Structure and Bonding 155

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David Scheschkewitz *Editor*

Functional Molecular Silicon Compounds I

Regular Oxidation States

Springer

155

Structure and Bonding

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Aims and Scope

The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table and addresses structure and bonding issues associated with all of the elements. It also focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of *Structure and Bonding* to the extent that the focus is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant

The individual volumes in the series are thematic. The goal of each volume is to give the reader, whether at a university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience. Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented using selected examples to illustrate the principles discussed. A description of the physical basis of the experimental techniques that have been used to provide the primary data may also be appropriate, if it has not been covered in detail elsewhere. The coverage need not be exhaustive in data, but should rather be conceptual, concentrating on the new principles being developed that will allow the reader, who is not a specialist in the area covered, to understand the data presented. Discussion of possible future research directions in the area is welcomed.

Review articles for the individual volumes are invited by the volume editors.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.

David Scheschkewitz
Editor

Functional Molecular Silicon Compounds I

Regular Oxidation States

With contributions by

U. Böhme • G. Kickelbick • E. Kroke • C. Marschner •
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Preface

Due to its unique properties, elemental silicon is a pivotal material in modern society. Even though a few other semiconductors, e.g., gallium arsenide, rival silicon in some performance indicators such as electron mobility, none of them can equally meet the technological and economic demands of current microprocessor technology: Electronic grade silicon is available at relatively low cost and its native oxide as an insulator is predisposed to effectively separate the conducting zones of microprocessors [1]. In this arguably most important application, silicon is thus present both in the elemental state (oxidation No. 0) and in its most highly oxidized form (oxidation No. +IV). In view of the prominent role of molecular silicon compounds in related industrial processes, this volume of *Structure&Bonding* is devoted to *Functional Molecular Silicon Compounds* with silicon in various oxidation states. It is divided into two sub-volumes: the first covers topics associated to silicon compounds in the "regular" oxidation state of +IV, while the second concerns compounds in lower oxidation states.

All industrial chemical processes involved in the production/purification/transformation of silicon in its elemental form have in common that silicon in lower oxidation states is prevalent in short-lived intermediates such as silylenes and larger unsaturated aggregates [2]. The chapter by Burgert Blom and Matthias Driess (Technical Universität Berlin, Germany) summarizes recent advances in the chemistry of stable silylenes, molecular compounds in the formal oxidation state +II (Volume 2, chapter titled "Recent Advances in Silylene Chemistry: Small Molecule Activation En-Route Towards Metal-Free Catalysis"). Saturated and unsaturated silicon clusters are several steps further on the way towards elemental silicon. Recent years have seen important progress with regard to the functionalization of stable derivatives of such clusters as well as the realization of surprising new structural motifs. In chapter titled "Substituted Polyhedral Silicon and Germanium Clusters" of Volume 2 Masafumi Unno (Gunma University, Kiryu, Japan) gives an account of the developments in this area. It is probably just a question of time before silicon clusters will be routinely connected to extended systems with exciting new properties as novel materials. Oligosilane chains are predisposed as linking units for such an endeavor. Christoph Marschner (University of Graz, Austria) updates comprehensively on the preparation and functionalization of oligosilane systems in chapter titled "Oligosilanes" of Volume 1.

Initially, the research into molecular silicon compounds was driven by the mostly academic question of how much the chemistry would parallel that of its lighter cousin carbon. Naturally, the stability of unsaturated derivatives was at the center of attention. Frederic Stanley Kipping – generally considered to be one of the most influential pioneers of organosilicon chemistry – eagerly pursued the synthesis of "silico ethylenes" [3] and "silicones" [4] – the heavier analogues of alkenes and ketones, respectively. The first reliable reports on stable compounds with heavier double bonds to silicon, however, only appeared in 1981. Since these milestone achievements on compounds with Si=Si (West et al.) [5] and Si=C bonds (Brook et al.) [6], the chemistry of molecular silicon compounds has matured considerably. Especially during the first decade of the new millennium the focus has shifted from the replication of well-known carbon motifs from organic chemistry to the introduction and tolerance of functional groups. The contribution by Takeaki Iwamoto and Shintaro Ishida (Tohoku University, Sendai, Japan) gives an overview of recent developments regarding Si=Si double bonds (Volume 2, chapter titled "Multiple Bonds with Silicon: Recent Advances in Synthesis, Structure, and Functions of Stable Disilenes").

With the powerful concept of stabilization of reactive main group species by strongly σ-donating *N*-heterocyclic carbenes pioneered inter alia by Greg Robinson [7], some of Kipping's initial targets are now available as derivatives stabilized by coordination of *N*-heterocyclic carbenes. Eric Rivard (University of Alberta, Edmonton, Canada) summarizes this emerging new field from the point of view of low valent silicon chemistry in chapter titled "Recent Advances in the *Heterocyclic Carbene-Supported Chemistry of Silicon*" of Volume 2. Interestingly, however, *N*-heterocyclic carbenes were initially employed by Kuhn et al. for the expansion of the coordination sphere of molecular silicon compounds beyond the usual four substituents [8]. Since it is now well established that this expansion does not entail hypervalency, low valent compounds with higher coordination numbers are one possible approach to increase the functionality of hypercoordinate silicon species. The various aspects of higher coordinate silicon compounds are comprehensively reviewed by Jörg Wagler, Uwe Böhme, and Edwin Kroke (Technical University Bergakademie Freiberg, Germany) in chapter titled "Higher-Coordinated Molecular Silicon" of Volume 1.

Having been unsuccessful in the original tasks, Kipping became disillusioned regarding any commercial value of his discoveries towards the end of his career [9]. As Thomas Edison said, however, "just because something doesn't do what you planned it to do does not mean it's useless" (As quoted in: [10]). Kipping's discoveries indeed laid the foundations for the nowadays ubiquitous application of polysiloxanes (colloquially known as silicones) in daily life. Silsequioxanes – already mentioned by Kipping as formally having the empirical formula of an anhydride $(R_2SiO)_2O$ [9] – are increasingly being used as precursors for sophisticated hybrid materials involving polysiloxanes. In his chapter, Guido Kickelbick

(Saarland University, Saarbrücken, Germany) gives an overview of the fundamental sciences and high-end applications of silsequioxanes (Volume 1, chapter titled "Silsesquioxanes").

Finally, two chapters are devoted to the most extreme of functionalization: ionization. The generation of silyl cations and anions provides valuable synthons, e.g., for the further extension of the silicon scaffold. In chapter titled "Silylium Ions" of Volume 1, Thomas Müller (University of Oldenburg, Germany) summarizes the many applications of silylium cations in catalysis and discusses recent trends towards low valent silicon cation chemistry thus completing the full circle to other chapters that are more explicitly devoted to low valent silicon species. Finally, the chemistry of silyl anions is summarized in chapter titled"Silyl Anions" of Volume 2.

Initially, only one volume was envisaged for the topic of functional molecular silicon chemistry, but it rapidly became clear that with the dedicated hard work and enthusiasm of all authors two volumes would be needed to accommodate the vast progress in that area during the last 10 years: the field keeps growing in an exponential manner. The ready availability of this exiting element at very low cost paired with the inquisitiveness and passion of organosilicon chemists will ensure that this trend continues for a long time to come.

Saarbrücken, Germany David Scheschkewitz
September 2013

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Silsesquioxanes

Guido Kickelbick

Abstract The diversity of structures of silsesquioxanes with the general composition $(RSiO_{1.5})_n$ is great and involves amorphous compounds, ladder structures, open cages, and polyhedral oligomeric silsesquioxane (POSS) molecules. The obtained structure morphology depends strongly on the applied reaction conditions. The enormous amount of potential substitution patterns combined with the chemical and thermal robust silicon oxide core makes silsesquioxanes ideal materials for a variety of applications. This review covers the structures and synthetic approaches of this type of compounds as well as their properties and potential applications. It focuses on results obtained in the last decade.

Keywords Functional materials · POSS · Silicon oxide · Silsesquioxanes

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Abbreviations

BET	Brunauer–Emmett–Teller method for surface area analysis
iPP	Isotactic polypropylene
MA-POSS	Methacrylcyclopentyl-POSS
Me_8T_8	Octamethyl-POSS

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MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
OLED	Organic light-emitting diode
PDA	1,4-Phenylenediamine
PDMS	Polydimethylsiloxane
PI	Polyimide
POF	Poly(9,9′-dioctylfluorene)
POSS	Polyhedral oligomeric silsesquioxanes
PP	Polypropylene
SCP	Stepwise coupling polymerization
TBAF	Tetrabutylammonium fluoride
TEOS	Tetraethylorthosilicate (or tetraethoxysilane)
TDSS	Tetrakisdimethylsiloxysilane

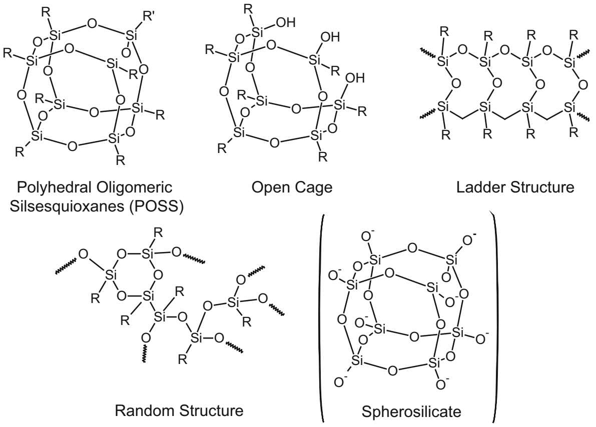
1 Introduction

Silsesquioxanes are a family of compounds that can be summarized by the general chemical formula $(RSiO_{1.5})_n$, in which R can be any kind of organic group and H, but not O. The name has its origin in the Latin prefix "sesqui" meaning one and a half, which represents the number of oxygen atoms per molecular unit.

While the chemical formula of the smallest building block is quite simple there is a large variety of structures of silsesquioxanes, which also lead to a broad range of properties and consequently to different applications of these molecules, not to mention the plethora of organic substituents R attached to the Si atom that also leads to variations in the properties of the final materials.

The four most common structures described in literature are (1) closed cage compounds known as polyhedral oligomeric silsesquioxanes (POSS), (2) open cage structures where at least one of the Si atoms in the vertices is removed, (3) ladder structures in which two chains are connected at regular intervals by Si–O–Si bonds, and (4) random structures that do not show any regular organization. The variations are based on the various substitution patterns of the Si atom in the precursor unit. It always carries four substituents in a tetrahedral environment, three of which are oxygen atoms that act as connecting units to other silicon atoms. From the point of view of dimensionality one-, two-, or three-dimensional objects can be formed by this type of connections.

The nanometer dimension of the formed silsesquioxane structures in combination with other properties moved this class of compounds in the focus of scientific interest in recent years, mainly because they can be used as building blocks in nanocomposites. The major advantage of silsesquioxane structures in the preparation of this materials class is the diversity of possible functional groups, which are combined with their three-dimensional structure. The silica core provides rigidity paired with thermal and mechanical properties, which are related to typical ceramics, while the organic groups provide functionalizations that can act not only as compatibilizers to enhance the processing of the materials but also as binding linkers to an organic matrix. This



Polyhedral Oligomeric Silsesquioxanes (POSS)

Open Cage

Ladder Structure

Random Structure

Spherosilicate

Fig. 1 Structural variety of silsesquioxane compounds and comparison to a spherosilicate

mixture of inorganic and organic functions with the nanometer-size dimensions leads to properties intermediate to those of classical ceramic and polymer materials. Due to the synergistic effects of both worlds new properties are generated when silsesquioxanes are combined with traditional molecules or materials, which in most cases are superior to that of the traditional materials.

In this chapter some major trends in silsesquioxane chemistry in the last decade are summarized, focusing on the formation of the structures and their use in various applications.

2 Main Text

2.1 *Structures, Synthesis and Properties*

The different structures of silsesquioxanes are based on the connection and the regularity of the basic $RSiO_{1.5}$ units. Cage structures are discrete one-dimensional objects with a symmetric core structure, while random structures are three-dimensional without any order (Fig. 1). In contrast, the two-dimensional ladder structures show a degree of order that is based on the substituents connected to each silicon atom. All morphologies have in common the same substitution pattern at each Si atom, namely three oxygen and one carbon or a hydrogen atom. Only compounds with this composition belong to the silsesquioxane class. In literature often spherosilicates are mixed with silsesquioxanes, particularly in literature regarding polyhedral silsesquioxanes, because of the similarity of their structural motifs, i.e., in both cases there exists a cube-like structure. In the case of spherosilicates, however, this cube has the composition $Si_8O_{20}{}^{8-}$. The vertices in this compound class feature a substitution pattern at the Si atom of four oxygen substituents; therefore this compound belongs not to the silsesquioxanes. This review will consequently focus on the chemistry of silsesquioxanes and spherosilicates are excluded from discussion.

The structural motif that is formed during the synthesis depends on the type of precursors, the stoichiometry of reactants in the solution, and the preparation method. As confirmed by various examples, small differences can lead to the formation of undesired structural motifs or to large amounts of side products.

2.1.1 Cage Compounds

In recent years a large interest in POSS materials developed in science and technology. This is particularly based on the properties of these cage compounds. They show a rigid framework structure closely related to that of silica, which is one of the major fillers in nanomaterials. Additionally, due to their size and the organic groups attached to the core, they offer a unique opportunity for preparing truly molecularly dispersed nanocomposites.

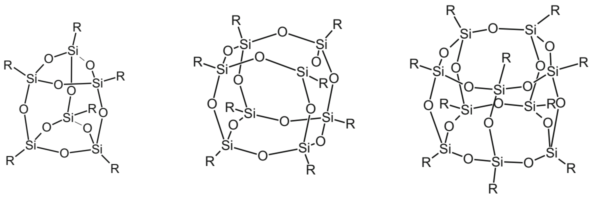
POSS cages with the chemical composition $(\mathrm{RSiO}_{1.5})_n$ exist in various sizes with $n = 6, 8, 10, \ldots$ (Fig. 2). By far the most prominent representative of this class is the cubic octahedron ($n = 8$). These compounds have nanoscale sizes with diameters ranging from 1 to 3 nm. Therefore they are ideal well-defined inorganic compounds for the preparation of nanocomposites. The internal core can be viewed to be the smallest cutout of the silica structure.

Different substitution patterns at the vertices of the cage structures can be achieved: identical substitution at each corner as in the cases of octa(hydrido) silsesquioxane and octa(vinyl)silsesquioxane or differing substitution at one corner as in the cases of methacrylate cyclohexyl POSS and glycidylisobutyl POSS (Fig. 3). Based on the different numbers of organic groups (R) with reactive functionalities, POSS can be classified as nonfunctional, monofunctional, or polyfunctional. The large variety of substitution patterns allows silsesquioxanes and specifically POSS to be incorporated into almost any conventional polymer either by blending or by covalent attachment. Therefore the compounds are ideal precursors for the synthesis of inorganic–organic hybrid nanomaterials.

In silicon chemistry building blocks of molecular structures containing Si–O bonds are often abbreviated by the following nomenclature: Q units represent Si atoms surrounded by four oxygen atoms, T units are those with three oxygen and one organic rest, and D and M units are consequently those with two or one oxygen supplemented by organic groups, respectively. Therefore silsesquioxanes are exclusively composed of T units.

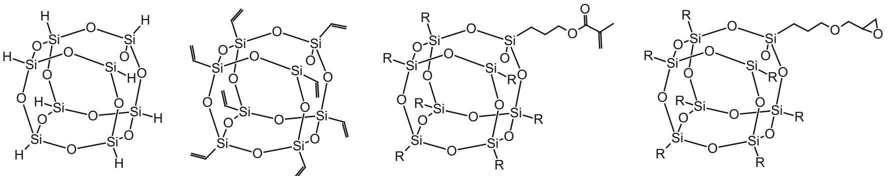
The first POSS cage compounds were synthesized in the 1940s when Scott isolated the highly symmetric $\mathrm{Me_8T_8}$ system by thermal rearrangement of branched-chain methylpolysiloxane [1]. However, a proper characterization was not possible until 1955 when X-ray crystallography revealed the structure of the compound [2]. Over the years both acid- and base-catalyzed methods have shown their capability in creating POSS molecules with a variety of organic groups R but often in relatively low yields [3].

Generally the formation of the cage structures is a difficult process that involves careful control of several parameters, such as the concentration of silane precursor in



$(RSiO_{1.5})_6$ $(RSiO_{1.5})_8$ $(RSiO_{1.5})_{10}$

Fig. 2 Silsesquioxane cages with different sizes



Octa(hydrido)-silsesquioxane H^8T^8

Octa(vinyl)-T^8-silsesquioxane

Methacrylate Cyclohexyl POSS (R = cyclohexyl)

Glycidylisobutyl POSS (R = isobutyl)

Fig. 3 Cubic POSS derivatives with different substitution patterns

the solution, nature of the solvent, type of catalyst employed, character of substituent R, and functional group in the initial silane precursor, temperature, solubility of the POSS in the reaction environment, quantity, and – most importantly – the rate of addition of water as the hydrolyzing reagent.

Critical parameters are the temperature: higher temperatures result in highly condensed polymers and therefore the temperature needs to be kept low. Slow addition of water helps to keep the concentration of silanol groups low in the reaction medium. Careful selection of the solvent, which is most of the times an alcohol, can stabilize the silanol groups formed.

Higher yields of POSS are available with a recently developed method by applying tetrabutylammonium fluoride (TBAF) as a catalyst under scarce-water hydrolysis conditions [4–7]. The resulting POSS materials contain a fluoride ion trapped in the center of the cage, and thus the materials are denoted $F^{-}@R_8T_8$. The resulting silsesquioxanes cage represents also a new type of POSS carrying a charge. It was shown that the effectiveness of the synthesis of a F^{-}@POSS molecule depends on the electronic properties of the organic groups connected to the silicon atoms. Electron-withdrawing capping groups induce a positive charge in the center of the cage, which stabilizes the F^{-}@POSS structure and also leads to an effective mechanism for F^{-} encapsulation [8].

Another intriguing property of POSS molecules is their tendency to crystallize, which is often observed in nanocomposites. This property renders the cage molecules potential “recognition elements” for supramolecular assembly processes. In consequence the methodology can be even applied for the assembly of nanoparticles. Au-nanoparticles were assembled using a two-stage assembly strategy coupling hydrogen bond-mediated interactions with POSS–POSS self-assembly [9]. Also electrostatic interactions between quaternary ammonium-ion functionalized POSS with

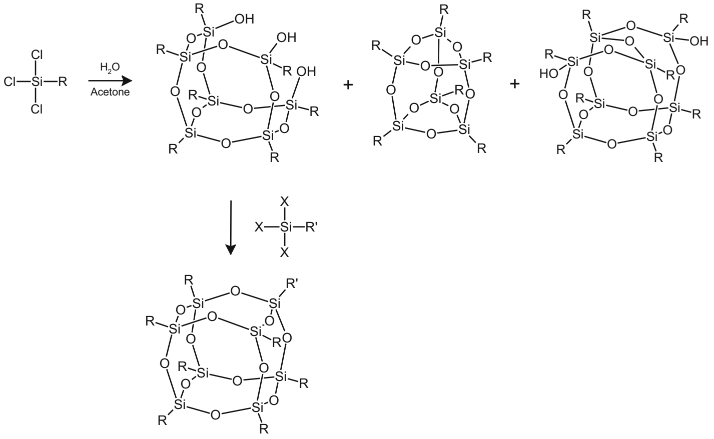


Fig. 4 Synthesis of monofunctional POSS derivatives

carboxylic acid modified Au-particles can be used for self-assembly of nanoparticles [10].

Monofunctional Polyhedral Silsesquioxanes

Monofunctional POSS cages received a great research boost in 1989 when Feher developed methods to synthesize well-defined incompletely condensed silsesquioxanes of the type $R_7T_4D_3(OH)_3$, which allowed for the straightforward synthesis of closed cages of the type $R_7T_8(R')$ by corner-capping using a variety of trichlorosilane coupling agents [11, 12]. The synthesis of monofunctional POSS derivatives typically starts with hydrolytic condensation of organotrichlorosilanes resulting in a mixture of siloxane cages [12, 13]. The desired silsesquioxane trisilanols are of the type $R_7Si_7O_9(OH)_3$, containing seven nonreactive organic groups (R) that provide increased solubility in monomers or organic solvents. The substituents that can be found most often are cyclopentyl, cyclohexyl, or isopropyl. Subsequent reaction of the trisilanols with silane coupling agents of the type $R'SiX_3$, where R′ bears a reactive site (vinyl, methycrylate, isocyanate, epoxy, etc.) and X=Cl or alkoxide, results in corner-capped POSS molecules, containing the requested functional group (Fig. 4). Monofunctional POSS derivatives are often used as so-called macromers which are incorporated as monomers in linear polymers. This leads to the incorporation of nanoscaled units in a polymer chain. In addition to corner-capping, trisilanol POSS reacts with a wide range of main group, transition metal, and lanthanide elements to afford fully condensed metal-silsesquioxanes [14–16]. The monofunctionalized POSS can be incorporated by copolymerization into a broad variety of polymers. Chemically bonded POSS can either dangle from, or be part of, the polymer backbone.

Recent studies show that closed cubic POSS structures can also be opened at least at one edge and the resulting disilanol can be functionalized, for example, with

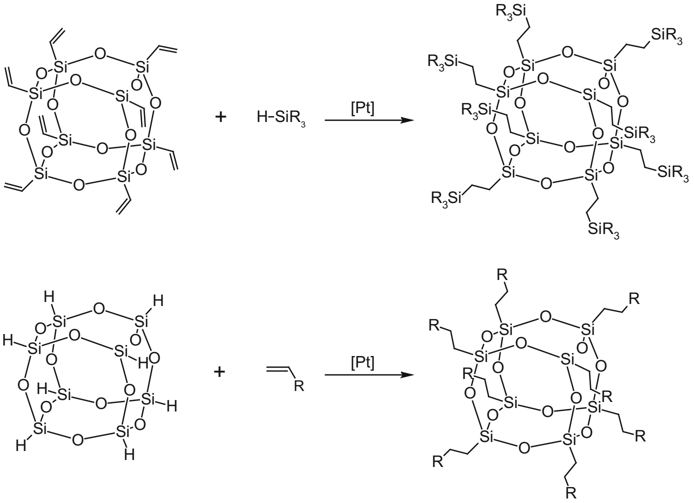


Fig. 5 Functionalization of the octavinyl- or octahydrido-POSS molecules by hydrosilation reactions

compounds of the type R_2SiCl_2, to again produce a closed polyhedron [17]. This method represents another route for the controlled functionalization of POSS systems and was applied to fluorinated POSS (F-POSS) molecules, which are useful as low surface energy materials for superhydrophobic and superoleophobic materials.

Multifunctional Polyhedral Silsesquioxanes

Various methods can be applied for the synthesis of POSS molecules with functionalizations at multiple silicon vertices. In the majority of cases eightfold-functionalized molecules are formed. The probably most studied octafunctional POSS molecules are octa(hydrido)silsesquioxane, octa(vinyl)silsesquioxane, and octa(phenyl)silsesquioxane. The first one is prepared via hydrolytic condensation of trichlorosilane in the presence of $FeCl_3$ [18]. The vinyl derivative can be prepared treating trichlorovinylsilane with hydrochloric acid and ethanol [19]. Both POSS molecules can be derivatized applying typical functionalization reactions for Si–H or Si–CH=CH_2 in the corners, such as platinum-catalyzed hydrosilation reactions (Fig. 5) [20, 21].

Octa(phenyl)silsesquioxane is prepared by hydrolysis and condensation of phenyltrichlorosilane and the subsequent rearrangement reaction catalyzed by benzyltrimethylammonium hydroxide [22]. For further derivatization this precursor has to be activated, for example, by halogenation of the phenyl rings. This complex reaction sequence is necessary because halogenated precursors such as bromophenyl silanes of the type $X_3SiC_6H_4Br$ may be readily accessible from Grignard reactions between the benzene derivative and either $SiCl_4$ or $Si(OR)_4$, but the following hydrolysis and condensation step results in only low yields of the targeted product. Therefore, octaphenylsilsesquioxane is usually brominated [23, 24]. The obtained products can undergo further derivatization by typical organic reactions [25, 26].

2.1.2 Ladder Polysilsesquioxanes

Silsesquioxane polymers can be obtained by the hydrolysis and condensation of the respective precursors of the type R–SiX_3 (X=Cl, OR′). If this condensation process is uncontrolled an amorphous product is formed, which shows different degrees of condensation and thus no well-defined structure. However, under controlled reaction conditions (specific water concentration, temperature for the initial hydrolysis and equilibrating condensation, the solvent, and the catalyst), it is possible that ladder silsesquioxanes are formed. The first example was a polyphenylsilsesquioxane reported by Brown in 1960 [27]. The high molecular weight (MW) ladder polyphenylsilsesquioxane was produced via a so called "equilibration polymerization." This discovery was the basis for further research on the formation mechanisms and variations in composition by many research groups, which was extensively reviewed in literature [28–30]. It was a long dispute between scientists whether under the reaction conditions of Brown the obtained systems have really a distinct ladder structure. In fact, the structure of polysilsesquioxanes depends enormously on the methods used for their preparation. Therefore, the preparation of a perfect stereoselective ladder polysilsesquioxane was the challenging target for many years.

Ladder polymers, which belong to the class of double-stranded polymers, possess much higher resistance to thermal, chemical, mechanical, and biological degradation than related single-chain polymers. The reasons for these special properties are that the probability of two bonds on the same ladder strand breaking simultaneously is far less than that of a single bond. Silicon-based compounds with a ladder structure are divided into two categories: oxygen-bridged ladder polysilsesquioxanes and organo-bridged ladder polysiloxanes (Fig. 6). Here, we will only deal with the silsesquioxanes.

From a synthetic point of view the synthesis of ladder polymers with a highly regular structure is very difficult, because not only bonds in one polymer chain have to be formed but also bonds to a second chain. Therefore, three bonds have to be established in a preferably stereoregular way. A very successful synthetic route towards ladder polysiloxanes is the so-called "stepwise coupling polymerization" (SCP) method (Fig. 7) [29, 31, 32]. The method involves pre-aminolysis of trichlorosilane with 1,4-phenylenediamine (PDA), hydrolysis, and polycondensation based on the H-bonding template effect. Applying this synthetic method, a large number of both nonreactive and reactive groups (such as hydrogen, methyl, phenyl, vinyl, and hydroxyl) were introduced into the structures of ladder polysilsesquioxanes.

Monomer self-organization is an important step to generate the well-ordered structure. Instead of amino-based bridges other precursor structures have been used as well. Ladder phenyl polysilsesquioxanes were formed using a three-step approach of self-assembly, lyophilization, and surface-confined polymerization [33]. For this approach the monomer 1,3-diphenyl-tetrahydroxy-disiloxane, $(Ph(OH)_2Si)_2O$, was

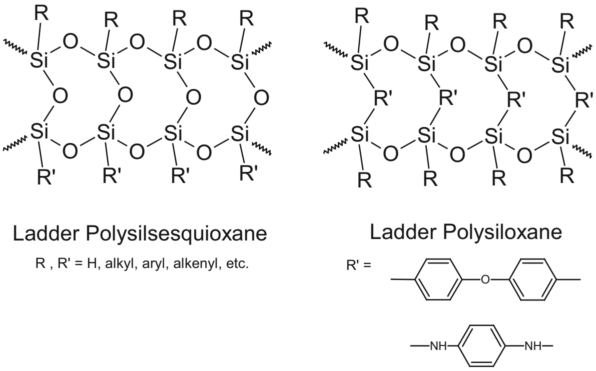


Fig. 6 Difference between ladder polysilsesquioxanes and ladder polysiloxanes

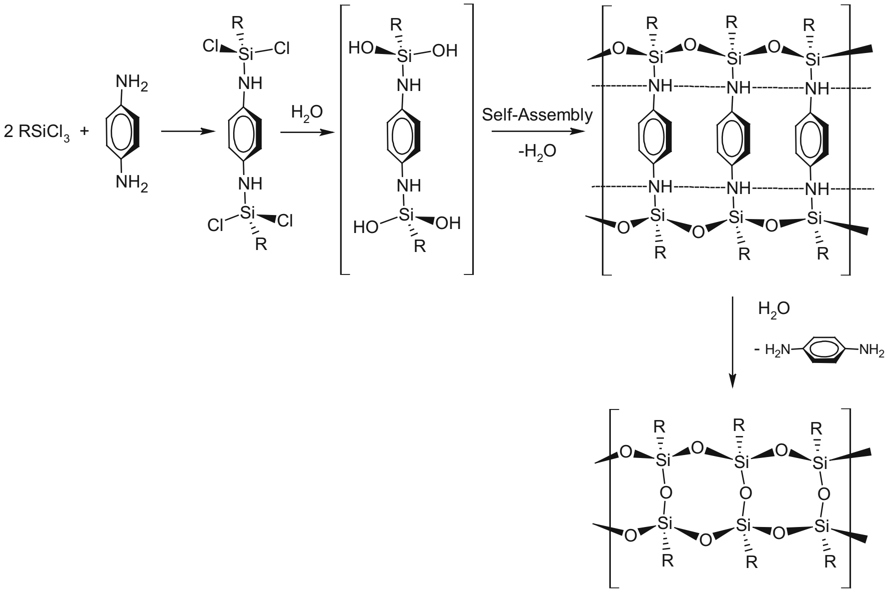


Fig. 7 Stepwise coupling polymerization in the synthesis of ladder polysilsesquioxanes

used, which already contains the Si–O–Si bridge and can be converted to polysilsesquioxane applying a dehydration reaction of the Si–OH groups. The method produces polysilsesquioxanes with a medium ladder tacticity, which was explained with the lack of organization of the monomers. An improvement of the method was achieved using additional concerted π–π stacking and H-bonding. By this approach a soluble, high molecular weight triphenylene-containing ladder polymer is formed by dehydration condensation [34].

Even quadruple-chain ladder polyphenylsiloxane structures are feasible by a supramolecular template-directed stepwise coupling and polymerization method [35].

The obtained structure possessed well-defined quadruple-chain ladder structure and extremely high thermal stability.

For the understanding of structure–property relationships in polysilsesquioxanes – particularly those based on tacticity – it is important to study smaller but well-defined and structurally characterized oligo-silsesquioxanes. The controlled synthesis of such compounds was proven by the formation of tricyclic laddersiloxanes; pentacyclic ladder siloxanes; bi-, tri-, tetra-, and pentacyclic laddersiloxanes with an all-*anti* conformation; extendible pentacyclic as well as heptacyclic ladder siloxanes; and methyl-substituted ladder polysilsesquioxane [36].

2.1.3 Other Silsesquioxane Structures

In contrast to the above-mentioned monoorgano-substituted alkoxysilanes hydrolysis and condensation of silanes with the general structure $X_3Si–R–SiX_3$ (X=OR) lead to bridged polysilsesquioxanes. The precursors contain a variable organic bridging group and at least two trialkoxysilyl groups. In these structures the organic moiety is not decorating the siloxane network structure in the periphery but is part of the overall network. Small changes in the organic component can result in large changes of the final materials properties (e.g., surface area, thermal stability). Early results in the synthesis and application of bridged polysilsesquioxane as a class of hybrid inorganic–organic materials are reviewed in literature [37]. Compared to other organosilanes as precursors in sol-gel reactions the high level of functionality of these monomers may result in their rapid gelation, even in dilute solution.

As mentioned above, in principle, all materials obtained by the hydrolysis and condensation of molecules from the type $RSiX_3$ (X=Cl, OR) lead to polysilsesquioxane. Therefore many sol-gel based materials formed from these precursors would also belong to this material class if the intermediately formed Si–OH groups completely condensed to Si–O–Si groups. In recent years particularly bridged polysilsesquioxanes starting from precursors of the type $X_3Si–R–SiX_3$ attracted much scientific interest. This type of compounds will not be covered by this article and interested readers are pointed to other review articles [38, 39].

2.2 Applications of Silsesquioxanes

2.2.1 Surface Chemistry

By far the most studied applications of silsesquioxanes are based on the POSS structures. The open POSS cubes of the type $R_7Si_7O_9(OH)_3$ as well as silanol group containing closed cage structures such as $R_7Si_7O_{12}SiOH$ are applied as molecular models of the silica surfaces. This is of particular interest in studies regarding the catalytic activity of immobilized transition metal complexes. The silsesquioxanes mimic the surface of silica supports on a molecular scale, which makes them interesting due to the fact that routine chemical analytic techniques such as liquid

NMR or X-ray structure analysis can be used to clarify the structure and reactivity of the catalytic active species on the surface. Examples are heterogeneous olefin metathesis catalysts [40]. A recent review gives an overview of POSS synthesis, derivatization, and properties [41]. Open cage structures are not only used for mimicking silica surfaces, but they can also react with silica surfaces to change their properties, for example, from hydrophilic to hydrophobic. This is achieved by an umbrella-type effect, where the silanol groups of the open cage interact with the silica surface and the bulky cage with its alkyl ligands is directed away from the surface and protects it from interactions with the environment. In addition open cage POSS molecules can be incorporated in sol-gel materials to alter their structure. One example is the use for functionalization of silica aerogels [42]. These compounds have very low densities and extremely high surface areas. However, their durability is often compromised by the inherent fragility and strong moisture absorption behavior of the silica networks. Open cage structure POSS molecules carrying phenyl, isobutyl, and cyclohexyl organic side groups were incorporated into the silica aerogel structures during their synthesis. Applying this procedure a large increase in compressive modulus was achieved with <5 wt % of POSS used and a dramatical decrease in polarity with negligible changes in density was observed in aerogels modified with <5 wt % trisilanol isobutyl POSS.

POSS-based molecules can alter the chemistry of surfaces drastically either based on their rigid design and an aforementioned umbrella effect where the molecules are located on top of a surface and protect this surface by their rigid body or by their chemical groups. One example of the role of the organic groups is shown in case of fluorinated POSS molecules which can be produced by a “one-pot” synthetic method and form highly hydrophobic fluorinated surfaces by a film formation [43]. A mixture of hydrolyzed fluorinated alkyl silanes containing well-dispersed fluorinated POSS molecules can be used to coat fabrics [44]. The obtained materials reveal a self-healing super-liquid-repellent surface with excellent durability against UV, acid exposure, repeated machine washes, and severe abrasion.

2.2.2 Precursors for Porous Materials

Silsesquioxanes are also a suitable silica source for the preparation of mesoporous materials after an assembly in block copolymer composites [45]. This was possible because the maleamic acid or aminophenyl group functionalized POSS molecules stabilized the well-ordered morphologies formed by the block copolymers. The maleamic ligands can be cross-linked by a thermal treatment which stabilized the structure of the composites prior to calcination at higher temperatures. The cylindrical and spherical morphologies of the parent composites were maintained in the resulting mesoporous silica. In another approach POSS molecules with hydrolyzable alkoxysilane functions were synthesized from octavinyl-substituted POSS. The compounds thus obtained were used in a template-directed synthesis for the production of mesoporous materials. Due to the fact that not all of the eight vinyl groups are transformed, the final material showed residual vinyl groups hanging in the mesopores that were available for conversion to other functions [46].

Recently, inorganic–organic hybrid frameworks on the basis of polyoctaphenylsilsesquioxane were prepared by cross-coupling reactions [47]. The resulting well-defined covalently linked microporous framework has a narrow pore size distribution, with a BET surface area of approximately 300 m^2 g^{-1}. The strategy of using POSS as a building block with Ullmann-type chemistry as a linking method may provide an approach for constructing a wide variety of functionalized zeolitic porous organic frameworks that bridge covalent organic frameworks and zeolites.

2.2.3 Nanocomposites

There is a large interest in recent years to prepare new materials with enhanced properties for increased performance in emerging technologies. One approach in the improvement of materials properties is the creation of inorganic–organic composites in which inorganic building blocks are incorporated into organic polymers. Silsesquioxanes can act as building blocks for such type of composites. The inorganic silicon–oxygen framework stabilizes the materials and the organic functional groups provide functional sites for versatile applications. By adding inorganic components into organic polymers, mechanical, thermal, electrical, and optical properties of the pristine polymer are altered. The resulting property advances have caused much interest in nanocomposite synthesis and analysis with the promise of new applications in many fields, including (opto)electrical materials, sensors, and biomaterials. A recent review shows the potential of silsesquioxanes in the preparation of multifunctional materials [48].

Most processing routes to incorporate the inorganic building blocks into organic polymers are based on solution methods. In many literature studies in situ polymerization was used. Functionalized POSS cubes are so attractive for this processing route, because their solubility properties could easily be tailored to fit the requirements for the incorporation into a polymer. In industrial application, however, melt processing is a major route towards composite systems. Therefore, POSS-based composites were also applied in the melt-blending processing of composites [49]. The crucial point for the synthesis of these systems is the capability to disperse the inorganic moieties on the molecular scale. Similar to the solution-based synthesis there has to be a balance between polymer–POSS interactions and POSS–POSS self-interactions to obtain a homogeneous material. Therefore, the organic groups attached to the POSS cube have to be matched to the polymer backbone.

Improvement of Mechanical Properties of Polymers by Silsesquioxane Incorporation

Polysilsesquioxanes, either cube-structured, ladder silsesquioxanes, or amorphous systems, are ideal compounds for improving mechanical properties of organic polymers if blended into these materials, because there is a high control over their composition. Their morphological structures mimic either very small particles (POSS) or polymer chains (ladder silsesquioxanes). Depending on their chemical composition they can induce similar properties as silica or polysiloxanes into a polymeric material. The probably most studied compounds for potential applications are POSS cages, which can be added to virtually all polymer types by either blending [50, 51], grafting [52–54], or copolymerization reactions [55–62]. The advantage of using POSS in the design of polymer nanocomposites is primarily based on the fact that organic substituents attached to the inorganic core can be tailored to facilitate incorporation of the POSS unit into the polymer matrix. One advantage of the POSS type macromers is that the nanosized cage structures have similar dimensions as most polymeric segments or coils and due to the substituents can be tailored in such a way that the desired solubility in the monomer or polymer is obtained.

The cage structures often improve the thermal and oxidation resistance and can also reduce the flammability of the polymeric materials. Structural studies on the final products reveal that the nanocomposites often have a hierarchical structure where the POSS units agglomerate and can form crystalline structures with diameters on the length scale of tens of nanometers in the polymer especially with increasing weight fraction of POSS [63]. Detailed studies on these materials revealed that there is a strong correlation between structure, segmental dynamics, and macroscopic properties in POSS-based nanocomposites. Mechanical properties of the resulting composites depend on the state of dispersion of POSS as well as the interactions between the POSS pendant groups and the matrix, resulting in dramatically different effects ranging from stiffening the polymer [64, 65] to plasticizing the polymer [65, 66].

Octamethyl-POSS was physically blended into isotactic polypropylene (iPP) at small loadings and it was shown that the POSS molecules exhibit nanocrystals and aggregate to form thread or network structure in the nanocomposites, which promotes the nucleation rate of iPP during crystallization [67, 68]. The thermal stability of iPP/POSS nanocomposites was lower than that of pure iPP, which was explained by the inferior interaction between octamethyl-POSS and the polymer.

The introduction of monofunctional POSS macromers into an organic polymer by polymerization at the single reactive site leads to POSS-modified polymers. POSS macromers were incorporated in linear polymers, such as methacrylates, styrenics, norbornenes, ethylenes, propylenes, and urethanes in order to improve mechanical or thermal properties. If a multifunctional POSS with cross-linkable functions is used cross-linked materials are indeed formed. Star polymers are achieved if a multifunctional POSS unit contains initiator groups and a controlled polymerization occurs, such as atom transfer radical polymerization.

The major interest in the incorporation of POSS derivatives in polymers is how the structures affect the polymer to which they are attached or in which they are blended. Many studies reveal that POSS groups undergo self-assembly/association to form POSS-rich domains that strongly affect polymer properties. For example, monofunctional epoxy derivatives of POSS were incorporated into an epoxy matrix and it was shown that phase separation occurs in such a matrix, most likely because of the incompatibility of the isobutyl groups attached to the cage [69]. The resulting macrophase separation led to epoxy-rich and POSS-rich regions in the polymer. A secondary-phase separation occurred in the epoxy-rich phase during the polymerization, producing a dispersion of small POSS domains.

POSS not only leads to self-assembling phenomena but also it has a strong effect on the chain mobility in polymers. POSS has a very low mobility in the polymer structures and therefore can be viewed as anchoring points linked to the macromolecules [70]. This effect is based not only on the rigid POSS core structure but also on the chemical structure of the organic ligands. Therefore different substitution patterns at the POSS cage can lead to variations in the macroscopic properties of the polymers.

Elastomeric nanocomposites were prepared of polydimethylsiloxane (PDMS) and POSS as cross-linker and filler at the same time by reaction of octasilane-POSS with vinyl-terminated PDMS chains using hydrosilylation chemistry [71]. Furthermore, so-called super-POSS cross-linkers, consisting of two pendant hepta (isobutyl)POSS molecules attached to a central octasilane-POSS core, were also used in the synthesis of the PDMS composites. Enhanced mechanical properties relative to polymer systems prepared with the commonly applied tetrafunctional tetrakisdimethylsiloxysilane (TDSS) cross-linker at equivalent loading levels were observed. The larger super-POSS molecule showed even improved mechanical properties relative to both the TDSS and octasilane-POSS composites due to the increased volume fraction of POSS filler in the polymer matrix.

Simple blending of POSS derivatives with unreactive organic groups in a polymer matrix can already have considerable effects on the macroscopic mechanical properties. Polypropylene blends with POSS bearing different alkyl groups revealed the effect of the alkyl group length on the mechanical behavior of the blends [51]. Systematic studies of polypropylene (PP) with either octamethyl-POSS, octaisobutyl-POSS, or octaisooctyl-POSS showed that the embedded molecules have only a minor influence on the degree of crystallinity compared to neat PP. Uniaxial tensile strength tests showed that the incorporation of octamethyl-POSS induces an increase in Young's modulus and a reduction of the yield strength in comparison with unfilled PP. Contrary, octaisobutyl-POSS and isooctyl-POSS result in a decrease of Young's modulus and yield strength by increasing POSS content. This behavior is explained by POSS behaving as a kind of particle with a siliceous hard core surrounded by a hydrocarbon soft-shell, which limits the stress transfer from the matrix to the core in dependence on the length of the alkyl groups.

Other polymers that were used for the preparation of POSS nanocomposites are polycarbonates [72], dicyclopentadiene norbornenyl-based copolymers [73], and polypropylene [74].

Silsesquioxanes in Electronic Devices

Silsesquioxanes should substitute SiO_2 in low-dielectric-constant (low-κ) materials for electronics applications [75]. The advantage of silsesquioxane-based materials is that its chemical properties are similar to traditional SiO_2, making it possible to use traditional processing technology. In addition, the rigidity of the structure induced in a polymer creates two types of porosity. On the one hand, the cage compound itself has a porous structure created by the free volume in the middle of the cage. On the other hand, porosity is created due to the fact that it is geometrically difficult to link cubes through only their corners and still fill all available space. This type of porosity is not an inherent property of the cage structure but determined by the type of processing used to incorporate the compounds in a polymer network. It depends on the efficiency of polymerization and the flexibility of the organic polymerizable group. Highly porous polymers can be prepared, for example, by the hydrosilation of octavinyl-POSS with octahydrido-POSS [76, 77].

Polyimides (PIs) are widely used as dielectric and encapsulating materials in the microelectronics industry because of their good mechanical, thermal, and dielectric properties. However, their quite high dielectric constant of 3.1–3.5 makes PIs insufficient in meeting the requirement of modern electronic applications with $\kappa < 2.5$ or even $\kappa < 2.2$ for the dielectrics of the future nm technologies. A method to decrease the dielectric constant is the inclusion of pores in the material. There are various physical methods to generate pores. These techniques, however, have also a large influence on the mechanical properties of the materials. In contrast, POSS incorporation follows another concept. POSS reveals a rigid cubic silica core and a nanopore of about 0.3 to 0.4 nm in size. The advantage of POSS in this case is that it reduces the dielectric constant, without significantly affecting the mechanical properties of the polymer hybrids compared to the pristine polymer. Nanoporous POSS was covalently tethered to the prefunctionalized PI chain ends or pendant groups. Nanocomposites consisting of polyimide with POSS have been successfully synthesized by thermally initiated free-radical graft copolymerization of methacrylcyclopentyl-POSS (MA-POSS) with the ozone-preactivated poly(amic acid), followed by thermal imidization [78]. The dielectric constants of the resulting nanocomposites are lower than that of the pristine polyimide because of the increase in free volume arising from the bulky side chains, the less polar nature of the MA-POSS molecules, and the nano-voids inherent in the POSS molecules. The dielectric constants of the film can be tuned by varying the molar ratio of the grafted PMA-POSS side chains in the copolymer. Copolymers with dielectric constants approaching 2.2 could be achieved in the PI-*g*-PMA-POSS film containing 23.5 mol % MA-POSS.

Nanocomposite prepared from methylmethacrylate-POSS and trifunctional furan derivatives exhibited an ultralow dielectric constant of 1.47 [79]. This very low κ value of the material was attributed to the formation of a POSS lamellar structure.

For optoelectronic applications three-dimensional photonic crystals with complete photonic bandgaps are very interesting materials, for example, in optical integrated circuits for various applications, including localizing, manipulating, and guiding light omnidirectionally. Calculations showed that the diamond symmetry structure offers the largest complete photonic bandgaps. Such diamond-like microstructures were prepared applying epoxy-functionalized cyclohexyl POSS through either by dual-beam quadruple exposure or four-beam interference

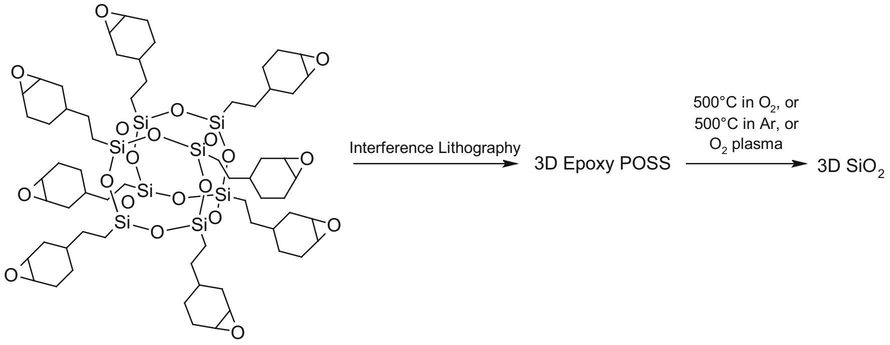


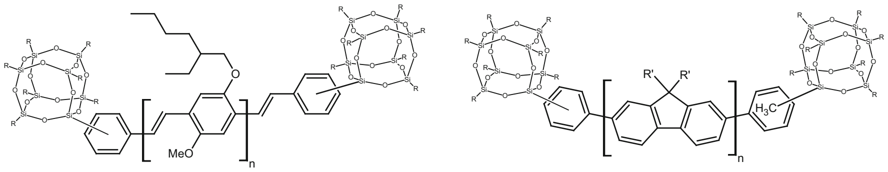
Fig. 8 Conversion of epoxycyclohexyl-functionalized POSS cage structure to silica-like structures under different conditions [80]

lithography (Fig. 8) [80, 81]. Due to the extraordinary properties of POSS like the high rigidity and content of silicon, the prepared materials showed no global volume shrinkage during thermal treatment. The resulting organosilicates can be conveniently converted to silica by thermal decomposition of the organic moieties [82]. Silica can be subsequently removed by aqueous HF treatment at room temperature. Therefore, the 3D POSS structures are attractive templates for infiltration of a wide range of organic and inorganic materials. The 3D structure resulting from the POSS cross-linking lithography method was maintained when calcinated at temperatures as high as 1100°C.

