investigations, as well as applications to synthetic organic and organometallic chemistry.

Several reviews have been devoted to the chemistry of silyllithium compounds; the most recent ones, by Lickiss and Smith [4], Tamao and Kawachi [5], and Belzner and Dehnert [6], cover the literature up to the middle of 1996. The present review, which summarizes the results in the field of silyllithium chemistry up to 1999, has some overlap with the previous reviews, but special attention has been paid to the synthetic applications of silyllithiums, particularly for the synthesis of polysilane dendritic molecules.

This review consists of two parts. In the first part, the common methods for synthesis of silyllithium compounds are presented, as well as the results of structural investigations of silyllithiums, including X-ray and ^{13}C-, ^{29}Si- and ^{6}Li (^{7}Li)-NMR data. The second part is devoted to the use of oligosilanyllithiums in the synthesis of polysilane dendrimers. The reactivity of silyllithium compounds has been the subject of several previous reviews [4,5] and will not be considered in the present article.

2. Preparation and structural studies of silyllithium compounds

2.1. Lithiosilanes with alkyl substituents

There are several methods for the preparation of lithiosilanes without aromatic substituents. The most common methods are: (1) cleavage of the Si–Si bond of disilanes by the action of nucleophiles (organolithium compound) (Eq. (1)); and (2) reaction of silylmercury compounds with lithium metal (lithium–mercury exchange reaction) (Eq. (2)).

$$R_3Si{-}SiR_3 + MeLi \rightarrow R_3SiLi + MeSiR_3 \quad (1)$$

$$2R_3SiCl \xrightarrow{Na/Hg} (R_3Si)_2Hg \xrightarrow{Li} 2R_3SiLi + Hg \quad (2)$$

Silyllithiums without aromatic substituents cannot be prepared by reaction of the corresponding chlorosilanes or disilanes with lithium metal. Reaction of lithium with chlorosilanes results in the formation of the Wurtz coupling products (e.g. disilanes) instead of silyllithiums. The latter compounds can be prepared by the reaction of organometallic nucleophiles with the corresponding disilanes. Thus, for example, Me_3SiLi has been prepared by reaction of $Me_3SiSiMe_3$ with MeLi in HMPA–THF mixed solvent [7,8] (Eq. (3)).

$$Me_3Si{-}SiMe_3 + MeLi \xrightarrow{THF-HMPA} Me_3SiLi + Me_4Si \quad (3)$$

The presence of a strongly coordinating solvent such as HMPA is essential for the reaction, which does not proceed without HMPA. The driving force of the reaction is the formation of a Si–C bond, which is stronger than the Si–Si bond of the starting disilane. This is the most convenient way for the synthesis of Me_3SiLi; however, it has some limitations. Thus, Me_3SiMe_2SiLi as a by-product was formed together with Me_3SiLi, depending on the reaction conditions [9–12].

Me_3SiLi is a hexamer in the solid state as was determined by an X-ray study (Fig. 1) [13]. The six lithium atoms form a 'folded chair' with an approximate D_{3d} symmetry and an average Li–Li bond distance of 2.7 Å, thus this 'chair' conformation is a strongly distorted octahedron, rather than a cyclohexane-type structure. All trimethylsilyl groups are located above the center of a triangle formed by three lithium atoms, with the average Si–Li distance being 2.68 Å. Such a kind of bonding between silicon and lithium was explained as a four-center two-electron interaction.

A complex of Me_3SiLi with TMEDA $(Me_3SiLi)_2 \cdot 3TMEDA$ was obtained during recrystallization of hexamer $(Me_3SiLi)_6$ from TMEDA [14]. The hexameric structure was transformed to a dimeric one due to complexation with TMEDA. Each lithium atom is coordinated with one Me_3Si substituent and one TMEDA molecule. The average Si–Li bond length is longer than that of uncomplexed hexamer: 2.70 versus 2.68 Å.

An alternative way to synthesize Me_3SiLi is the reaction of lithium metal with $(Me_3Si)_2Hg$, which can be prepared from Me_3SiCl with sodium amalgam in cyclopentane in the dark to avoid photochemically induced decomposition [15,16] (Eq. (4)).

$$2Me_3SiCl \xrightarrow[\text{cyclopentane}]{\text{Na/Hg}} (Me_3Si)_2Hg \overset{\text{Li}}{\rightarrow} 2Me_3SiLi \tag{4}$$

$LiHg(SiMe_3)_3$ and $Li_2Hg(SiMe_3)_4$ were postulated as reactive intermediates. Other types of silyllithium can also be prepared by the mercury–lithium exchange reaction, which usually proceeds in THF or even in non-polar solvents like benzene. Et_3SiLi was formed together with EtLi in the reaction of $EtHgSiEt_3$ with lithium in benzene [17] (Eq. (5)). However, when this reaction was performed in THF, only Et_3SiLi was obtained as a single product (Eq. (6)).

$$Et_3SiHgEt \xrightarrow[\text{benzene}]{\text{Li}} Et_3SiLi + EtLi + Hg \tag{5}$$

$$Et_3SiHgEt \underset{\text{THF}}{\overset{\text{Li}}{\rightarrow}} Et_3SiLi + Hg + C_2H_4 + C_2H_6 \tag{6}$$

Sterically crowded ${}^tBu_3SiLi$ cannot be produced by direct reaction with lithium metal, but it can be prepared by the exchange reaction of ${}^tBu_3SiNa$ with LiCl. Silylsodium ${}^tBu_3SiNa$ (or silylpotassium ${}^tBu_3SiK$) are the only examples of silyl anions, which can be prepared by the reaction of silylhalides with the corresponding metals [18–21] (Eq. (7)). A Wurtz-type reaction to give the coupling product ${}^tBu_3Si$–Si(${}^tBu_3$) does not take place because of great steric hindrance at the silicon atom.

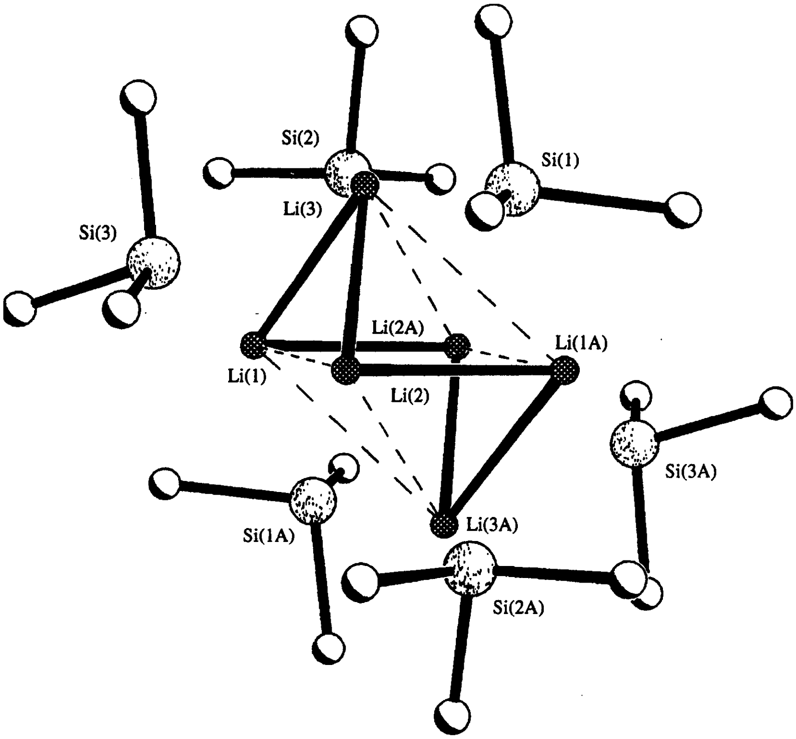


Fig. 1. Crystal structure of $(Me_3SiLi)_6$ (Ref. [13]). Reprinted with permission from the Journal of the American Chemical Society.

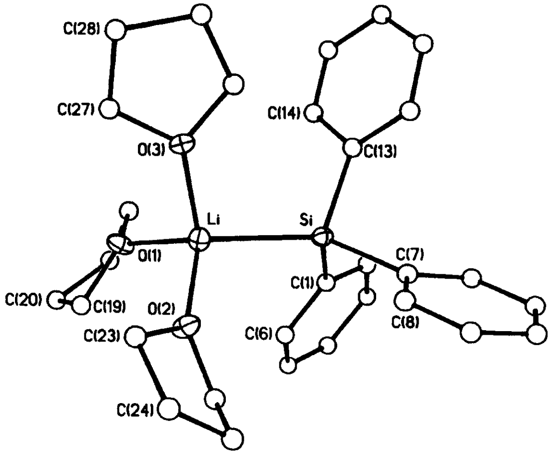


Fig. 2. Crystal structure of $Ph_3SiLi \cdot 3THF$ (Ref. [24]). Reprinted with permission from Elsevier Science.

$$^{t}Bu_3SiX + 2M \rightarrow {}^{t}Bu_3SiM + MX \qquad (7)$$

$$M = Na,\ K;\ X = Br,\ I$$

2.2. Lithiosilanes with aryl substituents

The most useful and simplest method for preparing aryllithiosilanes is reaction of the corresponding chlorosilanes with lithium in polar solvents such as THF or DME. Thus, Ph_3SiLi can be easily synthesized from Ph_3SiCl and Li in THF [22] (Eq. (8)).

$$Ph_3SiCl + 2Li \xrightarrow{THF} Ph_3SiLi + LiCl \qquad (8)$$

It is supposed that the first step is the formation of Ph_3SiLi. This compound undergoes subsequent nucleophilic attack by the excess Ph_3SiCl to give the disilane $Ph_3SiSiPh_3$ (second step), which can be isolated when stoichiometric amounts of reagents are used. However, in contrast to the alkylsilyllithium case, disilanes with aromatic substituents can be reduced with an excess of lithium, and, in fact, on the third step symmetrical Si–Si bond cleavage with lithium takes place with the final formation of silyllithiums. The last step is much slower than the initial formation of silyllithiums and requires electropositive alkali metals. For example, reaction of Ph_3SiCl with less electropositive Mg produces only $Ph_3SiSiPh_3$ [23].

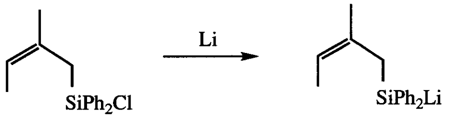
X-ray analysis of $Ph_3SiLi \cdot 3THF$ showed that both the lithium and silicon atoms are four-coordinated exhibiting distorted tetrahedral geometry [24] (Fig. 2). The Li–Si distance of 2.67 Å is normal and close to the average Li–Si bond length (2.68 Å) in the hexamer $(Me_3SiLi)_6$. In contrast, the average Si–C(phenyl) bond length of 1.94 Å is significantly longer than that of neutral compounds (1.85 Å). Such a lengthening may be the result of the increased negative charge on the silicon atom. The geometry around the silicon atom is completely different from that of the carbon analog $Ph_3CLi \cdot Et_2O$: tetrahedral for Ph_3SiLi versus planar coordination for Ph_3CLi.