The 3D diamond photonic crystals displayed a controllable nanoroughness, which is generated on the surfaces of the 3D network due to microphase separation of the polymer chain segments in a solvent not compatible with the polymer during the rinsing step in the lithography process [83]. The degree of roughness can be tuned by the reaction parameters in the lithographic process. By combining periodic microstructure and nanoroughness new materials can be realized with superhydrophobicity and enhanced dye adsorption in addition to the photon management in the 3D photonic crystal.

Silsesquioxanes in Organic Light Emitting Diode Devices

Silsesquioxanes have been introduced into organic light-emitting materials and led to significant improvements in the performance of OLEDs [84]. There are different ways how this type of molecules can improve OLED materials. Silsesquioxanes attached as pendant groups to conjugated polymers have provided materials with improved thermal and color stabilities, higher brightness, and improved quantum efficiencies compared with the pristine polymers. Silsesquioxanes can also function as the core of dendrimers, where they served as isolators for conjugated polymers by connecting and aligning them in a radial fashion. The resulting materials reveal property improvements of parameters such as low levels of defects, high glass



POSS end-capped MEH-PPV
R = cyclopentyl

POSS end-capped POF
R = cyclopentyl, R' = octyl

Fig. 9 POSS end-capped conjugated polymers

transition temperatures (T_g), and enhanced solubility. All of these parameters extend the lifetime of the devices and increase their output.

POSS molecules were attached as pendant units or as end-capping agents to conjugated-polymer chains. Thus functionalized conjugated polymers have shown great enhancements in terms of optical, thermal, and mechanical properties compared to the original polymers.

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly(9,9′-dioctylfluorene) (POF) (Fig. 9) belong to the first POSS chain-end-functionalized light-emitting polymers [85]. Electroluminescent devices made from MEH-PPV-POSS revealed higher brightness and external quantum efficiency compared to the pristine polymer. In addition a higher current density luminance was also observed in this device, implying better injection and transport of charge carriers. One reason for this observation may be the disturbance of aggregation of the polymers by the bulky POSS end groups. Devices using polymer POF-POSS as the active material displayed higher quantum efficiency and electroluminescence than the parent polymer. In both cases thermal stability and solubility of the modified polymers also improved, which is important for the fabrication of devices.

Copolymers where the POSS cages were tethered to the polymer chain of a POF polymer showed increased photoluminescence quantum yields as the amount of tethered POSS increases. This phenomenon was attributed to the presence of the bulky POSS units which prevent aggregation and dimer formation of the polyfluorene backbone [86]. Based on these two principles, i.e., end-capping and tethering of POSS molecules, a variety of other conjugated-polymer structures were modified. The gist of property enhancement in the majority of cases is that the stability of the polymers towards thermal and oxidative decomposition increased and that – in addition – in many cases quantum efficiency and other photophysical properties improved. Many of these advantages of the POSS-based polymers are due to morphological changes induced by the presence of the inorganic components.

Luminescence quantum yields in OLED materials are often hampered by the tendency of conjugated chromophores to engage in π–π interaction leading to molecular aggregation and quenching of the excited state. As mentioned before end-capping or tethering of POSS molecules might be a possibility to change this behavior. Alternatively, the chromophores can be directly attached to the eight

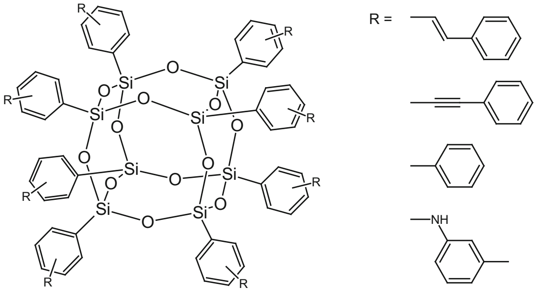


Fig. 10 POSS core with chromophores in the periphery

corners of POSS which leads to a radial alignment away from the central core. The rigid and bulky POSS core ensures that the chromophores within each molecule will be sterically and electronically isolated from one another and prevent aggregation of neighboring silsesquioxane–chromophore materials. This concept was applied based on the brominated octaphenyl-substituted core which was functionalized by various chromophores (Fig. 10) [23, 24]. For example stilbene-substituted POSS was compared with molecular stilbene and it was found that the quantum efficiency in solution was significantly higher than that of pure stilbene although the UV/Vis absorption behavior of both substituted and unsubstituted stilbene were nearly identical: This is an indication that a suppression of inter-chromophore aggregation and the ensuing self-quenching occurred.

Beside a covalent attachment of chromophores it is also possible to use supramolecular approaches, such as complementary hydrogen binding, to connect the chromophores to POSS cores. Applying such an approach, blue-light electroluminescent material based on 4-uracilbutyl-1-methylpyrene ether (U-PY)/octakis [dimethyl(*N*-(6-acetamidopyridin-2-yl))siloxy] silsesquioxane (ODAP-POSS) was synthesized, which contains eight pyrene chromophore arms [87]. The resulting compound exhibits high quantum efficiencies and good solution processing properties. Photoluminescence spectra of U-PY/ODAP-POSS (50/50) show that the color is stable after heating the sample. In contrast the covalent bond equivalent pyrene/ODAP-POSS (50/50) shows significant thermal quenching. Applying U-PY/ODAP-POSS in an electroluminescence device revealed higher maximum brightness and higher luminance efficiency relative to that of the U-PY. Furthermore, U-PY/ODAP-POSS can be used as an effective dopant that enhances energy transfer from itself to poly(2-methoxy,5-(20-ethylhexyloxy)-*para*-phenylenevinylene) (MEH-PPV). The U-PY/ODAP-POSS-doped MEH-PPV blends exhibit high luminance efficiency, 1.45 times greater than MEH-PPV.

Further examples of the use of POSS in polymers for OLEDs can be found in a recently published review [84].

Beside POSS structures also ladderlike polysilsesquioxanes can show the desired electroluminescent properties. Compounds with carbazole groups, for example, showed unexpected high photo- and electroluminescence efficiencies both in solution and solid states [88]. These observations are based – just as in the case of the POSS derivatives – on the rigid silicone ladder structures, which efficiently isolate the chromophore groups and thus suppress excimer formation.

Some square planar platinum complexes display a combination of monomer and red-shifted excimer/aggregate emission in concentrated solution and solid films, which is an interesting property for the fabrication of highly efficient white-emitting devices. These so-called phosphorescent excimer white-emitting devices are of a simple device structure, utilizing only one emissive dopant to achieve white emission, which can minimize color aging often encountered in white-emitting devices with multiple emissive dopants. If such platinum complexes are attached to a POSS core OLEDs can be produced with an external quantum efficiency which is significantly higher than that of the analogous devices produced as a physical blend of the platinum complexes and a polymer matrix [89]. In addition the formed devices represent noticeable improvement in the device efficiency of solution-processable phosphorescent excimer devices.

Beside the use of POSS-based compounds also ladder polysilsesquioxanes show interesting applications as materials for optical emission systems. The advantage of these systems is that they show a wide band-gap, good film-forming ability, high thermal and morphological stability, and good miscibility to the emission of dopant molecules. They can be prepared with side chains containing various groups showing photoluminescence (PL) and electroluminescence (EL) emission. Several compounds were used for the incorporation of the blue-light emitter iridium bis (4,6-difluorophenyl)pyridinato-N,C2-picolinate [90, 91]. The ladder structure of materials has not only a higher thermal resistance and could prevent molecular aggregation and effectively avoid quenching of fluorescence by the steric restrictions induced by the double-stranded polymer.

Applications in Catalysis

As mentioned earlier incompletely condensed silsesquioxanes of the type $R_7Si_7O_9(OH)_3$ mimic silica surfaces. Their open structure can be closed by metal coordination, resulting in metallasilsesquioxanes. These compounds are on the one hand suitable systems to study the influence of coordination of silica on the reactivity of the metal complexes. On the other hand, due to the good solubility, they represent the homogeneous homologues to heterogeneous catalysts. A second species that is important for this approach is the monosilanol-substituted POSS $R_7Si_8O_{12}(OH)$. The chemistry of incompletely condensed silsesquioxane structures with regard to their use in understanding and developing silica-supported catalyst was reviewed recently [92, 93]. The major contributions that silsesquioxane-based molecular compounds have offered to heterogeneous catalysis are the spectroscopic assignments of surface-bound organometallic and metal–inorganic fragments, the better understanding of elementary step and reaction mechanism occurring at the surface, and the molecularly precise structure–activity insight for heterogeneous catalysts [93].

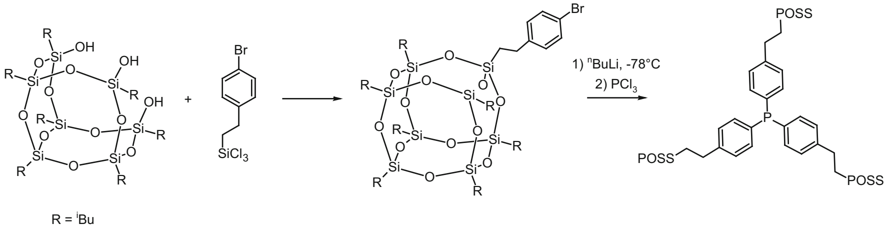


Fig. 11 Synthesis of POSS enlarged triphenylphosphine ligand

Some recent examples of the availability of these structures are presented here. POSS ligands were coordinated to molybdenum catalyst for alkyne metathesis by mixing a molybdenum(VI) trisamide alkylidyne with the mono- and trisilanol POSS ligands [94]. A resulting pentacoordinated complex showed activities analogous to that of the silica-supported Mo complex. The monosilanol POSS ligand stabilizes the monomeric Mo alkylidyne complex and shows no unwanted alkyne polymerization. In contrast, multidentate POSS ligands that have more than one silanol group were accompanied by considerable alkyne polymerization as well as alkyne metathesis.

An interesting route to use POSS in catalysis is the introduction into ligands which are originally used as homogeneous catalysts. This approach leads to molecular weight enlargement that allows for a better catalyst recycling, for example, by filtration [95]. Applying this method an Rh catalyst based on POSS-modified PPh_3 was applied in the hydroformylation of 1-octene in a continuous flow nanofiltration reactor [96]. The resulting systems showed exceptional properties with regard to activity, stability, and retention of the catalyst system. The hydroformylation setup was continuously operated for several weeks without any significant deactivation or leaching of the catalyst (Fig. 11).

The problem in the case of chiral catalysts is that usual methods to heterogenize them, for example, the use of silica formed by the sol-gel process limits the compatibility of functionalities, often make chiral functionalities anchor randomly within frameworks and thus can decrease the selectivity of the catalyst. Therefore, it is better to use preformed well-defined building blocks that allow for a heterogenization. This concept was used to prepare bifunctional octavinylsilsesquioxane-based organorhodium heterogeneous chiral catalyst [97]. These catalysts exhibited excellent catalytic activities and high enantioselectivities in the asymmetric transfer hydrogenation of aromatic ketones and analogues. The catalytic efficiency in a two-phase reaction system can be drastically enhanced by anchoring of quaternary ammonium salts onto the POSS molecules. Another advantage of the obtained catalyst is its high recycling potential.

Biomedical Applications

There is considerable interest in using POSS systems in biomedical and/or pharmaceutical applications, mainly due to the low toxicity of the POSS core and the large amount of functionalizations possible at the core vertices.

For example, quaternary ammonium functionalized POSS are attractive biocompatible drug carriers based on their nanoscale size, three-dimensional functionality, efficient cellular uptake, low toxicity, and high solubility. The efficient uptake in the cytoplasm was proven for Cos-1 cells [98]. It was shown that the migration pattern of the POSS derivatives functionalized with a fluorescent cellular membrane marker is drastically different from the non-conjugated control. The POSS marker was evenly dispersed in the cytosol, indicating that the conjugates enter the cell via diffusion, and not through endocytosis.

Conjugated oligoelectrolyte-POSS loaded and pH-triggered chitosan/poly(ethylene glycol) nanoparticles with folic acid functionalization were prepared for targeted imaging of cancer cell nuclei [99]. The nanoparticles can be assimilated in acidic lysosomes of MCF-7 breast cancer cells and trigger rapid release of the POSS compounds, which were used as fluorescent probes. Hence, the nanoparticles have shown low cytotoxicity with specific targeting capability for the nuclei of MCF-7 cancer cells.

POSS core conjugated-polymer (CP) shell structures, which were already described in the OLED section due to their high photoluminescent quantum yield, were also used in biomarker applications [100]. For this application they were loaded into poly(lactic-co-glycolic-acid) (PLGA) nanoparticles. The resulting particles showed high photoluminescent quantum yield, excellent stability, low cytotoxicity, and tunable surface protein density. The thus obtained nanoparticles were used in HER2-positive cancer cell detection.

The rigid structure of the POSS cubes can be beneficially used in the development of low-shrinkage dental composite resins. Octafunctionalized methacrylate-based compounds were incorporated in commonly used photoinitiated dental formulations. The study showed that the shrinkage of nanocomposites decreased and the nanocomposites incorporated with POSS showed improved mechanical properties at low POSS content [101].

A potential application of POSS nanocomposites is the coating of implants. Particularly cardiovascular implants got a great deal of interest [102]. The use of the inorganic structures in biocompatible nanocomposites resulted in improved hemocompatibility, antithrombogenicity, calcification resistance, reduced inflammatory response, as well as the already known enhanced mechanical and surface properties. For example, POSS/poly(carbonate–urea)urethane nanocomposites were prepared to coat NiTi stent alloys, which enhanced surface resistance and improve biocompatibility [103].

Flame Retardants

Different materials can be used as flame retardants in polymeric systems. Recent studies reveal that the use of nanodispersed silica structures such as montmorillonite clay shows large improvements in fire performance [104]. Beside these minerals also POSS incorporation in polymers revealed improvement in flammability associated to other properties enhancements [105–107].

Similar to other properties flame retardancy and thermal stability of POSS nanocomposites are strongly depending on the groups attached to the silicon-based core. These structure–property relationships are presented in a recent review [108].

An example where good fire-retardant performance was achieved is polyether-block-amide polymer reinforced by POSS. The peak of heat release rate in this polymeric system is dramatically decreased when using POSS compared to original polymer. It is suggested in this case that the fire-retardant mechanism is based on char formation at the surface of the material which can act as an insulative barrier [109]. POSS molecules undergo homolytic Si–C bond cleavage at 300–350°C in air which leads to a subsequent fusion of POSS cages to form a thermally insulating and oxidatively stable silicon-oxycarbide “blackglass” surface char.

3 Summary

Silsesquioxanes are unique molecular compounds, dominated in literature by polyhedral structures and ladder polymers. The synthesis of these molecules requires a high control over a variety of reaction parameters to obtain the targeted structures in good yield. Beside the structure the composition of silsesquioxanes can be varied over a wide range, particularly through the organic rests, and thus different types of functions can be included in the molecules. This opens a wide range of applications which are dominated from the nanocomposite materials class. In this review only a small selection could be presented.

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Higher-Coordinated Molecular Silicon Compounds

Jörg Wagler, Uwe Böhme, and Edwin Kroke

Abstract In silicon compounds the Si atoms are known to be fourfold coordinated in most cases. However, there are several cationic, anionic, and neutral molecular species containing hypercoordinated – i.e., five- and sixfold coordinated (and in few cases even higher coordinated) – silicon atoms. This class of compounds ranges from long known stable inorganic species such as SiF_6^{2-} to many different organometallic compounds with multidentate chelate ligands. Although this field has been known since the early nineteenth century and expanded significantly in the twentieth century, very interesting advances have been developed in the past decade. These include the extension of established synthesis routes to novel ligand systems via substitution, addition, and oxidative addition, among others. A number of new organic ligand systems have been successfully applied leading to unprecedented coordination modes of the silicon atoms. The structures of the obtained compounds have been analyzed thoroughly in many cases providing detailed insights into structure and bonding situations in hypercoordinated silicon complexes. Besides the classical silicon compounds with donor atoms such as H, C, Cl, F, O, and N, many novel examples with main group metal as well as transition metal atoms in the coordination sphere of silicon have been reported.

Keywords Chelate ligand · Donor atom · Hypercoordination · Silicon complex · Structure · Synthesis

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Abbreviations

AIM	Atoms in molecules (see also QTAIM)
Ar	Aryl
bipy	2,2’-Bipyridyl
Bn	Benzyl
Bu	Butyl
t-Bu	*Tert*-butyl
cat	Catalyst
CN	Coordination number
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
CSD	Cambridge Structural Database
Cy	Cyclohexyl

Dip	2,6-Diisopropylphenyl
DMAP	4-(Dimethylamino)pyridine
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Et	Ethyl
HMPA	Hexamethylphosphorictriamide
L	Ligand
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl (not methanesulfonyl)
mt	Methimazolyl (1-methyl-2-mercaptoimidazolyl)
NBO	Natural bond order
NHC	*N*-heterocyclic carbene
NHS	*N*-heterocyclic silylene
Nu	Nucleophile
Ph	Phenyl
phen	1,10-Phenantroline
Pr	Propyl
i-Pr	Isopropyl
py	Pyridine
pz	Pyrazolyl
pz*	3,5-Dimethylpyrazolyl
QTAIM	Quantum theory of atoms in molecules
SP	Square pyramid (or square pyramidal)
TBP	Trigonal bipyramid (or trigonal-bipyramidal)
Tf	Trifluoromethanesulfonyl (triflyl)
THF	Tetrahydrofuran
tmeda	*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine

1 Introduction

Silicon, as the heavier homolog of carbon, is fourfold coordinated in its compounds in most cases. This is, for example, reflected by the chemistry of silicates [1]. In these naturally occurring compounds, the silicon atoms are almost exclusively found in SiO_4-coordination. The situation is similar for synthetic solids, such as extended binary phases like pure silica zeolite-type frameworks [2], SiS_2, SiC or Si_3N_4, and related more complex ternary and multinary solids [3]. This is also valid for molecular silicon halides, hydrides, and metal organic (e.g., silicon alkoxides) as well as organometallic silicon compounds [3, 4].

Interestingly, for almost all mentioned classes of silicon compounds, there are also well-known examples containing higher-coordinated silicon atoms. For the silicates and silica phases, there are some naturally occurring minerals with SiO_6 moieties such as thaumasite [5] or the SiO_2 high-pressure phase stishovite [6]. Similarly, a high-pressure modification of silicon nitride (spinel-Si_3N_4) [7], selected nitridosilicates, and so-called sialons (silicon aluminum nitride oxides), which contain sixfold-coordinated silicon atoms, have been reported [8–10]. An even larger variety of *molecular* compounds containing higher-coordinated silicon atoms are known. These include neutral, anionic, as well as cationic species with mono-, bi-, and multidentate ligands. The probably best-known representative of this class of species is $[SiF_6]^{2-}$, its salts and its acid H_2SiF_6. In fact, for the first synthesis of elemental silicon in pure form, $K_2[SiF_6]$ was used as a starting material in 1825 [11], and the di-ammonia adduct of SiF_4 was reported as early as in 1811 [12].

The chemistry of higher-coordinated – sometimes also called hypercoordinated and/or hypervalent silicon compounds – has been reviewed in several publications in the past. These references provided general overviews in the 1960s [13, 14], 1970s [15], 1980s [16], and the 1990s [17, 18]. More recently, i.e., since the year 2000, additional review-papers appeared. Some are of general nature covering most classes of molecular higher-coordinated silicon compounds [19]. Many others of these newer reviews are focused on certain more specific topics, i.e., groups of compounds such as organosilicon derivatives containing nitrogen heterocycles [20], higher-coordinated silicon(IV) compounds with SiO_5 and SiO_6units [21], silicon (IV) complexes with SiO_2N_4 units, zwitterionic compounds with pentacoordinated silicon atoms [22], applications of higher-coordinated silicon compounds as a reactive site in (stereoselective) organic synthesis [23–26], pentacoordinated siliconium ion salts [27], pentaorganosilicates [28], silatranes and closely related compounds [29], silicon complexes with hydrazine derived N–O-donor ligands [30, 31], and silicon halides coordinated with neutral ligands [32]. Furthermore, a review is available on the role, properties, and fate of higher-coordinated fluorosilicates which are frequently used as additives for drinking water [33]. Another example of a class of compounds containing sixfold-coordinated silicon, which has been extensively studied over the past decades, is phthalocyanine derivatives with photosensitizing behavior which can be used for photodynamic therapies [34] or as electron acceptor components for the development of supramolecular solar cells [35].

Compounds which accommodate agostic interactions of Si–H moieties with transition metals may also be considered as a special type of higher-coordinated silicon compounds. A few reviews on this matter are also available [36]. These include a recent general overview [37] and further publications on selected subtopics such as platinum compounds [38] or niobium and tantalum complexes [39]. Complexes of this type are also discussed in comparison to C–H and H–H interactions with lanthanides [40].

In general, detailed explanations as to why and when higher-coordinated silicon atoms are formed remain limited, thus leaving the origin of silicon hypercoordination a matter of discussion. This holds also true for related heavier main group elements such as germanium, phosphorus or sulfur. There are many species which formally exceed the number of eight valence shell electrons and/or possess five, six, or more neighboring atoms with bonding interactions, i.e., distances below the sum of the van der Waals radii of the corresponding atoms.

For octahedral compounds a description using a sp^3d^2 hybridization was frequently discussed. However, due to the relatively high energy of the 3d orbitals of silicon, it is usually accepted that their role is not significant. Thus, two-electron–two-center bonds are not considered as the appropriate description for these “hypervalent” compounds.

Another well-accepted interpretation of hypercoordination of silicon is based on the ionicity of their bonding situations, which in general is very high. It can be stated that the ionicity increases with the coordination number. However, it is obvious that in higher-coordinated silicon compounds with different ligands such as SiXYZ, the bonding situation including its ionicity to the different atoms X, Y, and Z is different and depends on several factors. This can be related to the Lewis acidity of silicon atoms bound to electronegative atoms.

Due to the numerous overviews on the chemistry of hypercoordinated silicon compounds, the present review is primarily focused on the structural and synthetic aspects. Spectroscopic and other properties as well as (potential) applications are only briefly mentioned in selected cases. Nevertheless, the literature on higher-coordinated silicon complexes published in the past 5 years should be covered comprehensively, while relevant older literature is also considered.

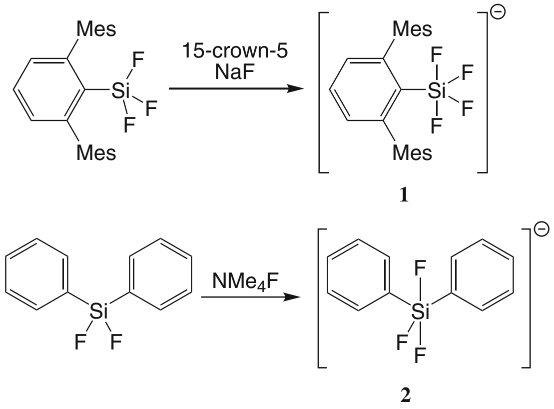
2 Synthesis of Hypercoordinated Silicon Compounds

Although a great variety of synthetic strategies is known to afford hypercoordinated silicon compounds, they can be classified as addition (and sometimes elimination), substitution, and rearrangement reactions or combinations thereof.

2.1 Addition of Anionic Nucleophiles

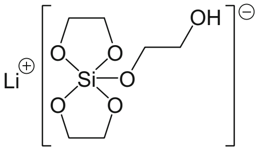
The most prominent examples of hexacoordinated silicon complexes – SiF_6^{2-}, $HSiF_6^-$ and H_2SiF_6 – form instantly in an addition reaction of SiF_4 and fluoride ions or HF in solution [11, 33] as well as in the gas phase [41]. In a similar manner, pentafluorosilicates (SiF_5^-) can be obtained [42] and organofluorosilanes form organofluorosilicates (e.g., **1** and **2**, Scheme 1) upon reaction with suitable fluoride sources [42, 43]. This noticeable susceptibility to fluoride addition is made use of in fluoride-catalyzed nucleophilic substitution reactions at silicon, where F^- serves as the first nucleophile to increase the silicon coordination number to five, thus creating a reactive species prone to addition of a sixth donor moiety (i.e., the new substituent) [44]. Also due to the high fluoride susceptibility of fluorosilanes, in syntheses of fluorosilanes out of chlorosilanes by halide exchange, one has to avoid excess of easily available fluoride. Thus, fluoride sources such as SbF_3 [45] and ZnF_2 [46] proved useful reagents for this purpose.

Scheme 1 Formation of pentacoordinated fluorosilicates from di- and trifluorosilanes



In sharp contrast, the anion $SiCl_6^{2-}$ has not been isolated yet, whereas the related compound of the heavier congener ($GeCl_6^{2-}$) is well known [47]. Even chlorosilicates with pentacoordinated Si atom are scarcely encountered, one of the rare exceptions being the anion $(Cl_3Si{-}SiMeCl_2{-}SiMeCl_2)^-$ with a pentacoordinated central silicon atom [48]. Instead, hexacoordinated chlorosilicon complexes are frequently found to undergo ionic dissociation under release of chloride and formation of cationic complexes with pentacoordinated Si atom, either as isolable cationic Si complexes (e.g., **3**) or in dynamic equilibrium in solution (e.g., **4a** and **4b**), thus reflecting the weakening of Si–Cl bonds upon hypercoordination of the silicon atom (Scheme 2) [49–52].

Oxysilanes (such as silanes comprising hydroxy, alkoxy, aryloxy, or carboxy groups) were found to add further oxy-anionic ligands (thus yielding silicates with penta- or hexacoordinated Si atom) in case of selected silanes with small chelate rings (five-membered OSiO chelates, e.g., **5** and **6**) [53–60]. Crystal structures of pentaalkoxysilicates with exclusively monodentate ligand moieties have not been reported yet, but formation of such species in the gas phase has been proven by mass spectrometry [61]. Interestingly, in the solid state the silicate $Si(OH)_6^{2-}$ is stabilized and encountered in the mineral thaumasite [5].



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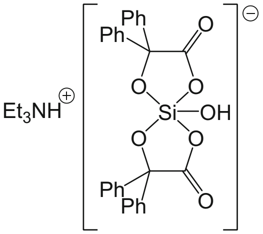

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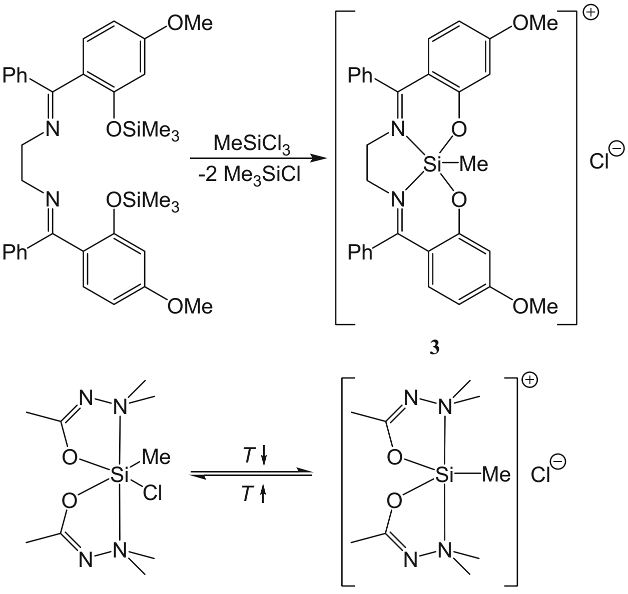

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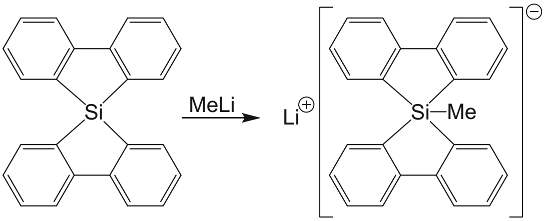
4a **4b**

Scheme 2 Cationic pentacoordinated silicon complexes formed upon ionic dissociation of a Si–Cl bond



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Scheme 3 Formation of a pentacoordinated silicate with five Si–C bonds

Anionic nitrogen nucleophiles (X^-), such as azide [62], cyanate [63, 64], thiocyanate [65, 66], and selenocyanate [67], are also well known to form hexacoordinated anionic silicon complexes of the type SiX_6^{2-} despite their monodentate nature.

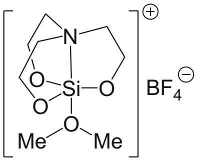
Carbanions have also been shown to add to certain tetraorganosilanes. Even though this route is also supported by five-membered chelates in the silicon coordination sphere (formation of **7**, Scheme 3) [28, 68–72], this structural feature is not essential to achieve the formation of pentacoordinated Si complexes with five Si−C bonds, as proven by the anion $[SiMe_3(CF_3)_2]^-$ [73].

Last but not least, hydridosilicates have been reported, which form upon addition of hydrides to hydridosilanes, e.g., formation of $K^+[(i\text{PrO})_3SiH_2]^-$ out of KH and $(i\text{PrO})_3SiH$ [74, 75].

2.2 Addition of Monodentate Charge-Neutral Nucleophiles

Basically, halocarbons should be capable of entering the silicon coordination sphere with a lone pair of one of their halogen atoms, as has been shown for the 1,2-dichlorobenzene solvate of a silicenium ion ($i\text{Pr}_3Si^+\ldots Cl{-}o{-}C_6H_4Cl$) [76]. To the best of our knowledge, this kind of solvate formation has not been proven relevant in hypercoordinated silicon chemistry yet.

Ethers were shown to form adducts with silicon compounds (e.g., **8**, **9** and **10**), but literature reports on crystallographic evidence are limited to few examples [77–80]. In the same manner, alcohols and water should be capable of forming related adducts. Surprisingly, no example of an alcohol solvate can be found in the CSD [81], but adduct formation with alcohols has already been reported [82]. Water, however, has already been demonstrated by X-ray crystallography to act as a ligand in hypercoordinated Si complexes (e.g., **11** and **12**) [82–85].



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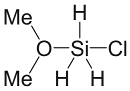

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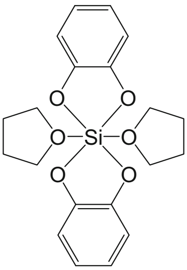

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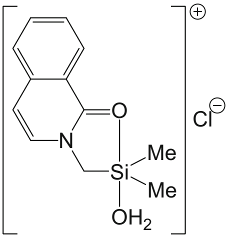

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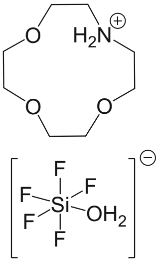

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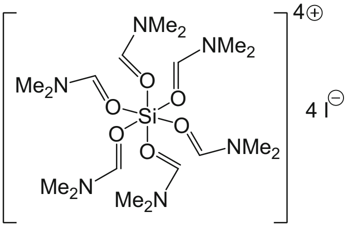
So far, no crystallographic evidence for adducts of silanes with aldehydes, ketones, esters, or acyl halides has been reported [81]. Dimethylformamide [86–88] and tetramethylurea [89], however, are known to enter the silicon coordination sphere (e.g., in **13** and **14**, respectively). In a similar manner amine-*N*-oxides (e.g., in **15**) [90], phosphine oxides (e.g., in **16** and **17**) [90, 91], and phosphoric amides [92–94] form hypercoordinated Si complexes. Although dimethyl sulfoxide (DMSO) increases the silicon coordination number (as shown ^{29}Si NMR spectroscopy) [49], crystallographic evidence for a silicon complex with DMSO ligand(s) is still lacking [81].



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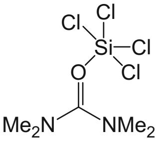

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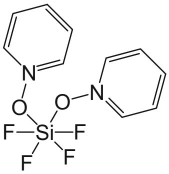

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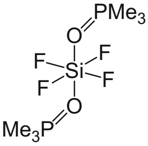

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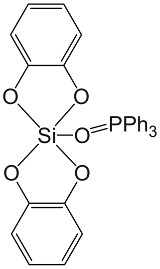

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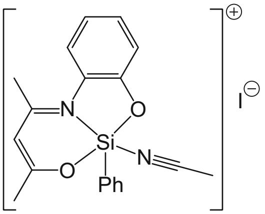
Only recently, nitriles were shown to increase the silicon coordination number to up to five in cationic complexes (**18**) [95], even though nitriles had already been shown to form adducts with silicenium ions, thus functioning as a donor moiety in a tetrahedral Si coordination sphere [96]. Amines are scarcely encountered in silicon coordination compounds, only few examples of crystallographically evidenced silicon complexes with monodentate amines have been reported so far, which include the adduct $SiF_4(NH_3)_2$ [97–100]. Imines, however, are well known to add to various halosilanes. Especially *N*-heterocycles with imine functionality, such as pyridines [101–103], imidazoles [104, 105], pyrazoles [106], and related compounds, can be found as ligands in various silicon complexes (e.g., in **19** and **20**).



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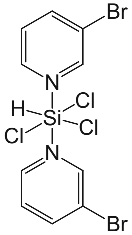

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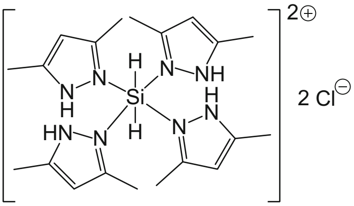

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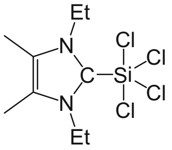
Recently, the set of donor molecules for the synthesis of silicon complexes has been extended to *N*-heterocyclic carbenes (NHCs). Even though some first examples of NHC silane adducts were reported earlier [107], a noticeable number of NHC silicon complexes entered literature in the past 5 years [108–112]. Interestingly, in pentacoordinated silicon complexes of the type (NHC)SiX_4 (X=halide), the carbene ligand was found capable of binding in both the axial (in **21** and **22**) and the equatorial position (in **23**) of the trigonal-bipyramidal coordination sphere. Computational analyses of a set of different NHCs and silanes have shown that in some cases, the energetic difference between axial and equatorial coordination of the NHC ligand is marginal [113]. In octahedral silicon complexes with two NHC ligands (**24**), the carbenes are found *trans* to each other [108], which is in agreement with computational predictions [113].



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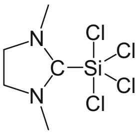

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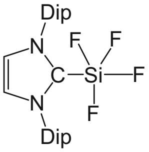

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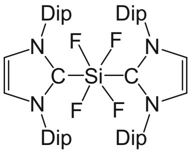

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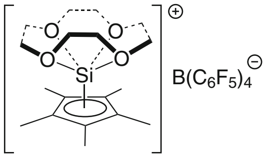
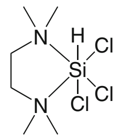
The above-listed monodentate donor moieties clearly demonstrate that, in addition to hydrocarbons (pentane, hexane, benzene, toluene, etc.), halogenated hydrocarbons (dichloromethane, chloroform, chlorobenzene, etc.), ethers (diethyl ether, tetrahydrofuran (THF), 1,4-dioxane, etc.), and nitriles (e.g., acetonitrile) should be suitable "innocent" solvents for syntheses and reactions of silicon complexes, as far as competitive solvent coordination has to be circumvented. The same holds true for trialkylamines as sacrificial bases (if required), as they appear least likely to compete in complex formation with other ligands. Nonetheless, care has to be taken when other side reactions appear likely. Solvolysis of Si−Cl, Si−OR (R=aryl, alkyl), or Si−N bonds by protic solvents such as alcohols or water is a well-known reaction in silicon chemistry [44, 114, 115] and may thus also apply to hypercoordinated silicon complexes [116, 117]. Although many reports can be found that deal with the syntheses of chlorosilicon complexes in alcohols as solvents, none of the resulting complexes has been confirmed crystallographically so far (to the best of our knowledge) [118–124]. Ether and ester cleavage represents another competitive reaction pathway and has to be considered in reactions of halosilanes (especially bromo and iodosilanes) in solvents of that kind [125, 126]. Enolization of carbonyl compounds (e.g., acetone), which may result in silylation of the enol, is another noteworthy competitor [127], whereas enols may also serve as the desired ligands, e.g., in compounds with acetylacetonato-derived ligand systems [128–130]. Dimethylformamide is known to transfer oxide to hydrosilanes, thus yielding siloxanes [131], and similarly dimethyl sulfoxide reacts with chlorosilanes under formation of siloxanes [132]. In some cases the solvent molecules participate in the formation of novel hypercoordinated silicon compounds in different ways than just acting as neutral donor ligands. Acetonitrile has been shown to undergo addition reactions with silicon-bound ligands, thus creating entirely new ligand systems [133, 134]. Recrystallization of a bromosilicon complex from 1,2-dichloroethane afforded a chlorosilicon complex upon halide exchange with the solvent [135].

2.3 Addition of Oligodentate Charge-Neutral Ligands

In general, silicon complex formation is favored when using chelating ligands. Thus, various kinds of chelators will be dealt with in the following sections, and just few examples are listed here. To the abovementioned monodentate ligands (from Sect. 2.2), various chelating combinations of one or more kinds of donor functions can be used to enhance the coordination number of silicon. Thus, 1,2-dimethoxyethane (**25a**) and 12-crown-4 (**25b**) [136] have also been successfully utilized as ligands at silicon (in this particular case in a silicon(II) compound). Many examples of N-donor chelates such as tetramethylethylenediamine (tmeda, e.g., in **26**) [137] and related amines [138, 139] as well as 2,2′-bipyridyl (bipy, e.g., in **27**) [140–143], 1,10-phenanthroline (phen, e.g., in **28**) [142, 143], and N-oxides thereof [144] were shown to form hypercoordinated silicon complexes.



25a (with MeO-CH_2CH_2-OMe)
25b (with 12-crown-4)



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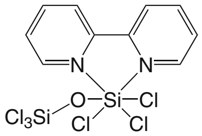

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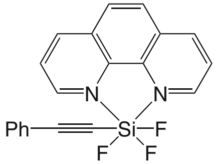

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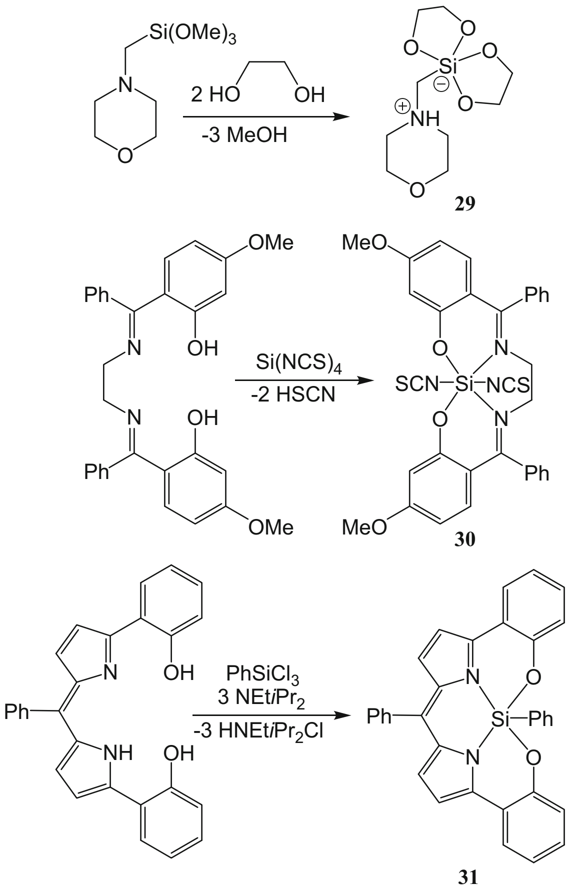
2.4 Metathesis with Anionic Chelating Ligands

A very successful strategy of anchoring charge neutral donor moieties is the substitution of anionic monodentate substituents by anionic chelators. In the same way, additional anionic donor moieties can be introduced in the Si coordination sphere, which are less likely to bind to Si if of monodentate nature. Various routes

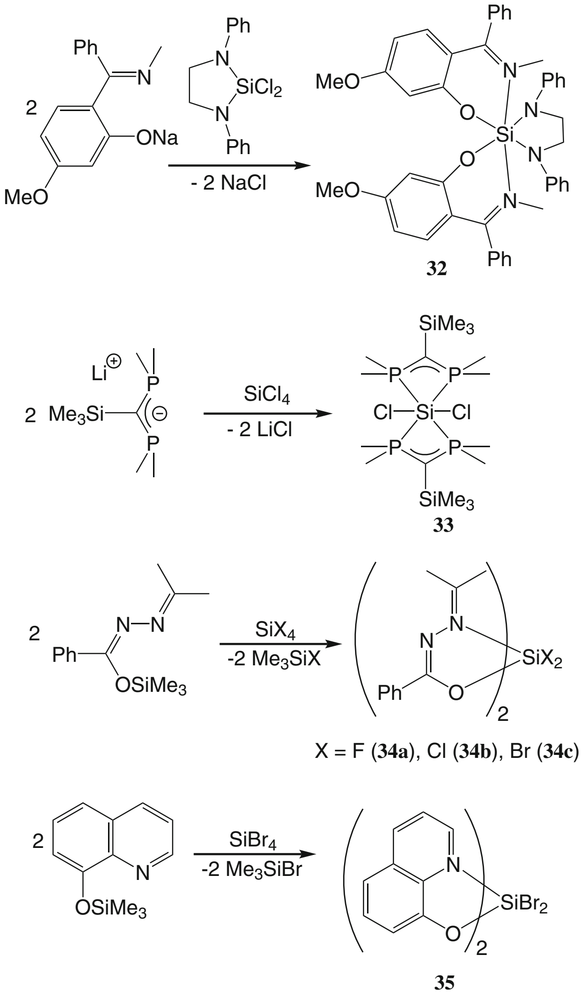


Scheme 4 Syntheses of penta- and hexacoordinated silicon complexes from ligand acids and alkoxy-, thiocyanato-, and chlorosilanes

have been developed for introducing new ligands in the silicon coordination sphere by metathesis, which include reaction of a ligand acid with an alkoxysilane (e.g., synthesis of **29**, Scheme 4) [145, 146], a cyanato- or thiocyanatosilane (e.g., synthesis of **30**, Scheme 4) [66, 128, 147], or a halosilane [148, 149], base-supported substitution of a ligand acid with a halosilane (e.g., synthesis of **31**, Scheme 4) [150–153], salt elimination from a ligand alkali metal salt and a halosilane (e.g., synthesis of **32** and **33**, Scheme 5) [153–155], and transsilylation between a trimethylsilylated ligand and a halosilane (e.g., synthesis of **34** and **35**, Scheme 5) [49, 156–158].

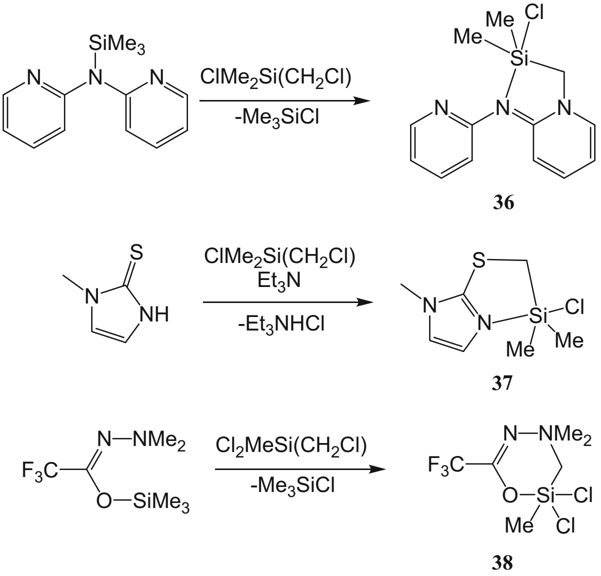
In addition to metathesis reactions at silicon, a substitution reaction in close proximity to the Si atom is also suitable for introducing chelators in the Si coordination sphere (Scheme 6). In this context, chloromethyl-substituted silanes have successfully been modified at the α-C-atom with amides (**36**) [84, 159–162],

Scheme 5 Syntheses of pentacoordinated silicon complexes from metalated and silylated ligands and halosilanes

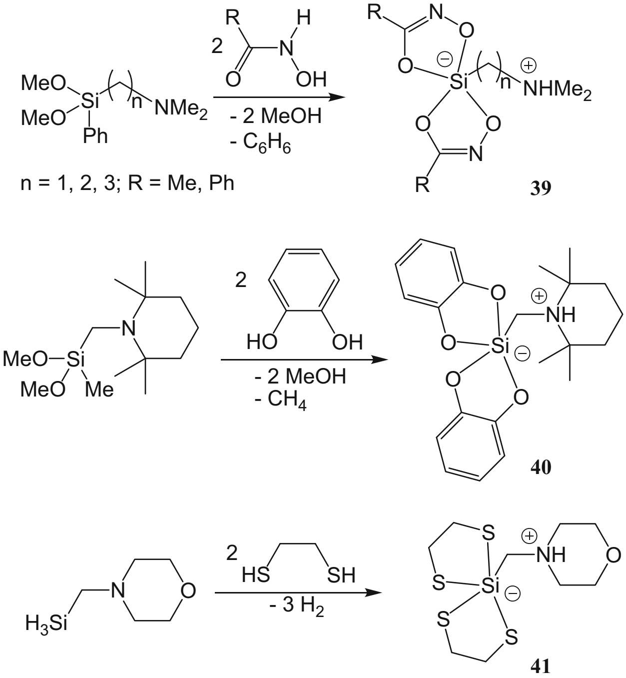


thiolates (**37**) [163], and other nucleophiles (**38**) [52, 164] to furnish new chelators anchored to silicon via Si–C bond. These nucleophilic substitution reactions again may be performed along various routes, which include base-supported reaction with a ligand acid and transsilylation with a trimethylsilylated ligand.