Many arylsilyllithiums besides Ph_3SiLi can be prepared by this method: (*o*-tolyl)$_3$SiLi [22], $Ph_2(^tBu)SiLi$ [25], Ph_2(*o*-tolyl)SiLi [26] and Ph(*o*-tolyl)$_2$SiLi [27] from the corresponding halosilanes. The obvious disadvantage of this method is the formation of lithium halides as by-products. The salt-free arylsilyllithiums can be synthesized by the reaction of disilanes with lithium in polar solvents such as THF or DME [28]. Another possibility for the synthesis of salt-free Ph_3SiLi is a transmetallation reaction of a silyl–cobalt complex and MeLi [29] (Eq. (9)).

$$Ph_3Si–Co(CO)_4 + MeLi \rightarrow Ph_3SiLi + MeCo(CO)_4 \tag{9}$$

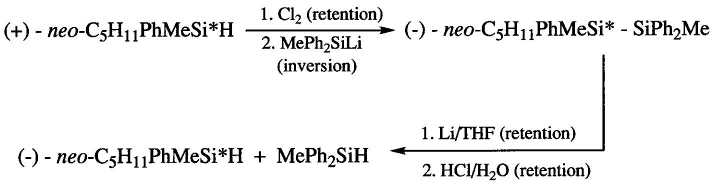
It seems that reductive cleavage of the Si–Si bond by alkali metals is the most convenient route to synthesize not only aryl, but also alkyl, benzyl and allyl silyllithiums [30–35]. Mixed arylalkylsilyllithiums, Ar_2(alkyl)SiLi and Ar(alkyl)$_2$SiLi, can be obtained by similar methods: cleavage of disilanes with Li in ether solvents such as THF or by the reaction of Li with chlorosilanes [36] (Eq. (10)). Silyllithiums with methyl, ethyl, *i*-propyl, *t*-butyl, benzyl and neo-pentyl substituents are available by this route. Allyl substituted silyllithium can also be synthesized from the corresponding chlorosilane and Li in THF at 0°C [37] (Eq. (11)).

$$\begin{aligned}&Ar_n(Alkyl)_{3-n}SiCl \xrightarrow{Li} Ar_n(Alkyl)_{3-n}SiLi\\&Ar_n(Alkyl)_{3-n}Si–Si(Alkyl)_{3-n}Ar_n \xrightarrow[THF]{Li} 2Ar_n(Alkyl)_{3-n}SiLi\end{aligned} \tag{10}$$



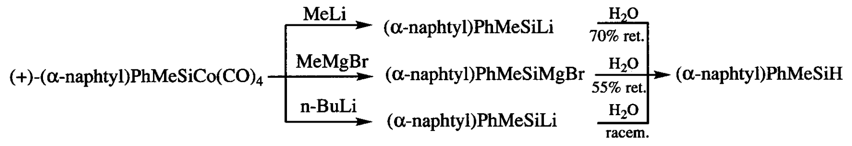
(11)

Sommer and Mason showed that reductive cleavage of the Si–Si bonds of an optically active disilane by lithium metal proceeds with retention of configuration at the chiral silicon atom [33] (Scheme 1). Optically active silyllithiums have been prepared by Corriu by the reaction of (+)-(α-naphtyl)PhMeSi*Co(CO)$_4$ with MeLi to give, after hydrolysis, (+)-(α-naphtyl)PhMeSiH with 70% retention of configuration [29]. The stereochemistry of the reaction strongly depends on the



Scheme 1.

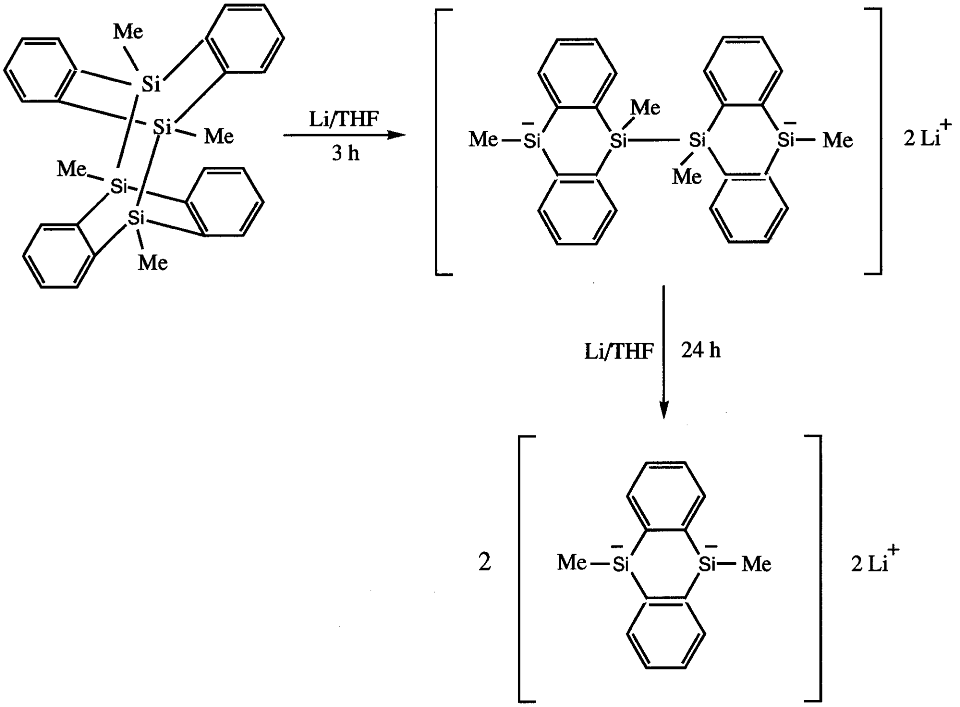
organometallic reagent. Thus, reaction with MeMgBr gave only 55% retention, and the reaction with ^{n}BuLi provided complete loss of chirality (Eq. (12)).



(12)

Reaction of lithium with the 9,10-disilaanthracene dimer caused cleavage of the Si–Si bond to give a dianion species, which was trapped by MeI [38] (Scheme 2). A longer reaction time with lithium produced 9,10-dilithio-9,10-disilaanthracene, which has been used for the synthesis of *cis*-substituted disilaanthracene derivatives.

Structural studies of aryllithiosilanes have been performed by means of NMR spectroscopy, especially ^{13}C-NMR, which has proved to be a very powerful method for elucidation of the electronic structure of aryllithiosilanes. For example, ^{13}C-NMR data give important information about the negative charge delocalization between the silicon atom and the phenyl groups. Thus, if ^{13}C-NMR chemical shifts of aromatic carbon atoms of chlorosilanes are compared with those of the corresponding lithiosilanes, the following trends are observed [39,40]. The *ipso* carbon atoms are significantly deshielded, whereas the *para* carbons are shielded. Such a



Scheme 2.

charge distribution is more characteristic of inductive π-polarization effects, rather than mesomeric effects. That means the negative charge in aryllithiosilanes is localized mainly on the silicon atom. On the other hand, the negative charge in phenyl substituted carbanions is significantly delocalized from the carbon atom into the aromatic rings through mesomeric effects. The same trends have been observed, as was mentioned above, in X-ray structures of Ph_3SiLi [24] and Ph_3CLi [42]. The tetrahedral configuration around the silicon center versus planar configuration around the carbon center means a reduced contribution of the resonance effects in silyl anions relative to carbanions. These conclusions have also been supported by UV data, which show almost no conjugation between the silicon atom and the phenyl rings [43,44]. Thus, for example, the absorption maximum of Ph_3SiLi in THF was found at 335 nm, whereas for Ph_3CLi it was observed at 500 nm.

^{13}C- as well as ^{6}Li (^{7}Li)-NMR data also gave some additional information about the nature of Si–Li bonds. Thus, it was found that ^{13}C-, ^{6}Li (^{7}Li)- and ^{29}Si-NMR chemical shifts of arylsilyllithiums are only slightly dependent on the solvent polarity [39,41,45,46], whereas arylsubstituted carbanions have a noticeable solvent dependence. For example, ^{29}Si-NMR chemical shifts of $Ph_3Si–^{6}Li$ does not exhibit any significant change on going from 2-methyl–THF to more polar solvents: 2-methyl–THF–THF–DME; δ (^{29}Si) = -9.2; -9.0; -8.7, respectively [41]. These results were explained by the partial covalent nature of Si–Li bonds. Such a conclusion was also supported by the coupling between Si and Li atoms in ^{29}Si-NMR. Thus, the ^{29}Si resonance of $Ph_3Si–^{6}Li$ in 2-methyl–THF at 173 K exhibits a triplet with equal intensities [41], whereas for $Ph_3Si–^{7}Li$ a quartet was found in toluene-d_8 at 193 K [24]. These data give evidence about the monomeric structure of Ph_3SiLi as well as the essentially covalent nature of the silicon–lithium bond. In contrast, for Ph_3CLi (as well as $PhCH_2Li$ and Ph_2CHLi) no coupling was observed down to 123 K, which could be consistent with a predominant ionic character of the carbon–lithium bond. However, intermolecular lithium–lithium exchange in Ph_3SiLi accelerates significantly on increase of temperature or by using the more polar THF, which leads to the disappearance of $^{29}Si–^{6}Li$ coupling [41]. This lithium–lithium exchange decreased when phenyl groups were changed to methyl groups: a well-resolved triplet was observed for $PhMe_2Si–^{6}Li$ at 173 K, even when THF was used as a solvent [41]. However, there is another point of view about the nature of the Si–Li bond. Thus, ^{7}Li-NMR shows rapid lithium exchange in mixtures of Ph_3SiLi and $Ph_2MeSiLi$ (or $PhMe_2SiLi$) in THF at about 183 K as well as the almost complete identity of the ^{7}Li chemical shifts of these compounds [46]. These results have been interpreted as indicating a predominantly ionic character for the silicon–lithium bond.

2.3. Lithiosilanes with functional groups

Functionalized silyllithiums have been studied less extensively. Nevertheless, there are some data on these compounds in the literature. In this section hydrogen, halogen, amino, alkoxy and carbonyl group substituted lithiosilanes will be considered, together with the results on silacyclopentadienide anions described in recent years.

2.3.1. Hydrogen-substituted silyllithiums

Silyllithiums with two aromatic substituents and a hydrogen atom were prepared by the reaction of Ar_2SiHCl (Ar = Ph, Mes) with Li [34,47,48] or lithium 1-(dimethylamino)naphthalenide (LDMAN) in THF [35]. However, $Ph_2(H)SiLi$ was obtained in low yield and polymerized easily during the long reaction time or at high temperatures. More bulky $Mes_2(H)SiLi$ was obtained as a stable compound in 71% yield as white crystals (Eq. (13)).

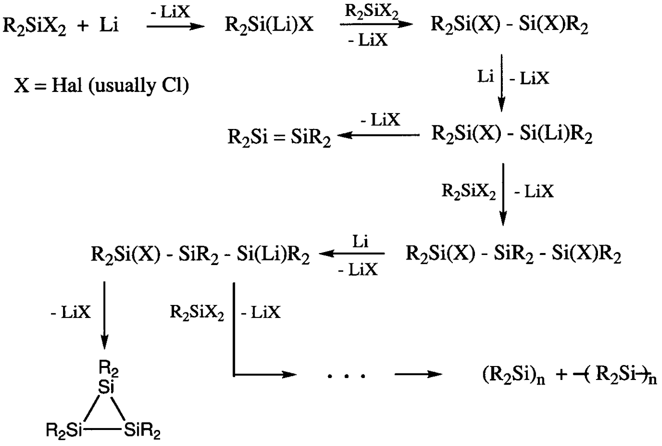
$$HMes_2SiCl + 2Li \xrightarrow{\text{THF, 0°C}} HMes_2SiLi \tag{13}$$

An alternative way for the synthesis of $Ar_2(H)SiLi$ is cleavage of the Si–Si bond of disilanes $Ar_2(H)Si–Si(H)Ar_2$ (Ar = Ph [34]) by Li in THF (Eq. (14)).

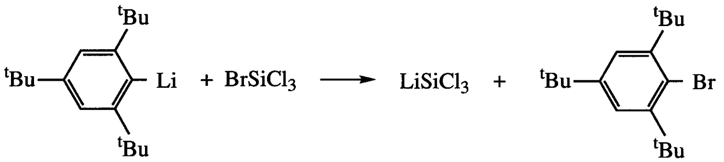
$$Ar_2(H)Si\text{–}Si(H)Ar_2 \xrightarrow{\text{Li/THF}} 2Ar_2Si(H)Li \tag{14}$$

2.3.2. Halogen-substituted silyllithiums

Formation of the lithiohalosilanes as reactive intermediates was assumed in the coupling reactions of dihalosilanes with lithium to produce linear and oligo- (or poly) silanes (Scheme 3). In the first step, intermediate lithiohalosilane was formed, which reacted with a second molecule of starting dihalosilane to form 1,2-dihalodisilane. This last compound underwent subsequent reduction with lithium, which resulted in the formation of 1-halo-2-lithiodisilane. Further transformations of the above compound strongly depend on the steric bulkiness around the silicon atoms. With very bulky substituents (e.g. Tip: 2,4,6-triisopropylphenyl [49]), the elimination of LiX with the formation of disilenes is favorable [50,51]. Less bulky substituents (^{t}Bu, ^{i}Pr) cause the formation of the cyclotri- (or tetra) silanes [50,52,53], whereas dihalosilanes with small substituents (Me, Ph) undergo further coupling reactions to produce larger cycles or linear polysilanes [54,55]. It was believed that $LiSiCl_3$ was formed by the bromine–lithium exchange reaction of $BrSiCl_3$ and 2,4,6-tri-*t*-butylphenyllithium [56] (Eq. (15)).



Scheme 3.



(15)

2.3.3. *Amino-substituted silyllithiums*

The first amino-substituted silyllithiums were synthesized by Tamao's group by reaction of the corresponding chlorosilanes with lithium dispersion [57] or lithium(α-dimethylaminonaphtalenide) (LDMAN) [35] (Eq. (16)) or by transmetallation of the corresponding aminosilylstannanes with *n*- or ^{t}BuLi [58] (Eq. (17)).

$$(\mathrm{Et_2N})_n\mathrm{Ph}_{3-n}\mathrm{SiCl} \xrightarrow[\mathrm{THF}]{\mathrm{Li}} (\mathrm{Et_2N})_n\mathrm{Ph}_{3-n}\mathrm{SiLi}$$

$$(\mathrm{Et_2N})\mathrm{Ph_2SiCl} \xrightarrow[\mathrm{THF}]{\mathrm{LDMAN}} (\mathrm{Et_2N})\mathrm{Ph_2SiLi}$$

LDMAN: lithium (α-dimethylaminonaphthalenide) (16)

$$(\mathrm{Et_2N})_n\mathrm{Ph}_{3-n}\mathrm{Si{-}SnMe_3} \xrightarrow[-\,\mathrm{RSnMe_3}]{\mathrm{RLi}} (\mathrm{Et_2N})_n\mathrm{Ph}_{3-n}\mathrm{SiLi} \qquad (17)$$

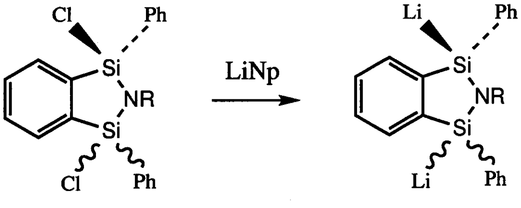
$n = 1,\ \mathrm{R} = \text{n-Bu};\ n = 2,\ \mathrm{R} = \text{t-Bu}$

Such functionalized silyllithiums, having at least one phenyl group attached to the silicon atom, are stable in an inert atmosphere at about 0°C in THF for several days. In contrast, alkyl-substituted mono- and diaminochlorosilanes react with lithium to form homocoupling products [59] (Eq. (18)).

$$2(\mathrm{Et_2N})_n\mathrm{R}_{3-n}\mathrm{SiCl} \xrightarrow[\mathrm{THF}]{\mathrm{Li}} (\mathrm{Et_2N})_n\mathrm{R}_{3-n}\mathrm{Si{-}SiR}_{3-n}(\mathrm{NEt_2})_n \qquad (18)$$

$\mathrm{R} = \text{Alkyl},\ n = 1,2$

Contrary to the stable amino(aryl)lithiosilanes, 1,3-dilithiosilanes, synthesized from the corresponding chlorosilanes with lithium naphthalenide, decompose in 3 h at 0°C [60] (Eq. (19)). The ^{29}Si-NMR signal of $(\mathrm{Et_2N})\mathrm{Ph_2SiLi}$ appeared at δ 19.34 (THF, 0°C) [5].



R = ^{n}Bu, ^{t}Bu (19)

The ^{13}C-NMR chemical shifts of the aromatic carbon atoms are almost the same as for $\mathrm{MePh_2SiLi}$, which means that there is no great influence of the $\mathrm{Et_2N}$ group on the charge distribution of both lithiosilanes. Using (aminosilyl)lithiums as a starting material many functional di- and oligosilanes have been prepared. Thus, the $\mathrm{Et_2N}$ group can be substituted by an alkoxy group or chlorine [57] (Eq. (20)).

$$(Et_2N)Ph_2SiLi + ClSiMe_2R \rightarrow (Et_2N)Ph_2Si\text{–}SiMe_2R \overset{AcCl}{\rightarrow} ClPh_2Si\text{–}SiMe_2X \quad (20)$$

$$R = H,\ NEt_2,\ O^{i}Pr,\ CH{=}CH_2;\ X = H,\ Cl$$

2.3.4. Alkoxy-substituted silyllithiums

Alkoxysilyllithiums, containing at least one aromatic substituent, can be prepared in several ways. For example, $(^{t}BuO)Ph_2SiLi$ was obtained by the reaction of $(^{t}BuO)Ph_2SiSnMe_3$ with $^{n}BuLi$ in THF [61] (Eq. (21)). This silyllithium is stable for several hours at −78°C and represents an ambident character.

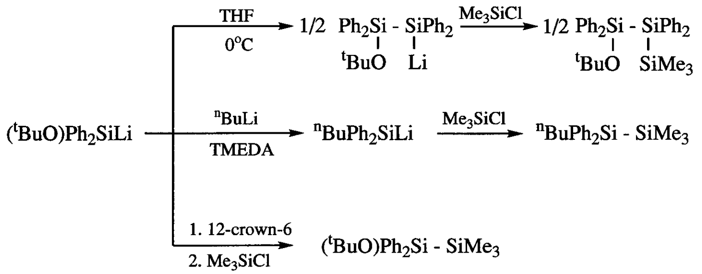
$$(t\text{-}BuO)Ph_2Si\text{–}SnMe_3 + n\text{-}BuLi \xrightarrow[-78°C]{THF} (t\text{-}BuO)Ph_2SiLi + n\text{-}BuSnMe_3 \quad (21)$$

It can react as a nucleophilic silyl anion as well as an electrophile. In other words, it has a silylenoid character. For example, upon warming up to 0°C this species undergoes self-condensation to produce, after quenching with Me_3SiCl, the compound $Ph_2(^{t}BuO)SiSiPh_2(SiMe_3)$. Reaction with an excess of $^{n}BuLi$ in the presence of TMEDA results in the formation of $^{n}BuPh_2SiLi$, a product of the nucleophilic attack of $^{n}BuLi$ [61] (Scheme 4). Addition of crown-ethers (12-crown-6) completely suppresses such an ambident character, because of the formation of solvent-separated ion pairs. Thus, self-condensation does not take place nor does butylation with $^{n}BuLi$; only reactions with electrophiles such as Me_3SiCl were observed. An analogous ambident character has been reported for $(^{i}PrO)Ph_2SiLi$ and $(MeO)Ph_2SiLi$, which can be prepared by reduction of the corresponding chlorosilanes with LDMAN at −78°C [35] (Eq. (22)).

$$(RO)_nPh_{3-n}SiCl \xrightarrow[-78°C]{LDMAN/THF} (RO)_nPh_{3-n}SiLi \quad (22)$$

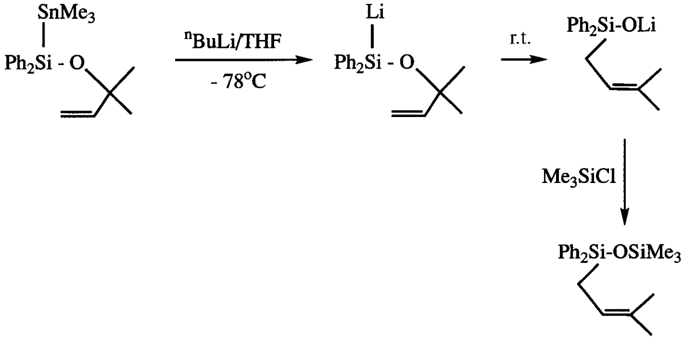
$$R = t\text{-}Bu\ (n = 1, 2),\ i\text{-}Pr\ (n = 1),\ Me\ (n = 1)$$

$(^{t}BuO)_2PhSiLi$ can also be prepared from the corresponding chlorosilane by the action of LDMAN at −50°C [35] or by reaction with lithium metal at 0°C [62]. This last compound, $(^{t}BuO)_2PhSiLi$, thermally is more stable than $(^{t}BuO)Ph_2SiLi$ and does not decompose in THF at room temperature (r.t.) [35]. Moreover, there is no reaction with $^{n}BuLi$ at r.t. due to a less electrophilic character for $(^{t}BuO)_2PhSiLi$.



Scheme 4.

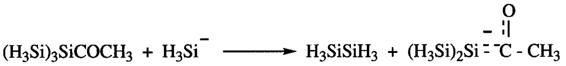
An interesting example is the reaction of stannyl(allyloxy)silanes with ^{n}BuLi in THF at −78°C to give, after quenching with Me_3SiCl, a rearranged product [63] (Eq. (23)). It is believed that the reaction proceeds through the intermediate formation of (allyloxy)silyllithiums, which undergo a Wittig-type intramolecular [2,3] sigmatropic rearrangement to form allylsilanolate anions.



(23)

2.3.5. Lithium sila-enolates

Sila-enolates, that is the silicon analogues of the well-known lithium enolates, were first prepared by Ishikawa et al. by the reaction of acyltris(trimethylsilyl)silane with tris(trimethylsilyl)silyllithium (or phenyldimethylsilyllithium) in THF [64–66]. Similar to the carbon analogues, sila-enolates exhibit an ambident character. Thus, trapping reactions of sila-enolates with H_2O give the products of the Si reaction site, whereas trapping with Et_3SiCl quantitatively produces sila-enol silyl ether (siloxysilene) (Scheme 5). Reaction of sila-enolates with $PdCl_2$ results in a coupling reaction with formation of hexasilanes, which can react (in the case of R = Mes) with $(Me_3Si)_3SiLi$ to give a new sila-enolate. The formation of sila-enolates is favorable, an observation supported by ab initio calculations, which show that the model reaction (Eq. (24)) is exothermic by −30 kcal mol^{-1} [66].

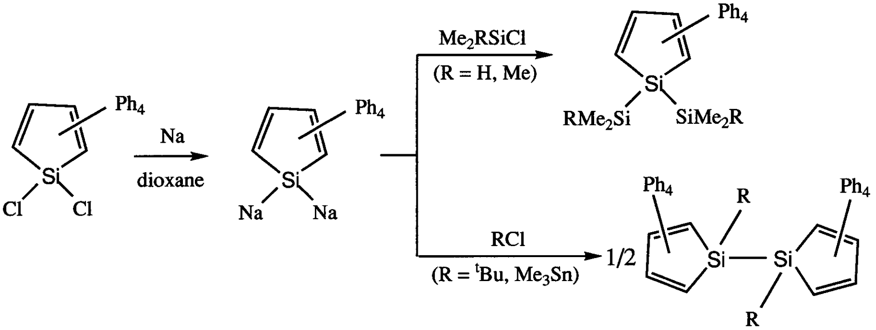


$$(H_3Si)_3SiCOCH_3 + H_3Si^- \longrightarrow H_3SiSiH_3 + (H_3Si)_2Si \overset{-}{=} \overset{\overset{O}{\|}}{C} - CH_3 \qquad (24)$$

Bulky substituents at the carbonyl center are necessary for successful preparation of the sila-enolates. For example, attempts to synthesize sila-enolates with less sterically hindered Ph or Me substituents have not been successful. Phenyl-substituted sila-enolates can be prepared by reaction of acylsilanes with $(Me_3Si)_3SiLi$, but then they quickly dimerize or undergo some other reaction. Reaction of methyl-substituted acylsilane with $(Me_3Si)_3SiLi$ causes deprotonation of the methyl group, yielding an enolate instead of a sila-enolate [66].