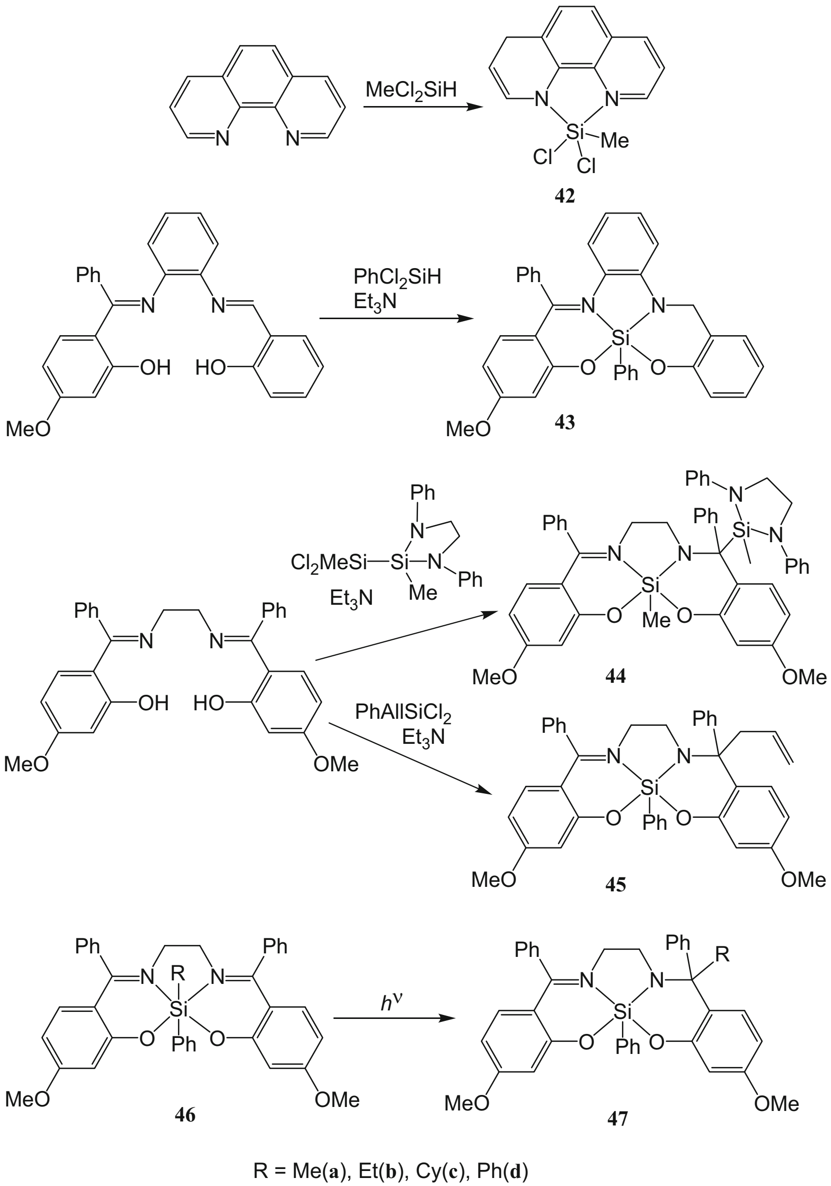
Last but not least, reactions of some organosilanes or hydridosilanes with ligand acids proceed under release of a hydrocarbon (e.g., **39** and **40**, Scheme 7) [165, 166] or hydrogen (e.g., **41**, Scheme 7) [145, 167], respectively, as very benign leaving groups.



Scheme 6 Syntheses of pentacoordinated silicon complexes from (chloromethyl)silanes



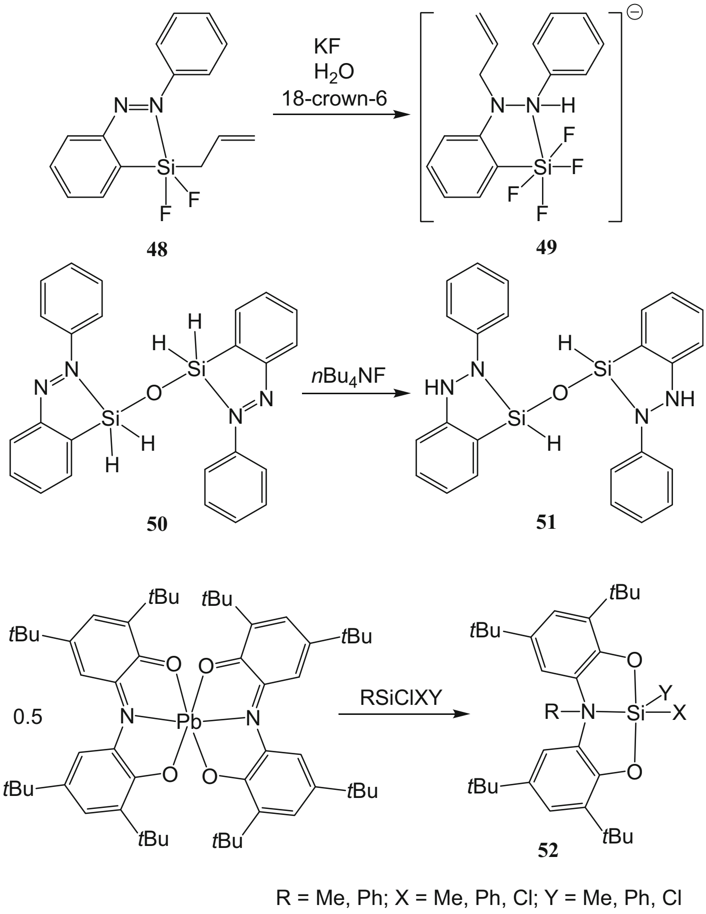
Scheme 7 Syntheses of pentacoordinated silicon complexes under release of hydrocarbons or hydrogen



Scheme 8 Syntheses of pentacoordinated silicon complexes under migration of a silicon-bound substituent to the chelating ligand

2.5 Rearrangement Reactions

The abovementioned routes can include molecular rearrangement (Scheme 8). Addition of 1,10-phenanthroline to methyldichlorosilane was shown to result in hydride migration, thus producing a pentacoordinated silicon complex (**42**) [168].

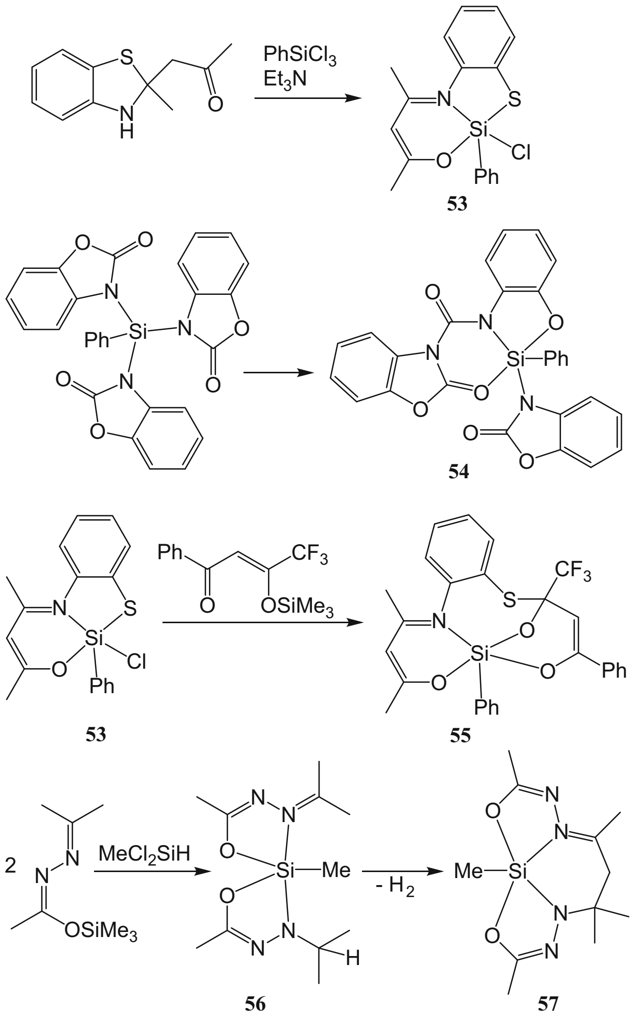


Scheme 9 Examples for migration of hydride and hydrocarbyl groups from silicon to an N atom of the chelating ligand

In a similar manner, hydride (**43**) [169, 170], silyl groups (**44**) [171], allyl groups (**45**) [169, 172], as well as alkyl (**47a-c**) and aryl groups (**47d**) [173–176] can migrate to imine carbon atoms of the ligand, either during the metathesis reaction or upon thermal or photochemical activation of an intermediate hypercoordinated silicon complex (**46a–d**).

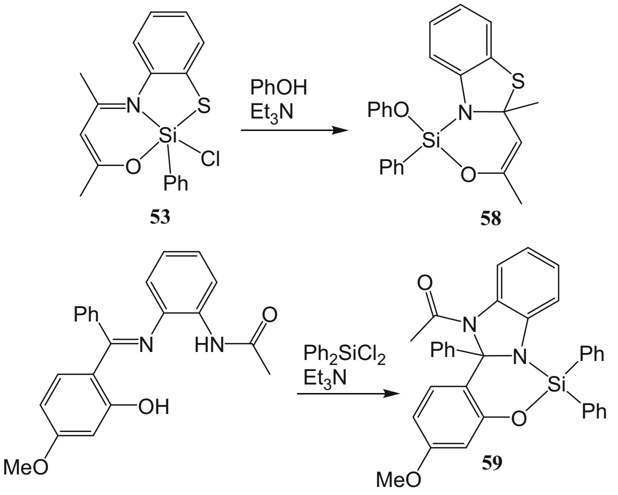
Related shift reactions were also observed in complexes with diazobenzene derived ligands (**48**–**51**) [177–179] and upon complex formation with aryloxyiminoquinones (**52**), as shown in Scheme 9 [180]. The allyl migration in particular, which is facilitated by silicon hexacoordination, is utilized for syntheses of various allylmethanols from aldehydes (or ketones) and allylsilanes [181–187].

Further examples of formation of hypercoordinated silicon complex by rearrangement reactions include silicon-templated ring opening reactions, which give rise



Scheme 10 Examples for Si-templated formation of multidentate chelators

to the installation of the chelator in the silicon coordination sphere (**53** and **54**, Scheme 10). The precursor may include all donor atoms in one molecule, as in case of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one [188–190], or two precursor ligands may rearrange to the new chelator, as shown in case of silylated benzoxazolinone [191, 192]. In a related rearrangement reaction, an ONS-chelator (in **53**) combined with an acetylacetone derivative to yield complex **55** [193]. Another type of Si-templated ligand rearrangement involves bidentate Si-bound hydrazide derivatives and a hydride shift from Si to one of these ligands (**56**) followed by condensation of the two ligand moieties (**57**) [170].



Scheme 11 Examples for rearrangement reactions of multidentate chelators in the Si coordination sphere

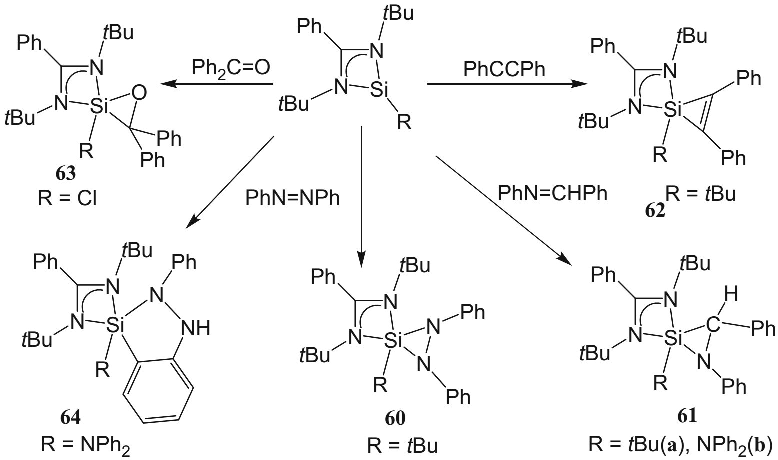
The opposite route, i.e., the withdrawal of a potential donor moiety by rearrangement and formation of a heterocycle, may also occur (Scheme 11), as shown for the formation of Si-bound 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one (in **58**) [194] and Si-bound benzimidazoline (in **59**) [195] out of tridentate chelators.

2.6 Oxidative Addition

In the past 5 years, much effort was dedicated to the exploration of the chemistry of amidinate-functionalized silylenes (Scheme 12). As the starting silylene already comprises a tricoordinated silicon atom, various oxidative addition reactions furnished silicon(IV) complexes with pentacoordinated Si atoms. Some of them comprise the striking features of three-membered SiNN (**60**) [196], SiNC (**61**) [196], SiCC (**62**) [196], or SiOC (**63**) [110] heterocycles, which are genuine novelties in silicon coordination chemistry. o-CH-activation of diazobenzene has also been observed (formation of **64**) [197].

Some related reactions (Scheme 13) have also been investigated for a disilylene (to afford **65**) [198], a related disilicon(I,III) system (to yield **66** and **67**) [199], and for a mononuclear silylene the oxidative addition of diphenylacetylene was found to proceed under formation of an Si–Si bond (formation of **68**) [200].

Further related reactions (Scheme 14) were found to result in cyclodimerization upon addition of diazomethane derivatives (**69**) [201], formation of cyclodisiloxane motifs with pentacoordinated Si atoms upon oxidation with N_2O (**70**), and insertion into the C–Cl bonds of dichloromethane (**71**) [202].



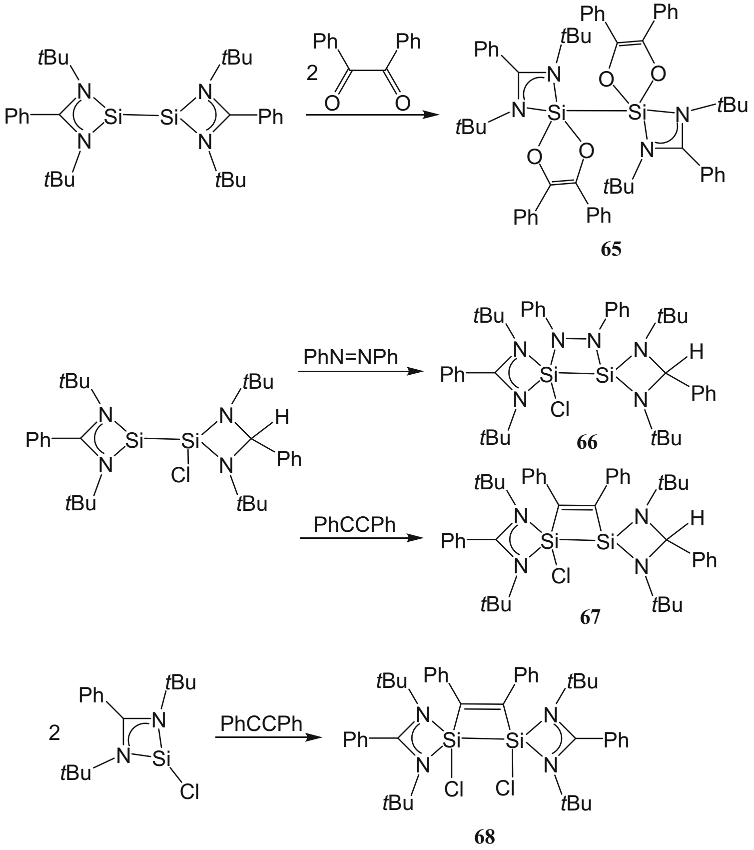
Scheme 12 Oxidative addition reactions of an amidinate stabilized silylene with various unsaturated compounds

Oxidative addition to a related silylene (Scheme 15) afforded a hexacoordinated silicon complex with two Si–I bonds (**72**), the first crystallographically evidenced hexacoordinated iodosilicon complex so far [203]. Furthermore, addition of chalcogens E (S, Se, Te) afforded pentacoordinated Si compounds with Si=E bonds (**73**) [204].

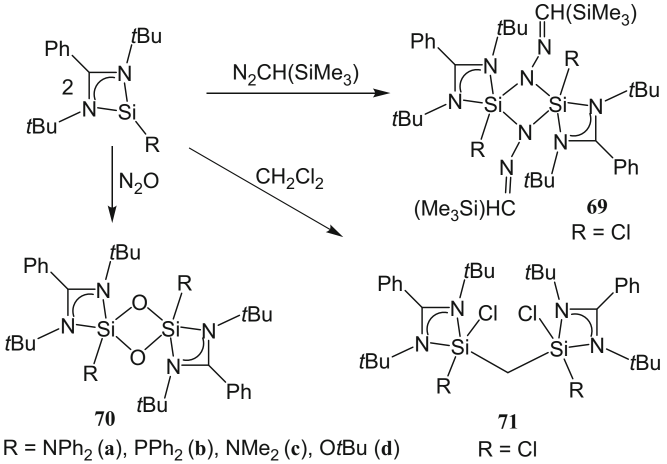
NHC-stabilized dichlorosilylene was shown to exhibit similar behavior in oxidative addition reactions (Scheme 16), i.e., formation of a SiOC three-membered heterocycle upon addition of benzophenone (**74**), whereas in the reaction with benzil, the formation of a five-membered heterocycle is favored (**75**) [110]. The reaction with diphenylacetylene involves silylene oligomerization to also yield a compound with five-membered silacycle (**76**) [109].

N-heterocyclic silylenes (NHSis) with acetylacetone diimine dianions as backbone were also shown to undergo oxidative addition which involves formation of hypercoordinated silicon complexes (Scheme 17). Particularly noteworthy appears the formation of a compound with SiOO three-membered heterocycle (**77**), which could be isolated on its way of rearranging into a urea-stabilized silanone [111]. Oxidative addition of a phenol to a similar NHSi followed by addition of another phenol to the resultant silyl enamine also afforded a pentacoordinated silicon complex (**78**) [205], and the addition of a carboxylic acid hydrazide proceeds in a similar manner (to afford **79**) [206]. The second step in these addition sequences, the addition reactions between silyl enamines and various Brønsted acids, has already been shown capable of augmenting the silicon coordination number [207–209].

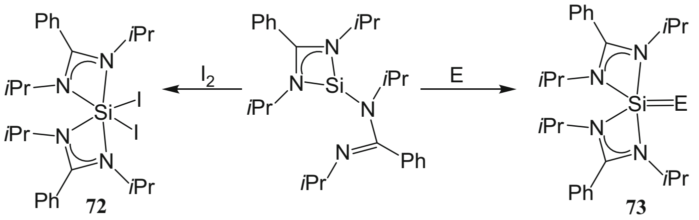
For structurally different P-donor-stabilized silylenes (Scheme 18) a related formation of a SiCO three-membered heterocycle (upon oxidative addition of mesityl carbaldehyde) was reported (formation of **80**) [210], and an oxidative addition of CO_2 (under release of CO) to a P-donor-stabilized disilylene afforded a bridged disiloxane motif with pentacoordinated Si atoms and a bridging carbonato ligand (**81**) [211].



Scheme 13 Further oxidative addition reactions with amidinate stabilized silylenes

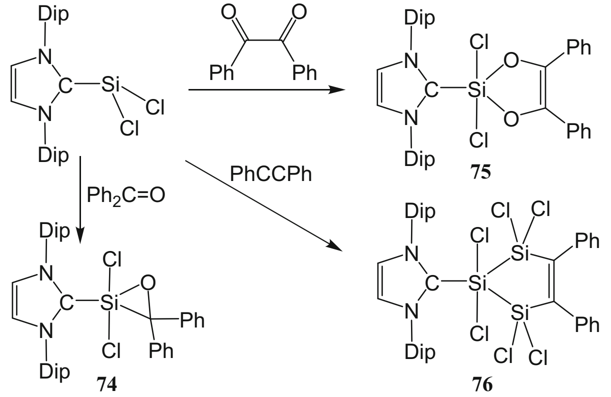


Scheme 14 Further oxidative addition reactions with amidinate stabilized silylenes

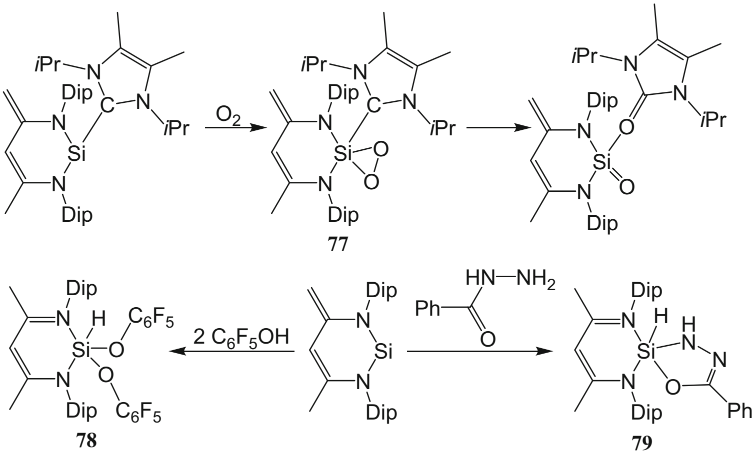


E = S (**a**), Se (**b**), Te (**c**)

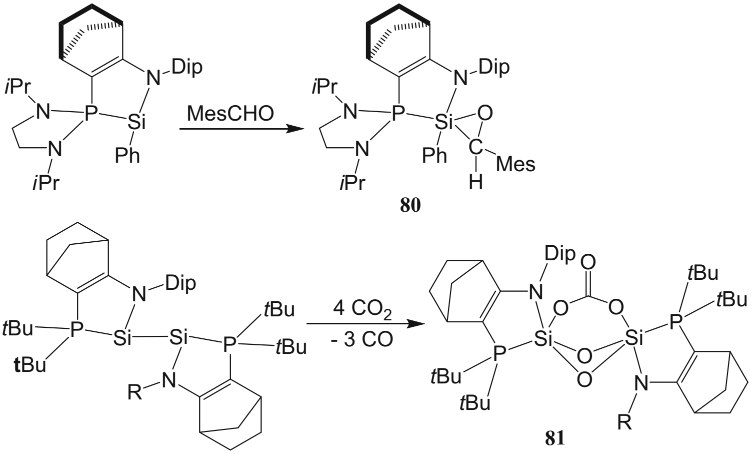
Scheme 15 Formation of a hexacoordinated iodosilicon complex and pentacoordinated silachalcogenones by oxidative addition reactions with an amidinate stabilized silylene



Scheme 16 Oxidative addition reactions with an NHC-stabilized silylene



Scheme 17 Oxidative addition reactions with six-membered *N*-heterocyclic silylenes

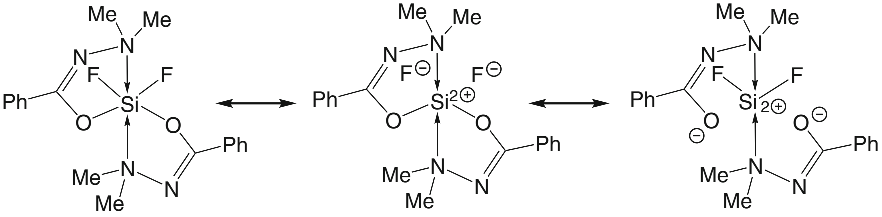


Scheme 18 Oxidative addition reactions with P-donor-stabilized silylenes

3 General Aspects of Structure

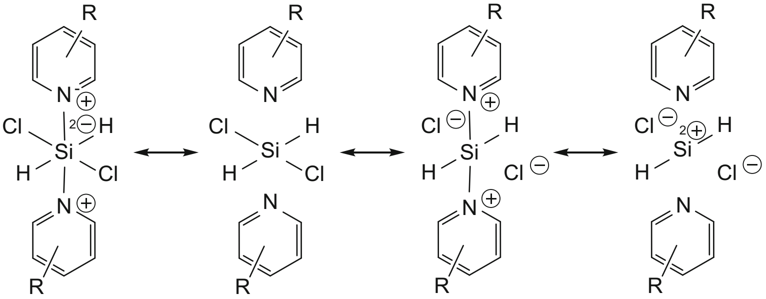
In a landmark paper Stalke et al. demonstrated with experimental and theoretical charge density studies on the molecule **82** (Scheme 19) that the silicon atom in this molecule is definitely not hyper*valent* (by means of more than four covalent bonds, thus exceeding the valence shell electron octet of silicon) [212]. Two different kinds of bonds around the hexacoordinated silicon atom are present. The Si–N bonds in **82** clearly are dative bonds with completely different properties than shorter nondative Si–N bonds. The question of whether dative bonds are to be classified as covalent or ionic remains controversial. Almost all properties in this molecule derived from both experiment and theory suggest ionic domination, and it is just the deformation of the lone pair charge concentration that might introduce a notable covalent contribution. The four remaining Si–O and Si–F bonds indicate predominantly ionic contributions and just a small covalent augmentation [212]. It was pointed out by the authors that "... all the electronic properties emphasize the dominance of the Lewis structures **82b** and **82c** in Scheme 19 to the appropriate bond description, and the covalent contribution obviously is much lower than commonly anticipated." A short summary of these results can also be found in [213].

A high degree of ionic bonding was also observed in adducts of dichlorosilane, trichlorosilane, and dichloromethylsilane with substituted pyridines [101, 103]. For example, four possible valence structures **a**–**d** (Scheme 20) have been investigated with the NBO method for compound **83**, with the valence structures **b**, **c**, and **d** being equally good descriptions of the bonding situation. The analysis of the topological properties of the electron density distribution (AIM) suggests that the Lewis structure **c** represents best the bonding situation in molecules of this type [101].



82a **82b** **82c**

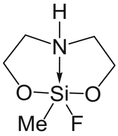
Scheme 19 Proposed Lewis structures for compound **82**



83a **83b** **83c** **83d**

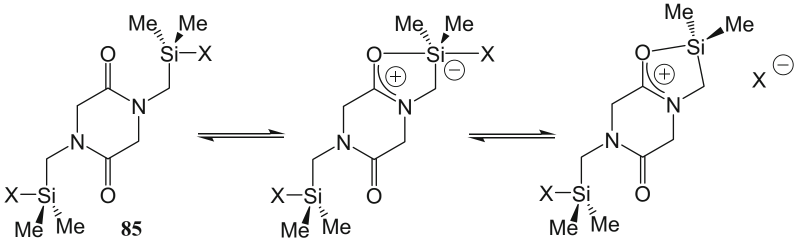
Scheme 20 Proposed Lewis structures for compound **83**

Experimentally determined and theoretically calculated electron density distribution functions of the fluoroquasisilatrane **84** have been investigated [214].



84

The quantum theory of atoms in molecules (QTAIM or AIM) [215–217] is now often used for the analysis of the electron density distribution in higher-coordinated silicon complexes. There are further works dealing with the properties of chemical bonding in 1-hydrosilatrane [218], 1-fluorosilatrane [219], several complexes of tris(pentafluorophenyl)silanes with neutral Lewis bases [92], and chlorosilanes of the composition $Cl_{3-n}H_nSiOCH_2CH_2NMe_2$ ($n = 1–3$) [220].



Scheme 21 S$_N$2 Profile at the silicon atom of compound **85** (X=F, Cl, OTf, Br, I)

3.1 Compounds with Pentacoordinated Silicon Atoms

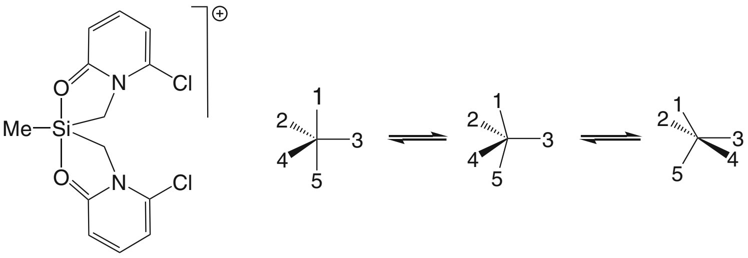
Pentacoordinated silicon compounds might form a trigonal bipyramid (TBP), a square pyramid (SP, or more generally rectangular pyramid), or all possible geometries in between. The coordination sphere in pentacoordinated silicon compounds is generally very flexible with low energy differences between TBP and SP structures [221]. Several methods have been applied to quantify the degree of deformation of a TBP towards a SP [222–224]. The geometric features of compounds with pentacoordinated main group and transition metal element atoms have been reviewed comprehensively by Holmes [225]. Only recently reported aspects of geometry in pentacoordinated silicon compounds will be briefly discussed here.

A series of binuclear pentacoordinated silicon complexes **85** of diketopiperazine have been synthesized and substituent (or leaving group) effects on the Si-O coordination have been studied for five analogues with X=F, Cl, OTf, Br, and I [226]. Variable-temperature NMR spectroscopy (supported by X-ray crystallography) shows, for the first time in binuclear pentacoordinated silicon complexes, a complex equilibrium with both nonionic (O–Si) and ionic (Si–X) dissociation of the axial bonds in the silicon-centered trigonal bipyramids. The two dissociation pathways are consistent with a model for nucleophilic substitution at the silicon atom in a binuclear pentacoordinated silicon compound (Scheme 21) [226].

The conformations of four independent cations of the compound **86** correspond to different points on the Berry pseudorotation pathway (Scheme 22) [221]. The percentage of square planar character varies between 19% and 40%.

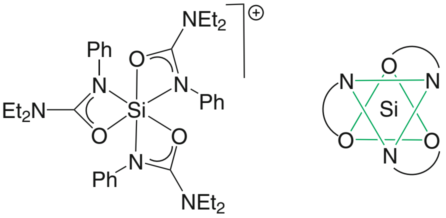
3.2 Compounds with Hexacoordinated Silicon Atoms

Hexacoordinated silicon complexes form octahedra in most cases, or with different ligands distorted octahedra. Deviations from this rule of thumb are seldom observed. One exception in the last 5 years was the distorted trigonal antiprismatic cationic silicon complex **87** with ureato ligands (Scheme 23) [227].



86

Scheme 22 S_N2 Cationic pentacoordinated silicon complex **86** (*left*) and schematic representation of a Berry pseudorotation process (*right*) [221]

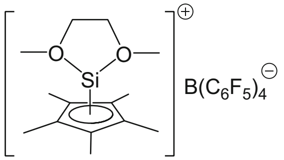


87

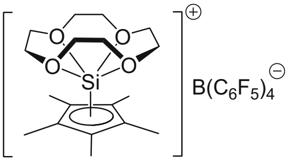
Scheme 23 Cationic silicon complex **87** with ureato ligands (*left*) and schematic representation of a trigonal antiprismatic coordination geometry (*right*)

3.3 Coordination Numbers Higher than Six

Whereas Si-hypercoordination is most frequently observed with five or six formal electron pair donors, silicon coordination numbers higher than six have also been realized. However, examples for such higher-coordinated silicon compounds bearing more than six formal lone pair donors in the coordination sphere are rare. Thus, only a few but quite fascinating compounds with Si coordination numbers higher than six have been reported during the last 5 years. Among these were ionic silicon(II) compounds derived from $[Cp^{*}Si]^{+}$. This highly reactive ion is stabilized by complexation with dimethoxyethane (DME) (in **25a**) and 12-crown-4 (in **25b**) [136]. Considering the Cp* anion a formal three-electron-pair donor, the hepta- and nona-coordinated Si atoms of **25a** and **25b**, respectively, are surrounded by five and seven formal electron pair donors, respectively.



25a



25b

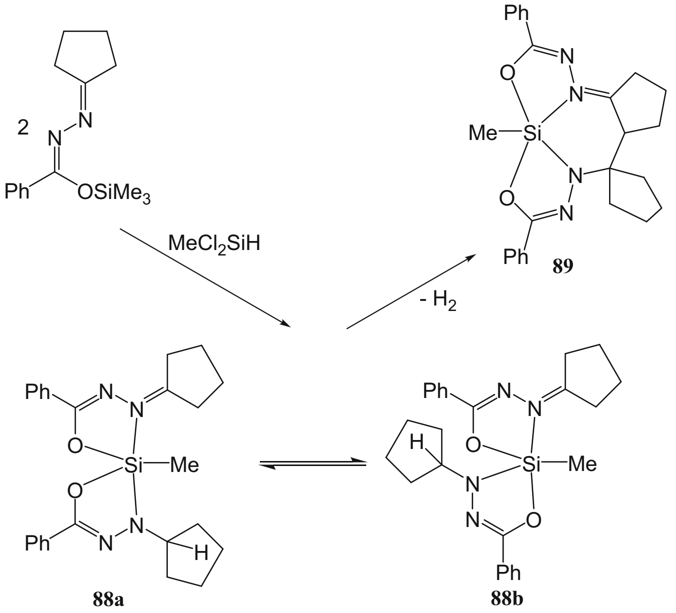
Further examples with Si coordination numbers greater than six are encountered with oligometallic (or oligometalloidic) clusters. The preparation and X-ray structures of $Si@Al_{14}R_6$ (R = Cp*, N(dip)SiMe$_3$; dip = 2,6-iPr$_2$-C$_6$H$_3$) are described via the disproportionation and substitution reaction of a metastable AlCl solution [228]. The silicon atom in these compounds occupies the center of an Al_8 cube. This central unit is stabilized through capping of six faces of the cube by AlR moieties.

Some new Zintl anions containing silicon atoms in high coordination numbers have been reported since 2008. Among these were [Rb(18-crown-6)]$Rb_3Si_9 \cdot 4NH_3$, $Rb_4Si_9 \cdot 4.75NH_3$, and $Rb_4Si_9 \cdot 5NH_3$ [229, 230]. Single-crystal X-ray diffraction analysis reveals the presence of Si_9^{4-} anions. The nonasilicide anions are coordinated by rubidium cations, thus expanding the coordination number of the silicon atoms above six. The reaction of $K_6Rb_6Si_{17}$, MesCu, and 18-crown-6 in liquid ammonia yielded crystals of [Rb(18-crown-6)]$_2$Rb$_{1.54}$K$_{0.46}$[(MesCu)$_2$Si$_4$](NH$_3$)$_{12}$ [230]. This compound contains a tetrahedral tetrasilicide(4−) anion which is stabilized by mesityl-copper units and rubidium cations thus yielding coordination numbers higher than six for the silicon atoms involved in this tetrasilicide. In a similar way the isotypic compound [Rb(18-crown-6)]$_2$Rb$_2$[(MesCu)$_2$(Si$_{3.3}$Ge$_{0.7}$)](NH$_3$)$_{12}$ has been synthesized [231].

Some recent publications deal with Keggin-type polyoxo-tungstates and polyoxomolybdates featuring central silicon atoms [232–234]. In CSD and CA registry database searches these compounds might appear as higher-coordinated silicon species probably due to complex nature of these anions. However, the central silicon atom in anions of composition $[SiM_{12}O_{40}]^{4-}$ (M = Mo, W) is tetracoordinated. These Keggin-type polyoxometalates therefore do not belong to the class of higher-coordinated silicon compounds considered here.

3.4 Equilibria Between Complexes with Different Coordination Numbers

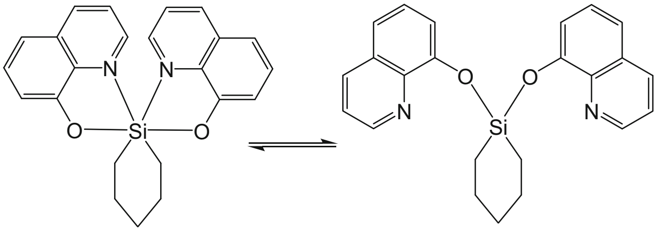
Equilibria between hexa- and pentacoordinated silicon complexes have been examined carefully by Kost et al. Exemplarily the following works might be cited here: Neutral hexacoordinated silicon complexes derived from hydrazide chelating ligands with imino-donor groups form pentacoordinated Si complexes in the course of ionic dissociation reactions. Such complexes were shown to undergo facile intramolecular aldol-type condensation [176]. In a related system



Scheme 24 Equilibrium between two isomeric silicon complexes (**88a** and **88b**) with pentacoordinated Si atom

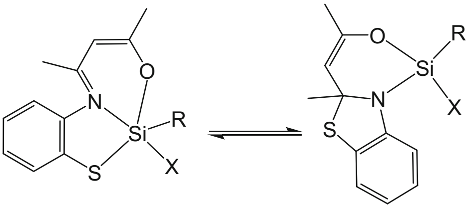
(Scheme 24), the hydride migration from silicon to an adjacent unsaturated imino carbon atom leads to a pentacoordinated silicon complex **89** as final product [170]. For the intermediate **88** a dynamic equilibrium between two conformers **88a** and **88b** with pentacoordinated Si atom was observed by NMR spectroscopy. For related compounds with hexacoordinated Si atom within a $(O,N)_2SiMe(H)$ coordination sphere, the authors observed reversible neutral dissociation of the N–Si dative bond, i.e., an equilibrium between hexa- and pentacoordinated hydrido complexes of silicon [235].

In several cases it was possible to observe equilibria or to isolate crystalline derivatives containing tetra- and hexacoordinated silicon atoms with the same ligand system. Some examples are listed here: A bicapped tetrahedral intermediate or transition state has been postulated in neutral hexacoordinated mixed trichelate silicon complexes on the basis of the temperature dependence of the ^1H NMR spectra and coalescence of signals due to diastereotopic *N*-methyl- and CH_2 groups [156]. The silacycloalkanes (8-oxyquinolinate)$_2$Si(CH_2)$_n$ ($n = 3, 4, 5, 6$) (for $n = 5$ see Scheme 25) reveal stepwise decreasing NSi coordination with increasing ring size. Whereas for $n = 3$ and 4 hexacoordinated silicon compounds were found at room temperature, $n = 5$ supports an equilibrium that allowed for the isolation of two coordination isomers (CN 4 and 6, compounds **90b** and **90a**, respectively) as crystalline solids, and $n = 6$ causes the equilibrium to shift towards the tetracoordinated Si compound [175].



90a **90b**

Scheme 25 Equilibrium between two isomeric silicon complexes (**90a** and **90b**) with hexa- and tetracoordinated Si atom



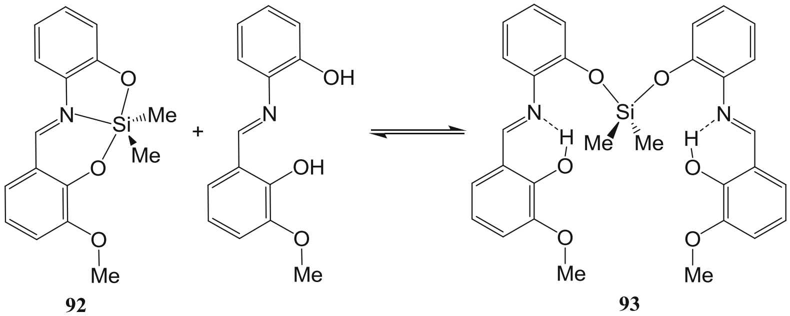
91a **91b**

Scheme 26 Dynamic equilibrium between penta-(**91a**) and tetracoordination (**91b**) in solution

Solution-state NMR studies of silicon complexes with tridentate O,N,S-ligands (Scheme 26) revealed the existence of dynamic equilibria between pentacoordinated silicon complexes (**91a**) and isomeric tetracoordinated species (**91b**) [190]. The ratio between tetra- and pentacoordinated complexes depends on the nature of the (pseudo) halogeno and organyl ligands and on the solvent. These effects are not yet fully understood. In the series of the halogenosilicon complexes, the halogeno ligands favor pentacoordination in the following rank order: $I \approx Br > Cl > F$. This is contrary to expectations if it is assumed that hard ligand atoms should favor pentacoordination of the hard silicon(IV) center [190].

A pentacoordinated (**92**) and a tetracoordinated silicon complex (**93**) were isolated from the reaction of 2-(2-hydroxy-3-methoxybenzylideneamino)phenol with dichlorodimethylsilane [236]. These complexes are related to one another via addition and elimination of one ligand molecule (Scheme 27). According to quantum chemical calculations, **93** is the thermodynamically stable product and **92** is the kinetically favored product.

Hexamethylphosphoramide (HMPA) adducts of tetrachlorosilane ($SiCl_4$) were investigated with NMR spectroscopy in solution and solid-state structures [93]. In solution, the meridional and facial isomers of the hexacoordinated cationic silicon complex $[SiCl_3(HMPA)_3]^+Cl^-$ predominate at all HMPA concentrations and are in equilibrium with the hexacoordinated neutral *trans*- and *cis*-$[SiCl_4(HMPA)_2]$ complexes, as well as the pentacoordinated cationic Si-complex *cis*-$[SiCl_3(HMPA)_2]^+Cl^-$ [93].



Scheme 27 Equilibrium between penta- (**92**) and tetracoordination (**93**) via addition and elimination of a ligand acid

4 Frequently Used Ligands and Donor Atoms

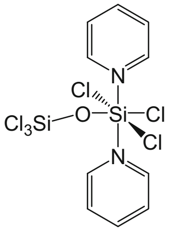
There are several types of ligand systems which have often been used to generate higher-coordinated silicon complexes within the last 5 years. These are:

1. Neutral mono- and bidentate nitrogen bases
2. Bidentate ionic ligands with oxygen and nitrogen as donor atoms
3. Bidentate ligands forming four-membered rings with silicon
4. Bidentate ligands derived from carboxylic acids
5. Tridentate chelate ligands
6. Triethanolamines forming silatranes
7. Tetradentate chelate ligands of "salen"-type
8. Phthalocyanines

These classes of silicon complexes will be discussed in the following sections.

4.1 Neutral Mono- and Bidentate Nitrogen Bases

Adducts of chlorosilanes with neutral nitrogen bases are known since more than 40 years [237–239]. Recently a series of new compounds of this type involving hydridochlorosilanes has been synthesized, characterized by X-ray structure analysis, and investigated under different aspects. These compounds are hexacoordinated adducts of trichlorosilane, dichloromethylsilane, and dichlorosilane with substituted pyridines [101–103]. The main focus of these articles was the structural and spectroscopic characterization of the new compounds, including ^{29}Si CP/MAS NMR investigation for experimental and theoretical evaluation of the tensor components of the ^{29}Si NMR shift anisotropy. These complexes prefer a *trans* arrangement of the nitrogen ligands. This is not possible in complexes bearing chelating ligands like 2,2′-bipyridine or 1,10-phenanthroline. Various hexacoordinated silicon complexes have also been prepared with these two nitrogen donor ligands, i.e., by complexation with H_2SiCl_2, $HSiCl_3$, $RSiCl_3$ (R = Me, Ph), and $[Na(CH_3CN)_n^+]_2$ $(Si(N_3)_6]^{2-}$ [142, 168]. Possible applications of silicon complexes with neutral nitrogen donor ligands have been outlined in a paper dealing with the preparation of sol–gel-derived Si/C/O/N materials. Therein the reactions of hexachlorodisiloxane ($Cl_3Si–O–SiCl_3$) with bis(trimethylsilyl)carbodiimide ($Me_3Si–NCN–SiMe_3$) were catalyzed with pyridine. The crystal structure of $Cl_3Si–O–SiCl_3(pyridine)_2$ **94** was determined and it was concluded that this compound is a potential intermediate in the pyridine catalyzed sol–gel process [240].



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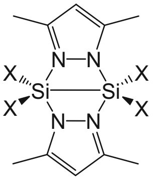


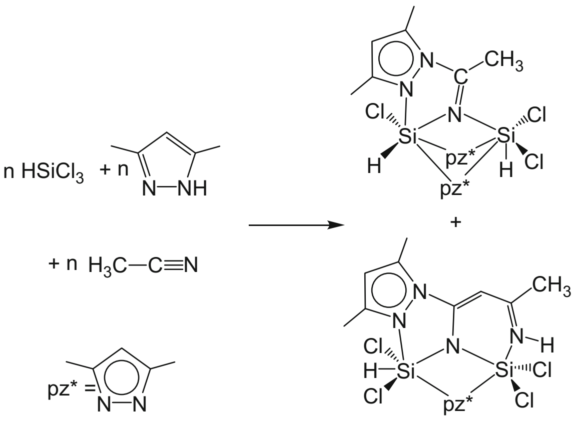
95

The reaction conditions for the synthesis of $[Si_2(pz^*)_6]$ and $[Si(pz^*)_4]$ have been investigated in detail in order to obtain suitable precursor compounds for the synthesis of the hitherto unknown Janus-head ligand tris(3,5-dimethylpyrazolyl) silanide ($[Si(pz^*)_3]^-$ [241]. The X-ray structures of several pentacoordinated disilanes of type **95** with X = Cl or 3,5-dimethylpyrazolyl have been presented in this work. The chemistry of 3,5-dimethylpyrazolyl silicon complexes has been further explored. Although pyrazolide is an anionic substituent, its second N atom (the imine N atom of N-silylated pyrazole) also coordinates to silicon, thus exhibiting features of a neutral nitrogen donor as well.

A complex system of equilibria of both Si–Cl vs. Si–N dismutation and intramolecular Si–N exchange was observed with NMR spectroscopy in $Si(pz^*)_4$ and $Si(pz^*)_3Cl$ [106]. The reaction of $Me_3Si(pz^*)$ with H_2SiCl_2 leads to the unexpected formation of a silicon complex with three silicon atoms [134]. The lateral silicon atoms are pentacoordinated; the central silicon atom is hexacoordinated. Furthermore, it was found that the reaction of $HSiCl_3$ with 3,5-dimethylpyrazole in acetonitrile gives 3,5-dimethylpyrazolyl silicon complexes where one (**96**) or two molecules acetonitrile (**97**) have been inserted into the bond between silicon and the 3,5-dimethylpyrazolyl ligand (see Scheme 28) [134].

Silicon-mediated nitrile activation has also been observed in trichloro [2-(dialkylphosphanyl)imidazol-1-yl]silanes (Scheme 29) [133]. These react with aceto- or propionitrile to yield the dinuclear pentacoordinated silicon complexes **98**. The reactions leading to **96**, **97**, and **98** hint to new pathways of catalytic activation mediated by dinuclear silicon complexes.

An unusual hydrolysis product **99**, which contains three hexacoordinated silicon atoms, was observed in reactions between $HSiCl_3$ and 3,5-dimethylpyrazole (Hpz*) [134]. The cationic complex consists of three pz* bridged Si–H units



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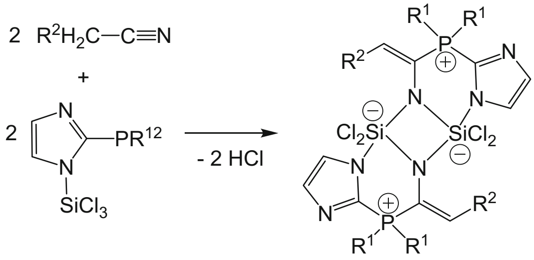
Scheme 28 Formation of binuclear silicon complexes as formal products of acetonitrile insertion



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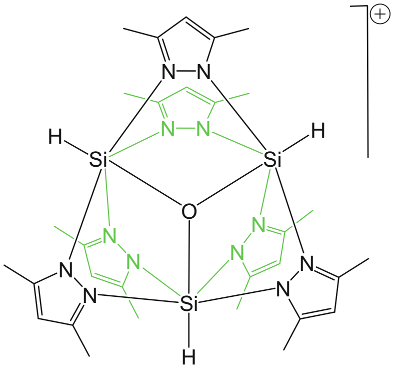
Scheme 29 Insertion of nitriles in trichloro[2-(dialkylphosphanyl)imidazol-1-yl]silanes (R^1 = Et, *i*-Pr; R^2 = H, Me)

and one oxo ligand in the center. Three crystal structures obtained from different reaction batches hint to the fact that this hydrolysis product might be exceptionally stable.