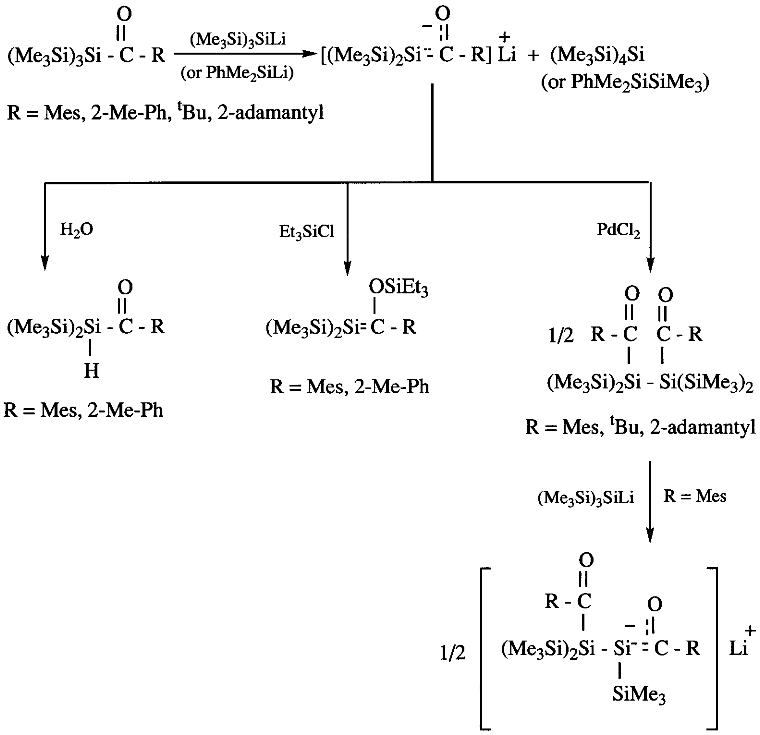
2.3.6. Silole mono- and dianions

The structure of silacyclopentadienyl anions (silole anions) is of special interest because of their similarity to the cyclopentadienide anion, which is well-known to be an aromatic species. After the first synthesis of dichlorosiloles [67], the first evidence for the formation of the silole dianion was obtained by Joo and co-workers in 1990 by the reduction of 1,1-dichlorosilole with sodium in refluxing dioxane in 80% yield. This dianion was trapped by electrophiles such as Me_2HSiCl and Me_3SiCl [68] (Eq. (25)).



(25)

Since this report, great progress has been made during the last decade, an especially strong contribution in this field being made by the Boudjouk and West groups [69–73]. Thus, 1,1-dilithiosilole was also synthesized from 1,1-dichlorosilole by reduction with four equivalents of Li in THF under ultrasonic activation. After the



Scheme 5.

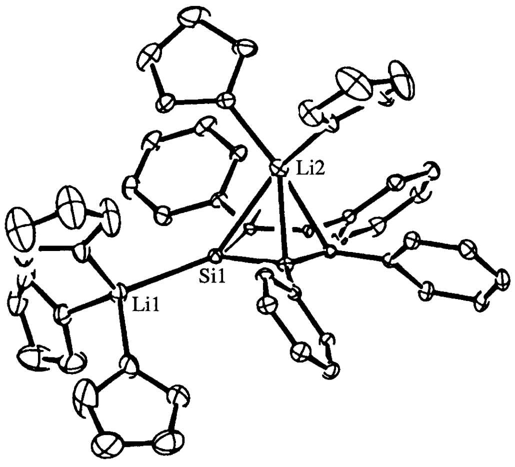
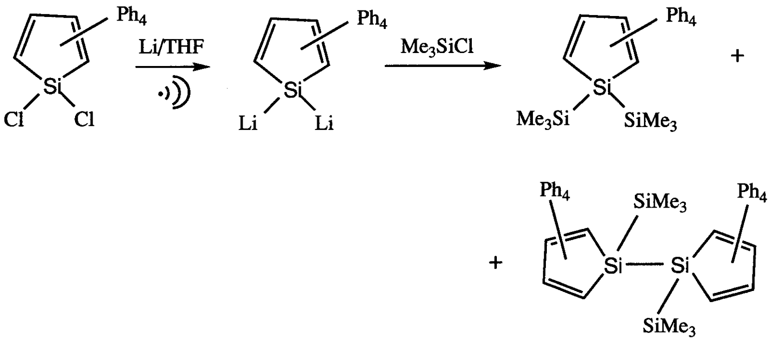


Fig. 3. Crystal structure of silole dianion dilithium (Ref. [73]). Reprinted with permission from the Journal of the American Chemical Society.

quenching reaction of the dianion with Me_3SiCl, the expected 1,1-bis(trimethylsilyl)silole was obtained together with a disilane [72] (Eq. (26)). Spectroscopic studies of the silole dianion show its aromatic character.

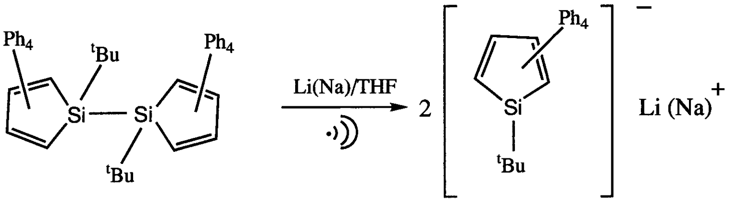


(26)

Thus, ^{29}Si-NMR reveals a significant down-field shift of the silicon atom resonance (δ 68.4), as well as shielding of the C_α and C_β atoms of the cyclopentadienyl ring in ^{13}C-NMR [72]. These results are in accordance with the theoretical calculations [74], which predicted that silole dianions as well as dimetallated siloles are aromatic compounds. The suggestion about aromaticity of the silole dianion has also been supported by the X-ray crystallography results reported by West [73] (Fig. 3).

According to these data, the cyclopentadienide ring is planar with almost equal C–C distances, which is normal for a delocalized system. However, the arrangement of Li atoms is in contrast to theoretical calculations [73,74]. It appears they are not equivalent — one of them lies above the ring plane (η^5-coordination) and another lies in the plane (η^1-bonding with silicon atom). Thus, this structure represents

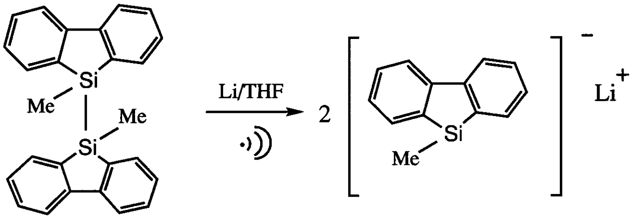
η^5-(1-lithiosilacyclopentadienyl)lithium. As was mentioned above, calculations predict another structure for the silole dianion — a symmetrical η^5–η^5 structure, which is more favorable than the η^1–η^5 structure by 21 kcal mol^{-1} [73]. The reason for this contradiction may bethe effects of THF ligands, which are coordinated with lithium cations, as well as specific features of the crystal packing. Opposite results have been obtained from the X-ray data of the 18-crown-6 complex of the dipotassium salt of tetramethylsilacyclopentadienide, which was prepared by reduction of the corresponding dibromosilole with potassium in the presence of two equivalents of 18-crown-6 [75,76]. In agreement with theoretical calculations, it has an inverted sandwich η^5–η^5-type structure. Silole monoanions were also generated from the corresponding siloles. The first example of such a monoanion was reported by Boudjouk, who obtained such a species by the reduction of disilane with Li or Na metal under ultrasonic activation [70] (Eq. (27)).



(27)

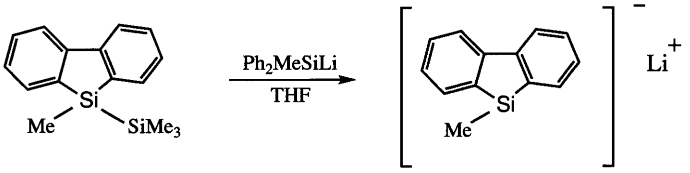
Most important is the down-field shift of silicon atom resonance in ^{29}Si-NMR at δ 25.10 for Li-anion and at δ 26.12 for Na-anion. The same tendency was observed in ^{13}C-NMR: shielding of the C_α and C_β atoms of the cyclopentadienyl ring. All these data display significant charge transfer into the cyclopentadienide ring, which is also supported by the calculated chemical shift for the silole monoanion $[SiC_4H_5]Li$ [77].

Another charge distribution was evidenced by the reduction of bis(silafluorene) with lithium [71] (Eq. (28)). The lithium salt of 1-silafluorenide exhibits some properties that are characteristic of a localized species. Thus, it shows a high-field shift for the ^{29}Si atom at δ -47.9. ^{13}C-NMR also does not show localization of electron density in a cyclopentadienide ring.



(28)

Another way to prepare this species is the reaction of 5-methyl-5-(trimethylsilyl)silafluorene with $Ph_2MeSiLi$ in THF at -78°C [78] (Eq. (29)).



(29)

2.4. Lithiooligosilanes

Generally, three methods are most commonly used for the preparation of the acyclic lithiooligosilanes: (1) Si–Si bond cleavage of oligosilanes by organo- or silyllithium reagents; (2) Si–Si bond cleavage of oligosilanes by lithium metal; and (3) transmetallation of silylmercury compounds by lithium metal. In that case it is possible to use non-polar solvents — toluene or even saturated hydrocarbons.

2.4.1. Linear lithiooligosilanes

2.4.1.1. Lithiodisilanes. The simplest representative of this class of compounds is $Me_3SiSiMe_2Li$, which has been obtained as a side product in the reaction of $Me_3SiSiMe_3$ with MeLi in HMPA–Et_2O [9]. However, by using a large amount of starting material it is possible to obtain $Me_3SiSiMe_2Li$ as a major product [12] (Eq. (30)).

$$Me_3Si\text{–}SiMe_3 + MeLi \xrightarrow[0°C]{HMPA/THF} Me_3Si\text{–}SiMe_2Li \qquad (30)$$

Another possibility for the synthesis of this silyllithium was demonstrated by Sekiguchi who described the lithium–mercury exchange reaction between $(Me_3SiSiMe_2)_2Hg$ and lithium metal in toluene [79] (Eq. (31)).

$$2Me_3Si\text{–}SiMe_2H \xrightarrow[heptane]{^tBu_2Hg} (Me_3Si\text{–}SiMe_2)_2Hg \xrightarrow[toluene]{Li} 2Me_3Si\text{–}SiMe_2Li + Hg \qquad (31)$$

The structure of solvent-free pentamethyldisilanyllithium was elucidated by X-ray crystallography [79,80] as well as by NMR data [79,81]. It was shown that this compound is tetrameric in the solid state, with four lithium atoms forming a tetrahedron having an average Li–Li distance of 2.780 Å, which is longer than that of the typical alkyllithium tetramers (Li–Li = 2.55–2.56 Å) (Fig. 4). All pentamethyldisilanyl units are located above one of the faces of the Li4 tetrahedron with three nearly equal Li–Si distances of 2.683 Å. The equal length of the Li–Si bonds shows that each silicon atom participates equally in bonding to the three lithium atoms. The distance between lithium atoms and hydrogen atoms of $SiMe_2$ units is rather short (Li–H = 2.08 Å), which is evidence for an agostic interaction between the lithium atoms and methyl groups. These structural features have also been supported by NMR data [79,81]. ^{29}Si-NMR shows the resonance of the silicon connected with lithium at δ -74.9 as a triplet with equal intensities in THF-d_8 at 180 K, which indicates that the negative charge is highly localized on this silicon atom. Thus, it appears that the silicon atom is coupled with only one lithium, indicating that silyllithium is monomeric in THF. In non-polar solvents, such as toluene, the ^{29}Si-NMR resonance appears as an unresolved multiplet at δ -79.6 to -81.4. That is, silyllithium is aggregated in hydrocarbons (probably a tetrameric structure is involved) and monomeric in more polar THF. Other types of aryl-substituted lithiodisilanes, Me_3SiPh_2SiLi and Me_3SiMes_2SiLi, were prepared from the corresponding trisilanes by Si–Si bond cleavage with MeLi in THF–Et_2O [82] (Eq. (32)).

$$(Me_3Si)_2SiR_2 \xrightarrow[THF-Et_2O]{MeLi} (Me_3Si)SiR_2Li + Me_4Si \tag{32}$$
$$R = Ph,\ Mes$$

Reduction of Ph_3SiPh_2SiCl with lithium metal selectively produces Ph_3SiPh_2SiLi, probably through the corresponding tetrasilane as an intermediate product [83]. In contrast, related chlorodisilane $PhMe_2SiMe_2SiCl$ produces a mixture of $PhMe_2SiMe_2SiLi$, $PhMe_2SiLi$ and $(Me_2Si)_6$ [84] (Eq. (33)).

$$Ph_3SiPh_2SiCl \overset{Li}{\rightarrow} Ph_3SiPh_2SiLi$$
$$PhMe_2SiMe_2SiCl \overset{Li}{\rightarrow} PhMe_2SiMe_2SiLi \rightleftharpoons PhMe_2SiLi + (Me_2Si)_6 \tag{33}$$

2.4.1.2. Lithiotrisilanes. The lithium–mercury exchange reaction has been used for the synthesis of two isomeric heptamethyltrisilanyllithiums [79–81] (Eq. (34)).

$$2R^1Me_2SiSiR^2MeH \xrightarrow[heptane]{^tBu_2Hg} (R^1Me_2SiSiR^2Me)_2Hg \xrightarrow[toluene]{Li} 2R^1Me_2SiSiR^2MeLi + Hg \tag{34}$$