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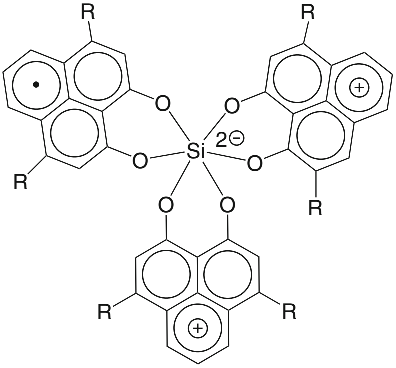
4.2 Bidentate Ionic Ligands with Oxygen and Nitrogen as Donor Atoms

Bidentate O,O-ligands like phenolates, glycolates, tartrates, and compounds bearing simple O,N and N,N chelating ligands are in the focus of this section. Trisphenalenylsilicon neutral radicals **100** (R=H, OMe) have been synthesized, characterized, and their solid-state properties have been investigated [242, 243]. Such compounds were proposed as building blocks for molecular conductors and provide an alternative approach to the conventional charge-transfer organic conductors and superconductors, in which the unpaired electrons of the neutral radicals serve as charge carriers. Several substituted catechols and sterically bulky natural flavones were used as 1,2-diolate anionic ligands to encapsulate silicon in an O_6 coordination sphere [244]. Electron-withdrawing groups at the aromatic ring favor a greater stability and better yields of the complexes. Octahedral silicon complexes bearing two 1,10-phenanthroline ligands and one arenediolate ligand as **101** were investigated as a structural motif for the design of hydrolytically stable bioactive complexes as demonstrated with the generation of silicon-based high-affinity DNA binders [245]. This proof-of-principle study suggests that octahedral silicon complexes are promising structural templates for widespread applications in chemical biology and medicinal chemistry.



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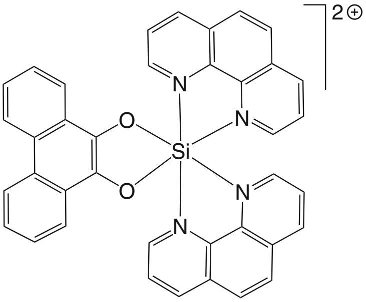
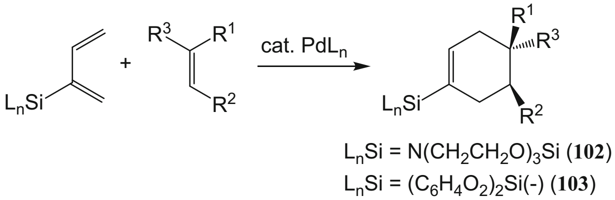


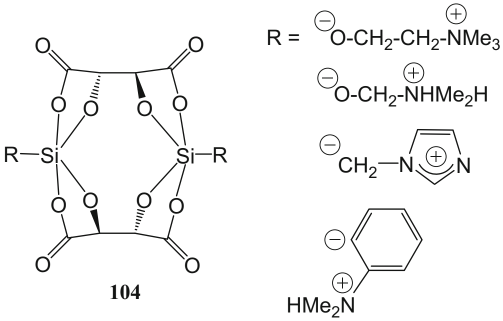
101

The use of 2-silyl-substituted 1,3-dienes in Diels–Alder and cross-coupling reactions was reported in [246]. Among other silicon compounds the authors utilized silatranyl (**102**) and catecholato-chelated silyl derivatives (**103**) with pentacoordinated Si atoms for the reactions shown in Scheme 30.

A series of zwitterionic and anionic dinuclear pentacoordinated silicon complexes with bridging (R,R)-tartrato ligands have been prepared and characterized [117, 247]. Common structural features of these compounds are two bridging tartrate ligands forming a cage-like unit with two silicon atoms. This leaves space for the coordination of a fifth ligand. For this purpose often zwitterionic groups are used, which



Scheme 30 Diels–Alder reactions of 2-silyl-substituted 1,3-dienes with pentacoordinated silicon atoms



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Scheme 31 Examples for zwitterionic dinuclear pentacoordinated silicon complexes with bridging (*R*,*R*)-tartrato ligands

render the complexes **104** charge neutral. Examples of such compounds are shown in Scheme 31. They were thoroughly characterized and their hydrolytic stability was investigated with respect to the role such complexes (or related compounds) might play in the biochemistry of silicon. Tartaric acid has been used in combination with (2-oxopiperidin-1-yl)methyl to prepare similar dinuclear silicon complexes such as **104**. Since the (2-oxopiperidin-1-yl)methyl ligand is a monoanion, dianionic complexes are obtained, which are stabilized by dicyclohexylammonium cations [248].

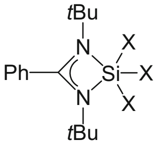
Simple α-amino acids have been utilized as dianionic and monoanionic chelating ligands to stabilize hexa- and pentacoordinated silicon complexes [249]. The hydrolysis reactions of these compounds lead to the formation of free α-amino acids and alkylsilanetriol $RSi(OH)_3$. In case of R=Me, methylsilanetriol is generated. This species is considered as a “silicon food supplement” for use in humans and is currently being discussed as a potential drug for the improvement of bone and other connective tissue health. Therefore, such silicon complexes might serve as silicon food supplements or as pro-drugs for methylsilanetriol. The reaction of *O*-trimethylsilyl-L-mandelic *N*,*N*-dimethylamide with tetrachlorosilane leads to a new complex with pentacoordinated silicon and a monoanionic (O,O) chelating ligand [250].

Penta- and hexacoordinated silicon complexes have been prepared with β-diketonato ligands generated from 1,3-diphenylpropane-1,3-dione and 1-phenylbutane-1,3-dione [128]. Several bidentate O,O-ligands and one O,N-ligand have been used to synthesize pentacoordinated silicon complexes containing the tris(pentafluorophenyl)silyl unit [92]. These bidentate ligands have been generated from salicyl aldehyde, *N*-(2-hydroxybenzoyl)pyrrolidine, *N*-methyl-*N*-(2-hydroxybenzylidene)amine, succindicyclopentylamide, and by aldol coupling of 1-tris(pentafluorophenyl) silyloxycyclopentene with isobutyraldehyde.

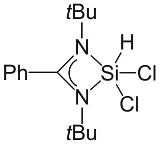
With 8-oxyquinolinate as an O,N-ligand it was shown that the donor–acceptor interaction between the nitrogen atom of the 8-oxoquinolinate ligand and the central silicon atom can be tuned by a stepwise increase of the ring size of a cycloalkyl group in the silacycloalkane series (8-oxyquinolinate)$_2$Si(CH$_2$)$_n$ ($n = 3, 4, 5, 6$) (see Scheme 25) [175]. Strong intramolecular Si–N interactions have been proven to exist in the chlorosilanes $Cl_{3-n}H_nSiOCH_2CH_2NMe_2$ ($n = 1–3$) [220]. Further work by the same group of Mitzel et al. shows that geminal Si–N interactions exist in compounds of the type $C_6F_5SiF_2$-X-NMe$_2$ with X = NSiMe$_3$ and X = O but not with X = CH$_2$ [251].

4.3 Bidentate Ligands Forming Four-Membered Rings with Silicon

Benzamidinates (and guanidinates) are able to stabilize pentacoordinated silicon complexes. The amidinate ligand coordinates via both nitrogen atoms to the central silicon atom, which is further supplemented by three other anionic ligands as it is shown exemplarily by the compounds **105–110** [200, 252–254].



X = Cl (**105**)
X = F (**106**)



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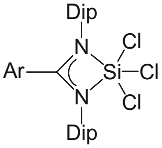

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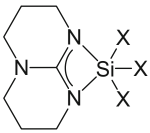
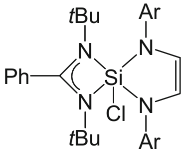


X = Cl (**109**)
X = F (**110**)

Starting from **107**, the heteroleptic chlorosilylene PhC(NtBu)$_2$SiCl is accessible [200]. This silylene has been utilized as a substrate to prepare various higher-coordinated silicon compounds. In a series of publications a rich chemistry was developed with several oxidative addition reactions and has therefore already been addressed in Sect. 2.6 (see Schemes 12, 13, and 14). Further reactions of this silylene include oxidative addition of a glyoxaldiimine to afford a formal [1+4]-cycloaddition product **111**. When treated with diphenyl disulfide, cleavage of the S–S bond occurs to form **112** [255].



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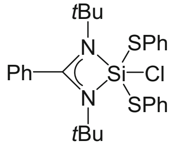

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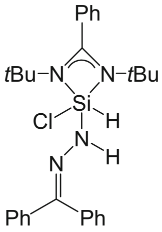

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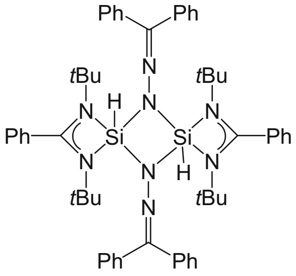
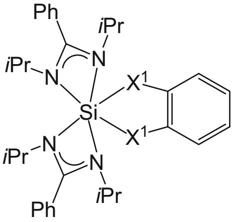


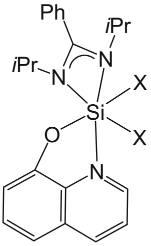
114

The reaction of chlorosilylene PhC(N*t*Bu)$_2$SiCl with diphenylhydrazone leads to a diphenylhydrazone derivative **113** with pentacoordinated silicon atom. Therefrom a disilicon compound **114** with a Si_2N_2 core is prepared under HCl elimination [256]. The reaction of PhC(N*t*-Bu)$_2$SiCl with N_2O afforded a trimer which contains a Si_3O_3 six-membered ring with pentacoordinated silicon atoms [257]. The reaction of PhC(N*t*-Bu)$_2$SiCl with 2-adamantanone furnishes a [1+2]-cycloaddition product, whereas treatment with 3,5-di-tert-butyl-*o*-benzoquinone leads to the [1+4]-cycloaddition product [258]. Both compounds contain pentacoordinated silicon atoms. The reaction of this silylene with diazobenzene afforded an unsymmetrical polycyclic product via chlorosilylene-mediated aromatic C–H bond activation. The reaction proceeds without the cleavage of the N–N bond of diazobenzene [259]. Another example of bond activation was demonstrated to occur in the reactions of PhC(N*t*Bu)$_2$SiCl with hexafluorobenzene and other fluorinated arenes, which afford silicon(IV) fluorides with pentacoordinated silicon atoms [260]. This chemistry was further explored recently by investigating the reactivity of LSi–SiL [198], LSi–Si(Cl)HL [199], LSi(*t*-Bu) [196], and LSi[C(SiMe$_3$)$_3$] [261] L = PhC(N*t*-Bu)$_2$. Cycloaddition and oxidative addition reactions with these silylenes and bis-silylenes give access to a steadily growing number of unusual silicon complexes with pentacoordinated silicon atoms (see also Sect. 2.6).

A number of hexacoordinated silicon complexes have been prepared by using benzamidinato ligands mainly in combination with other chelating ligands [154, 262]. Examples are compound **72** (Scheme 15) and the compound classes **115** and **116**.



115
(X^1 = S, Se)



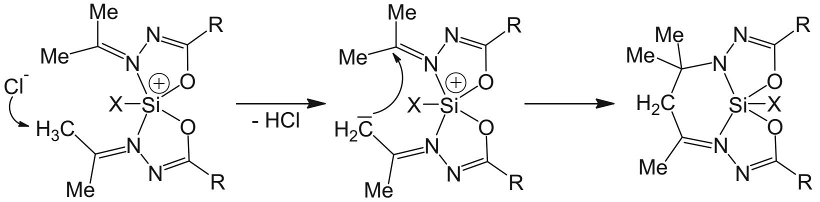
116
(X = Cl, Br, F, CN, N_3, NCO, NCS)

Ureato ligands with coordination ability via one carbonyl oxygen and a nitrogen atom represent an alternative to the benzamidinato ligands discussed above. They form also four-membered cycles with the silicon atom. Only one publication appeared in the past 5 years using this ligand system to prepare higher-coordinated silicon complexes. The distorted trigonal antiprismatic cationic silicon complex **87** (Scheme 23) with ureato ligands was characterized by X-ray structure analysis and ^{29}Si CP/MAS NMR spectroscopy [227].

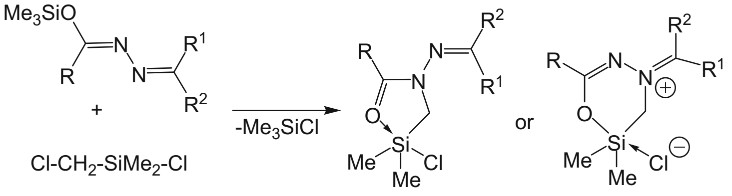
4.4 Bidentate Ligands Derived from Carboxylic Acids

A multifaceted chemistry of higher-coordinated silicon complexes has been developed utilizing hydrazide chelating ligands with imino-donor groups. Neutral hexacoordinated silicon complexes derived from these ligands and their pentacoordinated ionic dissociation products undergo facile intramolecular aldol-type condensation catalyzed by their chloride counterion leading to formation of a third chelate ring (Scheme 32) [176]. Furthermore, rearrangements involving silicon-bonded cyanide and *t*-Bu groups [176], hydride migration from silicon to an adjacent unsaturated imino carbon [170], reversible neutral dissociation of the N–Si dative bond [235], dynamic stereochemistry [156], and both chelate ligand exchange and central-element exchange [263] have been observed with complexes of this type.

Another effective route to pentacoordinated silicon complexes with ligand systems derived from carboxylic hydrazides is the reaction of *O*-trimethylsilylated hydrazide Schiff-base derivatives (at the terminal nitrogen atoms) [$RC(OSiMe_3){=}NN{=}CR'R''$] with chloro(chloromethyl)dimethylsilane [$ClCH_2SiMe_2Cl$] (Scheme 33) [264]. This reaction proceeds in a regioselective manner, forming either five-membered (**117**) or zwitterionic six-membered chelate complexes (**118**) with pentacoordinated silicon. The type of product is determined by the size of the substituent R. Bulky groups (R=Ph, *t*-Bu) lead to exclusive formation of complexes with six-membered chelate, whereas with the less bulky groups (Me, $PhCH_2$), only the five-membered



Scheme 32 Intramolecular aldol-type condensation catalyzed by a chloride counterion

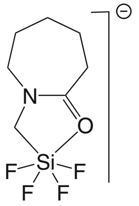


117 **118**

Scheme 33 Reaction of *O*-trimethylsilylated hydrazides with chloro(chloromethyl)dimethylsilane

chelate is obtained. Upon mild heating, the six-membered chelate complex **118** transforms into its five-membered isomer **117** [264].

Amides and hydrazides of carboxylic acids have been also used successfully by other groups to stabilize penta- and hexacoordinated silicon. The compounds **119** [265], **120** [266], and **79** [206] serve as examples.



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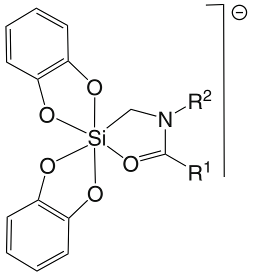

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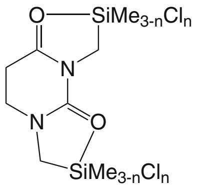
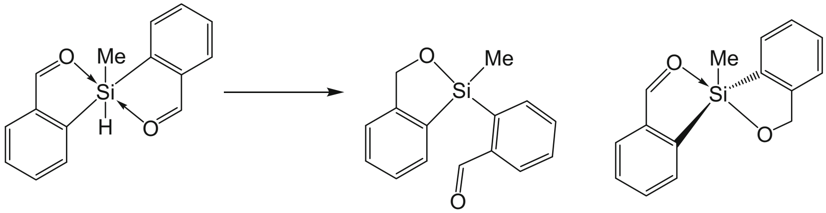


121

Compound **119** involves a cyclic amide of an ω-amino acid as ligand. Related to this are complexes containing cyclic amides like uracil (**121**), barbituric acid, 5,5-dimethylbarbituric acid [116], 2,5-piperazinedione (**85**) [226], and 2-chloro-6-hydroxypyridine (**86**) [221], respectively, to accomplish pentacoordination at silicon.



122 **123** **123a**

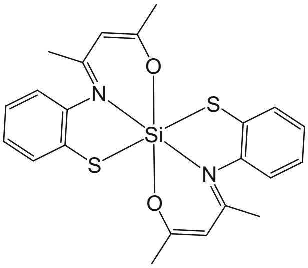
Scheme 34 Hydride migration from Si to an aldehyde C atom

These compounds were investigated with variable-temperature NMR spectroscopy supported by X-ray crystallography. It was shown that a complex equilibrium with both nonionic (O–Si) and ionic (Si–X) dissociation of the axial bonds in the silicon-centered trigonal bipyramids exists (*vide supra*) [226].

A hexacoordinated silicon complex with two ortho-silylated benzaldehyde ligands **122** has been proposed as an intermediate in the formation of compound **123** (Scheme 34) [267]. Notably, the authors have published a crystal structure and interpreted the molecule as compound **122**, but a closer inspection of the X-ray structure data shows (1) the silicon coordination sphere is trigonal-bipyramidal (equatorial situation of three Si–C bonds, axial situation of two Si–O bonds), (2) the Si-bound hydrogen atom has been refined in an unreasonable position (very close to one Si–O bond), (3) the quality of the structure is poor (R-factor 7.8%), (4) the thermal displacement ellipsoids of the Si and O atoms are unusually large, and (5) the C=O bond lengths are refined to 1.30 Å. Thus, we suspect that the crystal structure reported had been determined from compound **123a**, an isomer of the proposed compound **123** with pentacoordinated Si atom, and disorder of the two chelating ligands causes the unusually large ellipsoids of Si and O atoms and the C=O bond length which lies between the values expected for C=O and C–O bonds.

4.5 Tridentate Chelate Ligands

A large number of papers have been published in the last 5 years dealing with penta- and hexacoordinated silicon complexes stabilized by tridentate O,N,O-, O,N,S-, N,N,S-, and O,N,N-chelate ligands. A substantial part of these were produced by Tacke et al. [189, 190, 193, 194, 268–272]. Most of the tridentate ligand systems used in their investigations are Schiff bases of aromatic *o*-hydroxy- or *o*-mercaptoaniline derivatives. These were used to prepare penta- and hexacoordinated silicon complexes **124–130**.



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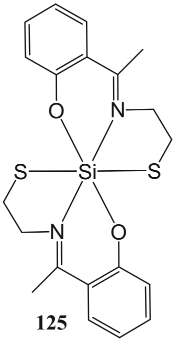

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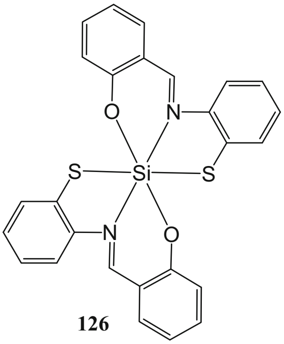

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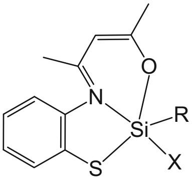

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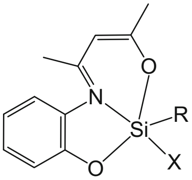

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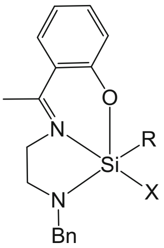

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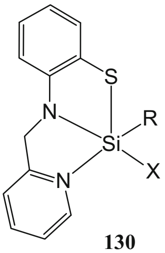

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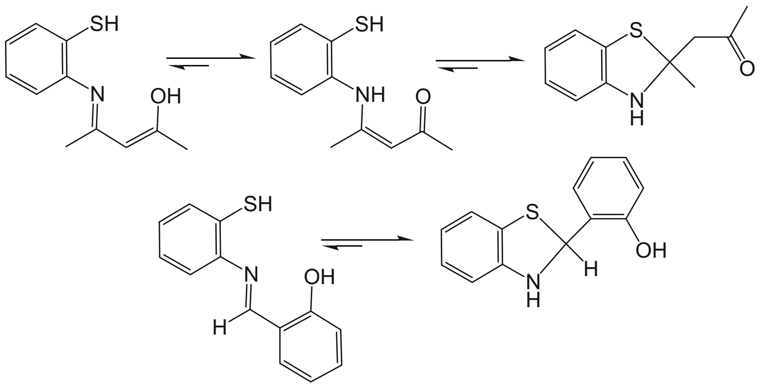
Ligands containing imine nitrogen and thiol groups in vicinal position can exist in a ring-opened form or in a ring-closed thiazol form (Scheme 35). It is difficult to predict which isomer will coordinate to silicon, as both coordination modes have been observed (e.g., compounds **53** and **58**, Scheme 11). Furthermore, one of these ligands was shown to react under formal loss of hydrogen (H_2) as a bidentate ligand and coordinates via the oxygen and nitrogen atom [269] to form the hexacoordinated silicon complex **131**(Scheme 36).

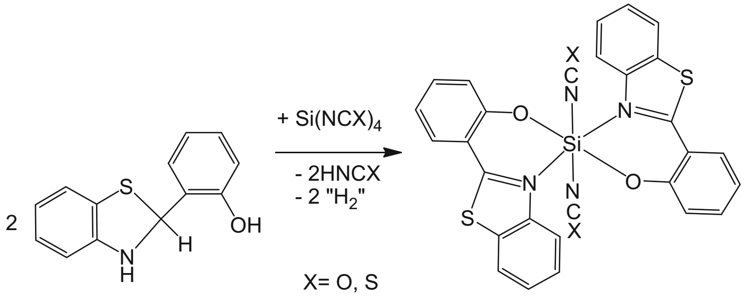
In a similar way the ring opening of organosilicon-substituted benzoxazolinone has been used as a convenient route to chelating ureato and carbamido ligands [192]. It was even possible to obtain three different coordination modes to silicon with the ligand *N*-(o-aminophenyl)-2-oxy-4-methoxybenzophenoneimine and its *N*-acylated derivatives, respectively (Scheme 37) [195, 273].

Further aspects which have been dealt with were the question whether ring-strain-formation Lewis acidity plays a role in pentacoordinated silacyclobutane derivatives [274]; intra-ligand π–π* transitions within a tridentate O,N,N-ligand [275]; dynamic disorder in a pentacoordinated silicon complex with 2,2′-diazenediyldiphenol [276]; pentacoordination vs. tetracoordination in silicon derivatives of an O,N,O-tridentate ligand [236] and the coordination of the pyridine moiety of an ONN-ligand in diorganosilicon complexes [277].

A few publications deal with silicon complexes of chiral O,N,O-ligands. Tridentate imine ligands were obtained from chiral amino alcohols by Schlecht et al. [278]. These ligands serve for the formation of bis-chelated silicon complexes. Whereas the complex based on 2-amino-1,1,2-triphenylethanol is obtained as a diastereomeric



Scheme 35 Ring-opened (*left*) and ring-closed isomers (*right*) of potential tridentate ligands with O,N,S-coordination ability



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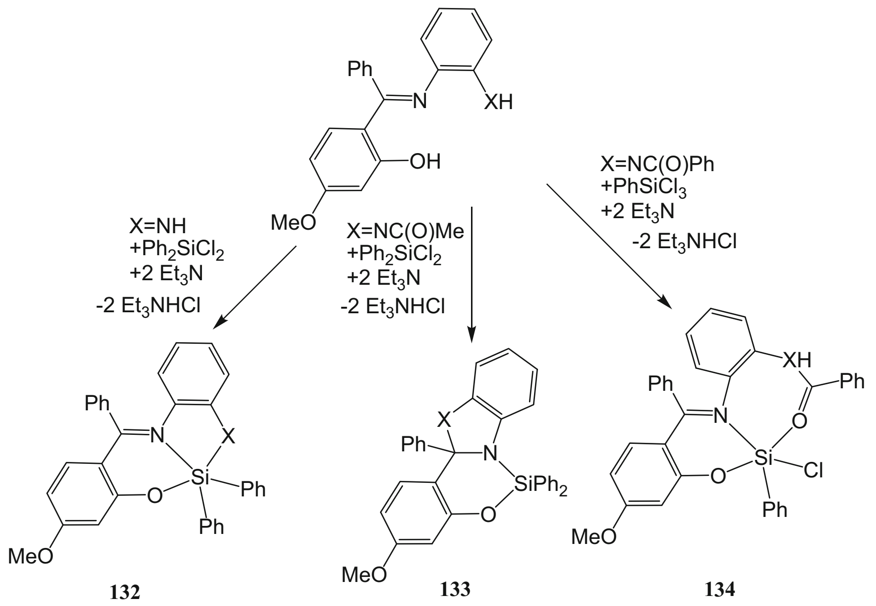
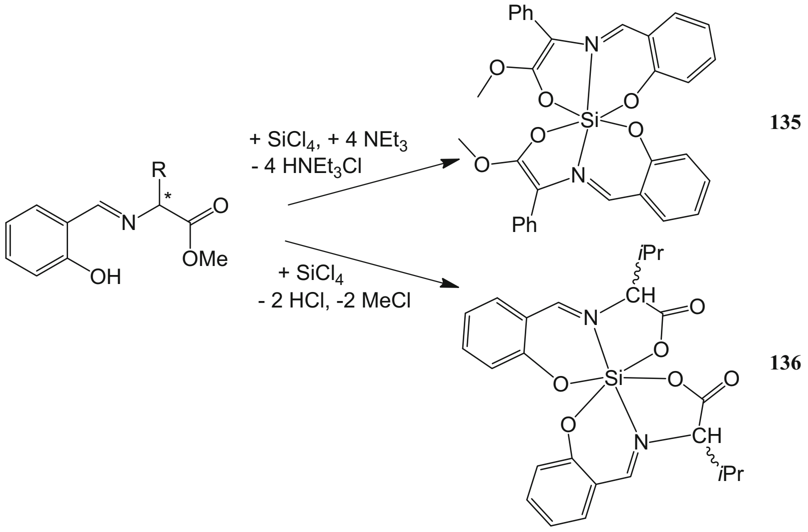
Scheme 36 Formation of a hexacoordinated silicon complex under loss of hydrogen

mixture, the complex that is derived from 1-amino-1,2,2-triphenylethanol forms in a completely diastereoselective manner. The new silicon complexes are found to be efficient dopants for the conversion of nematic liquid crystals into cholesteric phases [278]. Two turnstile rotamers of a pentacoordinated silicon complex with a chiral backbone derived from 2-amino-1,1,2-triphenylethanol have been confirmed by crystal structure analysis. In addition, the coexistence of two rotamers, which readily interconvert in solution, was demonstrated by NMR spectroscopy. A 120° turnstile rotation of three ligands at the silicon atom is assumed as the preferred path of the observed stereomutation [279]. Chiral Schiff-base ligands with O,N,O-coordination ability have been prepared with amino acid esters from the chiral pool [280]. The chiral information is lost during the formation of complexes with these chiral ligands with silicon tetrachloride (Scheme 38). The Schiff-base ligand yields a ketene acetal structure (**135**) or a racemized ligand system (**136**) depending on the reaction conditions and the nature of the amino acid group. The surprising structural features of **135** and **136** allowed to develop a uniform concept explaining the racemization of the ligand system during complex formation.

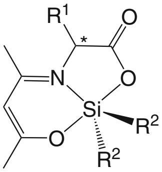


Scheme 37 Three different coordination modes to silicon with the ligand *N*-(*o*-aminophenyl)-2-oxy-4-methoxybenzophenoneimine and its acylated derivatives



Scheme 38 Formation of a ketene acetal structure (**135**) or a racemized ligand system (**136**) in the complex formation of $SiCl_4$ with chiral Schiff-base ligands

A new type of chiral silicon complexes have been developed recently. By preparation of a Schiff-base from acetylacetone and amino acids from the chiral pool a ligand system is available which allows the preparation of chiral pentacoordinated silicon complexes of type **137** [281]. No racemization has been observed during complex formation with dichlorodiorganosilanes.



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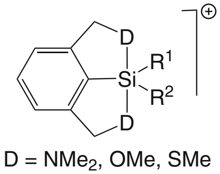

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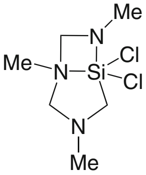

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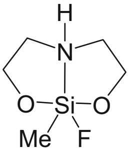
Only one investigation during the last 5 years employed pincer ligands (in this case to generate cationic higher-coordinated silicon complexes of type **138**) [282]. Pincer ligands are far more often used in transition metal chemistry, as it is reflected by numerous review articles published in the last years [283–285]. The molecule **139** was identified by X-ray structure analysis. It represents the formal insertion product of $SiCl_2$ into a C–N bond of 2,4,6-trimethyl-2,4,6-triaza-1,1-dichloro-1-sila-cycloheptane [286].

4.6 *Triethanolamines Forming Silatranes*

Silatranes are known since more than 50 years [287, 288] but are still fascinating molecules in the focus of an ongoing scientific interest. Fluoro-substituted quasisilatranes have been synthesized [214, 289–291]. Experimental and theoretically calculated electron density distribution functions in the crystal structure of **84** have been investigated [214]. Properties of chemical bonding in silatranes have also been studied in 1-hydrosilatrane [218] and 1-fluorosilatrane [219].



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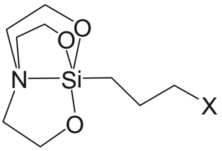
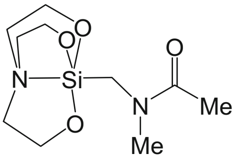


X = NCS (**140**)
X = N_3 (**141**)
X = NH_2 (**142**)



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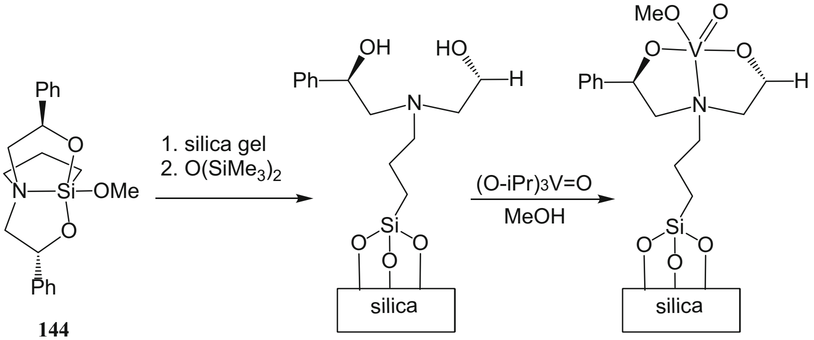
One aspect of recent interest is the functionalization of silatranes via a silicon-bound alkyl group. Examples for such compounds are 3-isothiocyanatopropylsilatrane



Scheme 39 Example for a carbasilatrane (**144**) as precursor to link the optically active ligand system to silica gel and to prepare vanadium(V) complexes

140 [292], 3-azidopropylsilatrane **141** [293], 3-aminopropylsilatrane **142** [294], 1-(2-pyridyloxy)silatrane [295], and *N*-(1-silatranylmethyl)succinimide and glutarimide [296], as well as urea and Schiff-base-functionalized propylsilatranes [297, 298]. These compounds offer opportunities, for instance, to build up larger ligand systems and to coordinate transition metals. Along these lines, a 1,3,2-dioxaphosphorinane unit was coupled to γ-aminopropylsilatrane to yield a compound which might have interesting biological properties [299]. The functionalization with *N*-methylacetamide (**143**) and *N*-(2-hydroxyethyl)acetamide delivers silatranes, which are partial muscarinic agonists and mimic the effect of acetylcholine by binding directly to cholinoreceptors of the ileal smooth muscle [300]. (Buta-1,3-dien-2-yl)silatrane has been used in Diels–Alder and cross-coupling reactions (Scheme 30 in Sect. 4.2) [246].

Carbasilatranes are another variation of the silatrane structure. The carbasilatrane**144** has been used as a precursor to fix the optically active ligand system via the incorporated silicon atom on silica gel or mesoporous silicas (Scheme 39) and to prepare vanadium(V) complexes therefrom, which act as functional models for the sulfide-peroxidase [301]. Several 3,7,10-trimethylsilatranes and carbasilatranes have been synthesized and investigated by NMR spectroscopy [302].

4.7 Tetradentate Chelate Ligands of "Salen"-Type

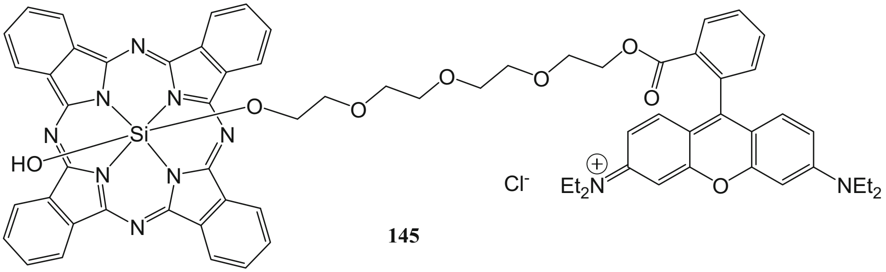
Salen-silicon complexes have been first crystallographically characterized in 1998 [148]. The studies on penta- and hexacoordinated silicon complexes containing salen-type ligands led to new insights in the field of silicon coordination chemistry; for instance, unusual activation of Si–C [173] and Si–Si [171] and other bonds (Schemes 2 and 8) or intramolecular ligand charge transfer promoted by hexacoordinated silicon(IV) complexes [153] has been observed in these compounds [147]. In continuation of this work, photo-driven Si–C bond cleavage in hexacoordinated silicon complexes [174] and the regio- and diastereoselectivity of rearrangement reactions in silicon−salphen complexes [169] have been investigated.

Hexacoordinated salen–silicon complexes can undergo Wurtz-type coupling reactions to produce the first examples of oligosilanes and polysilanes containing hexacoordinated silicon backbones [149]. This principle has been utilized to couple salen-type complexes containing thiocyanato ligands [Si(salen*)$(NCS)_2$] to a mixture of linear oligosilanes with a hexacoordinated silicon backbone SCN-[Si(salen*)$]_n$-NCS with $n = 2$–8 [147].

The structure of the salen ligand system has been modified by using a dipyrrin – instead of the ethylenediamine-unit. The novel pentacoordinated dipyrrin-silicon complexes (**31**, see Scheme 4, and some of its derivatives) showed efficient red or near-IR fluorescence, and the structural interconversion between silanol and siloxane derivatives resulted in significant changes in the optical properties [150].

4.8 Phthalocyanines

Metal phthalocyanines have a long-standing history as dyes and catalysts and are since recently being used in the manufacture of compact discs [303]. Only a few, but promising papers on silicon phthalocyanines, have been published in the last 5 years. Two new axially disubstituted silicon(IV) phthalocyanines containing adamantane moieties have been synthesized [304]. Both compounds are efficient singlet-oxygen generators with a quantum yield of 0.40–0.43. With two rigid bulky adamantane moieties at the axial positions, these phthalocyanines are essentially non-aggregated in common solvents but also exhibit a high photo stability. They are about 100 times more stable than zinc phthalocyanine under the same irradiation conditions [304]. Two axially ligated rhodamine-silicon(IV)-phthalocyanine complexes, bearing one (**145**) and two rhodamine B units, were synthesized and their photophysical, subcellular localization, and photocytotoxic properties were studied [305]. These phthalocyanine complexes exhibit an almost exclusive mitochondrial localizing property in human nasopharyngeal carcinoma (HK-1) cells and human cervical carcinoma (HeLa) cells. Strong photocytotoxic but low dark cytotoxic properties were also observed [305].



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Three publications deal with the synthesis of μ-oxo-linked silicon phthalocyanine and porphyrin derivatives. The stepwise syntheses of μ-oxo-linked hetero-chromophore arrays containing phthalocyanine, porphyrin, and sub phthalocyanine silicon and germanium complexes have been described [306, 307]. The μ-oxo linkage between the central group 14 metalloid atoms ensures π-overlap between the macrocycles, and an extension of the absorption profile to provide arrays that absorb across the whole UV-visible spectrum and into the near-IR. The strategy is sufficiently versatile to be extended to synthesis of higher defined oligomers and subsequent functionalization or attachment at either or both ends of the stack [307]. Similarly structured oxygen-bridged silicon phthalocyanine oligomers with $(Me_3SiO)_2MeSiO$-end groups give structural parameters for a matching set of three cofacial, oxygen-bridged silicon phthalocyanine oligomers for the first time [308]. The staggering angles between the six adjacent cofacial ring pairs in the three oligomers are neither in a random distribution nor in a cluster at the intuitively expected angle of 45° but rather are in two clusters, one at an angle of 15° and the other at an angle of 41°. These two clusters lead to the conclusion that long, directional interactions (LDI) exist between the adjacent ring pairs. An understanding of these interactions is provided by quantum chemical calculations [308].

5 Heavy Donor Atoms in the Silicon Coordination Sphere

A large number of penta- and hexacoordinated silicon compounds are known which comprise hydrogen, 2nd row elements (especially C, N, O, F), and/or chlorine in the silicon coordination sphere (as one can easily conclude from the contents of the previous sections).

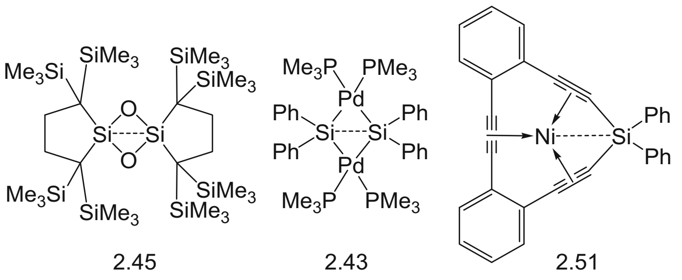
Far less compounds have been reported which comprise heavier elements in the coordination sphere of their penta- or hexacoordinated silicon atom. During the past decade significant contributions emerged on the field of silicon coordination chemistry with heavier lone pair donor atoms, and therefore this section will be dedicated to highlight these compounds.

As the silicon coordination number can be understood as the number of atoms located in proximity of the Si atom within the sum of the van der Waals radii and a large number of compounds without lone pair donation from atoms within this kind of coordination shell would fall into this section (such as those listed in Sect. 5.1), we focus on silicon compounds with five or six formal lone pair donors in the Si coordination sphere (Sects. 5.2–5.7).

5.1 Compounds with Si Coordination Number >4 but less than 5 Formal Lone Pair Donors

5.1.1 Silicon Hypercoordination due to Non-lone Pair Donors in Close Proximity, Apparent Absence of a Bond

This is encountered, e.g., with atoms in four-membered cycles (**146–148**, Scheme 40) [309–313]. Upon omission of the fifth atom in the silicon coordination sphere (omission of the coordination along the dashed line in Scheme 40), the almost tetrahedral coordination environment about silicon in these compounds is in support of the absence of significant M···Si electronic interaction (M = Si, Ni).



146 **147** **148**

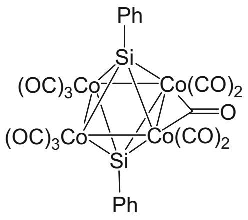
Scheme 40 The dashed lines indicate close interatomic contacts in the four-membered cycles. The interatomic separations in Å (Si···Si or Ni···Si, respectively) are given below the formula

5.1.2 Silicon Hypercoordination due to Lone Pair Acceptors in Close Proximity

This is encountered with various silanides, which can bridge two or more counter-cations with their Si-located lone pair (e.g., in compounds **149–151**) [314–317]. In a similar fashion, some silanides can μ^3-bridge assemblies of three transition metals (compounds **152** and **153**), which are stabilized by the additional ligand functionalities of the silanide, thus rendering the silanide Si atom formally hexacoordinated (Scheme 41) [318, 319]. The ^{29}Si NMR shifts of **152** and **153** clearly distinguish them from hexacoordinated Si complexes with six lone pair donors in the coordination sphere.

5.1.3 Silicon Within Oligoatomic (e.g., Oligometallic) Clusters

In these compounds the Si atom is constituent of a multicenter bonding system and the number of interatomic bonds drawn exceeds the number of electron pairs available for bonding. Some representative examples are compounds **154–156** [320–323].



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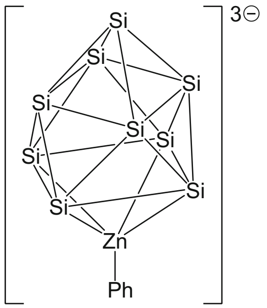

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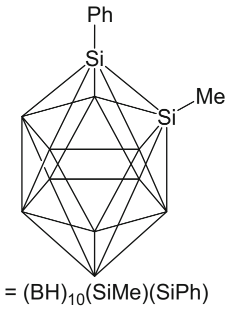

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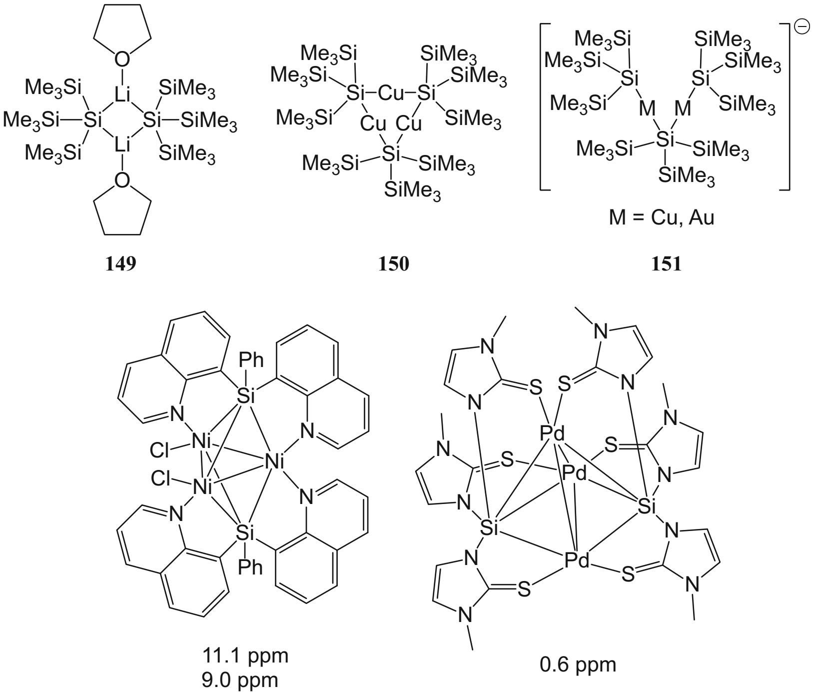


M = Cu, Au

149 **150** **151**

11.1 ppm
9.0 ppm

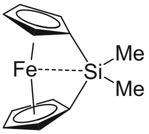
0.6 ppm

152 **153**

Scheme 41 Compounds with penta- and hexacoordinated Si atoms due to the presence of lone pair acceptors around the silanide Si atom. For compounds (**152**) and (**153**) the ^{29}Si NMR shifts are listed below the molecular formula

5.1.4 Silicon Atoms in Metallocenophane Bridge Positions

In these compounds the Si atom is sterically constrained to a position in close proximity to the metal atom, thus exhibiting an unusually short metal–silicon contact (dashed line in the structure of compound **157**), but the otherwise almost tetrahedral coordination sphere about silicon and the coordination geometry about the transition metal suggests absence of lone pair donation from the metal to silicon [324–326].



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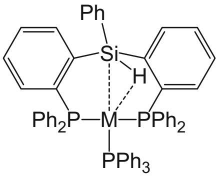
5.1.5 Silicon in Close Proximity to Transition Metal Atom via H-Bridge(s)

In these compounds the Si–H bond is likely to act as a σ-donor to the transition metal (agostic interaction), or the Si-bound hydrogen atoms act as σ-donors towards the transition metal, thus constraining the Si atom in close proximity to the transition metal even without σ-donor action from the latter to the Si atom. Besides, there are review articles on this topic, as mentioned in the introduction [36–40]. Hence, compounds such as **158** and **159** will not be discussed in detail here [327, 328]. Also, the same applies to compounds with Si transition metal bond which only achieve Si-hypercoordination by the presence of metal-bonded hydrogen atoms in closer proximity of the Si atom, while the rest of the Si coordination sphere is almost tetrahedral, thus less indicative of H→Si donor action (e.g., **160**) [329].



M = Ni, Pd

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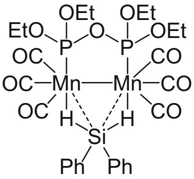

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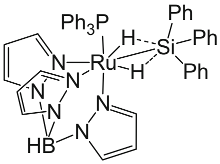

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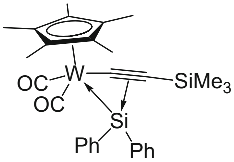
5.1.6 Multi-atomic Single-σ-Donor Stabilization of Silylene (Complexes)

Compound **161** represents a silylene ($SiPh_2$) complex of tungsten, the silylene ligand of which is stabilized by σ-donor action of the neighboring acetylene. Formally, the bonding environment of Si is comprised of only four electron pairs, even though the presence of the two acetylene carbon atoms in the coordination shell of Si accounts for the formal coordination number five [330].



161

These classes of compounds are briefly mentioned here (in Sect. 5.1), as their Si atoms are surrounded by more than four atoms, but in the following Sects. 5.2–5.7 we will only focus on compounds which are devoid of these features, i.e., compounds which, in addition to the presence of more than four atoms in the Si coordination sphere, comprise more than four formal σ-electron pairs in the Si valence shell, and if hydrogen atoms contribute to the enhanced coordination number, only compounds without Si transition metal bridging hydrogen are considered.

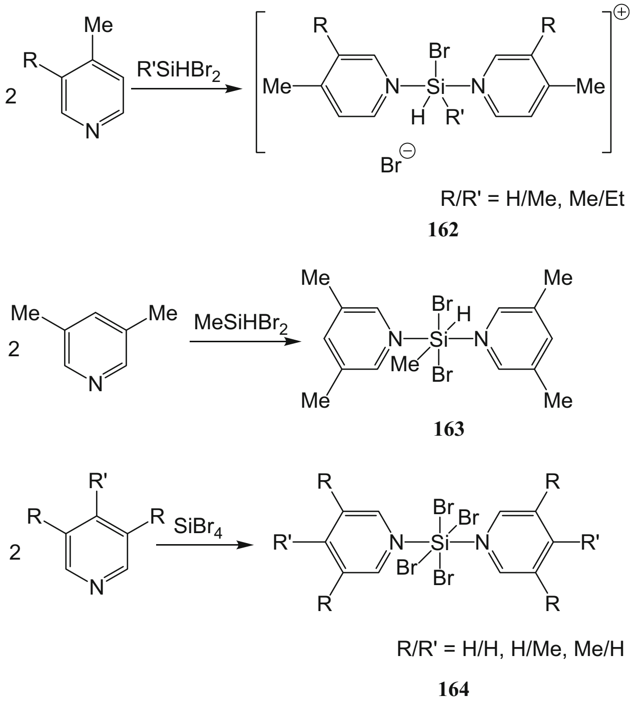
5.2 Penta- and Hexacoordinated Si Compounds with Heavier Halides (Br, I)

Alkylbromosilanes were shown to form pyridine adducts under ionic dissociation of an Si–Br bond (Scheme 42) [331, 332]. Thus, pentacoordinated Si complexes of the type **162** were isolated in which one out of two Si–Br bonds has been retained. Notably, this Si–Br bond occupies an equatorial position in the distorted trigonal-bipyramidal silicon coordination sphere (with bond lengths of 2.27 and 2.28 Å for the ethyl- and methylsilicon compound, respectively). In addition, a related compound with hexacoordinated Si atom and two Si–Br bonds (**163**) was characterized crystallographically [333]. The long Si–Br bonds (2.52 Å) already indicate the progress of Si–Br bond dissociation. Bromosilanes without electron-releasing alkyl groups (which most likely stabilize the cationic complex) form analogous pyridine adducts with hexacoordinated Si atom (compounds of type **164**) [334, 335]. The Si–Br bond lengths in the $SiBr_4$ adducts (ca. 2.38 Å) indicate the strengthening of this bond in these complexes. In the series of 4-methylpyridine complexes of the silicon tetrahalides $SiBr_nCl_{4\text{-}n}$ ($n = 0$–4), it was shown that the N–Si bond lengths are very similar despite the different number of Si-bonded Br vs. Cl atoms [335].