The linear isomer showed a triplet signal in ^{29}Si-NMR at δ −62.7 in THF-d_8 at 180 K, whereas the isopropyl-type isomer showed a singlet at δ −133.8 in THF-d_8 at 180 K. Other types of lithiotrisilanes, $LiSi(SiMe_2Ph)_2Me$ (**1a**) and $LiSi(SiMe_3)_2Ph$

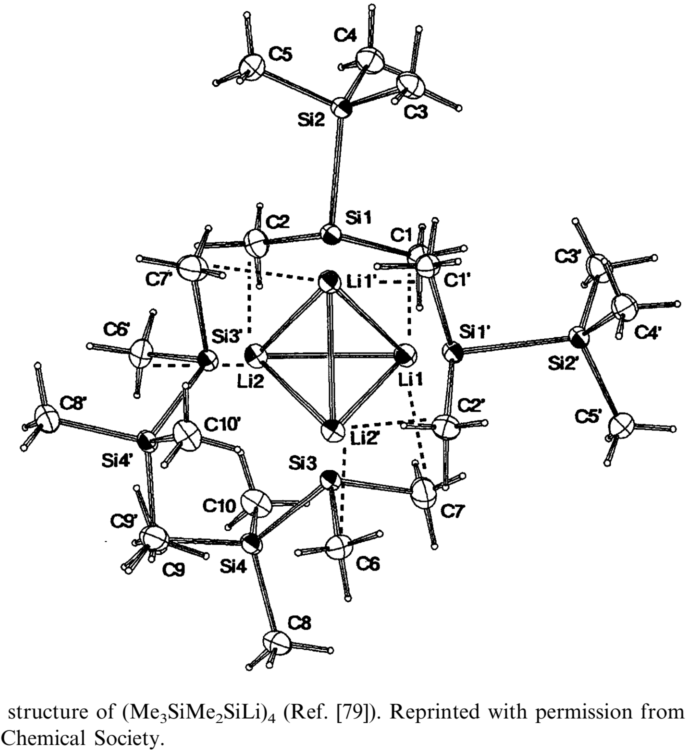


Fig. 4. Crystal structure of $(Me_3SiMe_2SiLi)_4$ (Ref. [79]). Reprinted with permission from the Journal of the American Chemical Society.

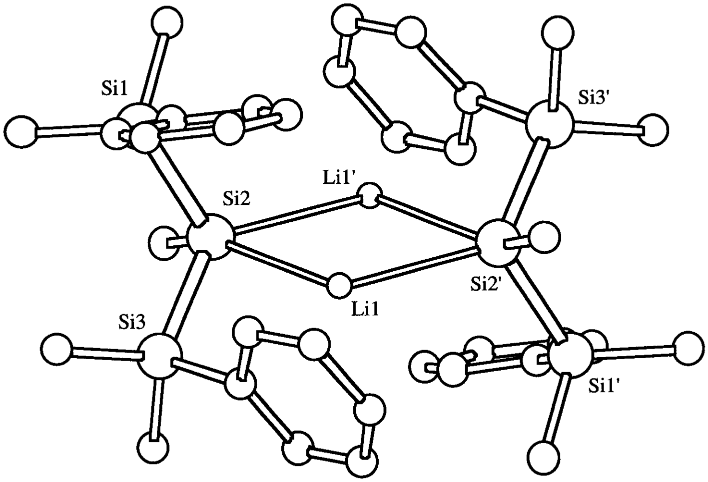


Fig. 5. Crystal structure of $[Me(PhMe_2Si)_2SiLi]_2$.

(**1b**), have been prepared using this methodology and their structures have been studied by means of X-ray crystallography and NMR spectroscopy [80,81,85] (Eq. (35)).

$$R^2Me_2SiSi(H)R^1Me_2R^2 \xrightarrow[\text{2. Li/toluene}]{\text{1. }^t\text{Bu}_2\text{Hg/heptane}} R^2Me_2SiSi(Li)R^1SiMe_2R^2 + Hg \qquad (35)$$

1a: $R^1 = Me$, $R^2 = Ph$; **1b**: $R^1 = Ph$, $R^2 = Me$

Both of these compounds were obtained as yellow crystals and are dimeric in the solid state, as was shown by X-ray crystallography (Figs. 5 and 6). The two lithium and two anionic silicon atoms constitute a planar four-membered ring with Li–Si

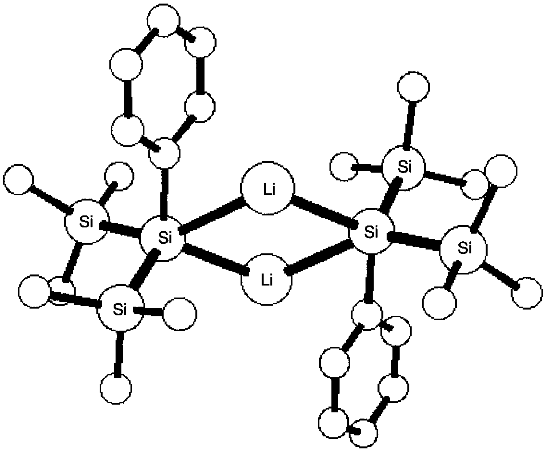


Fig. 6. Crystal structure of $[Ph(Me_3Si)_2SiLi]_2$.

distances of 2.664(5) and 2.778(7) Å for **1a**, 2.63(1) and 2.78(1) Å for **1b**. For the silyllithium **1a**, the two lithium atoms are surrounded by the four phenyl groups, thus each lithium atom contacts with two of the four neighboring benzene rings: the distances between Li and *ipso* and *ortho* carbon atoms of the nearby phenyl groups are typical for π-complexed organolithiums. For silyllithium **1b**, the electrostatic repulsion between the lithium atoms is increased, since only two benzene rings serve as electron donors to the electron deficient lithium atoms. Of further interest is the fact that **1b** not only has an intramolecular Li–Ph interaction, but also an intermolecular Li···CH_3 agostic interaction. Thus, an intermolecular interaction among the dimers with a Li···CH_3 distance of 2.64(1) Å and Li···H–C distance of 2.25(4) Å is observed. Since the dimer of **1b** has only two phenyl groups available for the intramolecular interaction with the electron deficient lithium atoms, the C–H bond may serve as an intermolecular donor.

^{7}Li-NMR data also provide additional support for the electrostatic interaction between the lithium ions and benzene rings. Thus, the ^{7}Li-NMR signal in **1a** is significantly shifted to high field: δ − 0.54 in toluene-d_8 and − 0.36 in cyclohexane-d_{12}, because of the shielding effect of the phenyl groups. However, the ^{7}Li-NMR signal is observed at δ 0.58 for a solution of **1a** in THF-d_8, indicating that the dimeric structure of **1a** is completely destroyed by complexation with THF. Consequently, the lithium atom can no longer be shielded by the phenyl groups. Lithiosilane **1b** also exhibits similar ^{7}Li-NMR spectra: δ − 0.42 in toluene-d_8, δ − 0.97 in cyclohexane-d_{12} and δ 0.69 in THF-d_8.

Various 2-lithiotrisilanes can be prepared by reaction of the corresponding branched tetrasilanes with MeLi in Et_2O [86–88] (Eq. (36)). It was found that the reaction rate depends on the aryl substituents: Tip > Mes > Ph. Such an order was explained by the relief of steric strain in the lithiosilane in comparison with the starting tetrasilanes.

$$RSi(SiMe_3)_3 \xrightarrow{MeLi} RSi(SiMe_3)_2Li + Me_4Si \tag{36}$$

$R = Me,\ Ph,\ Mes,\ Tip$

2.4.1.3. Lithiooligosilanes. Si–Si bond cleavage of the linear phenyloligosilanes by lithium metal usually produces mixtures of mono- and oligolithiosilanes. However, starting from the cyclic oligosilanes, it appears in some cases to produce selective cleavage of the Si–Si bond to form only one type of oligolithiosilane. The first example of such a reaction was demonstrated by Gilman who prepared 1,4-dilithiooctaphenyltetrasilane [89] (Eq. (37)).

$$(Ph_2Si)_4 \xrightarrow{Li} Li(SiPh_2)_4Li \tag{37}$$

1,5-Dilithiodecaphenylpentasilane has also been prepared in this way from decaphenylcyclopentasilane in THF [90], whereas lithiononaphenyltetrasilane was obtained from octaphenylcyclotetrasilane by reaction with PhLi [91]. 1,4-Dilithiooctaphenyltetrasilane was isolated in the form of orange–red crystals [92]. X-ray analysis showed that this compound is monomeric and centrosymmetric with a planar Li–Si4–Li unit (Fig. 7). The bond angle of Li–Si–Si is 126° and that of

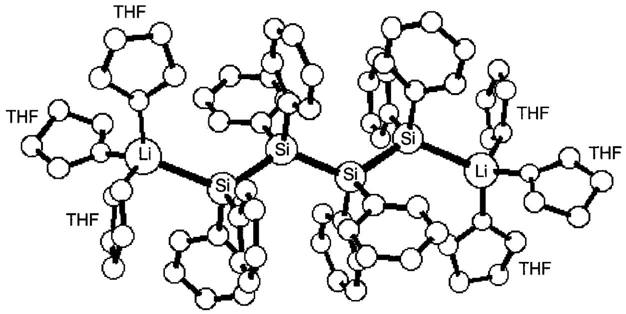
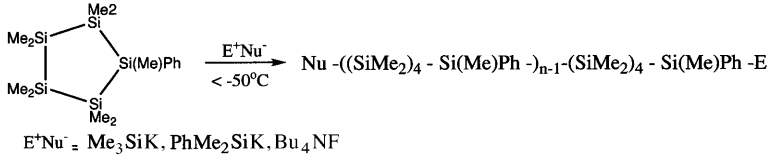


Fig. 7. Crystal structure of $Li(SiPh_2)_4Li \cdot 6THF$.

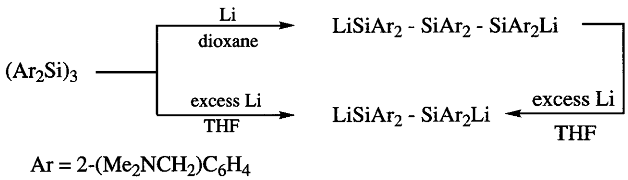
Si–Si–Si is 127°. The average Si–Li bond length is 2.68 Å, which is comparable with that of Ph_3SiLi, 2.67 Å.

The reaction of *trans*-$(PhMeSi)_4$ with a catalytic amount of nucleophile such as ^{n}BuLi, Me_3SiK or $(PhMe_2Si)_2CuLi$ caused an anionic ring-opening polymerization, which resulted in the formation of polysilanes [93]. Phenylnonamethylcyclopentasilane also undergoes such a type of polymerization in polar solvents under the action of catalytic amounts of Me_3SiK or $PhMe_2SiK$ below $-50°C$ [94]. These polymerizations proceed regioselectively to form the polymer with an ordered structure. Such regioselectivity was explained by the formation of the more favorable phenyl-substituted silyl anion [94] (Eq. (38)).



(38)

Reaction of cyclotrisilane with two equivalents of lithium metal in 1,4-dioxane provides access to 1,3-dilithiotrisilane [95]. This dilithiosilane is monomeric with an approximately antiperiplanar conformation of the Li–Si3–Li unit. Each lithium is bonded to a terminal silicon atom as well as to the two amino groups of the $(Me_2NCH_2)C_6H_4$ substituents and the oxygen atom of dioxane. Interaction of 1,3-dilithiotrisilane with an excess of lithium in THF unexpectedly gives 1,2-dilithiodisilane, which can be prepared directly from cyclotrisilane with an excess of lithium metal. 1,2-Dilithiodisilane is monomeric in THF with an Si–Li bond in solution, as was deduced from the ^{29}Si-NMR spectrum, which displayed a quartet with equal intensities at δ -32.8 (Eq. (39)).



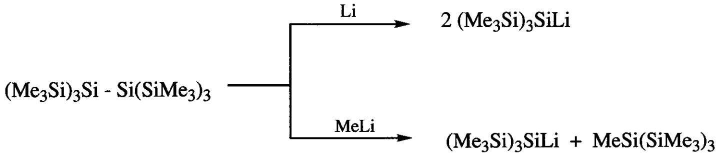
(39)

2.4.2. Branched lithiooligosilanes

One of the most important and thoroughly studied representatives of this class of lithiosilanes is $(\mathrm{Me_3Si})_3\mathrm{SiLi}$. This compound was prepared by cleavage of the Si–Si bond of tetrakis(trimethylsilyl)silane, which is readily available, with MeLi [96,97] (or even $\mathrm{Ph_3SiLi}$ [96]) in THF–$\mathrm{Et_2O}$ (Eq. (40)).

$$(\mathrm{Me_3Si})_4\mathrm{Si} + \mathrm{MeLi} \xrightarrow{\mathrm{THF-Et_2O}} (\mathrm{Me_3Si})_3\mathrm{SiLi} + \mathrm{SiMe_4} \tag{40}$$

$(\mathrm{Me_3Si})_3\mathrm{SiLi}$ cannot be synthesized by the direct metallation of $(\mathrm{Me_3Si})_4\mathrm{Si}$ with lithium metal, probably due to the formation of thermodynamically unfavorable $\mathrm{Me_3SiLi}$ [96]. Alternatively, $(\mathrm{Me_3Si})_3\mathrm{SiLi}$ can also be prepared from hexakis-(trimethylsilyl)disilane with lithium or MeLi [98] (Eq. (41)).

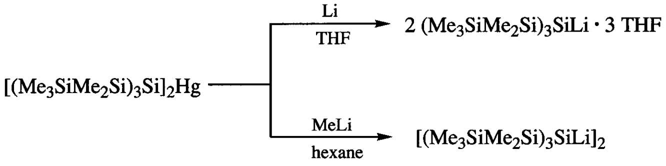


(41)

In contrast, using more bulky $\mathrm{Ph_3SiLi}$ (or $(\mathrm{Me_3Si})_3\mathrm{SiLi}$), results in the elimination of one or two peripheral trimethylsilyl groups by lithium atoms. Such results, probably, could be explained by steric effects, which cause elimination of terminal $\mathrm{Me_3Si}$-groups [98] (Eq. (42)).

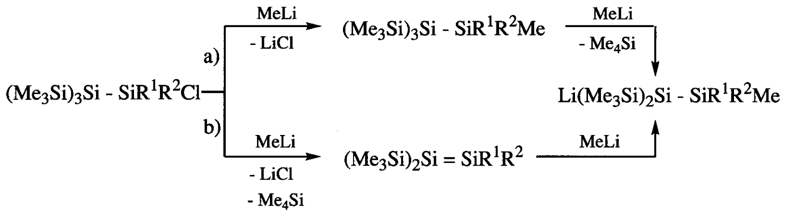
$$\begin{aligned}(\mathrm{Me_3Si})_3\mathrm{Si{-}Si(SiMe_3)_3} &\xrightarrow[\mathrm{R\,=\,SiMe_3,\ Ph}]{\mathrm{R_3SiLi}} (\mathrm{Me_3Si})_3\mathrm{Si{-}Si(SiMe_3)_2Li}\\ &+ \mathrm{Li(Me_3Si)_2Si{-}Si(SiMe_3)_2Li} + \mathrm{R_2Si{-}SiMe_3}\end{aligned} \tag{42}$$

However, treatment of phenyl-substituted unsymmetrical disilanes $\mathrm{Me_3Si{-}SiPh_3}$, $\mathrm{Me_3Si{-}SiMePh_2}$ or $\mathrm{Me_3Si{-}SiMe_2Ph}$ with ^{t}BuOK [99] or TBAF [100] produced the more stable phenyl-containing silyl anion by electronic factors. Transmetallation of silylmercury compounds by lithium metal was used by Apeloig's group for the synthesis of branched heptasilane $(\mathrm{Me_3SiMe_2Si})_3\mathrm{SiLi}\cdot 3\mathrm{THF}$ or its dimer $[(\mathrm{Me_3SiMe_2Si})_3\mathrm{SiLi}]_2$ [101] (Eq. (43)).



(43)

The reaction of MeLi with oligosilanes $(\mathrm{Me_3Si})_3\mathrm{Si{-}X}$ occurs on the less sterically hindered silicon atom, if X is a linear group with one or two silicon atoms: $-\mathrm{SiMe_2H}$, $-\mathrm{SiMe}_2^t\mathrm{Bu}$, $-\mathrm{SiMe_2SiMe_3}$, $-\mathrm{SiMe_2SiMe}_2^t\mathrm{Bu}$ [102]. For example, reaction of MeLi with $(\mathrm{Me_3Si})_3\mathrm{Si{-}SiMe_2H}$ produces $(\mathrm{Me_3Si})_3\mathrm{SiLi}$, whereas reaction of $(\mathrm{Me_3Si})_3\mathrm{Si{-}SiMe_2}(^t\mathrm{Bu})$ results in the formation of $\mathrm{Li(Me_3Si)_2Si{-}SiMe_2}(^t\mathrm{Bu})$. The opposite situation was observed when X is a branched oligosilyl group such as $-\mathrm{SiMe(SiMe_3)_2}$ or $-\mathrm{Si(SiMe_3)_3}$. MeLi reacts mainly with a silicon atom in the



Scheme 6.

α-position to the $(Me_3Si)_3Si$ group, yielding $(Me_3Si)_3SiLi$. Thus, in the last case, electronic factors could be responsible for such regioselectivity. On the other hand, when oligosilane $(Me_3Si)_3Si–SiR^1R^2Cl$, having a chlorine atom in the α-position to the $(Me_3Si)_3Si$ group, reacts with MeLi, $Li(Me_3Si)_2SiSiR^1R^2Me$ was formed. Two possible reaction pathways have been suggested for this reaction: (a) a substitution–metallation mechanism; or (b) a metallation–elimination–addition mechanism (Scheme 6).

$(Me_3Si)_3SiLi$ slowly decomposes in THF or Et_2O. However, if THF (or Et_2O) is changed to pentane, silyllithium can be isolated in a high yield to give colorless crystals containing THF as a solvate: $(Me_3Si)_3SiLi \cdot 3THF$ [97]. This material is soluble in hydrocarbon solvents such as pentane or toluene, and this is useful in performing the coupling reactions of $(Me_3Si)_3SiLi$ with electrophiles in non-polar solvents, in which these reactions usually proceed more cleanly and in higher yields. The ^{29}Si-NMR signal for the central silicon atom appears at a much higher field (δ -185.4) than that of the $(Me_3Si)_4Si$ (δ -135.5) [97]. In the mixed solvent $C_7D_8–C_6D_6$, the ^{29}Si resonance appeared at δ -189.4 in the form of a quartet due to coupling with the neighboring ^{7}Li atom, which means that $(Me_3Si)_3SiLi$ is monomeric under these conditions and the Si–Li bond has a partial covalent character [103]. X-ray crystallography [24,103] shows that $(Me_3Si)_3SiLi$ is monomeric in the solid state and has a shape of distorted tetrahedron; Si–Si–Si bond angles are reduced from the normal 109.5 to 102.4° (Fig. 8). Similar distorted structures have been reported also for $(Me_3Si)_3SiLi \cdot 1.5DME$ and for co-crystals of $(Me_3Si)_3SiLi \cdot (Me_3Si)_4Si$. Other alkali metal derivatives have been prepared by Klinkhammer by the alkali metal–Group 12 metal exchange reaction in pentane or heptane [104,105]. These compounds are dimeric in the solid state; in the case of Li and K derivatives, cyclic dimers are almost planar, whereas in the case of the Na compound, the folding angle is about 170.9° (Eq. (44)).

$$M'[Si(SiMe_3)_3]_2 \xrightarrow{M} 2MSi(SiMe_3)_3 + M' \tag{44}$$

$$M = Li,\ Na,\ K,\ Rb,\ Cs;\ M' = Zn,\ Cd,\ Hg$$

Other types of branched silyllithiums have also been prepared from the corresponding silanes by reaction with MeLi: $(HMe_2Si)_3SiLi$ [106], $({}^tBuMe_2Si)(Me_3Si)_2SiLi$ [102,107], and $({}^tBuMe_2Si)_2(Me_3Si)SiLi$ [107]. Trimethyltin-substituted silyllithium $(Me_3Sn)_3SiLi$ was synthesized by the reaction of $(Me_3Sn)_4Si$ with MeLi [108,109] (Eq. (45)).

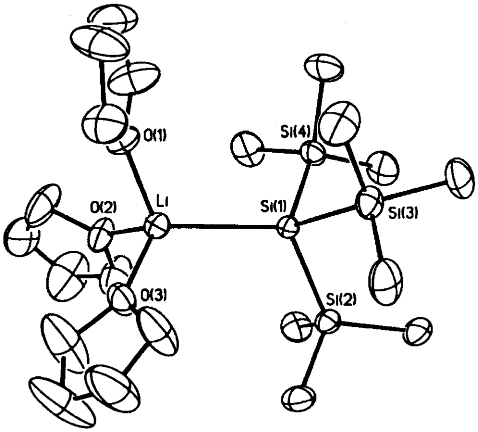


Fig. 8. Crystal structure of $(Me_3Si)_3SiLi \cdot 3THF$ (Ref. [24]). Reprinted with permission from Elsevier Science.

$$(Me_3Sn)_4Si + MeLi \xrightarrow{THF} (Me_3Sn)_3SiLi + SnMe_4 \tag{45}$$

An interesting example of 1,1-dilithiosilane $(Me_3Si)_2SiLi_2$ has been reported by the thermal redistribution of $(Me_3Si)_3SiLi$ at 140–150°C. Prolonging the reaction time caused the formation of the disilane $(Me_3Si)_3SiSi(SiMe_3)_3$ [110] (Eq. (46)).

$$(Me_3Si)_3SiLi \xrightarrow{140-150°C} (Me_3Si)_2SiLi_2 + (Me_3Si)_4Si + Me_3SiSiMe_3 + (Me_3Si)_3SiSi(SiMe_3)_3 \tag{46}$$

2,2-Dilithio-1,1,1,3,3,3-hexaisopropyltrisilane, $(^iPr_3Si)_2SiLi_2$, was isolated as air- and moisture-sensitive yellow crystals by the reaction of 3,3-bis(triisopropylsilyl)-1,2-bis-(trimethylsilyl)-3-silacyclopropene with lithium metal in THF [111] (Eq. (47)). The dilithiosilane has a monomeric structure, the central silicon atom having nearly tetrahedral geometry with a Li–Si distance of 2.55(1) Å (av.) (Fig. 9).

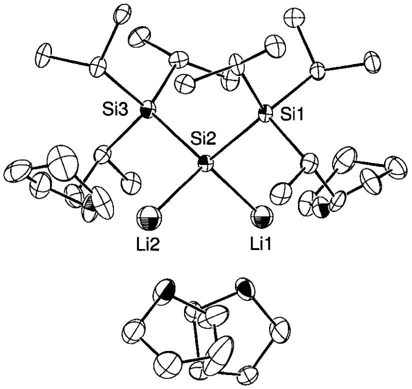
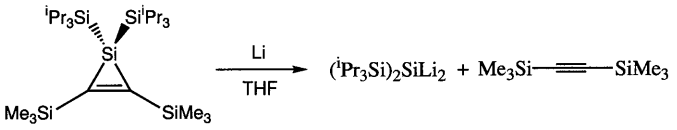


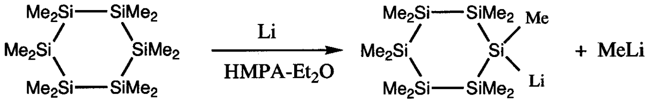
Fig. 9. Crystal structure of $(^iPr_3Si)_2SiLi_2 \cdot 4THF$ (Ref. [111]). Reprinted with permission from the Journal of the American Chemical Society.



(47)

2.4.3. Cyclic lithiooligosilanes

There is only one example of the successful preparation of a cyclic silyllithium compound: cyclohexasilanyllithium. This compound was prepared from dodecamethylcyclohexasilane by reaction with two equivalents of lithium metal in HMPA–Et$_2$O mixed solvent [112] (Eq. (48)).