Monoanionic bidentate chelators have also been shown useful to achieve hexacoordination of silicon under retention of Si–Br bonds (Scheme 43) [135, 154, 157, 262, 336, 337]. Although the Si atoms were shown to be hexacoordinated in the solid state, for some of those compounds (e.g., **168**, **169**) ionic dissociation of the Si–Br bond was found to occur in solution. As for the above pyridine adducts, the Si–Br bond lengths exhibit noticeable variability (ranging between 2.33 and 2.45 Å).

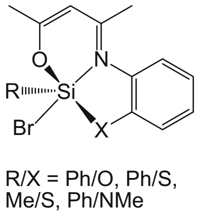
The weakness of the Si–Br bond, which is reflected by its ionic dissociation upon silicon hexacoordination, is also manifested in neutral pentacoordinated Si complexes. As shown by the related compounds in Scheme 44, the gradual approach of the additional donor moiety (O atom) causes a stepwise dissociation of the Si–X bond, which is reflected in the "umbrella inversion" of the equatorial Si-bound alkyl groups [338, 339]. In this course, a very long Si–Br bond (3.12 Å) has been observed for **172**.

In the compounds **170–172**, the halide (e.g., the Si–Br bond) occupies an axial position in the distorted trigonal-bipyramidal Si coordination sphere (cf. compounds in Scheme 42). The features of both axial [95, 190] and equatorial Si–Br bond situation [270] in pentacoordinated bromosilicon complexes have recently been



Scheme 42 Syntheses of bromosilane pyridine adducts

encountered with some tridentate chelates (compounds **173** and compound **174**). Apparently, the nature of the chelating ligand exerts great impact on the situation of the Si–Br bond (the same was observed for the related Si–Cl bearing compounds) in the silicon coordination sphere. The length of the Si–Br bond responds to the position within the trigonal-bipyramidal coordination sphere, i.e., 2.39–2.45 Å for axial positions and 2.33 Å for Br in an equatorial position.



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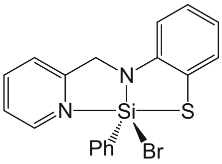

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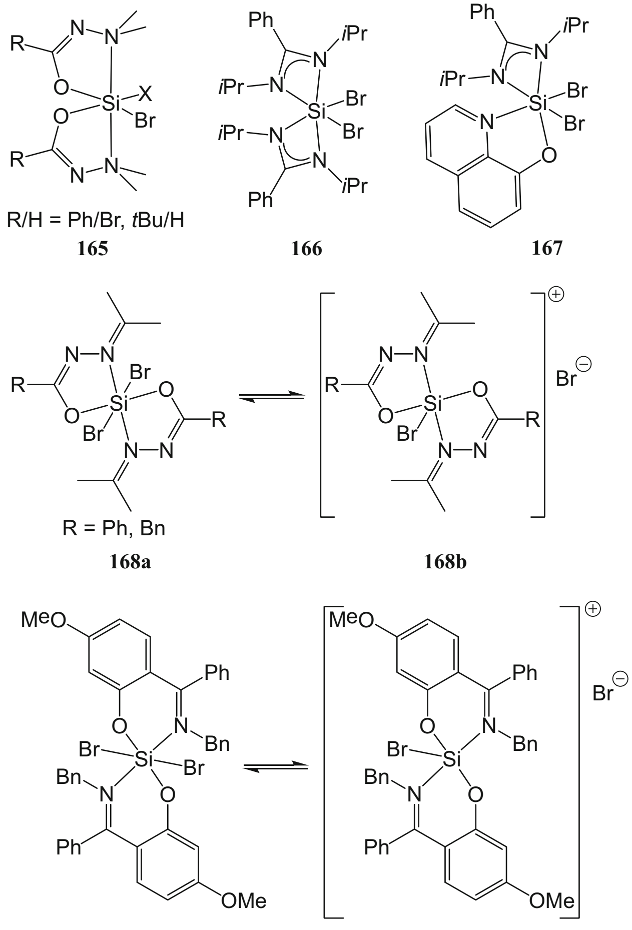
Last but not least, a carbene adduct of $SiBr_4$ (**175**) with pentacoordinated Si atom (with carbene ligand in equatorial position and Si–Br bond lengths of 2.24 and 2.38/2.41 Å for equatorial and axial sites, respectively) [108] and a dinuclear pentacoordinated bromosilicon compound (**176**) with a central Si_2N_2 four-membered cycle and rather short axial Si–Br bonds (ca. 2.28 Å) [340] have been reported.

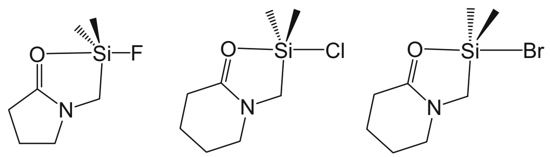


165 **166** **167**

168a **168b**

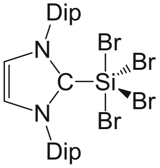
169a **169b**

Scheme 43 Syntheses of chelated bromosilicon complexes



2.31	1.95	1.80
355.1	359.7	355.9
170	**171**	**172**

Scheme 44 Model compounds for steps along an S_N2 reaction coordinate. Si–O bond lengths (in Å) and the sum of the equatorial C–Si–C angles (in °) are listed under each compound



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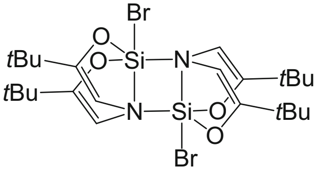
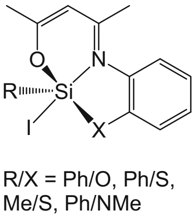


176

This variety of hypercoordinated bromosilicon compounds is in sharp contrast to hypercoordinated iodosilicon compounds, which are represented by far less crystallographically evidenced examples. In addition to some pentacoordinated monoiodosilicon compounds with tridentate chelators (compound **177**, Si–I bond lengths ranging between 2.74 and 2.82 Å) [95, 188, 190], the first crystallographically characterized hexacoordinated iodosilicon compound (with two Si–I bonds, 2.64 and 2.66 Å) [203] has been reported very recently (compound **72**, Scheme 15).



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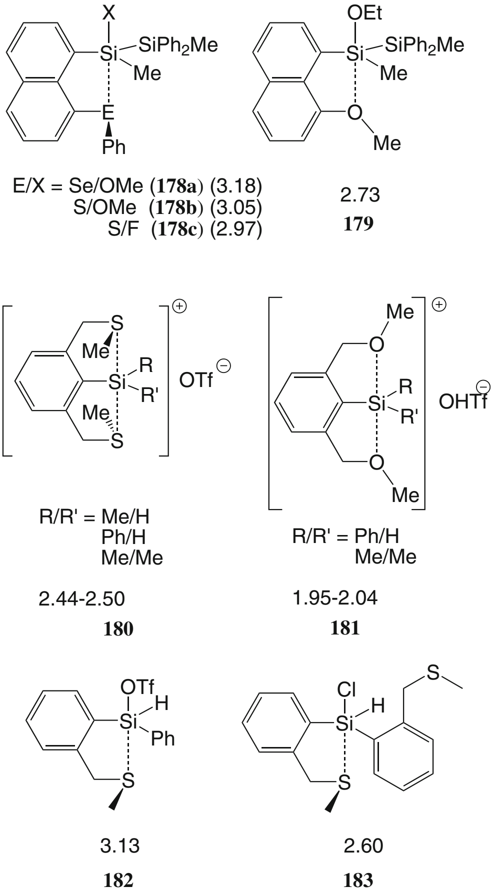
5.3 Penta- and Hexacoordination of Silicon with Heavier Chalcogens (S, Se, Te)

In case of silicon compounds with chalcogen donor moieties, we need to distinguish between chalcogenides and chalcogenolates as anionic ligands on the one hand and chalcogenoethers and chalcocarbonyl compounds as neutral donor moieties on the other hand. Only few examples of crystallographically characterized pentacoordinated Si complexes with chalcogenoether donor moieties have been reported to date (Scheme 45) [282, 341–343], but their characteristic features already allow deeper insights into the difference between ether and heavier chalcogenoether donor action towards silicon. Even though the particular kind of silicon hypercoordination which is forced by the short peri-distance of the naphthalene-1,8-diyl backbone can often be interpreted in terms of minimization of repulsive forces rather than deliberate attraction of silicon and its peri-situated additional donor atom [344, 345], the behavior of chalcogenoether S or Se atoms in compounds **178** systematically resembles that of related interactions in a much more flexible 2-methylthiomethyl substituted aryl group (compounds **180**, **182**, **183**). In detail, the methoxy O atom (in compounds **179** and **181**) approaches the Si atom in a sp^2-like fashion (Si atom located within the C–O–C plane). For compound **179**



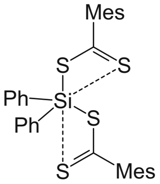
Scheme 45 Chalcogenoether coordination at silicon. The interatomic separations of Si and the chalcogen atom (*dashed line*) are given below the formula

the angles about the methoxy O atom sum up to 356.6°. For the related seleno- or thioether compounds **178** a non-hybrid approach of the chalcogen atom towards the Si atom is observed (both the E–C bonds and the E···Si interaction being aligned along the axes of p-orbitals). Thus, for compounds **178** the angles about the heavy chalcogen atom sum up to 309.6°, 310.6°, and 303.4° (for **178a–c**, respectively). Similar features are observed with the o-methylthiomethylphenyl-substituted compound **180** vs. their *o*-methoxymethylphenyl analogue **181**.

To our best knowledge, there is no crystallographic evidence for telluroether silicon coordination compounds to date.

Thiocarbonyl compounds as ligands in the Si coordination sphere are encountered with thiocarboxylate (**184**, **185**), thiocarbamate (**186**), and thiourea (**187**, **188**) derivatives [346–348]. Whereas in the first case (**184**, **185**) only capped tetrahedral

Si coordination spheres have been reported (with weak S···Si interactions indicated by interatomic separations of 3.05–3.48 Å), thiocarbamate was shown to form a noticeably shorter Si–S bond in **186** (2.70 Å) and the anion of the thiourea derivative methimazole was shown to be capable of forming a trisilane (**187**) with two adjacent octahedral Si coordination spheres, one of which comprises four Si–S bonds (with separations ranging between 2.35 and 2.48 Å). Notably, this trisilane with a central Si(Si_2S_4) skeleton is one out of only few crystallographically characterized hexacoordinated Si compounds which are devoid of first and second row elements in the octahedral Si coordination sphere of one of their Si atoms (further examples can be found with P and Cl in the coordination sphere, vide infra). The kind of tetrahedral capping by rather long Si···S separations of about 3.17–3.50 Å is encountered with various methimazolyl-substituted silanes such as **188** [349].



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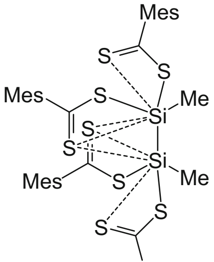

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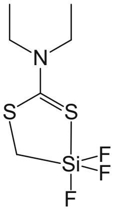

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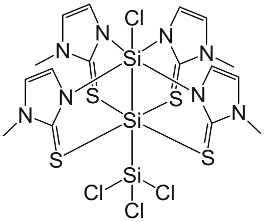

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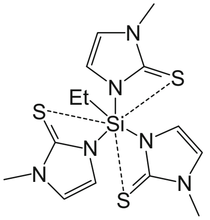
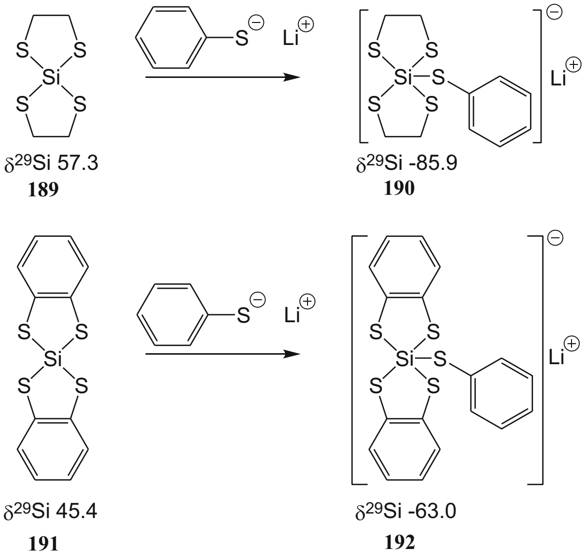


188

Apparently, silicon hypercoordination can be achieved more readily by utilizing anionic chelating S-donor ligands. Even though a hexacoordinated silicon compound with SiS_6 skeleton has not been reported yet, its left neighbor has already been shown to form compounds with AlS_6 skeleton [350–352]. Pentacoordinated Si compounds with SiS_5 skeleton have at least been evidenced by ^{29}Si NMR spectroscopy, as the spiro compounds **189** and **191** with SiS_4 skeleton (shown in Scheme 46) have been extensively characterized by crystallography, NMR spectroscopy, and quantum chemical calculations and a significant high-field shift of their ^{29}Si resonance has been observed upon addition of thiolates, wherefrom the formation of **190** and **192** has been concluded [353, 354].

In further studies this strategy of including thiolate donor moieties in chelating ligands (see compounds **41**, **124–127**, **130,** and **193–199**) proved successful to

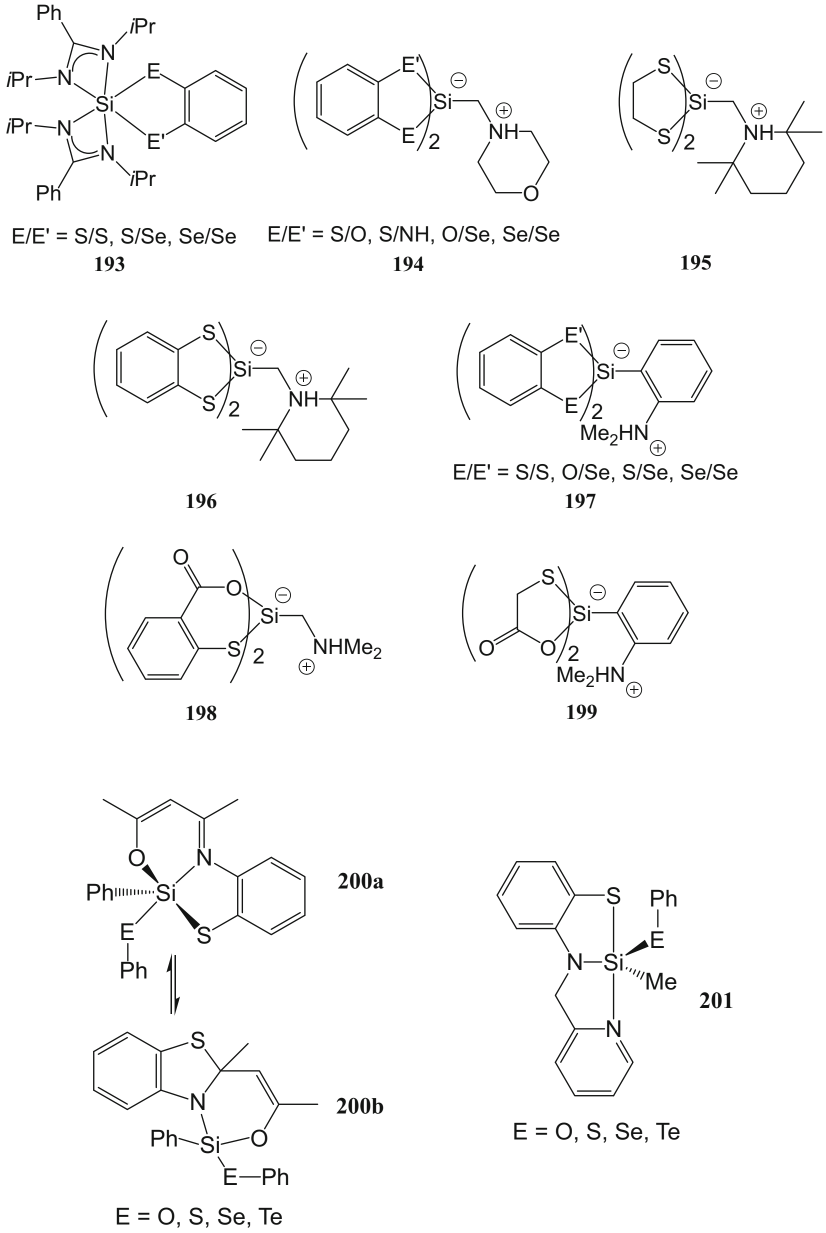


Scheme 46 Formation of compounds with SiS_5-skeleton (^{29}Si NMR shifts are given below the molecular formulae)

create a larger set of penta- and hexacoordinated Si compounds. Some related selenolato silicon compounds with heavier chalcocatecholate type ligands have also been reported [145, 154, 167, 188–190, 193, 194, 268, 270, 355–357]. In these compounds the chelators' S atoms can be found in axial and equatorial positions in the pentacoordinated Si compounds with equatorial and axial Si−S bonds in the ranges 2.13–2.18 Å and 2.23–2.39 Å, respectively (and in a particular case four S atoms were found to occupy the basal positions of a square pyramidal Si coordination sphere with Si−S separations of 2.23–2.26 Å [167]). In the hexacoordinated Si compounds of this class the Si−S bond lengths range between 2.26 and 2.31 Å. Si−Se bond lengths were found in the ranges 2.40–2.41, 2.46–2.58, and 2.29–2.32 Å for the hexacoordinated and the axial and equatorial positions in the almost trigonal-bipyramidal pentacoordinated Si compounds, respectively.

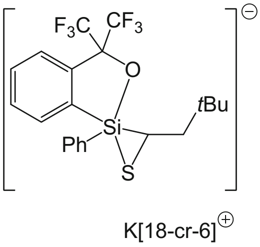
Some related monodentate chalcogenolates have also been successfully introduced in the coordination spheres of pentacoordinated Si compounds (Scheme 47) [190, 194, 270]. In these compounds the monodentate chalcogenolates occupy equatorial sites in the distorted trigonal-bipyramidal Si coordination spheres, and the Si−E bond lengths slightly exceed the ranges mentioned above (Si−S 2.19 and 2.21 Å, Si−Se 2.32 and 2.35 Å). Furthermore, equatorial Si−Te bonds with lengths of 2.52 and 2.56 Å have been reported. Interestingly, the equilibrium between isomeric tetra- and pentacoordinated Si compounds (**200b** and **200a**, respectively) was found to be shifted to the latter in case of the heavier chalcogenolates, whereas the phenoxy substituent promotes the formation of the compound with tetracoordinated Si atom (see also compound **58** Scheme 11) [194].

Finally, a pentacoordinated Si compound **202** with a thiolate type ligand as a 1,2-bidentate chelator (thus forming a thiasilirane, a three-membered Si,C,S heterocycle) is highly noteworthy [358]. In this compound the S atom occupies



Scheme 47 Silicon complexes with monodentate chalcogenolato ligands

an axial position (*trans* to O) in the distorted trigonal-bipyramidal Si coordination sphere. The Si–S bond (2.57 Å) is notably longer than those in the abovementioned compounds with axial thiolate ligands, most likely due to its S···K coordination (3.12 Å) in the crystal packing.



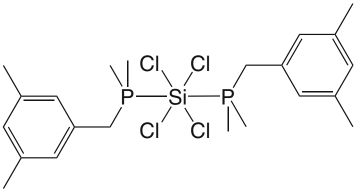
202

Last but not least, formally dianionic heavy chalcogeno ligands (i.e., chalcogenides) have recently been introduced in the Si coordination sphere (compounds **73**, Scheme 15) [204]. The Si=E bond lengths for the equatorially situated "chalcosilanone" bonds (2.02, 2.16, 2.40 Å for S, Se, Te, respectively) are noticeably shorter than those reported for the corresponding equatorially bonded chalcogenolates, as one would expect due to the lower coordination number of the chalcogen atom and the formally higher bond order.

5.4 Penta- and Hexacoordinated Si Compounds with Heavier Pnictogens (P)

To date hypercoordinated Si compounds with As, Sb, or Bi in the silicon coordination sphere have not been reported with any crystallographic evidence of their bonding situation. Phosphorus atoms in the coordination shell of such Si compounds, however, have been reported and the P-donor moieties cover the two classes of neutral (phosphane) and anionic (phosphanide) ligands.

In an earlier review it has already been pointed out that phosphane coordination at silicon is rarely encountered in the literature [359]. With the trialkylphosphane adduct of $SiCl_4$ (**203**), crystallographic evidence for the feasibility of the synthesis of this class of compounds from $SiCl_4$ and a phosphane has been delivered and the Si–P bond length was found to be 2.36 Å. The use of a chelating ligand (**204**) resulted in slightly stronger Si–P coordination (bond lengths 2.31 Å). In addition to the use of trialkylphosphanes, diphosphinomethanides proved suitable to enhance the silicon coordination number to five and six (**205**, **206,** and **33**) [155, 360]. The Si–P bond lengths in these compounds range between 2.30 and 2.48 Å.



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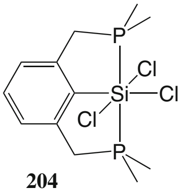

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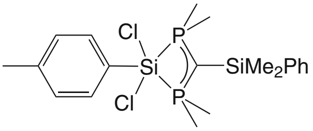

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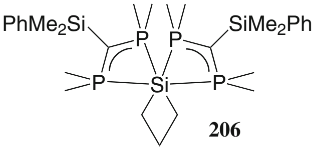

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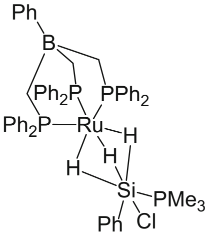
Recently, some further hypercoordinated Si compounds with crystallographically evidenced phosphane donor action have been published (**80**, **81**, **207**) [210, 211, 361]. Even though the overall coordination mode of the silicon atom in the Ru complex **207** does not fall into this class of hypercoordinated Si compounds (because of the Ru$\cdots$Si bridging hydrogen atoms and furthermore its ^{29}Si NMR shift of 9 ppm, which is far downfield from the ranges expected for "ordinary" penta- and hexacoordinated Si compounds), the silicon coordination of trimethylphosphane in this compound is still noteworthy, and the Si−P bond length of 2.34 Å matches the ranges reported for the abovementioned trialkylphosphane silicon complexes. Furthermore, the angles Cl−Si−C, Cl−Si−P, and P−Si−C sum up to 288.6°, which is much closer to the expected sum of three *cis* angles in an octahedron (270°) than three tetrahedral angles (328.5°). In the compounds **80** and **81** Si−P bond lengths of 2.50 and 2.49 Å have been found. These compounds constitute additional classes of phosphanes suitable for lone pair donation towards silicon. Silicon hypercoordination with the aid of triarylphosphanes has also been reported, but the crystallographically characterized example of a naphthalene-1,8-diyl bridged phosphorus silicon interaction (**208**) hints at rather repulsive forces with the Si−P separation of 2.99 Å [362]. As a diarylphosphanide, however, phosphorus has entered the trigonal-bipyramidal Si coordination sphere (in equatorial position) of the compound **70b** (Scheme 14) [202]. Surprisingly, the formally covalent Si−P bond in this compound (2.29 Å) is only little shorter than the formally dative Si−P bonds in the earlier mentioned trialkylphosphane adducts.



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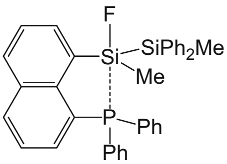

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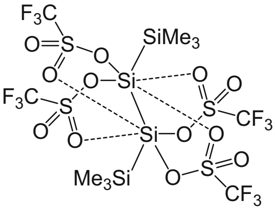
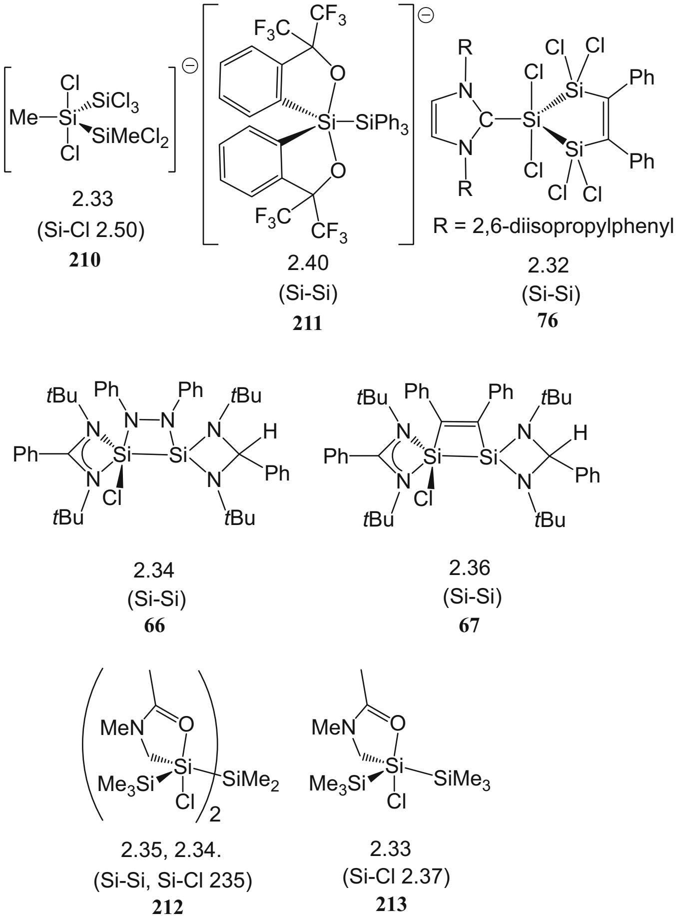
5.5 Penta- and Hexacoordinated Si Compounds with Heavier Tetrels (Si, Ge, Sn)

As di- and oligosilanes are a well-known class of silanes, which may bear a variety of functional groups (e.g., Si−Cl bonds) suitable for anchoring additional donor ligands, various oligosilanes with hypercoordinated Si atoms have already been reported in the literature. In order to assess the effect of hypercoordination on the Si−Si bond, we will only focus on crystallographically characterized compounds. Literature provides examples of some oligosilanes with relatively remote lone pair donor moieties in addition to four "regular" bonds in the Si coordination shell. This leads to capping of tetrahedral faces, but does not strongly distort the Si coordination spheres towards square-based pyramidal or trigonal-bipyramidal (for Si pentacoordination) or octahedral (for Si hexacoordination). Disilane **185** and tetrasilane **209** exhibit features of that kind [346, 363]. The interatomic separations between Si and the remote donor moieties are 3.05–3.48 Å (for S in **185**) and 2.72 and 2.84 Å (for O in **209**). The C−Si−Si and Si−Si−Si angles, which one would expect to be close to 180° or 90° in case of almost octahedral coordination, are 117.8/117.9° and 135.4°, respectively. The bond angles of the four noticeably shortest bonds around Si range between 97.5° and 117.9° in case of disilane **185** and between 96.9° and 135.4° in case of tetrasilane **209**. Thus, the particular geometrical parameters of these compounds do not match the expectations for octahedral coordination either, which would be 1 × 180° and 5 × 90° or 2 × 180° and 4 × 90°. The Si−Si bond lengths are 2.35 Å for the S-substituted disilane and 2.37 and 2.41 Å for the terminal and the central Si−Si bond in the O-substituted tetrasilane.



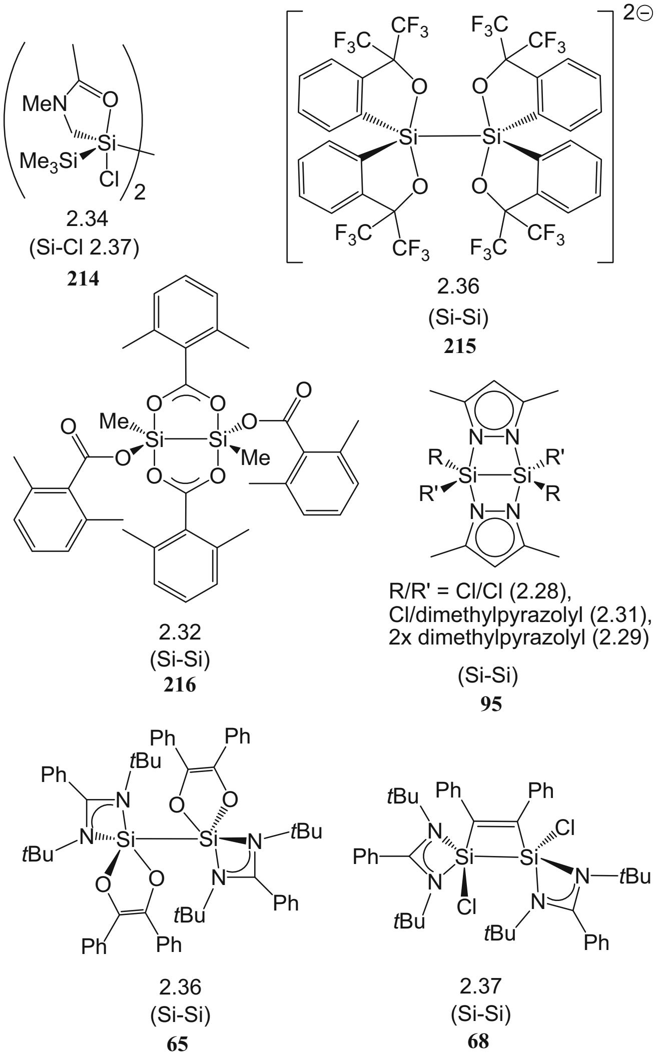
209

"Genuine" hypercoordination has been encountered with isolated and with adjacent hypercoordinated Si atoms within oligosilanes [48, 109, 134, 161, 162, 198–200, 241, 348, 364–368]. Schemes 48 and 49 show such compounds with isolated and with adjacent pentacoordinated Si atoms, respectively, and their Si−Si bond lengths (the value for the longest bond distance within the Si coordination sphere is given in the Schemes). Without exception, the Si−Si bonds are located in equatorial positions within the distorted trigonal-bipyramidal coordination spheres.



Scheme 48 Compounds with pentacoordinated Si atoms within an oligosilicon skeleton. Si–Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses

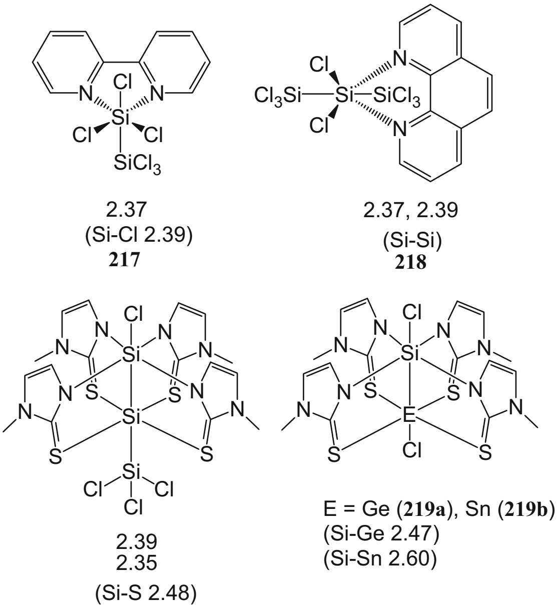
Far less compounds with octahedrally coordinated Si atom(s) within an oligosilicon compound have been reported, which are shown in Scheme 50 (again, in combination with their Si–Si bond lengths and the longest bond in the Si coordination sphere). Surprisingly, their Si–Si bond lengths are very similar to those of pentacoordinated Si atoms in oligosilicon compounds despite the now *trans*-disposed bond. The two compounds **219a** and **219b** are currently the only examples of crystallographically confirmed hypercoordinated Si compounds with Ge or Sn in the silicon coordination sphere.



Scheme 49 Compounds with adjacent pentacoordinated Si atoms within an oligosilicon skeleton. Si–Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses

5.6 Pentacoordinated Silicon Compounds with Coinage Metals (Cu, Ag, Au)

A phosphane-functionalized arylfluorosilane (**220**) has been shown to bind AuCl in almost linear P–Au–P arrangement and with an Au···Si separation of 3.09 Å (in **221**, Scheme 51) [369]. Although this interatomic distance is probably longer than one would expect for a strong Au→Si donor–acceptor interaction, the ^{29}Si



2.37
(Si-Cl 2.39)
217

2.37, 2.39
(Si-Si)
218

2.39
2.35
(Si-S 2.48)
187

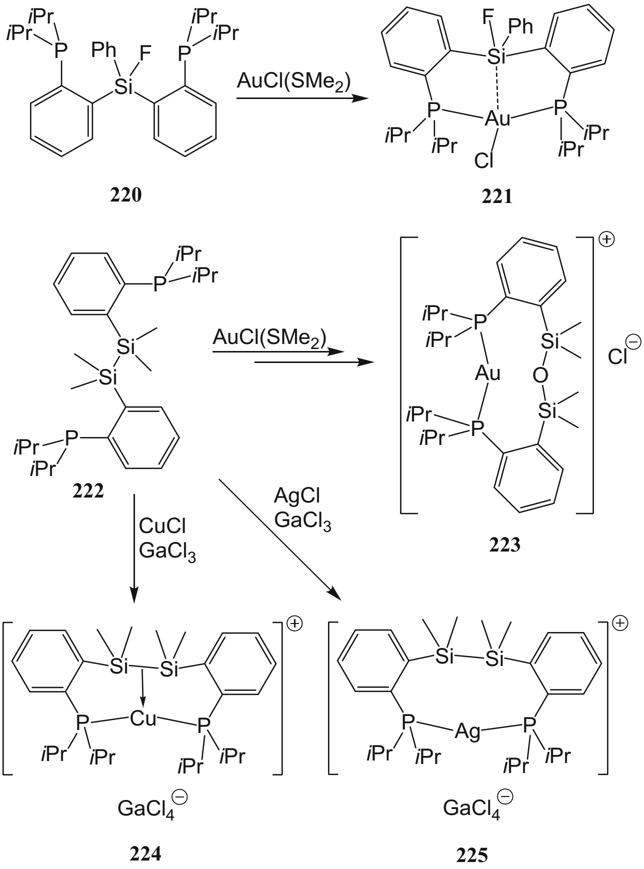
E = Ge (**219a**), Sn (**219b**)
(Si-Ge 2.47)
(Si-Sn 2.60)

Scheme 50 Compounds with octahedrally coordinated Si atoms within an oligosilicon or related skeleton. Si−Si bond lengths in Å are given below the formula; the longest bond in the Si coordination sphere in Å is given in parentheses

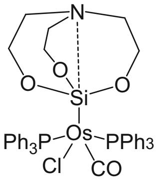
NMR shift of this compound (−21.4 ppm) already indicates effects of an enhanced coordination number of silicon, as this shift is significantly upfield (Δδ −23 ppm) with respect to triphenylfluorosilane [370]. In a related phosphane-functionalized disilane (**222**), complexation of gold activates the Si−Si bond for oxidation to afford **223** [371]. In sharp contrast, the related complexation of Cu(I) leads to a metal–silicon interaction in **224** (Cu−Si separations 2.72 Å) that has been interpreted as the Si−Si σ-orbital acting as an electron pair donor towards Cu(I), and complexation of Ag(I) (**225**) leads to a compound with noticeably larger intermetallic separations (3.39 and 3.48 Å) [372].

5.7 Penta- and Hexacoordinated Si Compounds with Transition Metals

An osmium-substituted silatrane (**226**) has been reported in 1998, which bears the transition metal atom as a formal covalently bonded substituent, whereas the silatrane N atom acts as the additional lone pair donor. In this particular compound, the transannular N→Si coordination is remarkably weak, which is reflected by the N−Si separation of 3.00 Å [373]. The use of electron rich transition metals as lone pair donors themselves to enhance the silicon coordination sphere has also been explored as early as 1994. The Ni(0) and Pd(0) centers in compounds **227** and **228**, however, exhibit poor σ-donor qualities, thus leading to transannular silicon metal separations of about 4 Å [373–378].



Scheme 51 Coinage metal atoms in the silicon coordination sphere



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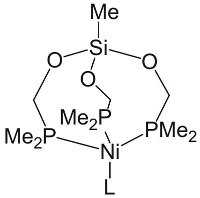
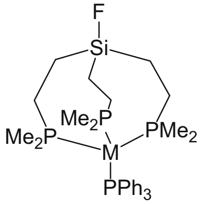


L = CO, PPh_3

227

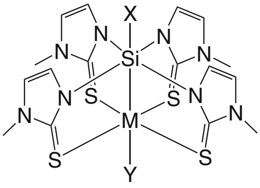


M = Ni, Pd

228

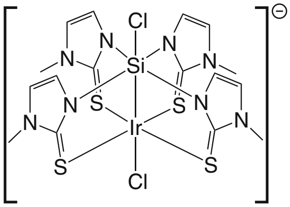
In the past 3 years, Ni(II), Pd(II), and Pt(II) proved suitable σ-donors in the octahedral silicon coordination sphere (compounds **229**) [377–379]. With ^{29}Si NMR shifts ranging between −175 and −216 ppm, the metal atom clearly acts as one out of six bonding partners at silicon, and the metal silicon separations of about 2.45–2.51 Å (M = Pt), 2.53–2.57 Å (M = Pd), and 2.56–2.61 Å (M = Ni) are in support of this interaction. In a series of these compounds it was shown that the spin-orbit effects on the ^{29}Si NMR shift are greater for M = Ni than for M = Pd, which appears unusual at first glance but can be rationalized as a result of the weaker ligand field splitting in case of M = Ni.

A related (hitherto not synthesized) Ir(I) compound (**230**) was predicted to exhibit similar structural features as the compound $ClSi(mt)_4PtCl$ (mt = methimazolyl), i.e., to accommodate a metal silicon bond [380].



various combinations of
X = F, Cl
M = Ni, Pd, Pt
Y = Cl, Br, I

229



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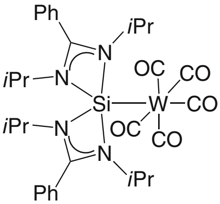
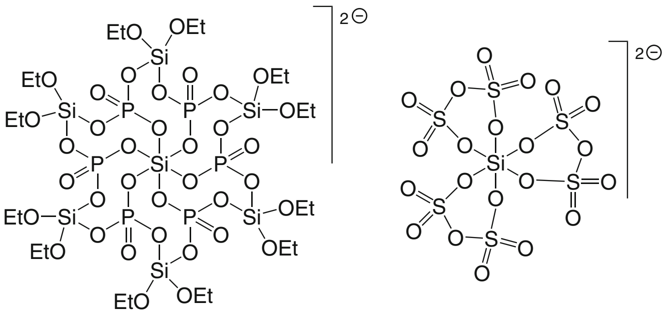


231

Last but not least, a pentacoordinated Si compound with Si–W bond (**231**) has been reported recently [203]. According to X-ray crystallographic results, the silicon coordination sphere in this compound is distorted trigonal-bipyramidal, with the Si–W bond (2.58 Å) in equatorial position. The ^{29}Si NMR shift of −13.3 ppm is noticeably downfield with respect to other pentacoordinated Si compounds with the same SiN_4 (bis-amidinate) skeleton, e.g., $N_4Si = S$ $\delta^{29}Si = -70.7$ ppm [204]. This observation can probably be attributed to the silylene character of the silicon bis-amidinate moiety in this tungsten compound, which renders the $W(CO)_5$ moiety a σ-lone pair acceptor, not a donor, and thus clearly distinguishes this metal–silicon interaction from the abovementioned Si–M (M = Ni, Pd, Pt) bonding situations, which have been shown to be rather covalent (M = Pt) or formally dative with the metal as lone pair donor (M = Ni, Pd) [378].

6 Hexacoordination of Silicon with Anions of Mineral Acids

Surprisingly, very few compounds with higher-coordinated silicon atoms and mineral oxoacids such as carbonic, nitric, phosphoric, and sulfuric acids are known. These involve oxygen-coordination which is – on the other hand – very common. An example is compound **81** (Scheme 18) in which the carbonate ion is generated from carbon dioxide. Recently, an unusual higher-coordinated molecular silicon



Scheme 52 Anions of **232** (*left*) and **233** (*right*) with hexacoordinated silicon atoms

compound has been prepared by the reaction of crystalline H_3PO_4 and $Si(OEt)_4$ in the presence of triethylamine. After recrystallization from chloroform the X-ray structure of $[Et_3NH]_2[Si(PO_4)_6(SiO_2Et_2)_6]\cdot 4(CHCl_3)$ (**232**) has been determined [381]. The silicophosphate anion contains a central hexacoordinated silicon atom which is surrounded by six PO_4 tetrahedra. These are supplemented by six diethoxysilicate groups, each one linking two phosphate groups. The structure of the anion is shown in Scheme 52. This compound illustrates possible structural motifs in silicophosphate glasses.

Another example of a hexacoordinated silicon atom generated by coordination of an inorganic acid anion is $Na_2[Si(S_2O_7)_3]$ (**233**) [382–384]. Herein the disulfate anion stabilizes the hexacoordinated silicon as a bidentate chelating ligand. Compounds like **232** and **233** might give insight into the possible genesis of naturally occurring silicates with hexacoordinated silicon [1, 385].

7 Conclusions

Although most of the known silicon compounds comprise tetracoordinated Si atoms, there are numerous and important classes of higher-coordinated silicon compounds. Some are long known such as the very stable hexafluorosilicate anion and its derivatives. Many more examples have been reported for (organometallic) higher-coordinated silicon compounds containing chelate ligands forming five- and six-membered silaheterocycles. The corresponding primary literature has been reviewed in the past decades. Nevertheless, similar to the field of lower-coordinated silicon compounds (silylenes, disilenes, etc.), the overall research in the field of higher-coordinated silicon compounds remains very active. This is indicated by the numerous publications on these topics that appeared in the past 5–10 years.

In this review we focused on the most recent literature, while at the same time trying to provide a comprehensive overview on the synthetic routes, structures, ligand types, and donor atoms in higher-coordinated silicon compounds. The syntheses can be subdivided into various (oxidative) addition, metathesis, and rearrangement reactions. The structures of pentacoordinated silicon compounds are either derived from (distorted) trigonal-bipyramidal or square (rectangular) pyramidal motives. Hexacoordinated compounds are based on (distorted) octahedra, while purely trigonal prismatic species are seldom. Only a few examples of compounds with coordination numbers higher than six are known. These either involve special ligands such as Cp*, or belong to cluster species (Zintl anions) or comprising donor moieties in greater distance (e.g., larger Si···S separations).

In most cases, bonding in higher-coordinated silicon compounds is significantly more ionic than in the corresponding tetrahedral or lower-coordinated species. However, the "nature" of a Si–E bond is strongly influenced by the type of atom E, the type of the other donor atoms at the silicon center, and steric and electronic constraints within the considered compound. The bonding "nature" may be roughly separated into covalent σ-bonds, ionic bonds, and dative interactions. The latter, however, may be considered as ionic as well, with some directionality, i.e., covalency. In many cases, bonding in the considered higher-coordinated silicon compounds can be described as 4e3c bonds. Nevertheless, especially in the cases of weak (additional) donor interaction with a Lewis-acidic, fourfold coordinated silicon atom 2e2c bonds are also present.

Apart from the well-known donor (or ligand) atoms such as C, N, O, F, and Cl, an increasing number of higher-coordinated silicon compounds with hydrogen, on the one hand, and heavy nonmetal as well as main group and transition metal donor atoms, on the other hand, have been reported. The latter may be separated into species without any bonding or donor–acceptor interaction (but distances below the sum of the van der Waals radii), compounds containing silicon atoms which act as electron pair acceptors as well as species where the Si is the Lewis donor.

Spectral and other properties and (potential) applications of higher-coordinated silicon compounds are not in the focus of this review. Nevertheless, interesting features and applications of selected subclasses of higher-coordinated silicon compounds include, for example, fluorination of drinking water involving fluorine complexes. It is well known that higher-coordinated silicon compounds act as reactive sites in (stereoselective) organic synthesis and in silicon chemistry in general. Octahedral silicon complexes bearing 1,10-phenanthroline and arenediolate ligands were investigated for the design of hydrolytically stable silicon-based high-affinity DNA binders, suggesting that similar silicon complexes are promising templates for applications in medicinal chemistry. Similarly, another class of compound containing hexacoordinated silicon, namely, phthalocyanine derivatives, is known to possess photosensitizing behavior, which can be used for photodynamic therapies. Zwitterionic and anionic (dinuclear) pentacoordinated silicon complexes with bridging tartrato ligands have been thoroughly characterized and their hydrolytic stability has been investigated with respect to the role of such complexes (or related compounds) in the biochemistry of silicon. Selected silatranes are partial muscarinic agonists and mimic the effect of acetylcholine, while others have been used in Diels–Alder and cross-coupling reactions, to name just a few examples.

Transition metal-containing compounds with higher-coordinated silicon atoms – especially those discussed in Sects. 5.6 and 5.7 – may be utilized as tunable homogeneous or heterogeneous catalysts. These (potential) applications and even more so the numerous fascinating fundamental results reported in the past few years, which have been summarized here, provide a promising and motivating basis for further research in the field of higher-coordinated molecular silicon compounds in the future.

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Silylium Ions

Thomas Müller

Abstract The chemistry of silylium ions and related silyl cations is reviewed. The discussion is focused on work since 2005 with recourse on investigation since the early 1990s. Structural and spectroscopic aspects of silylium ions are emphasized. Included is also survey of methods for their preparation and of their applications in organic synthesis and catalysis.

Keywords Bond activation · Silicon · NMR · Silylium ion · Lewis acid · XRD · Low coordinated compounds · Main group chemistry · Organosilicon chemistry · Hydrosilylation · Silicon cation · Small-molecule activation · Silyliumylidene

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Abbreviations

AE	Association energy
Ar	Aryl
Bu	Butyl
cat	Catalyst
Cp	Cyclopentadienyl
d	Day(s)
DFT	Density functional theory
Dipp	2,6-Di*iso*propylphenyl
Duryl	2,3,5,6-Tetramethylphenyl
Et	Ethyl
h	Hour(s)
^{i}Pr	*Iso*propyl
L	Litrer(s)
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl (not methanesulfonyl)
min	Minute(s)
mol	Mole(s)
NICS	Nucleus independent chemical shift
Nu	Nucleophile
odcb	*Ortho*-dichlorobenzene
Pemp	Pentamethylphenyl
Ph	Phenyl
Pr	Propyl
py	Pyridine
r.t.	Room temperature
s	Second(s)
^{t}Bu	*Tert* butyl
THF	Tetrahydrofuran
Tipp	2,4,6-Tri-*iso*-propylphenyl
Tol	4-Methylphenyl
Tr	Triphenylmethyl (trityl)
XRD	X-ray diffraction
Xylyl	2,6-Dimethylphenyl

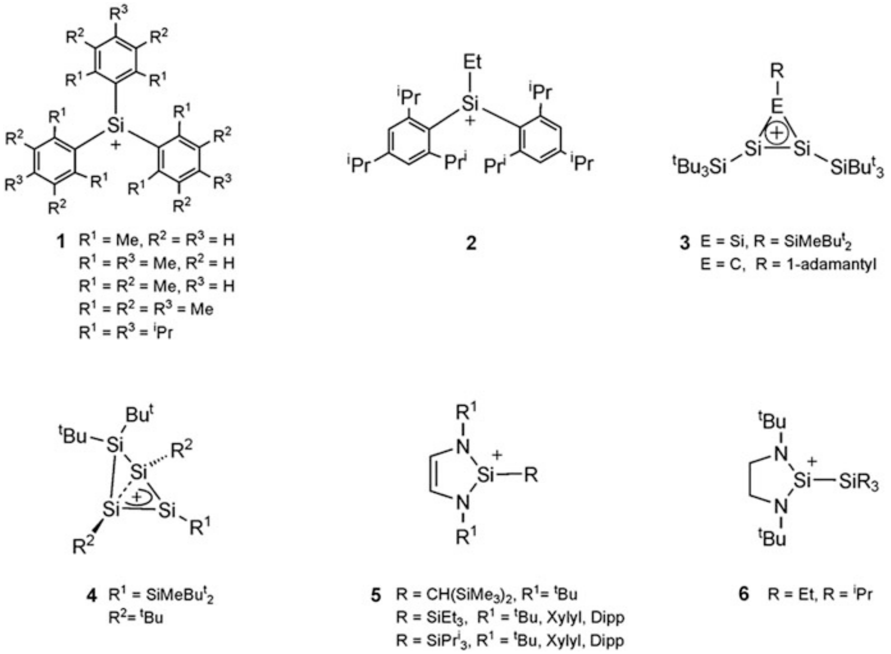
1 Introduction

The chemistry of silylium ions has been repeatedly reviewed over the past few decades, often in connection with the possibility of their existence in the condensed matter [1–7] and in relation of historical aspects of their synthesis [8]. Only in the last years reviews focused on the spectroscopic, structural and reactivity aspects of silylium ions [9–15]. This overview is a sequel to these previous reports and will summarize work in silylium ion chemistry starting from the 1990s but will concentrate on the development of this chemistry since 2005.

Silylium ions [R_3Si^+] are tricoordinated silicon species with a positively charged silicon atom. These six-valence electron species are isostructural and isolobal to boranes [R_3B] and they are the silicon analogues of classical carbenium ions [R_3C^+]. The striking difference between carbon and silicon chemistry in this respect is that carbenium ions are frequent intermediates in many chemical transformation in carbon chemistry, and their existence was recognized and firmly established already in 1901 [16]. In contrast, in organosilicon chemistry, there are only a few examples of reactions with silylium ions as established intermediates, and the first clear evidence for a silylium ion in condensed media was only presented in 1997 [17, 18]. This striking difference between these two so closely related species is not a result of the thermodynamic instability of the silicon compound. On the contrary, the silicon cation [R_3Si^+] is, for most of the synthetically important substituents R, more stable than the corresponding carbenium ion [R_3C^+] [9]. The major obstacle to the formation of silylium ions in the condensed phase is their high electrophilicity and, as a consequence, their high reactivity toward any nucleophile. The smaller electronegativity of silicon compared to carbon leads to an accumulation of positive charge at the central silicon atom for every organic substituent R. This accretion of positive charge is not dispersed by π-conjugation and/or hyperconjugative effects due to less-effective orbital overlap between the silicon atom and the carbon substituents. The larger size of the silicon atom means that steric protection by bulky substituents is less effective than for carbocations, and it allows extension of the coordination sphere at silicon to coordination numbers larger than 4. For these reasons many reactions in organic chemistry that proceed by a dissociative S_N1-type mechanism will in organosilicon chemistry follow an associative course via pentacoordinated transition states or even intermediates. As a consequence, only a small number of silylium ions **1**, **2** have been synthesized that are fully consistent with the textbook definition of a trigonal-planar coordinated silylium ion [R_3Si^+] [17, 19–22]. In addition, several silylium ions **3**–**6** in which the positively charged silicon atom is part of a delocalized π-system could be isolated and characterized under ambient conditions (Scheme 1) [23–27].

The synthetic efforts toward the isolation of silylium salts with an ideal trigonal-planar coordinated positively charged silicon atom in the cation created a series of stabilized silyl cations in which either the interaction with the solvent, the counteranion, or intramolecular donor groups pacify the high electron demand of the silyl cation. This electron donation leads to cationic species **7** in which the silicon atom adopts a distorted tetrahedral coordination environment (Scheme 2) [9]. Examples for siliconium ions **8** in which the silicon atom has expanded its coordination number to 5 by addition of two solvent molecules are known but are less frequently observed. Intermolecular species **7** and **8** as well as intramolecular variants **9** and **10** for both modes of stabilization have been structurally characterized [9, 28, 29].

Of particular interest in the context of this review are the solvent- or anion-stabilized tetracoordinated silyl cations **7**. In the case of the solvent complexes **11**–**16**, structural and/or NMR spectroscopic data clearly indicate a covalent



1 R^1 = Me, R^2 = R^3 = H
R^1 = R^3 = Me, R^2 = H
R^1 = R^2 = Me, R^3 = H
R^1 = R^2 = R^3 = Me
R^1 = R^3 = ^{i}Pr

2

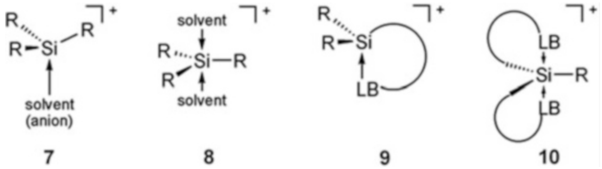
3 E = Si, R = $SiMeBu^t_2$
E = C, R = 1-adamantyl

4 R^1 = $SiMeBu^t_2$
R^2= ^{t}Bu

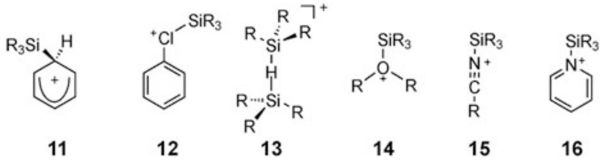
5 R = $CH(SiMe_3)_2$, R^1= ^{t}Bu
R = $SiEt_3$, R^1 = ^{t}Bu, Xylyl, Dipp
R = $SiPr^i_3$, R^1 = ^{t}Bu, Xylyl, Dipp

6 R = Et, R = ^{i}Pr

Scheme 1 Stable silylium ions [17, 19–27]

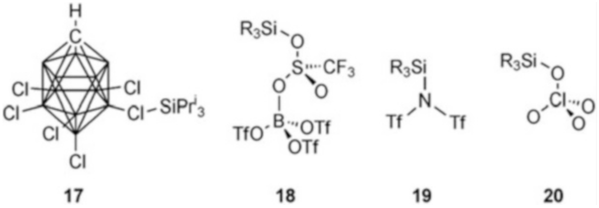


Scheme 2 Different modes of stabilization for silylium ions (LB Lewis Basic Group)

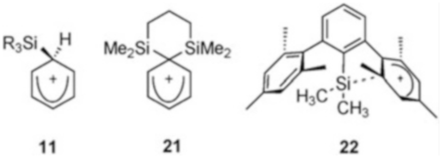


Scheme 3 Examples of solvent-stabilized silylium ions

interaction between the solvent and the silylium ion (Scheme 3). For example, cations **11** are accurately described as silylated arenium ions [9, 30]. Nevertheless, cations **11** as well as chloronium ions **12** and the bissilylated hydronium ions **13** are extremely valuable synthetic sources of silylium ions with an unmatched Lewis acidity. From a synthetic point of view, these species might be regarded as solvent-stabilized silylium



Scheme 4 The anion-stabilized silylium ion **17** and conventional silyl Lewis acids **18**–**20**



Scheme 5 Inter- and intramolecular arene-stabilized silylium ions

ions. In particular, their significant greater reactivity distinguishes them from silylated oxonium ions **14**, nitrilium ions **15** or pyridinium ions **16**.

Benzenium ions **11** are usually prepared using the weakly coordinating perfluorinated tetraphenylborate anion {$[B(C_6F_5)_4]^-$}. Switching to slightly more nucleophilic carborates as counteranions results in the formation of carborate-stabilized silylium ions; for example, with the {$[HCB_{11}H_5Cl_6]^-$} anion, the silylium carborate **17** is formed (Scheme 4). Extended structural studies for **17** and several related halogenated carborates and borates reveal in each case close contact between one halogen atom of the carborate anion and the silicon atom, which leads to a distorted tetrahedral coordination environment for the silicon atom [9, 31, 32]. Although the interaction between the carborate anion and the silicon atom determines the structure and spectroscopic properties of these silylium carborates and discriminates them from the free silylium ion, they represent possibly the nearest approach to simple trialkyl-substituted silylium ions in the condensed phase. Their high ability for silyl group transfer and their unprecedentedly high Lewis acidity, which outperforms by far those of the conventionally covalently bonded silyl Lewis acids **18**–**20**, justify, from a synthetic point of view, their description as anion-stabilized silylium ions.

In cases in which the high Lewis acidity of the cationic silicon is decreased by an intramolecular Lewis basic group (LB), as in the tetracoordinated cation **9** (and likewise in the siliconium ion **10**; Scheme 2), interactions between the positively charged silicon atom and the solvent and/or anion are of minor importance. The structures, spectroscopic properties, and reactivities of these silyl cations are greatly determined by the electron-donating ability of the LB groups. As a consequence, the structural and spectroscopic features of silyl cations **21** and **22**, which are stabilized by intramolecular electron donation from an aryl substituent, closely resemble those of benzenium ions **11** (Scheme 5) [33, 34]. The intramolecular stabilization operative in silylium ions **9** offers the intriguing possibility of controlling the Lewis acidity of the positively charged silicon atom by adjusting the electron-donating ability of the Lewis basic group. Several model systems for such tunable silyl Lewis acids have been suggested [34, 35].

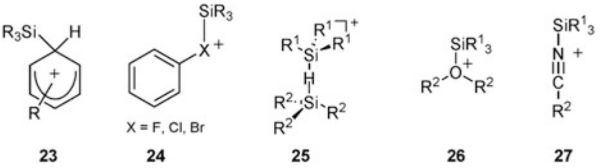
For the abovementioned reasons this review will concentrate on the silylium ions and related silicon cations with silicon in the oxidation state (+IV). In particular in view of silylium-like reactivity of species such as the solvent- or anion-stabilized silylium ions of the types **11–13**, **17** and intramolecular stabilized species, as, for example, **21**, **22** will be also included in this overview. Emphasis is given here to structural and ^{29}Si NMR spectroscopic properties of the silylium ions, synthetic aspects and the use of silylium ions in organic synthesis and catalysis will be also addressed.

2 Synthesis of Silylium Ions and Stabilized Silylium Ions

2.1 General Aspects

The major problem encountered during the synthesis of silylium ions is their inherent high electrophilicity and reactivity, which leads such species to interact in solution or the solid state with solvents or counteranions that are found to be innocent in other areas of chemistry. The ability of silicon to expand its coordination sphere facilitates nucleophilic attack and increases the requirements for the anion and the solvent. In addition its tendency to form strong bonds with oxygen and with halogens, here in particular with fluorine and chlorine, provides another major obstacle for the synthesis of silylium ions. In most cases aromatic hydrocarbons or halogenated arenes are the solvent of choice for the generation of silylium ions or silylium ion-like species. Depending on the substituents at the silicon atom and depending on the electron demand of the electron-deficient silicon center, either silyl arenium ions, **23** [9], or silylated arylhalonium ions, **24** [36, 37], are formed. Non-coordinated silylium ions are obtained only when sufficient steric or electronic stabilization is provided. Also silanes, $R^2{}_3SiH$, have found application as solvents. In these cases, it is a matter of the substrate which species is actually formed. Small aliphatic groups R^1 at the silicon atom of the incipient silylium ion give raise to hydrogen-bridged species of the composition $[R^1{}_3Si\text{-}H\text{-}SiR^2{}_3{}']^+$, **25** [36, 38]. On the other hand, the use of ethers and nitriles as solvents leads to the formation of either oxonium ions, **26**, or nitrilium ions, **27** (Scheme 6) [9]. Aliphatic halogenated hydrocarbons in particular methylene chloride are suitable alternatives to arenes only at low temperatures. At temperatures around $T = -50°C$ the reaction of the silyl cation with the halogenated solvent is very often slow enough to allow for its spectroscopic identification, for reactivity studies and, in certain cases, also for the isolation of silyl cation salts. At higher temperatures either formation of the corresponding silyl chloride is observed or complete decomposition occurs [9, 39–42].

As counteranions only very robust and extremely weakly coordinating anions [43] such as fluorinated tetraarylborates of the type $[B(C_6F_{5\text{-}n}R_n)_4]^-$ (R = $SiR^1{}_3$, H,



Scheme 6 Typical solvent complexes of silylium ions

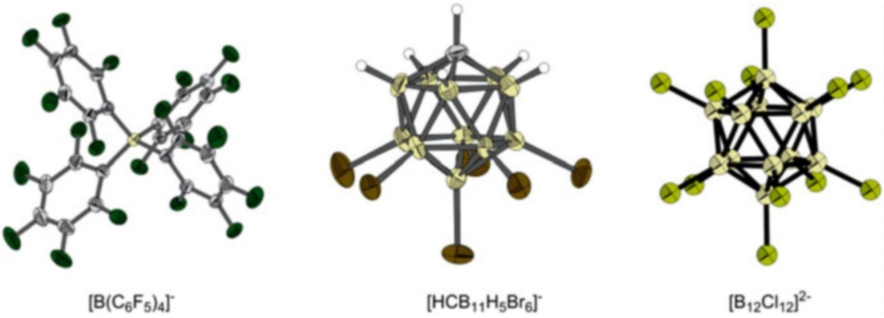
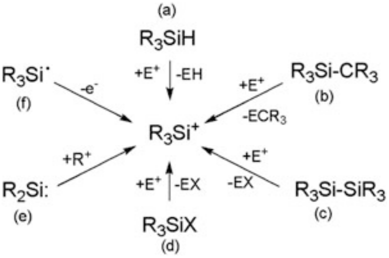

$[B(C_6F_5)_4]^-$ $[HCB_{11}H_5Br_6]^-$ $[B_{12}Cl_{12}]^{2-}$

Fig. 1 Weakly coordinating anions used in silylium ion chemistry



Scheme 7 Synthetic approaches to silylium ions

$n = 0$, 1), halogenated *closo*-carborates of the types $[RCB_{11}H_{11\text{-}n}X_n]^-$ and $[RCB_{11}Me_{11\text{-}n}X_n]^-$ (R = H, alkyl; X = F, Cl, Br, I, $n = 6$, 11) or perhalogenated *closo*-borates $[B_{12}X_{12}]^{2-}$ (X = Cl, Br) can be used (see Fig. 1 for prominent examples) [7, 9, 31, 32, 44]. Fluorinated tetraarylborates are usually applied in combination with arene solvents and depending on the substituents either silylarenium tetraarylborates or, in cases where the substituents at silicon provide enough steric and/or electronic stabilization, silylium borates are obtained. In contrast, with trialkylsilylium ions, *closo*-borate dianions or carborate anions form zwitterions (e.g., **17**) in which the silicon is bonded to one of the halogen atoms. Therefore depending on the weakly coordinating anion applied, different silyl cationic species may be present in arene solution.

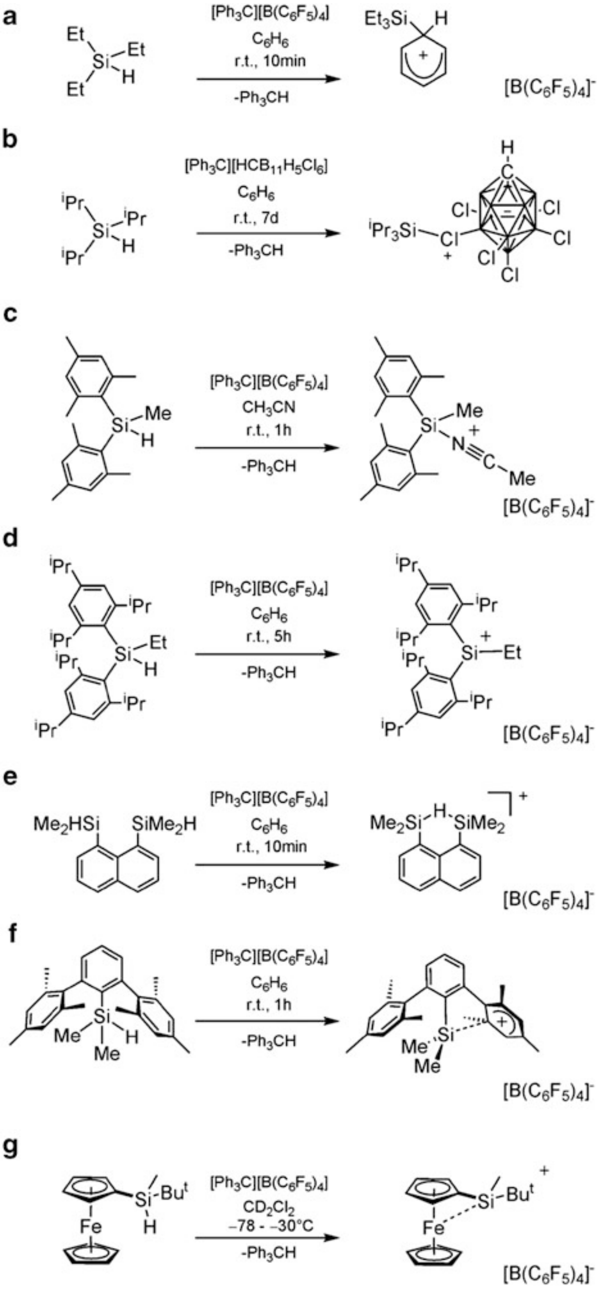
Scheme 7 shows the principal synthetic methods for the preparation of silylium ions or stabilized silylium ions. The most frequently used methods are, in the order of decreasing importance, the cleavage of Si–H, Si–C and Si–Si bonds (Scheme 7a–c) by strong electrophiles E^+. The cleavage of Si–X bonds (X = F, Cl, Br) (d) is successful only in the case of strongly stabilized silyl cations, and the scope of addition reactions of cationic species R^+ to silylenes (e) or the oxidation of silyl radicals (f) is rather limited, due to the small number of stable substrate compounds.

2.2 Synthesis of Silylium Ions by Heterolytic Cleavage of Si–H Bonds

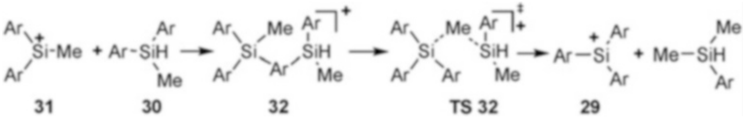
The most popular and most widespread method for the preparation of silylium ions in the condensed phase is a variant of the classical Bartlett–Condon–Schneider (BCS) hydride-transfer reaction [45, 46]. Silanes react with strong Lewis acids to give silylium ions and the hydride adduct of the Lewis acid. For this reaction, most frequently triphenylcarbenium (trityl) cation is the Lewis acid of choice. This is also fostered by the straightforward access of trityl salts with a wide variety of weakly coordinating anions [7, 31, 32, 43, 44]. The most commonly used weakly coordinating anions in this chemistry are perfluorinated tetraarylborates and halogenated *closo*-carborates or *closo*-borates. Scheme 8 summarizes representative examples for the synthesis of silylium ions or their stabilized variants with typical solvents and reaction conditions. The BCS reaction can be performed not only in polar solvents such as sulfolane, ethers, and nitriles but also in chlorinated or aromatic hydrocarbons or silanes. With trityl tetrakis(pentafluorophenyl)borate $[Ph_3C][B(C_6F_5)_4]$ as hydride acceptor, in aromatic solvents the reaction occurs within minutes at room temperature. At lower temperatures dichloromethane is usually used as the solvent. In this case special care must be taken due to the high reactivity of the generated silyl cations toward chlorinated hydrocarbons. Due to the size of the triphenylcarbenium cation, the hydride-transfer reaction with bulky silanes is very slow or is even thwarted [17, 19, 21]. Therefore, bulky triaryl- or trialkylsilanes cannot be used in hydride-transfer reactions with the triphenylcarbenium cation. Due to the low solubility of trityl *closo*-carborates and *closo*-borates in aromatic hydrocarbons the hydride transfer with these reagents requires very long reaction times at room temperature [47]. Several instances of decomposition of the products at higher reaction temperatures were reported [20, 21].

The BCS hydride-transfer reaction is a synthetic entry to a wide variety of cationic silicon species [4, 9, 14], which are stabilized either by intermolecular interaction with solvent molecules (Scheme 8a, c) [22, 27] or with the counteranion (Scheme 7b) [47] or by intramolecular interactions (Scheme 8e–g) [34, 41, 48]. Even silylium ions without a stabilizing attachment can be prepared according to this synthetic route (Scheme 8d) [21]. The examples brought together in Scheme 8 nicely demonstrate that the nature and in particular the reactivity of the generated stabilized silylium ion crucially depends on the substituents at the silicon atom and on the solvent and counteranion.

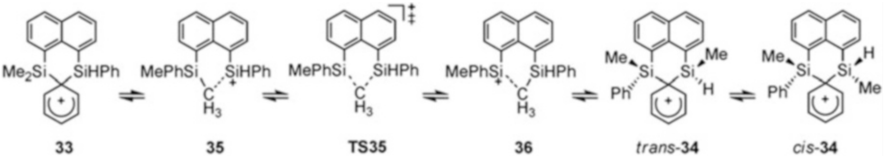
Scheme 8 Synthesis of silylium ions by the BCS hydride-transfer reaction [21, 22, 27, 34, 41, 47, 48]



Scheme 9 Preparation of trimesitylsilylium borate, **28**[B(C_6F_5)$_4$], by the BCS hydride-transfer reaction with substituent exchange [21, 22]

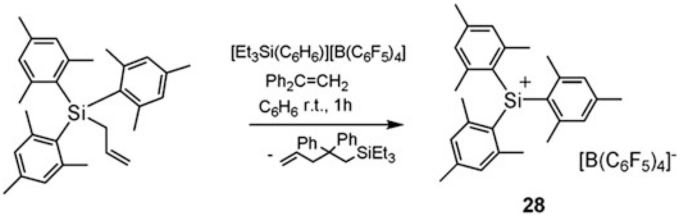


Scheme 10 Substituent exchange reaction between diarylmethyl silylium ions **31** and diarylalkyl silanes **30**

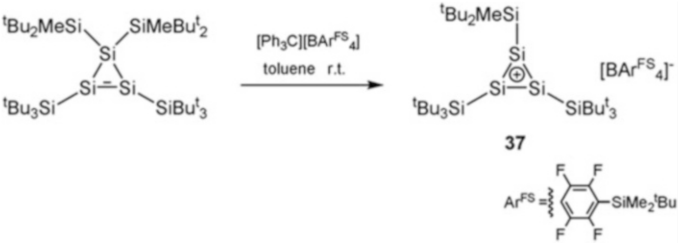


Scheme 11 Isomerization reaction between disilylarenium ions **33** and *cis-*/*trans-***34** [49]

A synthetically extremely useful follow-up reaction of the BCS hydride transfer between silanes and trityl cation is a substituent exchange reaction between the starting silane and the formed silylium ion. This reaction can be used for the preparation of sterically hindered triarylsilylium ions [Ar_3Si^+], **29**, from diarylmethylsilanes [Ar_2MeSi^+], **30** (see Scheme 9 for an example and Scheme 10 for the general reaction) [21, 22]. The synthesis of these triarylsilylium ions from the corresponding triarylsilanes is not possible by the standard hydride-transfer reaction due to the exceeding steric hindrance between the reactants. Therefore, this variant of the BCS hydride-transfer reaction provides a facile synthetic route to bulky triarylsilylium ions. Cross experiments suggested that the reaction proceeds stepwise via diarylmethyl silylium ions **31**. For the central alkyl/aryl substituent exchange reaction disilylated arenium ions **32** are suggested as intermediates. In these cations the methyl group transfer occurs via a methonium-like transition state **TS32** (Scheme 10). This is supported by an investigation of the isomerization reaction between the arenium ions **33** and *cis*- and *trans*-**34** (Scheme 11) [49]. This reaction occurs at room temperature and yields an equilibrium mixture of all three cations. For this example, DFT calculations suggest that the methyl exchange necessary for the transformation of **33** → *trans*-**34** proceeds via energetically high-lying silyl cations **35**, **36** and the methonium-like transition state **TS35** with an overall free energy barrier of 90 kJ mol^{-1} at room temperature.



Scheme 12 Synthesis of trimesitylsilylium borate, **28**$[B(C_6F_5)_4]$, using the allyl leaving group methodology [17, 19]



Scheme 13 Synthesis of the trisilacyclopropenylium cation **37** [24]

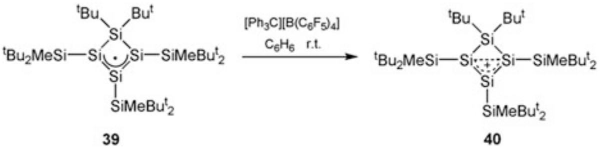
2.3 *Synthesis of Silylium Ions by Heterolytic Cleavage of Si–C and Si–Si Bonds*

The heterolytic cleavage of Si–C bonds by strong electrophiles to liberate silylium ions has found only niche applications. Nevertheless this method is applicable when silanes with good leaving groups such as allyl groups are used [19]. From a historic perspective, it is appropriate to note that this synthetic approach was the method of choice for the synthesis of the trimesitylsilylium, Mes_3Si^+, **28**, the first silylium ion not stabilized by inter- or intramolecular interaction with donors (Scheme 12) [17, 19]. The cleavage of Si–C bonds requires very potent electrophiles such as carbocations, protonated ethers or silylarenium ions. In a broader context, it is also of interest that cleavage of Sn–C bonds to form stannylium ions has found more widespread applications [9].

The cleavage of Si–Si bonds by trityl cation has been applied in the synthesis of the aromatic trisilacyclopropenium ion **37** (Scheme 13) [24]. Interestingly it has been claimed that trityl cation acts as a one-electron oxidant and that the resulting radical cation underwent a fragmentation reaction into cation and a silyl radical. In regard of Wagner–Meerwein-type rearrangements of polysilanes, this method has the potential to develop into an important synthetic method for the generation of polysilylsilylium ions from electron-rich polysilanes [50–52].

Scheme 14 Oxidation of hexa-*tert*-butylsilane by trityl cation [53]

Scheme 15 Synthesis of the tetrasilacyclobutenyl cation 40 [23]



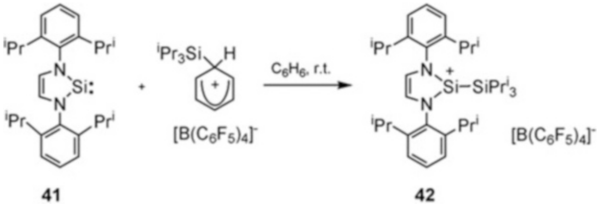
2.4 Synthesis of Silylium Ions by Oxidation of Disilanes and Silyl Radicals

The oxidation of sterically hindered disilanes by trityl cation in pivaloyl nitrile was shown to yield silylium ions which form with the solvent silylnitrilium ions, e.g., **38** (Scheme 14) [53]. The generation of silyl cations was, however, only observed for sterically overloaded disilanes, such as hexa-*tert*.-butyldisilane. Hexaethyldisilane for example was found to be inert under the applied reaction conditions [53]. In view of the problems with bulky silanes in the standard hydride-transfer reaction, the oxidation of disilanes is a complementary addendum to the synthetic methodology. The very limited preparative access to stable radicals restricts the oxidation of silyl radicals to give silylium ions to only a few selected examples. The most prominent example is the oxidation of the stable radical **39** to the homoaromatic silylium ion **40** by trityl cation (Scheme 15) [23].

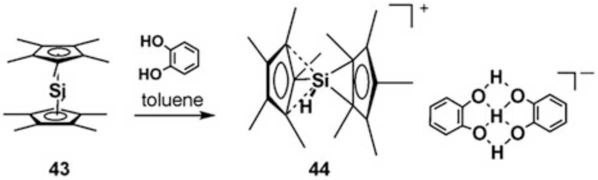
2.5 Synthesis of Silylium Ions by Addition of Electrophiles to Silylenes

All stable isolated silylenes have a singlet ground state and therefore they show in principle an amphiphilic reactivity pattern. In the case of N-heterocyclic silylenes (NHSi) such as compound **41** the electronic contribution of the heteroallylic NSiN resonance form quenches their electrophilicity and they behave in many of their reactions as Lewis bases. As a consequence, silaimidazolium ions, e.g., **42** are formed upon reaction of NHSi's with strongly silylating reagents such as silylated arenium ions (Scheme 16) [27]. This reaction proceeds for several examples under mild conditions and the silaimidazolium ions can be isolated in the form of their $[B(C_6F_5)_4]^-$ salts in excellent yields. The very limited number of stable silylenes clearly narrows the scope of this synthetic methodology to silylium ions. Recent

Scheme 16 Synthesis of silaimidazolium borate **42** $[B(C_6F_5)_4]$ [27]



Scheme 17 Protonation of decamethylsilicocene **43** [56]



progress in the chemistry of stabilized silylenes might improve this situation in the future significantly [54, 55]. Only one example of a successful protonation of silylenes to give hydrogen-substituted silylium ions is reported. Decamethylsilicocene **43** was protonated by catechol to give the unique H-substituted silylium ion **44** (Scheme 17). Notably, with stronger acids than catechol, a fragmentation of the cation **44** occurs (see Sect. 5) [56, 57].

3 Spectroscopic and Structural Aspects of Silylium Ions and Stabilized Silylium Ions

3.1 General Aspects

^{29}Si NMR spectroscopy and X-ray diffraction (XRD) methods are of major importance in the development of silicon cation chemistry and are the most significant source for structural information [6, 7, 9, 10]. Theoretical investigations in particular in combination with ^{29}Si NMR spectroscopic results played a dominant role in silicon cation chemistry in the 1990s [5]. In particular, the contributions of theory to the debate on the existence of silylium ions in the condensed phase proved to be fruitful and decisive. This has been comprehensively illustrated by several authors [5, 15]. In this chapter emphasis is laid on experimental structural data which results from XRD measurements or is deduced from ^{29}Si NMR spectroscopy. Theoretical results are only quoted as supplement to the experimental data. Similarly ^{1}H, ^{13}C NMR data or results from IR spectroscopy are only provided when significant structural insights were obtained from these data.

3.2 Molecular Structures and ^{29}Si NMR Spectroscopic Properties of Silylium Ions

3.2.1 Aryl-Substituted Silylium Ions

Experimental structural information about silylium ions is still rather limited. At the time this review was finalized solid-state structures of only five different silylium salts have been published in which the positively charged silicon atom fulfils the strict structural criteria for a six-valence-electron, tricoordinated main group molecule [20, 22–25]. For example, the molecular structures of only two archetypical representatives for R_3Si^+ cations, Mes_3Si^+, **28**, and $Pemp_3Si^+$, **45**, have been reported to date. The trimesityl species was isolated in the form of the *closo*-carborane salt $[Mes_3Si][HCB_{11}Me_5Br_6]$ [20] while in the case of the pentamethylphenyl-substituted compound the dodecachloro-*closo*-borate dianion was applied to obtain the silylium salt $[Pemp_3Si]_2[B_{12}Cl_{12}]$ [22]. In both cations the silicon atom adopts the expected trigonal-planar coordination environment as indicated by values for the sum of the bond angles around the central silicon atom, $\Sigma\alpha(Si)$, close or equal to 360°. The bulky aryl substituents are twisted out of the central plane and lead to an overall propeller-like molecular shape of the silylium ions. Pertinent structural data are summarized in Table 1 and the molecular structure of $Pemp_3Si^+$ as found by XRD analysis of single crystals of $[Pemp_3Si]_2[B_{12}Cl_{12}]$ is shown in Fig. 2. A noticeable dactylic (long–short–short) C–C bond length alternation of the aryl substituents in Mes_3Si^+, **28**, indicates some resonance stabilization for this silylium ion (C^{ipso}–C^{ortho}:140.5 pm; C^{ortho}–C^{meta}:138.4 pm; C^{meta}–C^{para}:137.9 pm). Due to its larger twist angle δ, this structural indication of resonance vanishes in the case of $Pemp_3Si^+$, **45**, (C^{ipso}–C^{ortho}:140.5 pm; C^{ortho}–C^{meta}:140.2 pm; C^{meta}–C^{para}:139.8 pm). On the other hand, the average Si–C^{ipso} bond in cation **45** (Si-C^{ipso} = 184.7 pm) is significantly shorter than found experimentally for tetracoordinated silanes such as tris(pentamethylphenyl)silane, $Pemp_3SiH$ (Si-C^{ipso} = 194.96 pm), and bis (pentamethylphenyl)methylsilane, $Pemp_2(Me)SiH$, (Si-C^{ipso} = 190.18 pm). This bond length shortening results from the superposition of two effects. The reduced steric congestion in the trigonal-planar coordinated cation **45** compared to the tetrahedral silanes allows for shorter Si–C^{ipso} bonds. In addition, the smaller covalent radii of tricoordinated silicon and the onset of π-conjugation between the Pemp substituent and the central silicon atom contribute to the shorter Si–C^{ipso} bond in silylium ion **45**. At this point it is maybe worth mentioning that DFT methods even at a moderate level predict molecular structures of triarylsilylium ions which are very near to the experiment (see Table 1) [58]. This suggests that for silylium ions the structure optimization using DFT methods is a reliable source for structural information.

^{29}Si NMR spectroscopy is of high diagnostic value for the identification and characterization of silylium ions. Typically, the positively charged silicon atom in triarylsilylium ions resonates in arene solutions at very low field (δ ^{29}Si = 230–216; see Table 2). The only reported example for a diarylalkyl

Table 1 Pertinent structural parameter for triarylsilylium ions **28**, **45** from XRD investigations. Computed values in parenthesis are given for comparison (B3LYP/6-311G(d,p)) [20, 22, 58]

	Si-C^{ipso}(av) [pm]	Σα(Si) [°]	δ (av) [°]
Mes_3Si^+, **28**	181.7 (184.1)	359.9 (360.0)	49.2 (49)
$Pemp_3Si^+$, **45**	184.7 (185.4)	360.0 (360.0)	60.0 (52)

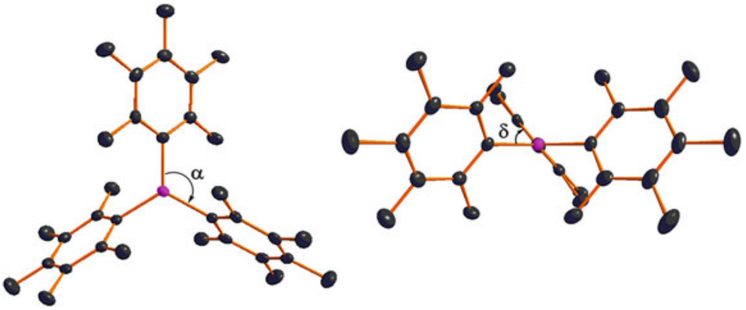


Fig. 2 Molecular structure of $Pemp_3Si^+$, **45**, as determined by XRD from the borate $[Pemp_3Si]_2[B_{12}Cl_{12}]$. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) *Left* view perpendicular to the $SiC^{ipso}{}_3$ plane. *Right* view along one Si–C^{ipso} vector [22]

silylium ion, di-Tipp-substituted cation **2**, is characterized by an even stronger deshielding of the silicon atom (δ ^{29}Si = 244) [21]. The ^{29}Si NMR chemical shift of these triarylsilylium ions shows virtually no dependence on the solvent used. This fact can be used to distinguish the free silylium ions from silylarenium ions formed between trialkylsilylium ions and the arene solvent. For example, the ^{29}Si NMR chemical shift difference between the arenium ions $[Et_3Si(C_6D_6)]^+$ and $[Et_3Si(C_7D_8)]^+$is nearly 9 ppm (Table 2) [27]. The corresponding solvent complexes of triarylsilylium ions are also formed in solvents with higher nucleophilicity than aromatic hydrocarbons. This is revealed by a significant high-field shift of the ^{29}Si NMR resonance (see Table 2). Therefore, for NMR work with silylium borates, aromatic hydrocarbons and fluorinated or chlorinated aromatic hydrocarbons are the solvents of choice.

The comparison of the experimental data for silylium ions with theoretical estimates for their ^{29}Si NMR chemical shift (B3LYP/IGLOIII//B3LYP/6-311G(d, p)), which is provided in Table 2, emphasizes the applicability of theoretical data at this level of theory for the identification and characterization of these compounds.

Slow-spinning ^{29}Si NMR CPMAS solid-state NMR spectroscopy for silylium borates **28**$[HCB_{11}Me_5Br_6]$ and **45**$_2[B_{12}Cl_{12}]$ (see Fig. 3 for an example) revealed within the limits of accuracy an almost axial symmetric ^{29}Si NMR chemical shift tensor ($\delta_{11} = \delta_{22} > \delta_{33}$ and skew κ close to +1) in agreement with the local molecular C_3-symmetry of silylium ions **28** and **45** (see Table 3) [20, 22]. A very large anisotropy of the ^{29}Si NMR chemical shift tensor is indicated by the determined span $\Omega = \delta_{11}–\delta_{33}$. Therefore, the anisotropy of the ^{29}Si chemical shift tensor is significantly larger for triarylsilylium ions than for tetrahedral

Table 2 ^{29}Si NMR chemical shift of triaryl silylium ions $Ar_2Ar'Si^+$ and diarylalkyl silylium ions Ar_2EtSi^+. ^{29}Si NMR data for $[Et_3Si(C_6D_6)]^+$, $[Et_3Si(C_7D_8)]^+$ and calculated ^{29}Si NMR chemical shifts (in parenthesis) are given for comparison (GIAO/B3LYP/IGLOIII//B3LYP/ 6-311G(d,p))

Ion	Ar/Ar'(*R*)	δ^{29}Si	Solvent	References
28	Mes/Mes	225.3	C_6D_6	[17, 21]
		223.8	C_7D_8	[21]
		225.5	C_6D_5Cl	[21]
		(229.6)	–	[58]
		37.0	C_6D_6/CD_3CN (1/3)	[17]
45	Pemp/Pemp	216.2	C_6D_6	[21]
		216.4	C_7D_8	[22]
		216.8	C_6D_5Cl	[22]
		(223.2)	–	[58]
46	Xylyl/Xylyl	229.9	C_6D_6	[21]
		(239.4)	–	[58]
47	Duryl/Duryl	226.5	C_6D_6	[22, 59]
		(237.5)	–	[58]
48	Tipp/Tipp	229.8	C_6D_6	[21]
		(242.6)	–	[58]
49	Mes/Tipp	217.0	C_6D_6	[21]
2	Tipp/Et	244.7	C_6D_6	[22]
		240.6	C_6D_5Cl	[22]
$[Et_3Si(C_6D_6)]^+$, **50**	–	97.6	C_6D_6	[27]
$[Et_3Si(C_7D_8)]^+$, **51**	–	88.7	C_7D_8	[27]

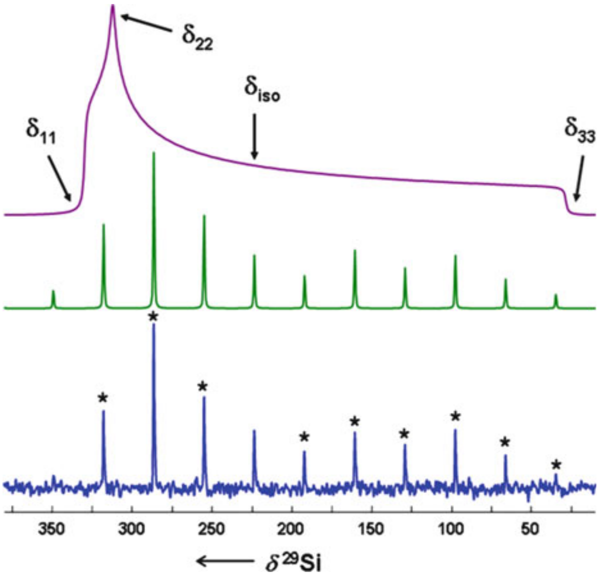


Fig. 3 ^{29}Si solid-state NMR spectra of the borate $[Pemp_3Si]_2[B_{12}Cl_{12}]$ 6 *o*-$Cl_2C_6H_4$. Lower trace: Experimental slow-spinning CP MAS spectra at 4 kHz spinning frequency (* spinning side bands). Middle trace: Simulated slow-spinning spectra. Upper trace: static spectra [22]

Table 3 ^{29}Si NMR chemical shift tensor of silylium ions **28**, **45** (Span $\Omega = \delta_{11}$-δ_{33}; Skew $\kappa = 3(\delta_{22}-\delta_{iso})/\Omega$). Values calculated at GIAO/B3LYP/IGLOIII//B3LYP/6-311G(d,p) are given in parenthesis [20, 22]

Ion	Ar/Ar'	δ^{29}Si	δ_{11}	δ_{22}	δ_{33}	Ω	κ
28	Mes/Mes	226.7	319.5	319.5	41.2	278.3	1.00
45	Pemp/Pemp	223.5	329	312	30	299	0.89
		(221.6)	(320)	(318)	(27)	(293)	(0.99)

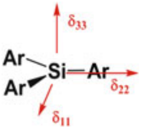
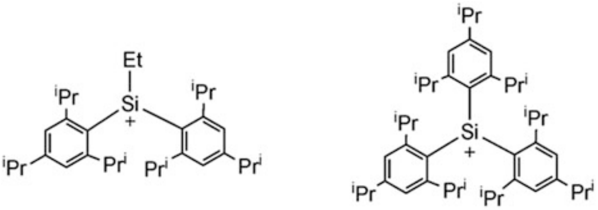


Fig. 4 Orientation of the principal components of the ^{29}Si NMR chemical shift tensor in triarylsilylium ions

coordinated silicon compounds (i.e., for triphenylsilane, Ph_3SiH $\Omega = 52$). The origin of this high anisotropy of the ^{29}Si NMR chemical shift tensor of silylium ions is the strongly deshielded δ_{11} and δ_{22} components, while the high-field component δ_{33} is in the chemical shift range for tetracoordinated silicon atoms ($\delta_{33} = +30$ to -60; see also Table 3). For symmetry reasons both deshielded principal components are located in the SiC^{ipso}_3 plane of silylium ions **28** and **45**, and the shielded component δ_{33} is oriented perpendicular to that plane and along the local C_3 axis (see Fig. 4). This orientation of the ^{29}Si NMR chemical shift tensor relative to the molecular structure and also the size of the principal components are confirmed by the results of NMR chemical shift computations (see Table 3). A more detailed analysis of the calculations suggests that the strong deshielding of the in-plane components δ_{11} and δ_{22} is mainly the result of paramagnetic currents induced by the magnetic field that correlate the degenerate Si–C σ-bonding orbitals with the LUMO which is dominated by contributions from the 3p(Si). These deshielding currents are very efficient due to the low energy of the LUMO and the consequentially small energy difference between Si–C σ-bonds and the LUMO [22].

In view of the extreme electron deficit of the central silicon atom in triarylsilylium ions and in regard of the fact that silyl cationic species have been isolated that are stabilized by formation of intra- or intermolecular Si–H–Si 3c2e bonds, the possible formation of related Si–H–C bonds or the onset of such a bonding interaction is clearly a matter of discussion. Pertinent candidates for the occurrence of such agostic interactions are all triarylsilylium ions substituted with alkyl groups in the *ortho*-positions. Available structural and NMR data for most of the investigated silylium ions are in this respect unremarkable. The ^{1}H and ^{13}C NMR data obtained for the Tipp-substituted cations **2** and **48** (Scheme 18) reveal, however, clear indications for multicenter bonding between the positively charged silicon atom and the *ortho*-methine groups of the iso-propyl substituents of the Tipp substituent. In particular, the ^{1}H NMR resonances of the *ortho*-methine protons are



2 **48**

Scheme 18 Silylium ions with NMR spectroscopic indications for $Si^{+}\cdots H$–C multicenter bonding

high-field-shifted by $\Delta\delta\ ^{1}H = -1.11$ to -1.37, and the *ortho*-methine carbon atoms are deshielded by $\Delta\delta\ ^{13}C = 8.4-9.6$, compared to the corresponding reference silanes. Similar significant changes in the ^{1}H and ^{13}C NMR chemical shifts were not detected for the *para*-isopropyl groups. In addition, the ^{1}J(*ortho*-CH) coupling constants in cations **2** and **48** are significantly smaller than those detected for the *para*-methine groups ($\Delta^{1}J(CH) = 14$ Hz). Although these effects appear to be relatively small compared to prototypical compounds that exhibit three-center M−H−C bonding, [60] the NMR spectroscopic data for **2** and **48** indicate the onset of a multicenter $Si^{+}\cdots H-C$ interaction [22].

3.2.2 Aromatic and Homoaromatic Silylium Ions

Significantly more complex structures are revealed by the work of Sekiguchi's group on cyclic polysila-silylium ions. The 2π-Hückel aromatic trisilacyclopropenylium cation **37** was synthesized starting from cyclotrisilene **52** by cleavage of an exocyclic Si–Si bond at the tetracoordinated silicon atom (Scheme 13) [24]. In the solid state it showed the expected symmetric structure with an almost equilateral triangle of silicon atoms (endocyclic SiSiSi bond angles: 59.8–60.2°) (Fig. 5). The nearly identical endocyclic Si–Si bond lengths (Si–Si (av) = 221.7) are intermediate between Si–Si single (237.3 pm) and Si=Si double bonds (216.1 pm) in cyclotrisilene **52**. All three ring-forming silicon atoms adopt a trigonal-planar coordination sphere. These structural features clearly classify cation **37** as a persilaaromatic compound and rank it in one series with its carbon analogues, the cyclopropenylium cations and its germanium congener **53** and the isoelectronic dianionic cyclotrigallane **54** [61, 62]. This is further supported by nucleus-independent chemical shift (NICS) computations for model compounds [63]. NICS(1) values, commonly recognized as an aromaticity probe, were calculated to be −13.7 for $[(Me_3SiSi)_3]^{+}$ and −14.3 for $[(Me_3CC)_3]^{+}$. These strongly negative NICS values indicate the presence of a diamagnetic ring current in the model cations and aromaticity also for cation **37**. Strongly deshielded ^{29}Si NMR chemical shifts are reported for both representative of this class of silylium ions, for **37**$[B(p\text{-}C_6F_4SiMe_2t\text{-}Bu)_4]$ ($\delta^{29}Si = 284.6$, 288.1) and for the disilacyclopropenylium borate **55**$[B(C_6F_5)_4]$ ($\delta^{29}Si = 208.2$).