(48)

Surprisingly, in this reaction not Si–Si, but selectively Si–C bond cleavage was detected, even in the presence of excess lithium. This silyllithium $Me_{11}Si_6Li$ is quite stable in HMPA for several weeks at r.t. in the dark and can be trapped by different electrophiles, such as ethylbromide or trimethylchlorosilane to produce the expected products in moderate yields. The negatively charged silicon atom shows a signal in the ^{29}Si-NMR at δ -108.1. Alternatively, $Me_{11}Si_6Li$ can be synthesized from cyclohexasilane by the action of MeLi, ^{n}BuLi or PhLi in HMPA–Et$_2$O [112]. Such reactions are not completely clean; some linear oligosilanes were also formed, due to Si–Si bond cleavage. In contrast, cyclotri-, tetra- and pentasilyllithiums cannot be prepared by this route from the corresponding cyclotri-, tetra- or pentasilanes, because of cleavage of the Si–Si bonds upon the action of lithium metal. Thus, reaction of cyclopentasilane with lithium produces 1,5-dilithiosilane $Li(Ph_{10}Si_5)Li$ [90] because of Si–Si bond cleavage, whereas reaction of cyclopentasilane with MeLi in HMPA gives a complex mixture of acyclic oligosilanes [112]. The reason for such a difference in the reactions of cyclic oligosilanes with lithium is still unknown. One possible explanation is the thermodynamic stabilization of $Me_{11}Si_6Li$ due to the negative charge delocalization into the silicon framework [112]. Thus, for example, it is known, that thermodynamic stability increases from Me_3SiLi to $(Me_3Si)_3SiLi$: $Me_3SiLi < (Me_3Si)Me_2SiLi < (Me_3Si)_3SiLi$ [96].

3. Application of lithiosilanes to the synthesis of polysilane dendrimers

Dendrimers are highly branched, regular, three-dimensional, tree-like monodisperse macromolecules, later generations of which have a globular shape [113]. Dendrimers with functional groups on the surface have some specific properties, such as solubility, viscosity, thermal behavior, etc. therefore they are very interesting and promising as precursors for new advanced materials. After the pioneering work on the first preparation of dendritic molecules by Vögtle in 1978

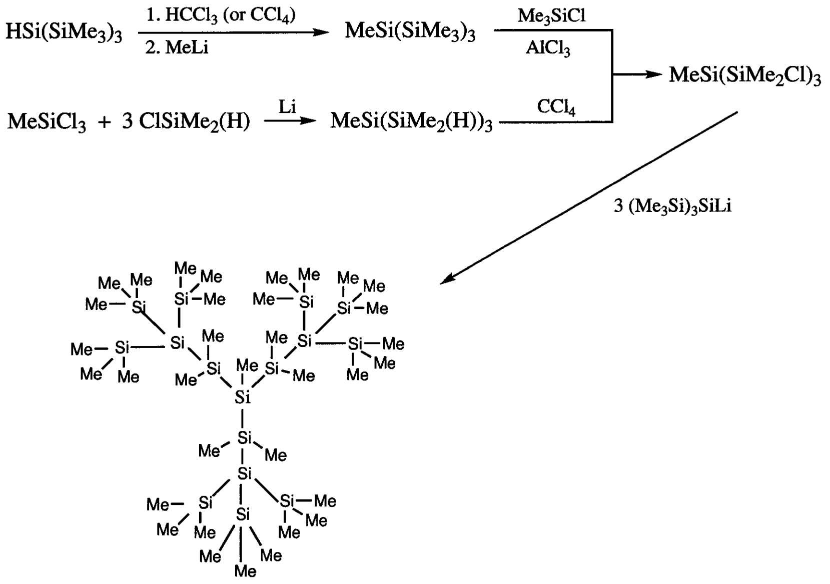
[114], great attention has been paid to the synthesis and study of new dendrimers. Two synthetic strategies have been used: the divergent growth approach developed independently by Tomalia [115,116] and Newkome in 1985 [117], and the convergent approach introduced by Hawker and Fréchet in 1990 [118]. Both methods consist of repetition of the reaction sequence, allowing growth of the dendrimers step-by-step, that is, generation by generation.

Using these two synthetic routes, a variety of dendritic molecules has been prepared, which is reflected in the number of recent reviews devoted to this field of chemistry [119–126]. They are concerned mainly with organic dendrimers, and only a few of them were devoted to main group elements containing dendrimers [127–132], although these can have interesting and unusual characteristics, such as optical properties and the possibility of surface functionalization. The latest reviews were thoroughly written by Majoral and Caminade [133] concerning the synthesis of B-, Si-, Ge-, P- and Bi-containing dendrimers, and Newkome et al. [134] devoted to metallodendrimers, including both main group and transition metals.

There are three types of linkage, which are used at the branching points: Si–O (siloxane dendrimers), Si–C (carbosilane dendrimers) and Si–Si (polysilane dendrimers). Historically, siloxane-type dendrimers were synthesized as the first example of heteroatom-containing dendrimers in 1989 by Rebrov et al. [135]. Carbosilane dendrimers, which are the most important class of silicon-containing dendrimers because of their chemical and thermal stability and the possibility of synthesis high generations of these molecules, were prepared for the first time in 1992 by van der Made et al. [136]. Polysilane dendrimers have been known since 1995, when the groups of Lambert [137], Suzuki [138] and Sekiguchi [139] independently reported the synthesis of such dendrimers with homocatenated chains composed of silicon atoms. Silicon-containing dendrimers represent a very large field in dendrimer chemistry and they have been the subject of several previous reviews (see, for example: Refs. [133,134]). Therefore, only polysilane dendrimers will be considered in the present article in the light of the application of silyllithium compounds for their synthesis.

The first dendrimers reported by Lambert [137] and Suzuki [138] had the same structure. They were characterized by X-ray analysis after synthesis by the coupling reaction of $MeSi(SiMe_2Cl)_3$ and $(Me_3Si)_3SiLi$, thus affording the first generation dendrimer containing 15 Si atoms (Scheme 7).

Other types of polysilane dendrimers (up to the second generation) have also been prepared and structurally characterized by Lambert: $MeSi[SiMe(SiMe_3)_2]_3$ [140], $MeSi[SiMe_2Si(SiMe_3)_3]_3$ [140], $HSi[SiMe_2SiMe(SiMe_3)_2]_3$ [140], $MeSi[SiMe_2SiMe(SiMe_3)_2]_3$ [141] and $MeSi[SiMe_2(SiMe_3)_2SiSiMe_2SiMe_2Si(SiMe_3)_3]_3$ [142]. Another methodology using silyllithium compounds as the versatile building block for the preparation of polysilane dendrimers up to the second generation has been adopted by Sekiguchi's group. The first example of the second generation permethylated polysilane dendrimer, which was the largest pure synthetic polysilane at that time, prepared by the divergent method, was described in 1995 [139]. Silyllithium compounds necessary for this dendrimer were synthesized by the lithium–mercury exchange reaction. Thus, $PhMe_2SiMeSi(Li)SiMe_2Ph$ (**1a**) was used



Scheme 7.

as a key intermediate, which was prepared and isolated as yellow crystals by reaction of $Hg[Si(SiMe_2Ph)Me]_2$ and Li in toluene in 80% yield (see Eq. (35)).

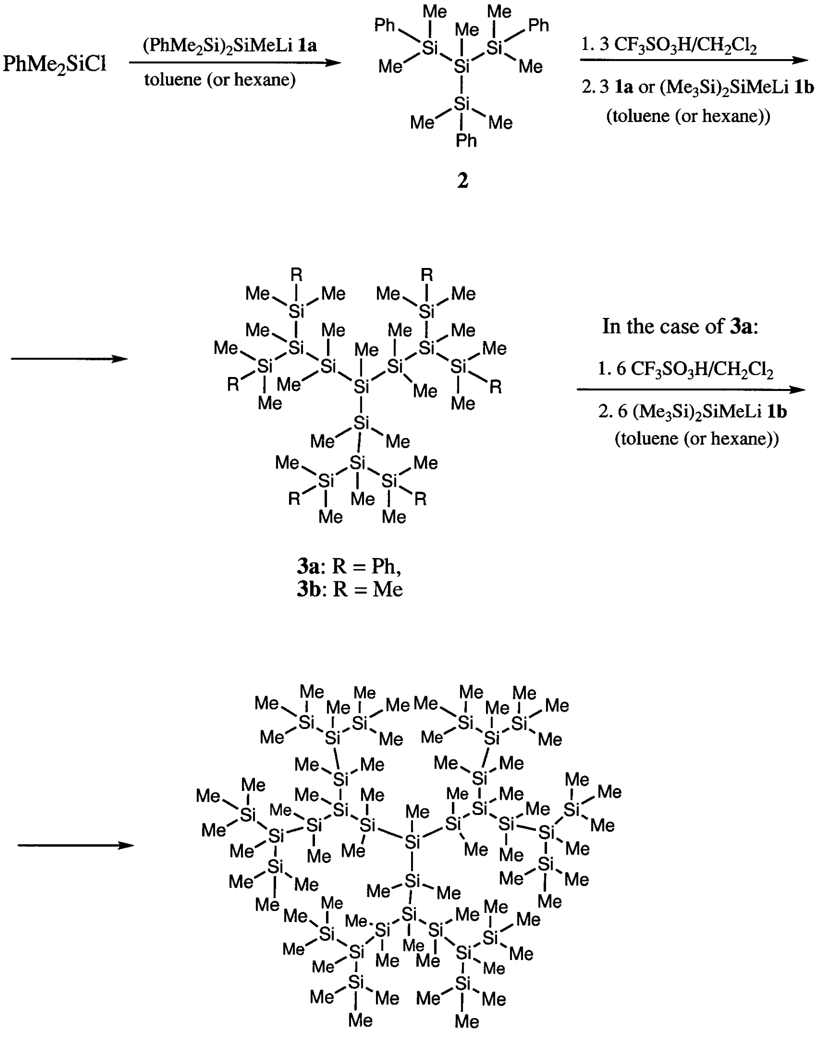
For the preparation of polysilane dendrimer, $PhMe_2SiCl$ was first reacted with **1a** in toluene to give colorless crystals of **2** possessing a core and three branching points for the polysilane dendrimer. The resulting compound **2** was then treated with three equivalents of trifluoromethanesulfonic acid in dichloromethane followed by reaction with **1a** in toluene to yield the first generation, **3a**, in 43% yield. The permethyl-substituted polysilane dendrimers were synthesized by use of $Me_3SiMeSi(Li)SiMe_3$ (**1b**). Thus, treatment of **3a** with six equivalents of trifluoromethanesulfonic acid in dichloromethane followed by reaction with **1b** resulted in the formation of the second generation **4** in 29% yield as colorless crystals (Scheme 8). Dendrimer **4** contains 31 silicon atoms and 30 Si–Si bonds. Its enhanced electronic properties include an extinction coefficient $\varepsilon = 9.64 \times 10^4$ at $\lambda_{max} = 279$ nm, which is two times larger than that of **3b** ($\lambda_{max} = 269$ nm, $\varepsilon = 4.91 \times 10^4$).

The structure of **4** was confirmed by X-ray crystallography (Fig. 10). The longest chain has 11 silicon atoms. The polysilane chain of the dendrimer consists of orthogonal (*O*) and anti (*A*) conformations (*O* and *A* are torsion angles of the Si–Si–Si unit in the range of 80.4–99.6 and 139.9–164.4°, respectively).

The structures of the first generation of phenyl- and permethyl-substituted polysilane dendrimers **3a** and **3b** were also determined by X-ray crystallography [143]. $PhMe_2SiMeSi(Li)SiMe_2Ph$ (**1a**), a key synthon in this synthesis, was previously synthesized by a lithium–mercury exchange reaction, which is not suitable for a gram scale synthesis of dendritic polysilanes. Therefore, another method for the preparation of silyllithium reagent was applied; treatment of $\mathrm{MeSi(SiMe_2Ph)_3}$ with MeLi in $\mathrm{THF{-}Et_2O}$ produced the desired silyllithium together with the formation of $\mathrm{PhSiMe_3}$ (Eq. (49)).

$$\mathrm{Me(PhMe_2Si)_3Si} \xrightarrow[\mathrm{THF/Et_2O}]{\mathrm{MeLi}} \mathrm{Me(PhMe_2Si)_2SiLi} + \mathrm{PhSiMe_3} \qquad (49)$$

The synthetic strategy for the preparation of phenyl-substituted first generation dendrimer **3a** was described above (see Scheme 8). The molecular structure of **3a**



Scheme 8.