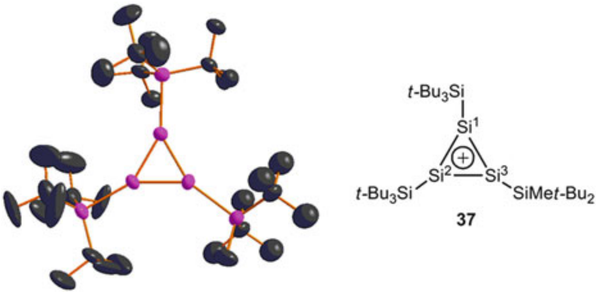
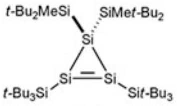


Fig. 5 Molecular structure of cyclotrisilenium, **37**, as determined by XRD from the borate 37[B(*p*-$C_6F_4SiMe_2t$-Bu)$_4$]. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Pertinent bond lengths [pm]: Si^1–Si^2 = 222.1; Si^1–Si^3 = 221.8; Si^2–Si^3 = 221.1 [24]



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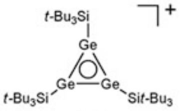

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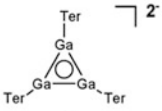

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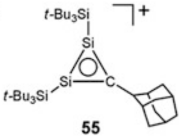

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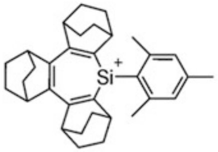

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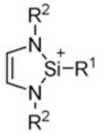
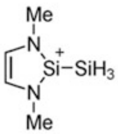


5

$R^1 = CH(SiMe_3)_2$; $R^2 = {}^tBu$
$R^2 = SiEt_3$; $R^2 = {}^tBu$, Xylyl, Dipp
$R^2 = Si^iPr_3$; $R^2 = {}^tBu$, Xylyl, Dipp



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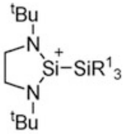


6

R^1 = Et, ^{i}Pr

Prior to these spectacular achievements the synthesis of the marginally stable cationic silaaromatic compound **56** was reported [39, 40]. Silatropylium cation **56** was identified by its strongly deshielded ^{29}Si resonance at $\delta^{29}Si = 149$, which is downfield shifted compared to its precursor silane by $\Delta\delta^{29}Si = 192$. Cation **56** is stable only at −50° in methylene chloride and decomposes at higher temperatures. The identification of silatropylium cation **56** gained further support from ^{29}Si NMR chemical shift calculations, which predict an NMR chemical shift close to the experimental value for cation **56** ($\delta^{29}Si(calc) = 160$). The computed NICS (1) value of −7.5 indicates a diamagnetic ring current for cation **56**. The same method indicates also for the recently synthesized silaimidazolium tetraarylborates **5**[$B(C_6F_5)_4$] a certain degree of aromaticity, i.e., the computed NICS(1) aromaticity index for the model compound **57** is −8.0. For comparison,

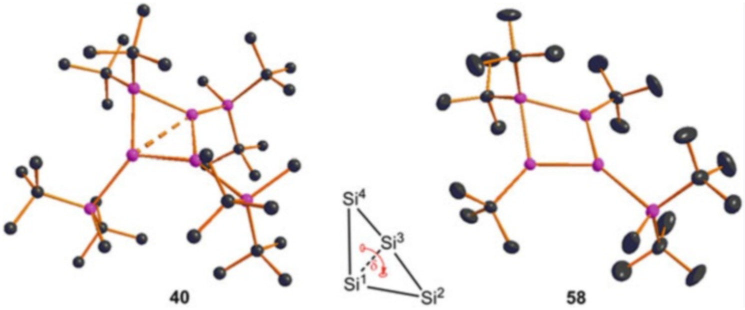
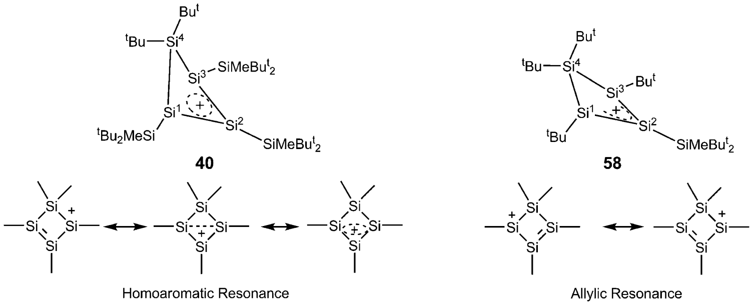


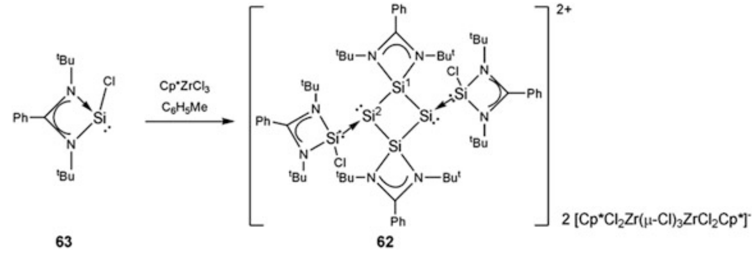
Fig. 6 Molecular structures of tetrasilacyclobutenyl cations **40** and **58** as determined by XRD in the borates **40**$[B(C_6F_5)_4]$ and **58**$[B(C_6F_5)_4]$. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and dihedral angles [°]: **40**: Si^1–Si^2 = 224.0; Si^1–Si^3 = 269.2; Si^2–Si^3 = 224.4; Si^1–Si^4 = 233.6; Si^3–Si^4 = 232.5; δ = 46.6. **58**: Si^1–Si^2 = 222.6; Si^1–Si^3 = 280.7; Si^2–Si^3 = 221.9; Si^1–Si^4 = 234.0; Si^3–Si^4 = 234.3; δ = 28 [23, 64]



Scheme 19 Homoaromaticity versus allylic resonance in tetrasilacyclobutenyl cations

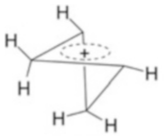
the NICS(1) values for textbook aromatic compounds such as benzene and imidazolium cation are −12.3 and −10.5. The silaimidazolium cations **5** are strongly stabilized by this electronic situation and were identified by ^{29}Si NMR chemical shifts for the endocyclic silicon atoms in the region of δ^{29}Si (**5**) = 53–67 [26, 27]. The related nonaromatic cations **6** for which stabilization by a heteroallylic resonance is operative show somewhat more deshielded ring silicon atoms δ^{29}Si(**6**) = 91–92 [27].

A remarkable substituent effect on the molecular structure and – as a consequence – also on the electronic situation is revealed by the comparison of the structural parameters of the tetrasilacyclobutenyl cations **40** and **58** (see Fig. 6) [23, 64]. Both cations were obtained in the form of their tetraarylborates in benzene. In cations **40** and **58**, the tri-substituted silicon atoms Si^1–Si^3 are coordinated in a trigonal-planar fashion and the Si–Si bond lengths between these three atoms are intermediate between Si–Si single and Si=Si double bonds. The intriguing and decisive structural differences between both closely related silicon cations are the smaller Si^1Si^3 separation and the larger folding of the four-membered ring in cation



Scheme 20 Synthesis of tetrasilacyclobutadiene dication **62** [67]

40. The Si^1–Si^3 distance of 269.2 pm is only around 15% longer than a regular Si–Si single bond (235 pm). This indicates bonding orbital interaction between these silicon atoms and classifies cation **40** as a homoaromatic compound similar to the carbon congener, the cyclobutenylium ion **59** (Scheme 19) [65]. The Si^{1}Si^3 separation in cation **58** is significantly larger (280.7 pm) and the folding of the four-membered ring is less pronounced ($\delta = 28°$). The 1,3-orbital interaction in cation **58** is apparently reduced and the electronic situation is thus dominated by allylic resonance (Scheme 19). ^{29}Si NMR spectroscopy reflects the different bonding situations in cations **40** and **58** much more sensitively than the structural parameters. The allylic resonance in cation **58** is manifested by the low-field-shifted ^{29}Si NMR signal for the silicon atoms Si^1 and Si^3 (δ^{29}Si$^{1/3}$ = 286.8) while the central silicon atom Si^2 gives rise to a ^{29}Si NMR resonance in a chemical shift region typical for doubly bonded silicon atoms in polysilyldisilenes (δ^{29}Si^2 = 183.8, compared to δ^{29}Si = 155.5 in disilene **60**). In contrast, the homoaromatic cation **40** is distinguished by an enormous deshielding of the central silicon atom Si^2 (δ^{29}Si^2 = 315.7) and significant high-field-shifted resonances for the silicon atoms Si^1 and Si^3 (δ^{29}Si$^{1/3}$ = 77.3). It was concluded that these pronounced differences in the bonding situation in cations **40** and **58** are due to the different electronegativities of the substituents at Si^1 and Si^3. The more electronegative alkyl substituent increases the electrostatic repulsion between both silicon atoms and weakens the 1,3-bonding interaction [64].



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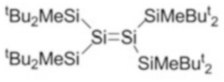

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61

Cyclobutadiene dication, **61**, is a 2π-aromatic cation. In the carbon case, tetramethyl- and tetraphenyl-substituted derivatives of this dication were characterized in superacidic media already in 1976 [66]. A related persila-analogue, the tetrasilacyclobutadiene dication **62**, was obtained only recently in an unexpected reaction between donor-stabilized silylene **63** and Cp*ZrCl$_3$. in 29% yield (Scheme 20) [67]. As an intermediate, a silicon(II) cation, [LSi]$^+$, resulting from

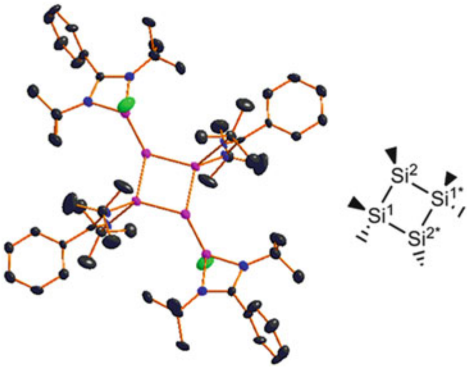
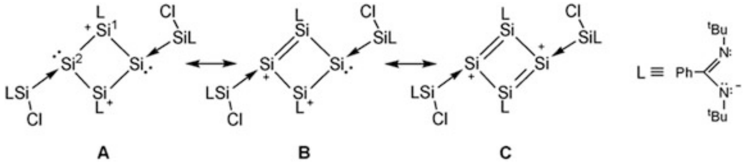


Fig. 7 Molecular structures of tetrasilacyclobutadiene dication **62** as determined by XRD in the salt **62**[$Zr_2Cp^*{}_2Cl_7]_2$. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level, color code: Si *pink*, C *black*, N *blue*, Cl *green*.) Important bond lengths [pm] and dihedral angles [°]:$Si^1–Si^2$ = 232.1; $Si^{1*}–Si^2$ = 233.1; $Si^1...Si^{1*}$ = 302.6; $Si^2...Si^{2*}$ = 353.4; $Si^1–Si^2–Si^{1*}$ = 81.15; $Si^2–Si^1–Si^{2*}$ = 98.85 [67]



Scheme 21 Electron delocalization in tetrasilacyclobutadiene dication **62** [67]

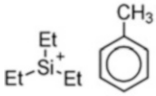
chloride abstraction from chlorosilylene **63**, was suggested. The molecular structure of the dication reveals a planar Si_4 core of rhombic shape (see Fig. 7). The Si_4 core consists of two N-donor-stabilized silyl cationic subunits (Si^1) and two silylene-like groups (Si^2). NICS calculation suggests cyclic delocalization although all endocyclic Si–Si bond lengths approach the regular SiSi single bonds length for tetracoordinated silicon atoms (Si–Si: 234 pm). Based on the combined theoretical and experimental data, it was concluded that dication **62** is best depicted by the charge-localized resonance structure **A** with some π-electron delocalization as represented by canonical structure **B** (Scheme 21).

3.3 Molecular Structures of Stabilized Silylium Ions

In this chapter the structural and NMR spectroscopic features of stabilized silylium ions are summarized. As already outlined and justified in the introductory paragraph this overview focuses on species, which are stabilized by interaction with aryl groups or by silane functionalities. Both modes of stabilization, intra- or intermolecularly, will be discussed here in comparison. In addition, the structures of silylium ion-like cation–anion aggregates of silyl cations with weakly coordinating halogenated *closo*-borate and *closo*-carborate anions will be discussed.

3.3.1 Arene-Stabilized Silylium Ions

The interpretation of the first solid-state structure of an intermolecular silylium/arene complex was subject of an intense debate [68–71]. Originally, the molecular structure of the cation in the crystal structure of $[Et_3SiC_6H_5CH_3][B(C_6F_5)_4]$ was presented as that of a triethylsilyl cation with distant coordination to toluene, **64** [68]. The now commonly accepted understanding of the structure is that of a triethylsilylated toluenium ion **65** [70, 71]. Beyond the historical dissents on the interpretation of the structure, very soon it became clear that these species are very strong silyl Lewis acids and outstanding silylating agents and during the last two decades several groups provided more reliable spectroscopic and structural information on these compounds.



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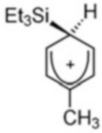

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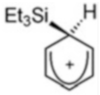

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A concluding structural study was recently presented by the Schulz and Villinger group [30]. A series of trimethylsilylated arenium ions **67** were synthesized from bis(trimethylsilyl)hydronium, **66**, and excess arene according to Scheme 22 and solid-state structures of eleven different trimethylsilyl arenium borates were reported (Table 4).

It was pointed out that the identification of consistent structural trends was severely hampered by the soft potential for all structural parameter related to the Si–C^{ipso} bond; nevertheless the following general structural features could be recognized. The molecular structures of silylated arenium ions are characterized by long Si–C^{ipso} bonds (212.1–217.1 pm; see Fig. 8, for the molecular structure of the toluenium ion and Table 4 for a summary of the important data), which exceed the length of a regular Si–C^{ar} bond (187.9 pm) by 11–15%. Despite these long Si–C^{ipso} bonds the silicon atom in these cations is clearly tetracoordinated. This is indicated by the significant pyramidalization of the silicon atom as measured by the sum of the bond angles around the silicon atom, $\Sigma\alpha(Si)$. For all structurally investigated arenium ions $\Sigma\alpha(Si)$ is reported to be 334–342° (see Table 4) which is markedly smaller than expected for an ideal trigonal-planar coordination ($\Sigma\alpha(Si) = 360°$). The noteworthy C–C bond lengths alternations in the arene parts of the cations provide a second structural indication for the arenium ion nature of the cation (Scheme 23, see also Fig. 8 for an example). The angles γ between the Si–C^{ipso} bond vectors and the line defined by the C^{ipso} and C^{para} carbon atoms of the srenes fall in a narrow range for all structurally investigated silylarenium ions

Scheme 22 Synthesis of trimethylsilylated arenium borates according to [30]

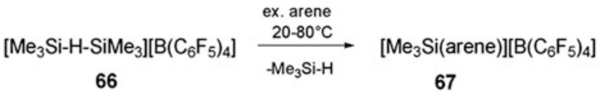


Table 4 Selected structural parameter for trimethylsilylated arenium ions, $[Me_3Si(arene)]^+$, from XRD investigations and computed values of the association energy, AE, for Me_3Si^+ and the arene (PBE1PBE/aug-cc-VDZ). For comparison data, of the triethylsilyltoluenium, **65**, is provided. Computed structural parameters are given in parenthesis [30]

arene	$Si\text{-}C^{ipso}$ [pm]	$\Sigma\alpha(Si)$ [°]	γ [°]	AE (kJ mol^{-1})
C_6H_6	216.9 (219.6)	341.8 (342.4)	103.5	−123
4-Me-C_6H_5	212.1 (214.6)	340.4 (341.0)	106.4	−141
4-Et-C_6H_5	214.0 (214.4)	341.5 (340.7)	103.3	−144
4-n-Pr-C_6H_5	213.7 (214.2)	340.9 (340.7)	104.3	−146
4-i-Pr-C_6H_5	216.9 (214.2)	342.1 (340.7)	101.9	−146
3,4-Me_2-C_6H_4	213.7 (214.2)	341.4 (340.5)	108.2	−150
2,4-Me_2-C_6H_4	214.8 (213.2)	338.3 (338.5)	102.0	−154
2,5-Me_2-C_6H_4	216.7 (215.9)	341.2 (338.7)	101.8	−146
2,3,4-Me_3-C_6H_3	212.9 (213.0)	339.2 (338.0)	102.0	−155
2,4,5-Me_3-C_6H_3	212.1 (212.5)	336.2 (337.7)	102.4	−162
2,4,6-Me_3-C_6H_3[a]	217.1	336.5	99.6	
	213.9 (212.6)	334.2 (335.0)	99.8	−163
$Et_3Si(4\text{-}Me\text{-}C_6H_5)]^+$	219	341	104	

[a] Two independent cations in the elementary cell

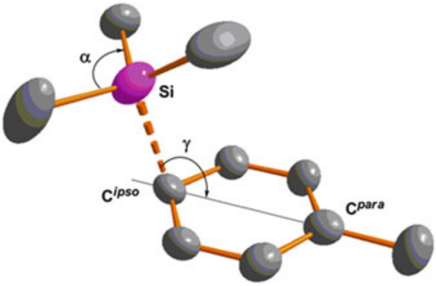
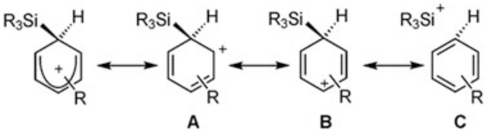


Fig. 8 Molecular structure of $[Me_3Si(C_6H_5CH_3)]^+$ in the compound $[Me_3Si(C_6H_5CH_3)][B(C_6F_5)_4]$. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: Si – C^{ipso} = 212.1; C^{ipso}–C^{ortho} = 140.9; C^{ortho}–C^{meta} = 136.6; C^{meta}–C^{para} = 139.8; $\Sigma\alpha(Si)$ = 340.4; γ = 106.4° [21]

(γ = 99–108°). Therefore, the angles γ are significantly smaller than expected for arenium ions with a sp^3-hybridized *ipso*-carbon atom (γ = 120–125°). This can be rationalized as a structural consequence of β-silyl hyperconjugation as indicated by the no-bond resonance structure **C** in Scheme 23. The smaller angle γ provides better overlap of the σ-SiC^{ipso} bond with the π-system of the arene. Reed pointed out that silylated arenium ions should be viewed as neither a traditional σ-complex



Scheme 23 Resonance in silylated arenium ions **23**

Table 5 Selected structural parameter and association energy, AE, calculated for triethylsilyl benzenium, **68**, using different methods. For all methods the 6-311+G(d,p) basis set was applied [58]

Method	Si–C^{ipso} [pm]	$\Sigma\alpha$(Si) [°]	γ [°]	AE (kJ mol^{-1})
B3LYP	229.8	347.3	108.9	−71
M06-2X	225.0	344.3	103.3	−129
MP2	224.2	345.9	102.8	−136

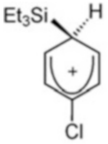
nor a π-complex, but as a point along a σ–π-continuum [69]. Both seemingly diverging views can be brought together if one accepts the extreme no-bond resonance formulation of hyperconjugation as a traditional π-complex.

In agreement with several previous investigations in this field [5, 15, 70, 71] the study by Schulz and Villinger showed that molecular structures obtained by DFT methods closely match in many cases those obtained experimentally in the solid state (see Table 4) [30]. In view of the relatively weak bonds in silylated arenium ions and the soft bonding potentials associated with, it is appropriate to point out that the choice of the right functional might be decisive to obtain meaningful theoretical results with DFT methods. Simply the neglect of dispersion energy contributions when the very popular B3LYP functional is applied can lead to significant deviations compared to results from higher level ab initio calculations, in particular for energies. The M0X series of functionals provides results which are much closer to, for example, MP2 results. As an example the results for energy and structure calculations of triethylsilyl benzenium, **68**, are summarized in Table 5 [58].

As suggested by the distinct structural features of trimethylsilylated arenium ions, the calculated association energies (AE) between the Me_3Si^+ ion and the arenes are substantial and increase with the degree of substitution at the aromatic hydrocarbon. The relative high predicted AE values imply that silylated arenium ions are also stable in solution. In many cases they can be detected at room temperature in solution of the arene by ^{29}Si NMR spectroscopy (see Table 6). Strongly deshielded ^{29}Si NMR resonances in the chemical shift range of δ^{29}Si = 80–115 are characteristic for these cations. Although the data set is rather limited, the following trends can be identified: For a given silyl group a more electron-rich arene leads to a more shielded ^{29}Si NMR resonance. In contrast, increasing steric bulk at the silicon atom results in a deshielding of the ^{29}Si nuclei. In several cases, the ^{29}Si NMR signals of the silylated arenium ions are very broad (i.e., for $[Et_3Si(C_7D_8)]^+$, **51**, $\nu_{1/2}$ = 98 Hz at 99 MHz and r.t.) and the line width is temperature dependent. In addition, usually no ^{13}C NMR signal for the coordinated arene can be detected. This indicates that at room temperature the arene exchanges at a rate, which is fast on the NMR time scale.

Table 6 ^{29}Si NMR chemical shifts observed for silylated arenium borates $[R_3Si(arene)][B(C_6F_5)_4]$

Cation	δ^{29}Si	References
$[Me_3Si(C_6D_6)]^+$	83.6	[72]
$[Et_3Si(C_6D_6)]^+$	92.3	[72]
	97.4	[27]
$[Et_3Si(C_7D_8)]^+$	81.8	[72]
	88.7	[27]
$[^iPr_3Si(C_6D_6)]^+$	107.5	[72]
$[^iPr_3Si(C_7D_8)]^+$	94.3	[27]
$[^iBu_3Si(C_6D_6)]^+$	99.5	[72]
$[^nHex_3Si(C_6D_6)]^+$	90.3	[72]
$[^iPr_2MeSi(C_6D_6)]^+$	96.9	[72]
$[(Me_3Si)_3Si(C_6D_6)]^+$	111.1	[72]



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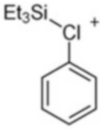

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Broad ^{29}Si NMR signals in the region for silylated arenium ions were also detected when silanes were ionized in chlorobenzene, PhCl (e.g., $\delta^{29}Si(Et_3Si(PhCl)) = 99.9$; $\nu_{1/2} = 33$ Hz; $\delta^{29}Si(^iPr_3Si(PhCl)) = 103.4$; $\nu_{1/2} = 170$ Hz; both at 99 MHz and r.t.) [58]. In these cases the results of DFT calculations suggest that coordination of the solvent via the chlorine substituent is energetically favored, the difference in the free enthalpies between the two isomeric cations **69** and **70** at 298 K being 24.2 kJ mol^{-1}, in favor of chloronium ion **70** [37]. The coordination of silyl cations to halogenated aromatic solvents via the halogen atom is also shown by the solid-state structure of the *o*-dichlorobenzene (odcb) complex of $^iPr_3Si^+$ in the carborate $[^iPr_3Si(odcb)][CHB_{11}Cl_{11}]$ [36]. The molecular structure of the cation $[^iPr_3Si(odcb)]^+$ reveals a tetracoordinated silicon atom with the fourth coordination side occupied with a chlorine atom of the coordinated odcb molecule (see Fig. 9). The Si–Cl bond length (average 233 pm) is 25 pm longer than a typical Si–Cl covalent bond, indicative of weaker, dative bonding.

The results presented in the previous paragraphs demonstrate that the extreme reactivity of three-coordinate silyl cations is significantly reduced in arene solvents by intermolecular polar–π (p–π) interaction between the cation and the π-system of the arene. Two model systems have been suggested and have been experimentally verified in which this p–π interaction is employed to modulate the cation character of the silicon atom intramolecularly and to control the reactivity of the silicon cation [34, 35]. Both classes of silyl cations, the cyclic disilyl-substituted arenium ions **71**, **72** synthesized in our group [33, 49, 73] and the *meta*-terphenyl-substituted silyl cations **73** from the Siegel group [34, 74, 75], will be discussed here as examples for intramolecular stabilized silylated arenium ions. Both classes of silyl cations were synthesized by the standard BCS hydride-transfer reaction

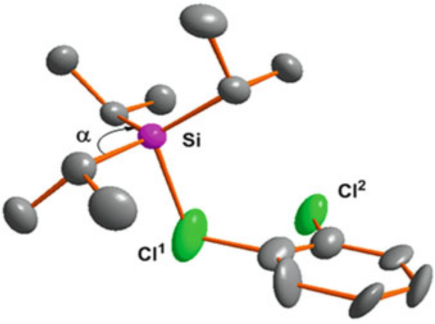
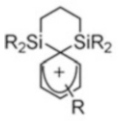


Fig. 9 Molecular structure of [^{i}Pr$_3$Si(odcb)]$^+$ in the compound [^{i}Pr$_3$Si(odcb)][CHB$_{11}$Cl$_{11}$]. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level; only one from two disordered molecules is shown.) Important bond lengths [pm] and angles [°]: Si–Cl^1 = 237.0; 229.3; Cl^1–C = 177.4; Cl^2–C = 170.9; Σα(Si) = 350.3 [36]

using trityl tetrakis(pentafluorophenyl)borate as hydride acceptor in aromatic hydrocarbons. The borates were isolated in high yields and were found to be stable at ambient conditions.



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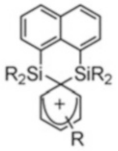

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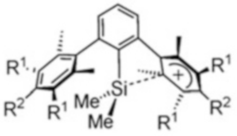

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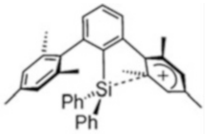

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The terphenyl-substituted silyl cations **73**, **74** were identified by ^{29}Si NMR chemical shifts between δ^{29}Si = 52.7–80.1, a spectral region characteristic for silylated arenium ions (see Table 7) [34, 76]. No significant interactions between cation and solvent or counteranion are present in arene solutions of cations **73**. This is indicated by the solvent- and anion-independent ^{29}Si NMR chemical shift of these species. Both flanking aryl groups are isochronous at r.t., which suggests either a symmetric silyl cation structure or an equilibrium between two identical cations **73** which is fast on the NMR time scale (see Scheme 24). The results of quantum-mechanical calculations for silyl cation **73b** showed that isomer **73b**(C$_2$) is the transition state for the equilibration of two mirror-image structures of the intramolecular arenium ion **73b**. The barrier for this process was predicted to be merely 15–17 kJ mol^{-1} and the computed ^{29}Si NMR chemical shifts for cations **73** match closely the experimental results. Final evidence for the arenium ion nature of cations **73** came from an XRD analysis from single crystals obtained from the borate **73b**[B(C$_6$F$_5$)$_4$] (see Fig. 10) [34]. The characteristic structural features of arenium ions (see Fig. 8) can be clearly recognized also in the molecular structure of cation **73b** in solid state.

Table 7 ^{29}Si NMR chemical shifts observed in benzene-d_6 at r.t. for *meta*-terphenyl-substituted silyl cations **73**–**77**. The counteranion was in each case $[B(C_6F_5)_4]^-$

Cation		$\delta^{29}Si^{exp}$	$\delta^{29}Si^{calc}$	References
73a	$R^1 = R^2 = H$	80.1	74.2[d]	[34]
73b	$R^1 = H$; $R^2 = Me$	79.1	72.8[d]	[34]
		79.1[a]		[34]
73c	$R^1 = Me$; $R^2 = H$	60.6	54.2[d]	[34]
73d	$R^1 = Me$; $R^2 = Me$	58.6	49.7[d]	[34]
74		52.7	63.2[e]	[76]
75a	X = F	89 (quin) J(SiF) = 32 Hz	87.6[c]	[74]
75b	X = Cl	91	93.8[c]	[74]
76a	$R^1 = R^2 = H$	101.3	98.9[b]	[75]
76b	$R^1 = H$; $R^2 = Me$	95.5 (tr) J(SiF) = 42 Hz	97.6[b]	[75]
76c	$R^1 = Me$; $R^2 = H$	60.1	61.6[b]	[75]
76d	$R^1 = Me$; $R^2 = Me$	61.6	56.2[b]	[75]
77		95.4		[75]

[a] Toluene-d_8

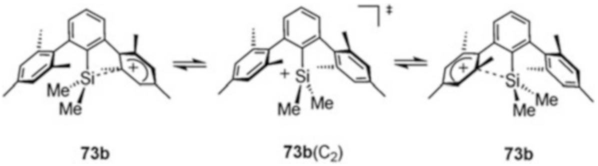
[b] Calculated at CSGT/M06-L/def2-TZVPP//M06-2X/ Def2-TZVPP

[c] Calculated at GIAO/B98/DZ+(2df,pd)//B98/DZ(2df,pd)

[d] Calculated at GIAO/B3LYP/DZ(2df,pd)//B3LYP/DZ(2df,pd)

[e] Calculated at GIAO/B3LYP/IGLOIII//PCM/M06-2X/6-311+G(d,p))

Scheme 24 Fast equilibrium between two mirror-image isomers of **73**b via transition state **73**b (C_2)



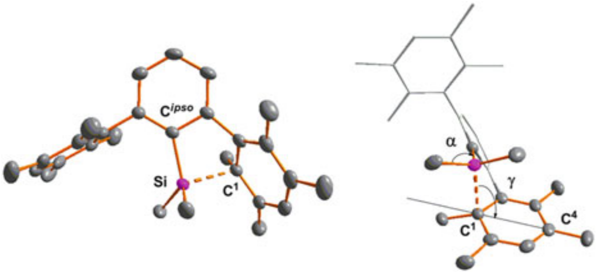
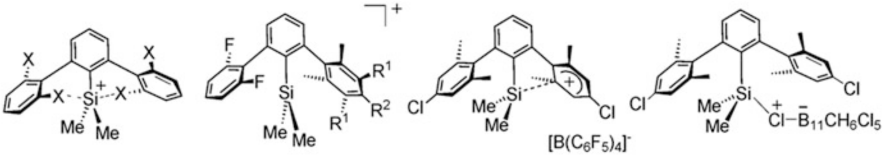


Fig. 10 Molecular structure of silyl cation **73b** in the crystal structure of **73b**$[B(C_6F_5)_4]$. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) In the structure on the right side, the silylated arenium part is emphasized. Important bond lengths [pm] and angles [°]: Si–C^1 = 212.5; av. C^1–C^2 = 144.6; av. C^2–C^3 = 138.7; av. C^3–C^4 = 140.4; $\Sigma\alpha(Si)$ = 346.1; γ = 102.8 [34]

The cations **73** and **74** represent a class of silyl cations which are stabilized by intramolecular π-donation from the flanking aryl groups of the *meta*-terphenyl substituent. This offers the possibility to tune their reactivity by suitable choice of the substituent. Some evidence for this is provided by the high-field-shifted ^{29}Si NMR resonance detected for cation **73d** with the electron-rich pentamethylaryl substituent compared to that of the xylyl-substituted cation **73a** (δ^{29}Si (**73d**) $= 58.6$ vs. δ^{29}Si (**73a**) $= 80.1$).



75 **76** **77**[B(C_6F_5)$_4$] **78**[$CB_{11}H_6Cl_6$]

	X
a	F
b	Cl

	R^1	R^2
a	H	H
b	H	Me
c	Me	H
d	Me	Me

As already pointed out in the previous paragraph aryl–halogen functionalities can serve as intermolecular donors for silylium ions as well (see, e.g., Fig. 9). Related intramolecular halogen stabilization was nicely probed by the Siegel group with the synthesis of cations **75** and **76** bearing 2,6-dihalophenyl substituents [74]. The XRD analysis of a single crystal of **75a**[$CB_{11}H_6Cl_6$] showed that the silicon atom in cation **75a** is pentacoordinated with the two fluorine atoms at the apical position of the trigonal bipyramidal coordination environment of the silicon atom (see Fig. 11a). The SiF distances are by 29 and 35% longer than a regular Si–F bond (159.0 pm), but significantly smaller than the sum of the van der Waals radii of silicon and fluorine (357 pm). On the basis of DFT calculations of the molecular structures of cations **75** and their possible conformers and supported by quantum-mechanical predictions of the ^{29}Si NMR chemical shifts, it was concluded that the pentacoordination of the silicon atom prevails also in solution for both cations **75** (Table 5). Similar to the situation found for the terphenyl-substituted silyl cations **73**, an intramolecular gearing process is operative in their halosubstituted congeners **75** and renders both flanking aryl substituents and in particular all four fluorine atoms in cation **75a** equivalent on the NMR time scale. The interaction of the $SiMe_2$ unit in silyl cation **75a** with all four fluorine atoms is clearly demonstrated by the quintet splitting of the NMR signals of this group (see Table 5). The synthesis of the mixed-substituted silyl cations **76** allowed for the investigation of the competition between π-aryl and lone-pair halogen coordination [75]. A combined NMR, XRD and quantum-mechanical study revealed that in the case of the xylyl- and mesityl-substituted silyl cations **76a**, **b** with relative low π-basicity the fluorine–silicon interaction dominates. This is shown by the substantial J-coupling between the fluorine atoms and the atoms of the central $SiMe_2$ unit

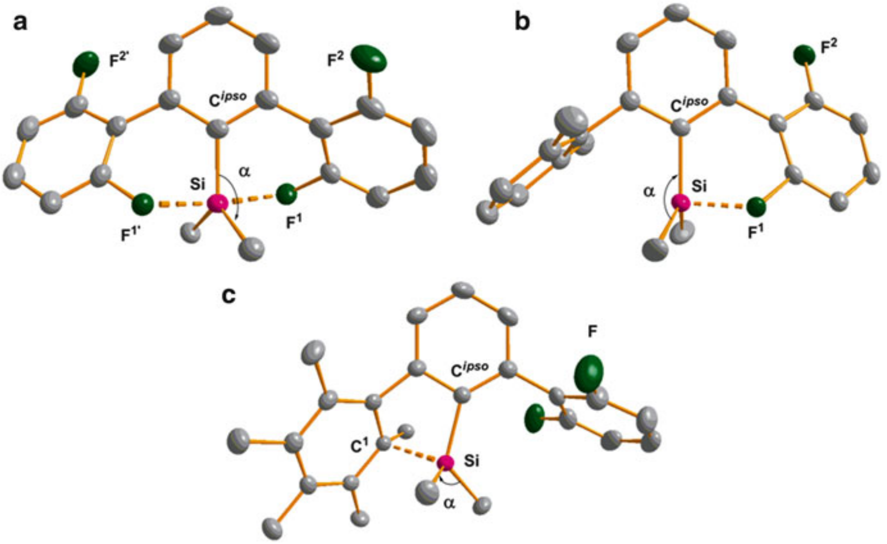
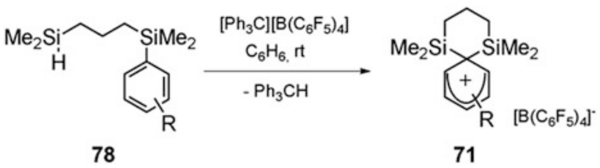


Fig. 11 Molecular structures of terphenyl-substituted silyl cations as determined by XRD from their [$CB_{11}H_6Cl_6$] salts. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) In the structure on the right side, the silylated arenium part is emphasized. Important bond lengths [pm] and angles [°]: (**a**) **75a**; Si–F^1 = 215.06; Si–$F^{1'}$ = 206.5; Si–$F^{1'}$–Si = 174.2; C–F^1 = 141.0; C–$F^{1'}$ = 142.1; C–F^2 = 135.1; C–$F^{2'}$ = 135.2; Σα(Si) = 359.9. (**b**) **76a**; Si–F^1 = 186.6; C–F^1 = 144.8; C–F^2 = 134.6; Σα(Si) = 356.8. (**c**) **76d**. Si–C^1 = 208.9; Σα(Si) = 345.5 [74, 75]

and by an XRD analysis of the carborate **76a**[$CB_{11}H_6Cl_6$] (see Fig. 11b). The most prominent feature of the molecular structure of silyl cation **76a** is the tetracoordinated silicon atom with a long Si–F^1 distance, which is by 17% longer than a typical Si–F bond in tetracoordinated silicon compounds. In solution, both fluorine atoms, F^1 and F^2, are equivalent on the NMR time scale. This is illustrated by only one ^{19}F NMR signal and by the triplet multiplicity of the NMR signals of the central $SiMe_2$ group. The equivalence of both fluorine atoms at r.t. and below indicates that the intramolecular Si/F interaction is not substantial enough to suppress the intramolecular dynamics. The electronic situation of cations **76c**,**d** with π-electron-rich lateral rings is dominated by π-arene/Si electron donation and a η^1-arenium ion structure results. This is pictorially demonstrated by the molecular structure of the silyl cation **76d** (Fig. 11c). The molecular structure of cation **76d** features all characteristics of a silylated arenium ion and the fluorinated flanking aryl ring in **76d** is a pure spectator substituent. That the electron demand of these *meta*-terphenyl-substituted silyl cations can be controlled by the substituents at the lateral aryl rings is nicely demonstrated for the cation **77**. When paired with the perfluorinated tetraarylborate NMR investigations suggest in solution a η^1-arenium ion structure. In contrast, with the more silicophilic carborane anion [$CB_{11}H_6Cl_6$]$^-$, an intimate cation/anion aggregate is formed as disclosed by the solid-state structure of **77** [$CB_{11}H_6Cl_6$] [75]. These results illustrate that *meta*-terphenyl-substituted



Scheme 25 Synthesis of bissilylated arenium ions **71**

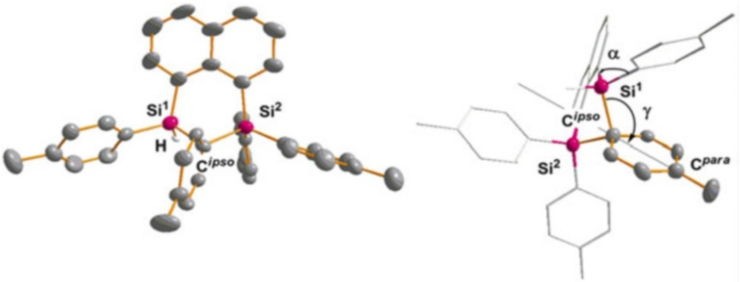


Fig. 12 Molecular structure of silyl cation **79** in the crystal structure of **79**[B(C_6F_5)$_4$]. (Ellipsoid presentation. H-atoms but the SiH are omitted for clarity, thermal ellipsoids at 50% probability level.) In the structure on the right side, the bissilylated arenium part is emphasized. Important bond lengths [pm] and angles [°]: Si^1–C^{ipso} = 199.6; Si^2–C^{ipso} = 198.3; av. C^{ipso}–C^{ortho} = 144.1; av. C^{ortho}–C^{meta} = 135.4; av. C^{meta}–C^{para} = 140.7; Σα(Si^1) = 337.6; Σα(Si^2) = 335.4; γ = 121.5 [73]

silyl cations such as **73**–**77** are a new class of extremely powerful and tuneable silicon-based Lewis acids.

A related class of cations was synthesized in our group. The bissilylated arenium ions **71** were obtained by hydride-transfer reaction from disilahexanes **78** (Scheme 25) and it was shown that their characteristic ^{29}Si NMR chemical shifts at δ^{29}Si = 19–27 depend on the position and the number of alkyl substituents at the aryl ring [33]. This suggests that the electron demand of these silicon cations can also be controlled by the electron-donating ability of the arene ring. Therefore, they represent another class of tuneable silyl Lewis acids. From a structural point of view, the arenium ions **71** are clearly identified as σ-complexes by their ^{13}C NMR spectroscopic parameter. In particular, the high-field ^{13}C NMR signal for the tetracoordinated C^{ipso} atom (δ^{13}C^{ipso} = 89–103) is indicative for a classical structure resembling the Wheland intermediate. The low-field resonances of the C^{ortho} and C^{para} carbon atoms are reminiscent of the dienyl resonance that is operative in arenium ions (δ^{13}C^{orth} = 161–182; δ^{13}C^{ortho} = 150–170). This is further supported by the molecular structure of the bissilylated toluenium ion **79** in the salt **79**[B(C_6F_5)$_4$] (Fig. 12) [73]. The clear long–short–intermediate-bond length alternation and the large $^{\mathrm{SiC}ipso}$C^{para} bond angle ε are in agreement with resonance structures **A** and **B** (Scheme 26). Although the SiC^{ipso} bonds in **79** are significantly longer than regular Si–C single bonds, these bonds are relatively short compared to related SiC bonds in other silylarenium ions such as [$Me_3Si(C_7H_8)$]$^+$ or **73b** (see Table 8). This suggests for toluenium ion **79** a smaller contribution of the no-bond resonance structure **C**.

Scheme 26 Canonical representation for bisilylated benzenium ions

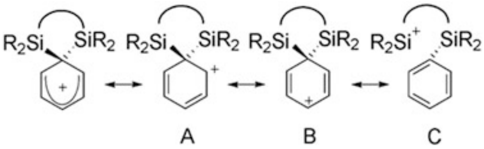
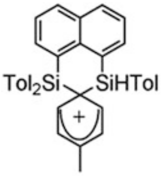


Table 8 Comparison of structural parameter of different silylarenium ions (bond lengths [pm]) as determined by XRD from their $[B(C_6F_5)_4]$ salts

Cation	$Si–C^{ipso}$ [a]	$C^{ipso}–C^{ortho}$ [a]	$C^{ortho}–C^{meta}$ [a]	$C^{meta}–C^{para}$ [a]
65	212.1	140.9	136.6	139.8
73b	212.5	144.6	138.7	140.4
79	199.6	144.1	135.4	140.7
80[a]	207.1	139.9	136.9	136.6

[a]For equivalent bonds average values are reported



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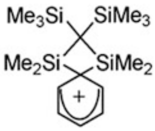


80

In this respect the molecular structure of the closely related silicon cation **80** is of interest which fails to show the expected CC bond length alternation in the bridging phenyl ring (see Fig. 13 and Table 8) [77]. In addition, the relatively long $Si–C^{ipso}$ bonds are noticeable. The reported structural data for cation **80** closely resemble that of toluenium ion **65** and suggest that β-silyl hyperconjugation as it is pictorially represented by the canonical structure **C** is important in these cations.

3.3.2 Silane-Stabilized Silylium Ions

The use of excess alkylsilane R_3SiH (R = Me, Et, ^{i}Pr) as reactant and as solvent in the standard hydride-transfer reaction with triphenylcarbenium tetrakis (pentafluorophenyl)borate results in the formation of bissilylhydronium ions $[R_3Si\text{-}H\text{-}SiR_3]^+$ **13** that might be regarded as silane-stabilized silylium ions. These cations are characterized by a Si–H–Si three-center, two-electron bond and feature tetracoordinated silicon atoms [36, 38]. In publications prior to 2011, the obtained colorless salts were often erroneously identified as simple silylium salts of the type $[R_3Si][B(C_6F_5)_4]$ [38]. The silane in cations **13** is easily replaced by even weak donors such as sulfur dioxide, trimethylsilyl halides, or benzene. Therefore, these bissilylhydronium borates can be used as synthetic equivalents for silylium borates. In cases where triphenylcarbenium carborates $[Ph_3C][HCB_{11}R_5X_6]$ (X = Cl, Br; R = Cl, Br, Me, H) are applied for the synthesis, the corresponding anion-

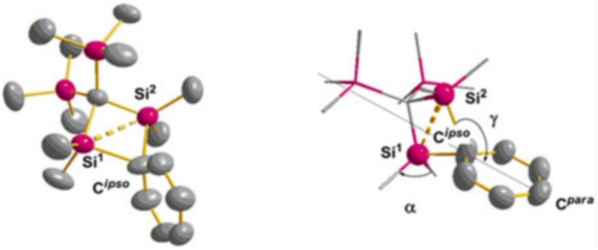


Fig. 13 Molecular structure of silyl cation **80** in the crystal structure of **80**[B(C_6F_5)$_4$]. (Ellipsoid presentation. H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) In the structure on the right side the bissilylated arenium part is emphasized. Important bond lengths [pm] and angles [°]: $Si^1–Si^2 = 261.8$; $Si^1–C^{ipso} = 202.3$; $Si^2–C^{ipso} = 211.8$; av. $C^{ipso}–C^{ortho} = 139.9$; av. $C^{ortho}–C^{meta} = 136.9$; av. $C^{meta}–C^{para} = 136.3$; $\Sigma\alpha(Si^1) = 346.2$; $\Sigma\alpha(Si^2) = 347.2$; $\gamma = 131.0$ [77]

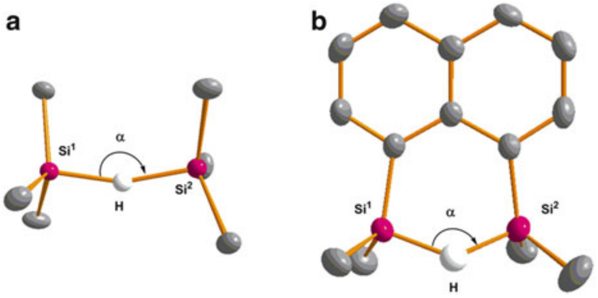


Fig. 14 (**a**) Molecular structure of bissilylhydronium ion $[Me_3SiHSiMe_3]^+$ **66** in the crystal structure of **66**[$HCB_{11}Cl_{11}$]. (Ellipsoid presentation. All H-atoms but the bridging H-atom are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: $Si^1–Si^2 = 317.32(5)$; $Si^1–H = 160(2)$; $Si^2–H = 162(2)$; $\alpha = 160(1)$. (**b**) Molecular structure of bissilylhydronium ion **81** in the crystal structure of **81**[B(C_6F_5)$_4$]•C_6F_6. (Ellipsoid presentation. All H-atoms but the bridging H-atom are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: $Si^1–Si^2 = 297.7(2)$; $Si^1–H = 167(4)$; $Si^2 – H = 158(5)$; $\alpha = 131(3)$ [36, 48]

stabilized species are isolated [7, 47]. Also intramolecular variants of these bissilylhydronium ions, **81**–**85**, have been prepared [48, 78–80]. Cations **81**, **82**, **84**, and **85** were obtained by the standard hydride-transfer protocol from di- or polysilanes in the form of their [B(C_6F_5)$_4$]$^-$ salts. These intramolecular stabilized cations are less reactive, and cations **81** and **82**, for example, are stable in aromatic solvents at r.t. as in these cases no formation of arenium ions was detected. The silyl cations **84** and **85** are reported to be stable even in chlorinated solvents at ambient conditions. Structural information about these unusual hydrogen-bridged disilyl cations came from XRD analysis of compounds **66**[$HCB_{11}Cl_{11}$] and **81**[B(C_6F_5)$_4$]. The molecular structures in the solid state revealed an almost symmetrical Si–H–Si bridge in both cations corresponding to the single minimum potential expected for 3c2e bond and confirmed by the results of quantum-mechanical calculations (Fig. 14). The

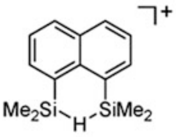
Table 9 NMR and IR data of silylium borates and carborates having a Si–H–Si bond

Compound	δ ^{29}Si	^{1}J(SiH) (Hz)	δ ^{1}H	υ(SiHSi) (cm^{-1})	References
[$Me_3SiHSiMe_3$] [[$HCB_{11}Cl_{11}$]	85.4; 82.2[a]			1,950	[36]
[$Me_3SiHSiMe_3$] [$B(C_6F_5)_4$]	84.6[b]			1,941	[38, 72]
[$Et_3SiHSiEt_3$] [$HCB_{11}Cl_{11}$]				1,900	[36]
[$Et_3SiHSiEt_3$] [$B_{12}Cl_{12}$]				1,879	[32]
[$Et_3SiHSiEt_3$] [$B_{12}Br_{12}$]				1,872	[32]
[$Et_3SiHSiEt_3$] [$B(C_6F_5)_4$]	94.3[b]			1,899	[38, 72]
[$^{i}Pr_3SiHSiPr^{i}_3$] [$B(C_6F_5)_4$]	107.6			1,750	[38, 72]
81[$B(C_6F_5)_4$]	54.4[c]	39	3.34[c]	1,834	[48]
82[$B(C_6F_5)_4$]	76.7[c]	46	1.47[c]		[78]
83[$B(C_6F_5)_4$]	99.1[c]	26			[80]
84[$B(C_6F_5)_4$]	24.9; 15.3; -5.3[d]	46; 119; 171	4.26; 4.41; 4.64[d]	1,725; 1,978; 2,140	[79]
85[$B(C_6F_5)_4$]	34.3, 33.5; -4.5[e]	16; 87; 166	4.28; 4.53[e]	1,747; 1,810; 2,107	[79]

[a] CPMAS solid-state NMR data; two crystallographic different Si atoms
[b] CPMAS solid-state NMR data
[c] At r.t., in C_6D_6
[d] At −85°C in CD_2Cl_2
[e] At r.t. in $CDCl_3$

Si–H–Si linkage in cation **66** is predicted to be linear in the gas phase by DFT calculations (α(Si–H–Si) = 179.7°, at B3LYP/6-311+G(d,p)). In contrast, the experimentally determined molecular structure of cation **66** (Fig. 14a) revealed a slightly bent Si–H–Si bridge. The DFT calculations also indicated a rather flat bending potential for the SiHSi unit in cation **66**. Therefore simple crystal lattice forces may account for the disagreement between theoretical gas phase structure and molecular structure of cation **66** in the crystal. The cyclic structure of disilyl cation **81** forces an even stronger bending of the SiHSi group [36, 48].