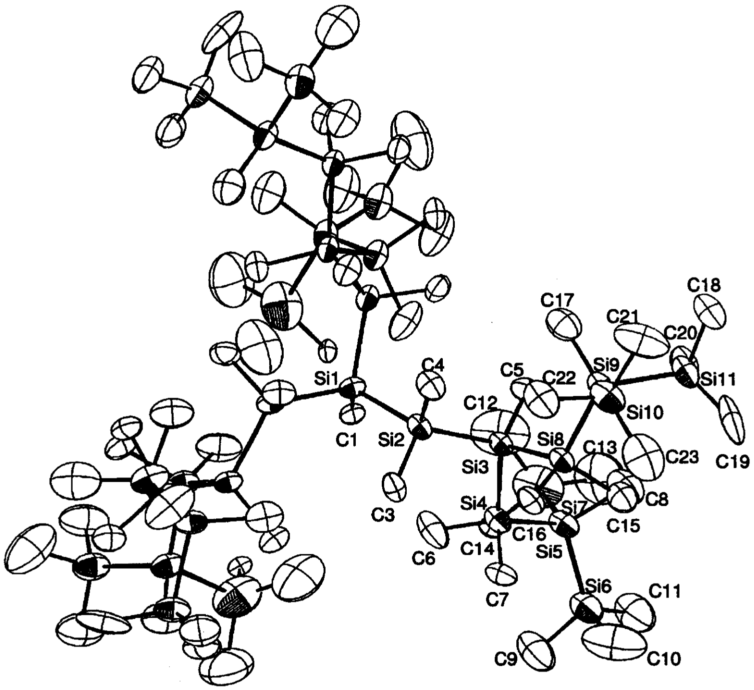


Fig. 10. Crystal structure of polysilane dendrimer **4**.

was confirmed by X-ray crystallography (Fig. 11). The Si–Si bond lengths (2.352(1)–2.384(1) Å) are within the normal range of 2.33–2.37 Å, and th inner Si–Si distances (av. 2.380 Å) are slightly longer than the outermost ones (av. 2.359 Å). Although the geometries at the branching points are nearly tetrahedral (av. 110.5°), the bond angles at the spacer are expanded (av. 114.6°). The corresponding permethyl-substituted polysilane dendrimer **3b** was prepared in 76% yield by conversion of the six phenyl groups in **3a** into methyl groups (Scheme 9).

A first generation of hybrid dendrimer with alternating Si and Ge atoms in the chains has also been synthesized by the divergent method using the above mentioned methodology [144]. $Me(PhMe_2Ge)_2SiLi$, a branching reagent for the preparation of the dendrimer, was synthesized by a lithium–mercury exchange reaction of $Hg[Si(GeMe_2Ph)_2Me]_2$ in ether. The first step in the divergent growth method was the reaction of $PhMe_2GeCl$ with branching reagent $Me(PhMe_2Ge)_2$-$SiLi \cdot (Et_2O)_n$ to give the coupled product $MeSi(GeMe_2Ph)_3$ (**5**) as the initiator core. First generation phenyl-substituted dendrimer **6** was obtained by treatment of **5** with trifluoromethanesulfonic acid followed by reaction with $Me(PhMe_2Ge)_2$-$SiLi \cdot (Et_2O)_n$ (Scheme 10). The hybrid permethyl-substituted dendrimer

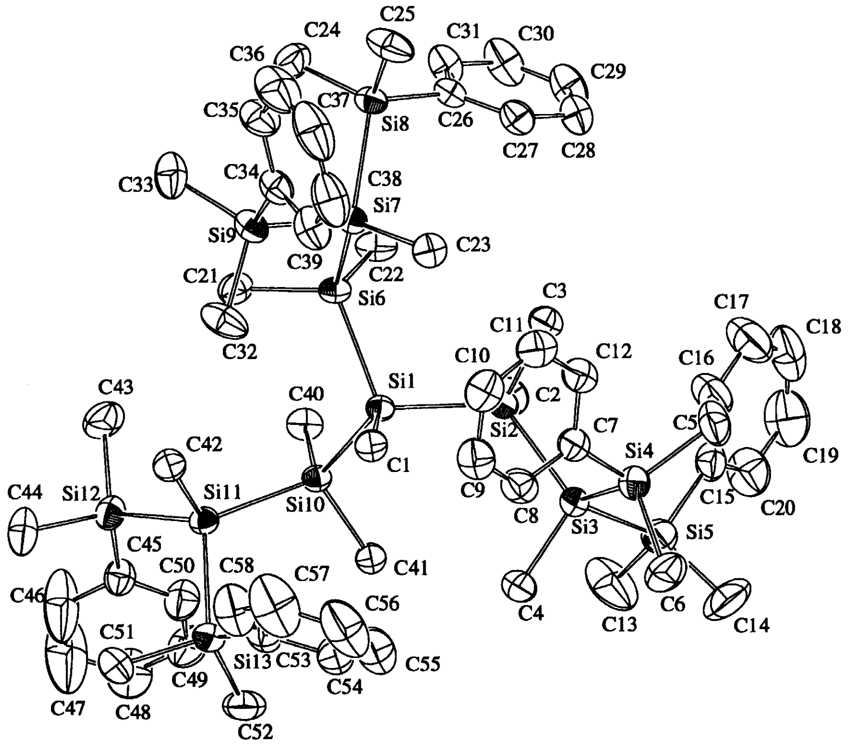
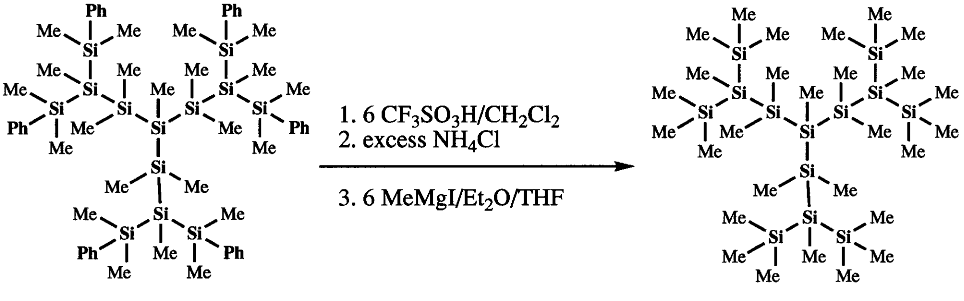


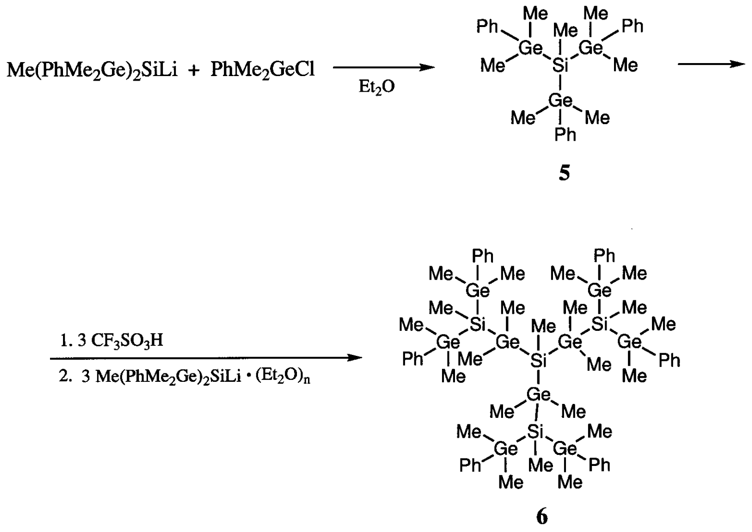
Fig. 11. Crystal structure of polysilane dendrimer **3a** (Ref. [143]). Reprinted with permission from Elsevier Science.



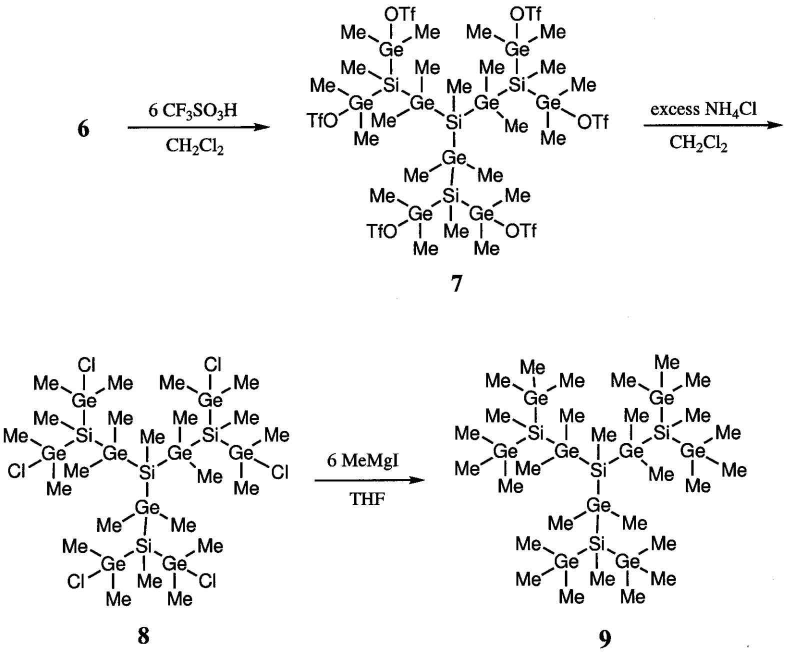
3a **3b**

Scheme 9.

was synthesized by substitution of six phenyl groups with methyl groups (Scheme 11). First, dephenylation of **6** by trifluoromethanesulfonic acid gave the hexatriflate **7** which was treated without isolation with excess of ammonium chloride to yield the hexachloride **8**. This last compound was subsequently reacted



Scheme 10.



Scheme 11.

with MeMgI in THF to finally produce **9** as colorless crystals in 74% yield. The molecular structure of **9** was determined by X-ray crystallography (Fig. 12).

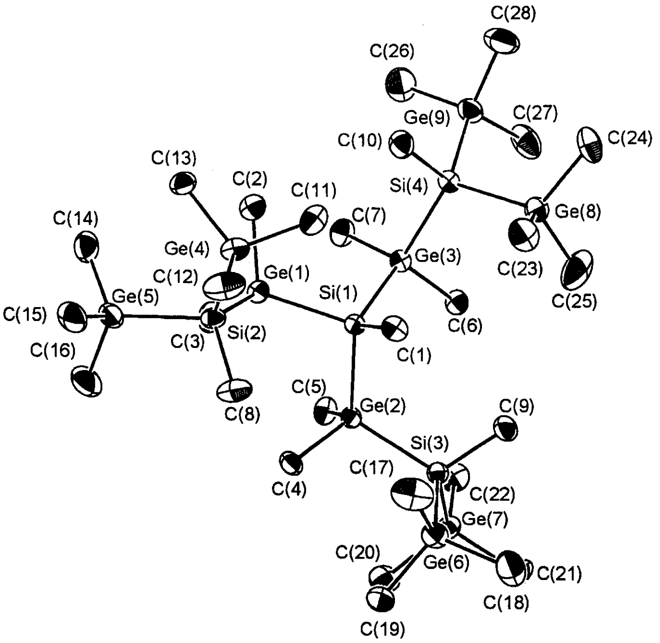


Fig. 12. Crystal structure of Si/Ge hybrid dendrimer **9** (Ref. [144]). Reprinted with permission from the Journal of the American Chemical Society.

4. Conclusions

The chemistry of silyllithium compounds remains a very interesting and intriguing field of both organosilicon and organolithium chemistry. Despite the significant progress that has been made recently, especially concerning the structural investigations of lithiosilanes, many questions still have to be clarified and developed. These concern, first of all, the preparation methods of silyllithiums (especially with functional groups) as well as their characterization by means of X-ray crystallography and NMR studies. Another reason for the study of silyllithium compounds is their application in organic and organometallic chemistry, in particular in dendrimer chemistry. Great synthetic possibilities of lithiosilanes in the synthesis of a variety of polysilane dendrimers could stimulate a new stage in the development of silyllithium compounds. Undoubtedly, one can expect great progress at the beginning of this century.

Acknowledgements

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Appendix A. Abbreviations

DME	1,2-dimethoxyethane
HMPA	hexamethylphosphoramide
LDMAN	lithium (α-dimethylaminonaphthalenide)
Mes	2,4,6-trimethylphenyl
TfO	trifluoromethylsulfonate
THF	tetrahydrofuran
Tip	2,4,6-triisopropylphenyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine

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