The intramolecular stabilized silyl cations **81–85** are easily identified by their characteristic ^{29}Si NMR spectroscopic data, that is, a ^{29}Si NMR chemical shift in the region of $\delta = 25–90$ and, in particular, a strongly reduced direct J-coupling constant $^{1}J(SiH) = 16–46$ Hz (see Table 9). This small ^{1}J(SiH) coupling constant indicates the reduced bond order between the silicon and hydrogen atom compared to regular silanes. ^{29}Si NMR data in solution for intermolecular silane-stabilized cations [R_3Si-H-SiR_3]$^{+}$, **13**, are not available, due to the fast equilibria between **13** and arene- or anion-stabilized trialkylsilylium ions. The hydrogen-bridged species are, however, easily identified in the solid state by a broad absorption in the IR spectra in the region of ν(SiHSi) = 1,750–1,950 cm^{-1}, which is significantly shifted to lower energy compared to regular Si–H stretch vibrations (ν(SiH) = 2,150 cm^{-1}).



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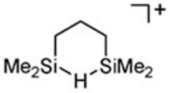

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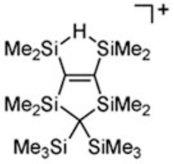

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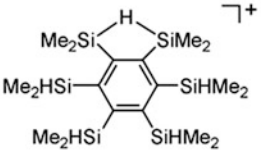

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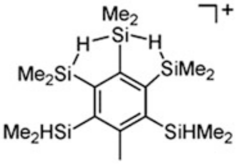

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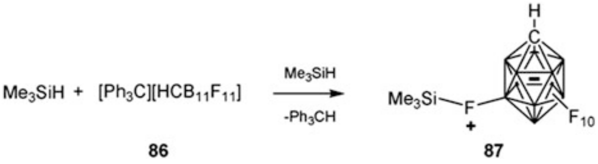
3.3.3 Anion-Stabilized Silylium Ions

It was already pointed out in the introductory remarks that non-nucleophilic reaction conditions are one prerequisite for the synthesis of silylium ions in the condensed phase. The use of weakly coordinating anions is particularly decisive. Halogenated *closo*-carborate monoanions and – more recently – *closo*-borate dianions have found the most widespread use besides fluorinated tetraarylborates. While with bulky substituents these anions form silylium ions salts with well-separated cations and borate anions [10, 20, 22, 42], silylium ions with smaller alkyl substituents tend to coordinate directly to the anion forming zwitterionic compounds [7, 31, 32, 47]. For example, upon reaction of trimethylsilane with trityl-*closo*-carborate **86** in excess trimethylsilane the trimethylsilylium carborate **87** is formed (Scheme 27) [44].

A structural study for **87** and several related halogenated trialkylsilylium carborates and borates reveals in each case a close contact between one halogen atom of the anion and the silicon atom, which leads to a distorted tetrahedral coordination environment for the silicon atom [7, 9, 31, 32, 47]. The molecular structure of silylium carborate **87** serves here as a typical example for this type of compounds. It is characterized by a long Si–F bond (190.2 pm, see Fig. 15a), which

Scheme 27 Preparation of trimethylsilylium carba-*closo*-borate **87** [44]



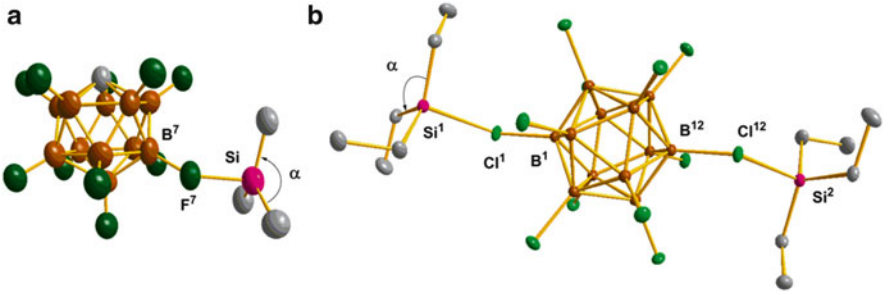
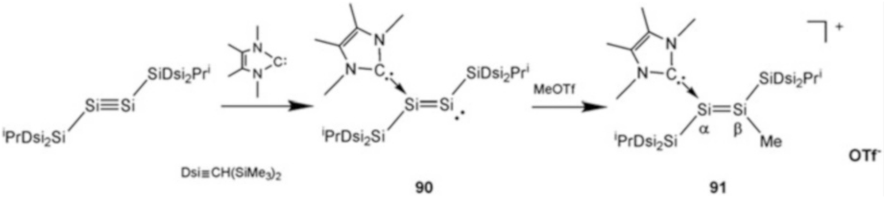


Fig. 15 (**a**) Molecular structure of $[Me_3Si][HCB_{11}F_{11}]$, 87, in the crystal. (Ellipsoid presentation. All H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: Si–F^7 = 190.2; F^7–B^7 = 145.7; mean B-F distance: B–F^{mean} = 137.2; Σα(Si) = 354.4 [44]. (**b**) Molecular structure of $[Et_3Si]_2[B_{12}Cl_{12}]$, 88, in the crystal. (Ellipsoid presentation. All H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: Si^1–Cl^1 = 231.1; Cl^1–B^1 = 184.5; mean B-Cl distance: B – Cl^{mean} = 178.0; Σα(Si)= 348.1 [31, 32]

exceeds the length of a standard Si–F bond (163 pm) by 17%. Despite this long Si–F bond the silicon atom in compound **87** is clearly tetracoordinated. This is indicated by the significant pyramidalization of the silicon atom as measured by the sum of the bond angles around the silicon atom, Σα(Si) = 354°. The coordination of the silylium ion to the fluorine atom causes also a significant elongation of the B–F bond compared to the mean B–F bond length in the carborane anion (B7–F7 = 145.7 pm vs. mean B–F = 137.2 pm; see Fig. 15a). Small trialkylsilylium ions coordinate to the $[B_{12}Cl_{12}]^{2-}$ dianion in a 1,12 regiochemistry, as it is shown for the triethylsilylium dodecachloro-*closo*-dodecaborate **88** in Fig. 15b [31, 32].

The zwitterionic nature of the silylium carborate **87** is also reflected by the relatively small ^{29}Si NMR chemical shift (δ^{29}Si = 138, neat) compared to that of free triarylsilylium ions or compared to the theoretical estimate for Me_3Si^+ (δ^{29}Si = 404) [44]. ^{29}Si NMR investigations on a complete series of silylium carborates suggest that the coordination of the silicon cation to the carborate anion prevails in solution. For example, the ^{29}Si NMR chemical shift detected for $[^iPr_3Si][HCB_{11}H_5Cl_6]$ in benzene-d_6 (δ^{29}Si = 103) differs significantly from that measured for tri-*iso*-propylsilylium tetrakis(pentafluorophenyl)borate $[^iPr_3Si][B(C_6F_5)_4]$ in the same solvent (δ^{29}Si = 108) [9]. This indicates that, depending on the weakly coordinating anion, different silyl cationic species are present in benzene solution. Although the interaction between the carborate anion and the silicon

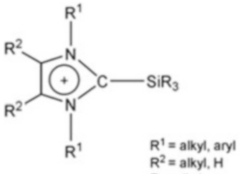


Scheme 28 Synthesis of disilenyl triflate **91**[OTf] [81]

atom determines the structure and spectroscopic properties of these silylium carborates and discriminates them from the free silylium ion, they represent possibly the nearest approach to simple trialkyl-substituted silylium ions in the condensed phase and their specific reactivity justifies their description as anion-stabilized silylium ions.

3.3.4 A N-Heterocyclic Carbene-Stabilized Disilenyl Cation

N-heterocyclic carbenes (NHCs) are strong donors and they form stable complexes with silylium ions which are accurately described as being 2-silylimidazolium ions **89**. A remarkable NHC-stabilized silyl cation was recently prepared by the Sekiguchi group [81]. Addition of methyl triflate to the NHC/disilyne complex **90** yields the triflate of disilenyl cation, **91**, the persila-variant of a vinyl cation, in good yields (Scheme 28).



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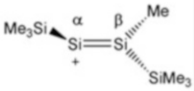

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Disilenyl cation **91** is identified by two characteristic low-field signals in the ^{29}Si NMR spectrum (δ^{29}Si = 54 and 168.8) with the most deshielded signal assigned to the Si$^{\beta}$ atom. The results of computations predict a bent structure for disilenyl cation **92**, in contrast to vinyl cations which feature a linear dicoordinated positively charged carbon atom. The molecular structure of NHC-stabilized disilenyl cation **91** differs significantly from the theoretical prediction and closely resembles in many characteristics that of a disilene (Fig. 16). Based on the analysis of theoretical results and spectroscopic data, the authors suggested for disilenyl cation **91** a electronic structure described by resonance between Lewis representations **A** and **B** with only minor contributions of the canonical form **C** (Scheme 29).

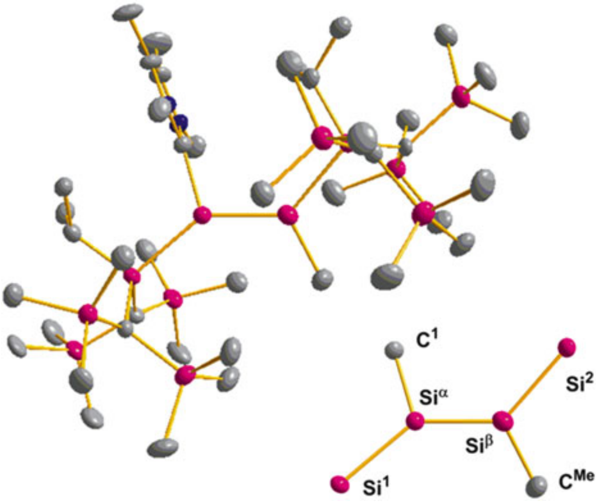
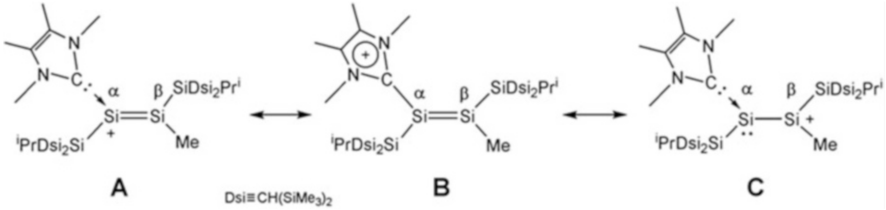


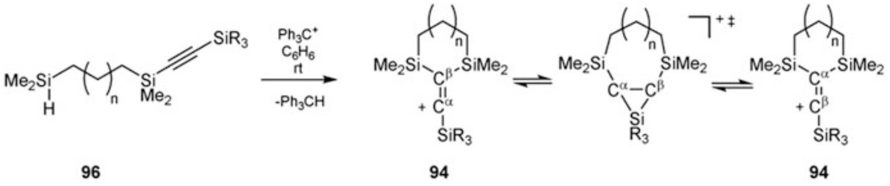
Fig. 16 Molecular structure of disilenyl cation **91** in the crystal of **91**[OTf]. (Ellipsoid presentation. All H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and bond and dihedral angles [°]: $Si^{\alpha}–Si^{\beta}$ = 219.2; $C^{1}–Si^{\alpha}$ = 190.4; $Si^{\alpha}–Si^{1}$ = 243.42; $Si^{\beta}–Si^{2}$ = 240.64; $Si^{\beta}–C^{Me}$ = 186.5; $Si^{\beta}–Si^{\alpha}–Si^{1}$ = 139.87; $Si^{\beta}–Si^{\alpha}–C^{1}$ = 112.71; $Si^{\alpha}–Si^{\beta}–C^{Me}$ = 117.61; $C^{Me}–Si^{\beta}–Si^{\alpha}–Si^{1}$ = 0.0; $C^{1}–Si^{\alpha}–Si^{\beta}–Si^{2}$ = 20.7 [81]



Scheme 29 Resonance structures of disilenyl cation **91** [81]

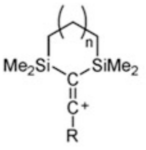
3.3.5 Intramolecular π-Stabilized Silylium Ions

Intramolecular silyl arenium ions such as the terphenyl-substituted cations **73** prepared in the Siegel group or the bissilylated arenium ions **71**, **72** from our laboratories are prominent representatives for intramolecular π-stabilized silylium ions. When the aryl substituents are replaced by CC multiple bonds as electron-donating groups for the incipient silylium ion, carbocations are formed which are significantly stabilized due to their β-silyl substitution. The non-nucleophilic reaction conditions needed for the generation of the silylium ions are also advantageous for the isolation of carbocations in the form of their tetraarylborates or carborates [82–86]. A series of β-silyl-substituted vinyl cations **93** were synthesized by this approach at ambient conditions and several examples of vinyl cation salts have been crystallized [83, 84]. While for most of these compounds the description as carbocations is undisputable, the highly dynamic trisilyl-substituted vinyl cations **94** [86] and the silanorbornyl cations **95** [82]



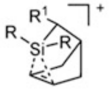
Scheme 30 Synthesis of trisilyl-substituted vinyl cations **94** and their degenerate rearrangement

are regarded as borderline cases. Trisilyl-substituted vinyl cations of type **94** are synthesized by hydride transfer from the corresponding alkinylsilanes **96**. ^{13}C and ^{29}Si NMR studies confirm the degenerate rearrangement of the central dicarbyne $[C{\equiv}C]^{2-}$ unit within the triangle defined by the three positively charged silyl groups (Scheme 30) [86]. For silanorbornyl cations **95** a [3+1] coordination of the positively charged silicon atom was established by NMR investigations, which is supported by quantum-mechanical calculations. The extra coordination side at the silicon atom is occupied by the C=C double bond of the methylene cyclopentene substituent which leads to a symmetrical η^2-coordination for the silicon atom. The silanorbornyl cations **95** are characterized by a ^{29}Si resonance in the NMR spectra at relative low field (δ^{29}Si = 80–87) and the interaction between the vinyl group and the positively charged silicon atom is shown by a downfield shift of the ^{13}C NMR resonances of the vinylic carbon atoms by $\Delta\delta^{13}$C = 20 compared to the precursor silanes [82].



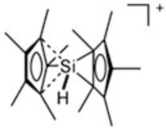
93

R^1 = alkyl, aryl
n = 0-2



95

R = alkyl
R^1 = CH_2-*t*Bu, H



44

A very unusual representative of the π-stabilized silylium ions is cation **44**, which is obtained from protonation of decamethylsilicocene **43** (see Sect. 2.5) [56]. Its very high field shifted ^{29}Si NMR resonance at δ^{29}Si = −12.1 is independent from the solvent, which indicates no significant interaction between solvent and cation. A computational study suggests that this very high field ^{29}Si NMR resonance reflects the unusual bonding situation in protonated silicocene **44** [57]. The cation is predicted to be highly fluxional and in the predominant isomer the Cp* substituents are bonded in a η^2:η^3 fashion to the silicon atom. Clearly, experimental structural investigations based on XRD results for the highly intriguing species **44**, **94**, and **95** are extremely desirable to further substantiate the theoretical structure predictions. This demand becomes even more pressing as quite often the extreme electron deficit at silicon in silylium ions is the source for previously unprecedented structural motifs. This is nicely demonstrated by the structure determination of the intramolecular stabilized silylium ion **97** [42]. Silylium ion **97** is synthesized by hydride transfer starting from the corresponding ferrocenyl monosilane FcSiHMe^{t}Bu, **98**, and it is characterized by a

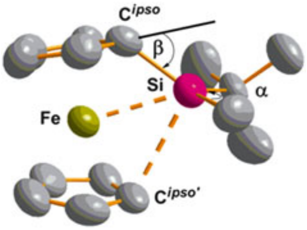
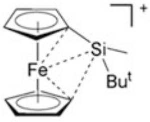
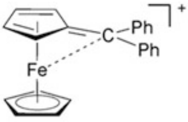


Fig. 17 (**a**) Molecular structure of ferrocenylsilylium ion, **97**, in the crystal of $\mathbf{97}_2[B_{12}Cl_{12}]$. (Ellipsoid presentation. All H-atoms are omitted for clarity, thermal ellipsoids at 50% probability level.) Important bond lengths [pm] and angles [°]: Si–Fe = 249.2; $Si–C^{ipso}$ = 182.9; $Si–C^{ipso}$ = 278.4; $\Sigma\alpha(Si) = 353.5$; $\beta = 44.8$ [42]

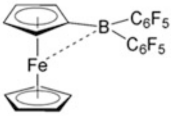
low-field ^{29}Si NMR signal at $\delta^{29}Si = 114.6$. Its molecular structure as determined by an XRD study from the *closo*-borate $[B_{12}Cl_{12}]^{2-}$ salt (Fig. 17) is markedly different from those found previously for the isoelectronic carbocation **99** and the neutral boron compound **100**. In all three compounds **97**, **99**, and **100** interaction between the iron and the electron-deficient center is displayed by a significant bending of the exocyclic group in direction to the iron atom. This bending as measured by the dip angle β is only moderate for the carbocation **99** ($\beta = 20.7°$) and the boryl ferrocene **100** ($\beta = 16.0°$), but it becomes extreme for silylium ion **97** ($\beta = 44.8°$). This extreme dip angle places the silicon atom near to both cyclopentadienyl rings of the ferrocenyl backbone and a quantum-mechanical analysis of the bonding situation suggests that the presence of two Fe–Si–C–3c2e bonds involving the iron, silicon, and both C^{ipso} carbon atoms accounts for the unconventional molecular structure of silylium ion **97**.



97



99



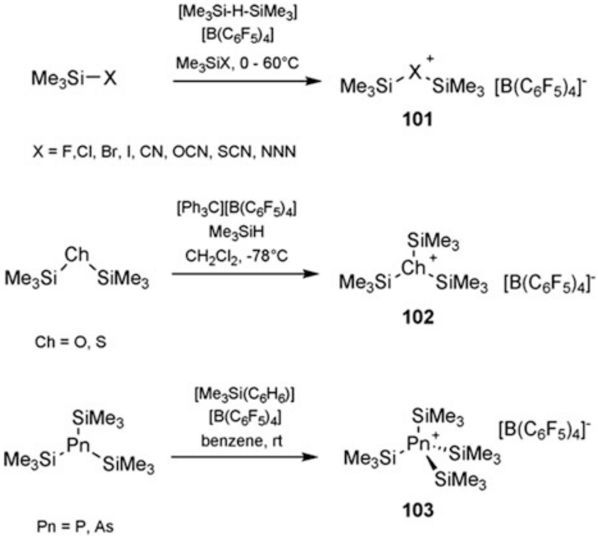
100

4 Applications of Silylium Ions and Stabilized Silylium Ions in Synthesis and Catalysis

4.1 General Aspects

More than one decade after the first reports on the synthesis and NMR spectroscopic characterization of silylium ions, the ingenious use of their enormous electrophilicity for applications in synthesis or catalysis has attracted considerable attention. The reactivity of silylium ions is dominated by their extreme Lewis acidity, which found advantageous use in organic synthesis, in polymerization reactions and is of interest in

Scheme 31 Preparation of onium ions from solvent-stabilized silylium ions [87–91]

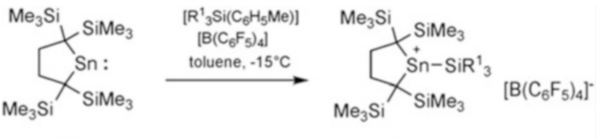


the context of frustrated Lewis pair (FLP) chemistry. A second important factor for the understanding of the chemistry of silylium ions is the high affinity of silicon to fluorine and oxygen. The combination of both factors provides opportunities for catalytic bond activation processes and for the preparation of extremely potent Brønsted acids and alkylating reagents. By their very nature, silylium ions and stabilized silylium ions are perfect silylating reagents which were applied in the synthesis of new cationic species. Beneficial for the synthesis of many of these new compounds proved to be the weakly coordinating reaction condition needed for the preparation of the silylium salts. This part will give a survey of some of these addition reactions of stabilized silylium ions and then it will focus on application of silylium ions in hydrosilylation reactions, C–F activation chemistry and in Lewis acid catalysis.

4.2 *Addition Reactions of Stabilized Silylium Ions*

From the high Lewis acidity of silylium ions follows that they undergo addition reactions with almost any nucleophile. This opened synthetic avenues for the synthesis of persilylated onium ions of halogens [87], pseudohalogens [88], chalcogens [89, 90], and pnictogens [91] **101–103**. For the preparation of these onium ions, the superb silylating properties of solvent- or anion-stabilized silylium ions are an essential requirement. Conventional silylating agents fail to give the desired products. Scheme 31 provides a concise survey of these synthetic achievements.

Stabilized silylium ions can be also used to transfer silyl groups to singlet carbene analogues. As outlined previously, silylation of N-heterocyclic silylenes gives access to aromatic silaimidazolium ions [27]. Likewise, the reaction of stannylene **104** with arene-stabilized silylium borates results in the formation of stable



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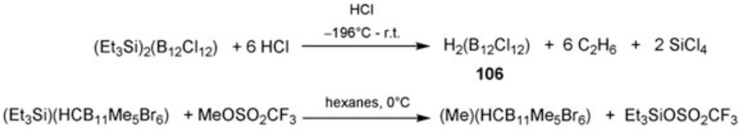
105

Scheme 32 Synthesis of stannylium borates **105**[B(C_6F_5)$_4$] [92]



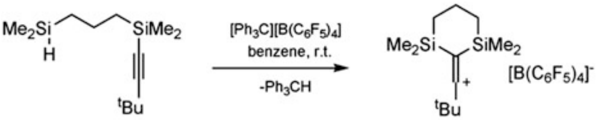
$$(Et_3Si)_2(B_{12}Cl_{12}) + 6\,HCl \xrightarrow[-196°C\text{ - r.t.}]{HCl} H_2(B_{12}Cl_{12}) + 6\,C_2H_6 + 2\,SiCl_4$$

106

$$(Et_3Si)(HCB_{11}Me_5Br_6) + MeOSO_2CF_3 \xrightarrow{\text{hexanes, }0°C} (Me)(HCB_{11}Me_5Br_6) + Et_3SiOSO_2CF_3$$

107

Scheme 33 Preparation of *closo*-borate Brønsted superacid, **106**, and a *closo*-carborane-based methylating reagent, **107** [94, 95]



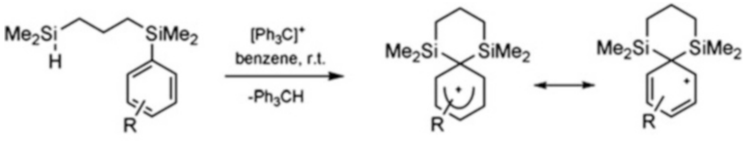
108

Scheme 34 Synthesis of the stable β-silyl vinyl cation borate, **108**[B(C_6F_5)$_4$] [83]

stannylium borates **105**[B(C_6F_5)$_4$] (Scheme 32) [92]. These results indicate that in general the silylation of heavy carbene analogues using silylium ions or stabilized silylium ions is a promising route to the corresponding cationic species [93].

The high affinity of silicon to halogens and oxygen was exploited for the synthesis of series of extremely strong Brønsted acids, e.g., **106** [10, 32, 44, 94], and methylating reagents, e.g., **107** [10, 95], from *closo*-carborate- or -borate-stabilized silylium ions (Scheme 33). The driving force for the formation of these strong electrophiles is the creation of strong silicon–halogen or silicon–oxygen bonds at the expense of weaker hydrogen–halogen or carbon–oxygen bonds. These extremely strong Brønsted acids are able to protonate benzene and fullerene C_{60}. Likewise the methylcarborate **107** was used to generate tertiary carbenium ions such as *tert*.-butyl cation or *tert*.-pentyl cation in an environment that allows the isolation of the carbocation *closo*-carborates at ambient conditions [10].

The addition of silylium ions to CC unsaturated compounds results in the formation of carbocations that are stabilized due their β-silyl substitution. As already mentioned in Sect. 3.3.5 β-silyl-substituted vinyl cations **93** were prepared by intramolecular addition of an incipient silylium ion to a C≡C triple bond. A prominent example is *tert*.-butyl-substituted vinyl cation **108** that could be isolated in the form of its [B(C_6F_5)$_4$]$^-$ salt and was investigated by XRD (Scheme 34). The molecular structures of **108** and related vinyl cations showed the linear coordination at the positively charged carbon atom and indicated the structural consequences of β-silyl hyperconjugation [83, 84]. While



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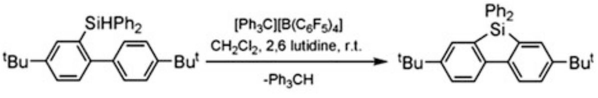
Scheme 35 Synthesis of the disilylarenium ion, **71** (anion omitted) [33]

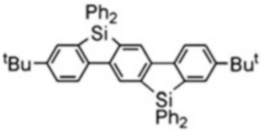


109

Scheme 36 Synthesis of dibenzosilafluorene **109** by a sila-Friedel–Crafts reaction [100]

several examples for such intramolecular additions of silylium ions to CC multiple bonds are reported [82–86, 96] only two well-documented examples for an intermolecular addition of silylium ions are reported [97–99].

Bissilylated arenium ions, **71**, synthesized by intramolecular addition of incipient silylium ions to arenes are clearly related to this chemistry (Scheme 35) [33]. These compounds were described in the previous chapter as examples for intramolecular arene-stabilized silylium ions; however, their description as silyl-substituted dienyl cations is equally justified which underscores the double-edged nature of the terminology “stabilized silylium ions.” A very interesting synthetic application of the intramolecular addition of silylium ions to arenes is the development of a sila-Friedel–Crafts reaction protocol for the synthesis of dibenzosilole derivatives, e.g., **109** (Scheme 36). Using this method, the synthesis of ladder-type silafluorenes **110** and trisilasumanene **111** was achieved [100].



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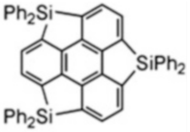

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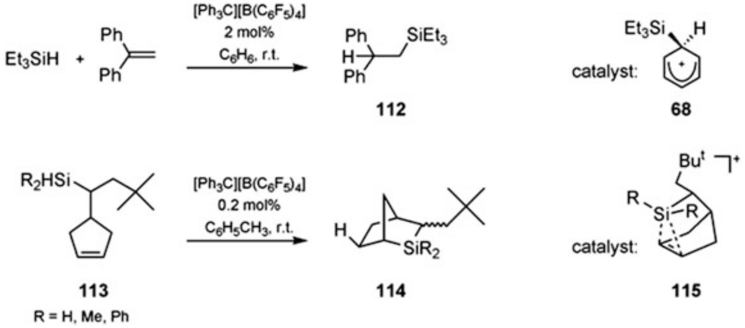
4.3 *Hydrosilylation Reactions*

The addition of silylium ions to CC multiple bonds provides a synthetic route to β-silyl-substituted carbocations (see Sect. 4.2). On the other hand carbocations are good hydride acceptors and are used for the generation of silylium ions from silanes in the BCS reaction (see Sect. 2.2). On the basis of these considerations a catalytic hydrosilylation reaction seems possible, provided a favorable matching of the bond

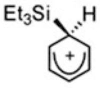


Scheme 37 Hydrosilylation reactions of alkenes catalyzed by stabilized silylium ions [98, 101]

energies of the participating silanes, alkenes and silyl-substituted alkanes can be achieved. Surprisingly, only two early examples for this transition metal-free catalytic hydrosilylation reaction are reported [97, 98, 101]. The hydrosilylation reaction of 1,1-diphenylethene to give silane **112** is catalyzed by triethylsilyl-benzenium which is formed from triethylsilane and trityl cation during the reaction (Scheme 37) [98]. In the case of the intramolecular hydrosilylation reaction of cyclopentenes **113** to give the silanorbornane systems **114**, silanorbornyl cations **115** are suggested as catalytic active species (Scheme 37) [101].

Silylium-catalyzed hydrosilylation of carbonyl compounds gives deoxygenated compounds [102, 103]. For example, ketones are reduced to the corresponding hydrocarbons by the reaction with 2 equivalents of triethylsilane using triethylsilyl toluenium borate, **65**[B(C_6F_5)$_4$], as catalyst (Scheme 38) [102]. The catalytic reaction can be efficiently stopped at the stage of the silylated alcohol when more hydridic silanes, such as **98**, are used. The ferrocenyl-substituted silylium ion **97** is suggested as active species in this transformation [104].

Carbon dioxide can be efficiently reduced by silanes in chlorobenzene when it is activated by stoichiometric amounts of trityl cation [37]. Silylated chloronium ions **116**, **117**, which are formed in situ by reaction of the applied silanes with trityl cation, are thought to activate CO_2 by *O*-silylation and prepare it for hydrosilylation by a second equivalent of the silanes to yield the formic acid derivatives **118a**, **b** (Scheme 39a, b). While the reaction stops with tri-*iso*-propyl silane at this stage with triethylsilane further hydrosilylation occurs to give the oxonium ion **119** (Scheme 39a) Thus, depending on the bulkiness of the silanes, either formic acid or methanol is obtained after hydrolysis. When benzene is used as solvent, triethylsilylbenzenium, **68**, is formed in the first step. After activation of CO_2 by *O*-silylation the benzylic carbocation **120** is obtained (Scheme 39c). Subsequent hydrolysis affords benzoic acid [37].



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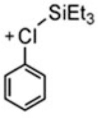

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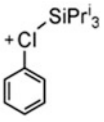

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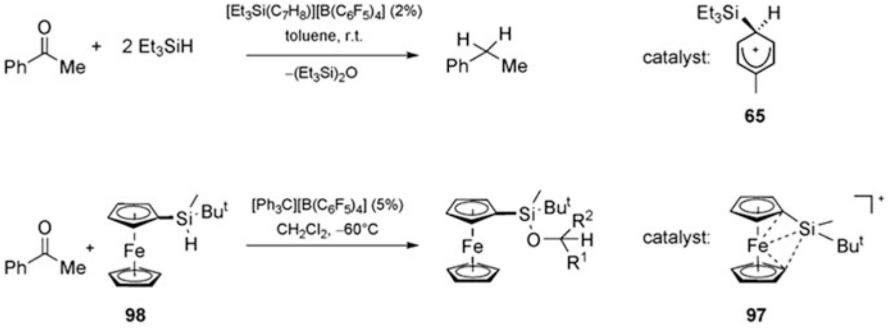
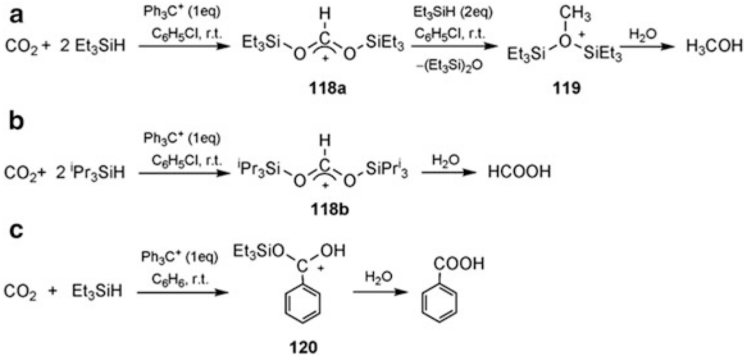


Scheme 38 Hydrosilylation reactions of carbonyl compounds catalyzed by stabilized silylium ions [102, 104]

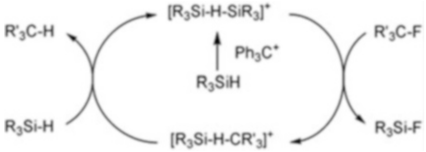


Scheme 39 Stoichiometric reduction of CO_2 by silanes mediated by solvent-stabilized silylium ions [37]

4.4 C–F Bond Activation Chemistry

The combination of high Lewis acidity and the ability to form strong Si–F bonds makes silylium ions ideally suited for ionic C–F bond activation. When silanes are applied as reducing agents for the generated carbocations, an effective silylium-catalyzed hydrodefluorination (HDF) reaction is achieved. Benzyltrifluorides, alkyl fluorides, and polyfluorinated alkanes undergo the catalytic HDF reaction with silylium ions, but perfluorinated arenes, such as hexafluorobenzenes, are inert. For several cases turn over numbers (TON) up to 2,700 are reported. The central concept of the catalytic replacement of C–F bonds by C–H bonds is outlined in Scheme 40 [105–109].

The overall Si–H/F–C metathesis is thermodynamically strongly favored as C–H bonds are stronger than Si–H bonds and Si–F bonds stronger than C–F bonds as shown by the following bond dissociation energies (BDE): BDE(H_3C-H) = 439

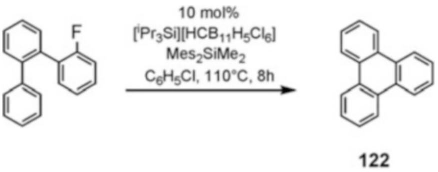


Scheme 40 Hydrodefluorination reaction of alkyl fluorides catalyzed by trialkylsilylium ions in silanes (anion omitted)

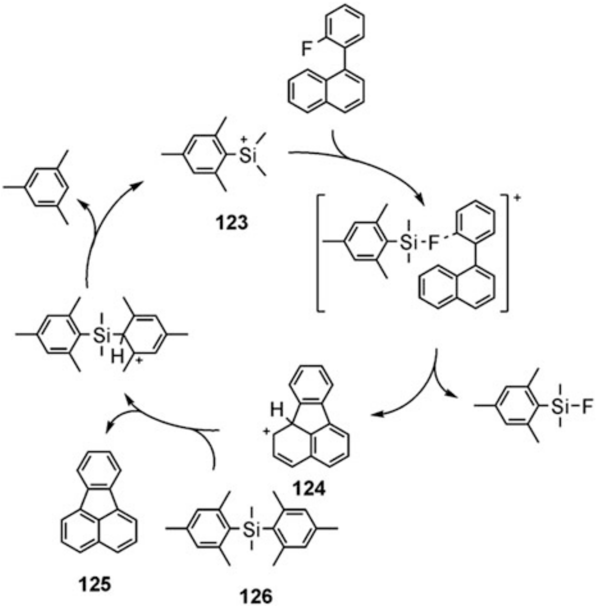
kJ mol^{-1}; BDE(H_3Si-H) = 396 kJ mol^{-1}; BDE(Me_3Si-F) = 662 kJ mol^{-1}; BDE (H_3C-F) = 481 kJ mol^{-1}). The catalytic C–F bond activation by silylium ions is restricted to aliphatic C–F bonds; compounds with C(sp^2)–F bond are inert. Therefore, this method is complementary to most transition metal mediated C–F activation reactions that show the opposite chemoselectivity. The reaction is usually performed in excess silane; the most commonly used silane is triethylsilane. Trityl cation paired with a weakly coordinating anion is then used as precatalyst to generate the cationic catalyst. The catalytic active species in silanes are silane-stabilized silylium ions such as $[Et_3Si\text{-H-}SiEt_3]^+$, **121** [38]. Alternatively, the bissilylhydronium ions, **81**, can be directly applied as catalyst [48]. The stability of the catalysts and therefore the TON of the catalysis strongly depend on the applied weakly coordinating anion. The use of the perfluorinated tetraarylborate anion $[B(C_6F_5)_4]^-$ restricts the TON to values below 100, due to decomposition of the anion during the reaction [48, 49]. The more robust halogenated carborates, e.g., $[HCB_{11}H_5Cl_6]^-$, enable maximum TON up to 2,700 [107]. In aromatic hydrocarbons as solvents the HDF reaction of alkyl fluorides using silylium ions as catalyst is accompanied by significant Friedel–Crafts alkylation of the solvent [107, 110]. Although this reaction is not selective it is an example for a C(sp^3)–F activation combined with the desirable formation of a new C(sp^3)–C(sp^2) bond. An attempt to circumvent the selectivity issue in this reaction through the use of aryl silanes as coupling partners in *ipso*-directed substitutions had only limited success [110].

The high potential of silylium ions for C–F bond activation was recently demonstrated by the Siegel group through the discovery that $Et_3Si[HCB_{11}Cl_{11}]$ is able to activate even fluorobenzene at elevated temperatures [111]. Product studies and reaction kinetics suggested intermediates of phenyl cationic character. Based on these results a synthetic protocol for a catalytic C(aryl)–C(aryl) coupling of fluoroarenes was developed, which allows to prepare a series of polycyclic arenes in high yields, for example, triphenylene, **122**, was synthesized in 97% yield (Scheme 41) [112]. The central step of this catalysis is the activation of the C (sp^2)–F bond by the silylium ion **123**, followed by an intramolecular electrophilic aromatic substitution. The proton released in the rearomatization step of cation **124** to give the neutral fluoranthene **125** is scavenged by the electron-rich silane **126** which undergoes a protodesilylation and regenerates the silylium ion catalyst **123** (Scheme 42) [112].

Scheme 41 Preparation of triphenylene **122** by intramolecular Friedel–Crafts arylation [112]

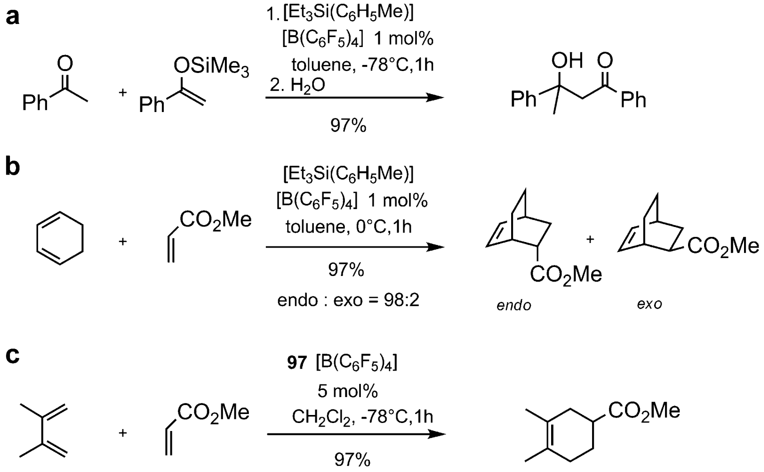


Scheme 42 Suggested catalytic cycle for the intramolecular Friedel–Crafts arylation, shown here for the synthesis of fluoranthene **125** (anion omitted) [112]

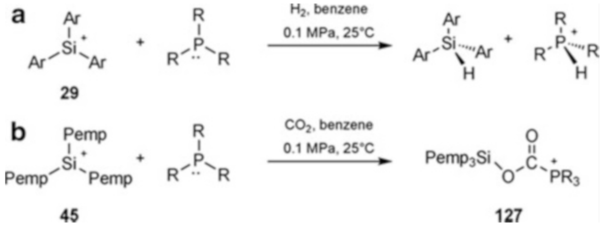


4.5 Lewis Acid Catalysis and FLP Chemistry

Various silyl Lewis acids such as silyl trifluormethanesulfonate, R_3SiOTf, or silyl trifluoromethanesulfonimides, R_3SiNTf_2, have been employed as catalysts for synthetic transformations [113]. The activity of these tetracoordinated trialkylsilyl Lewis acids is clearly defined by the Lewis basicity of the fourth substituent. The logical extrapolation is to use silylium-based Lewis acids. Indeed, triethylsilyl toluenium borate, $[Et_3Si(C_6H_5Me)][B(C_6F_4)_4]$, shows excellent activity as catalyst in C–C bond-forming reactions such as Mukaiyama aldol condensations and Diels–Alder cyclizations (see Scheme 43a, b) [114]. These reactions can be performed with low loading of the silylium catalyst at room temperature or even below. The silylium-based catalyst clearly outperforms conventional silyl Lewis acids; however, a pronounced solvent effect on the catalyst's activity was observed. The catalytic activity is efficiently quenched by nucleophilic solvents such as acetonitrile or diethyl ether. An even higher activity in Diels–Alder cyclization reactions is shown by the internally stabilized ferrocenylsilylium ion **97** [41, 115]. Diels–Alder reactions between unreactive dienes such as 2,3-dimethylbuta-1,3-diene and methacrylate are catalyzed by silylium ion **97**;



Scheme 43 Examples for Mukaiyama aldol condensations (**a**) and Diels–Alder cyclizations (**b**, **c**) catalyzed by silylium borates [41, 114, 115]



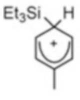
Scheme 44 (**a**) Dihydrogen activation by silylium/phosphane Lewis pairs (Ar = Mes, Duryl, Pemp; R = *o*-tolyl, Mes, Pemp, *tert*-butyl, *cyclo*-hexyl) (**b**) CO_2 fixation by silylium/phosphane Lewis pairs (R = *tert*-butyl, *cyclo*-hexyl) [116]

full conversion of the dienophile at temperatures as low as −78°C is achieved (Scheme 43c).

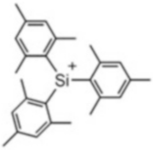
The high Lewis acidity of silylium ions is clearly of interest in respect to bond activation chemistry using the concept of frustrated Lewis pairs. Triarylsilylium ions, **29**, with their unrivalled Lewis acidity in combination with high steric protection are here of particular interest. Silylium ion/phosphane Lewis pairs, in which triaryl silylium ions, **29**, are partnered with bulky phosphanes, are able to cleave dihydrogen heterolytically to give the corresponding silanes and phosphonium ions at ambient temperatures and pressure (Scheme 44a) [21, 116]. The mixture of silylium ion, **45**, with bulky trialkylphosphanes in benzene reacts with carbon dioxide to give acylphosphonium borates **127**$[B(C_6F_5)_4]$, which can be isolated in good yields and are stable at ambient conditions (Scheme 44b). In solution, decomposition of phosphonium ions **127** occurs at higher temperatures without regeneration of CO_2.

5 Conclusion and Perspectives

Two decades after the first characterization of a stabilized silylium ion, the triethylsilyl toluenium, **65**, and ten years after the unequivocal structural identification of trimesitylsilylium, **28**, silylium ions have developed from a laboratory curiosity to a well-recognized and valued piece of the tool box of organic synthesis and catalysis. In the previous chapters, it was shown that their unmatched silylating potential was beneficially used for the design of novel molecular structures and for creating substances with outstanding functionalities. It was also demonstrated that the combination of the extreme Lewis acidity of silylium ions with the high affinity of silicon to fluorine and oxygen has paved the way to new catalytic processes for C–F bond activation and hydrosilylation of carbonyl compounds. These properties of silylium ions fuelled also their application in ring-opening polymerizations processes of phosphazene cyclotrimers [117], cyclosiloxanes [90], and lactones [118] and for their use as catalysts for polymerization of oxygen containing monomers such as methylmetacrylate [119]. Clearly, with the advent and success of the FLP chemistry, the high Lewis acidity of silylium ions and their potential for small-molecule activation came into focus. These development directions for silyl cation chemistry are clearly visible and more interesting chemistry will arise from these investigations.



65



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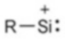
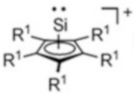
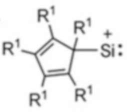


128



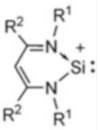
129

R^1 = Me, ${}^iPr$



130

R^1 = Me, ${}^iPr$

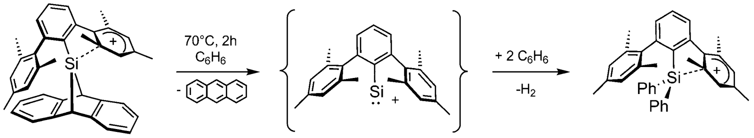


131

R^1 = Dipp

R^2 = Me

Quite recently a previously completely neglected part of silyl cation chemistry came into focus: the chemistry of cationic silicon in the oxidation state +II. Peter Gaspar pointed out that the combination of the high Lewis acidity of silylium ions with the amphiphilic character of non-stabilized silylenes as accomplished in the shape of silyliumylidenes $RSi:^+$, **128**, creates silicon cations with an extraordinary high reactivity and synthetic potential [120]. These species having only four valence electrons could create up to three bonds in one single reaction step. Furthermore, their specific electronic situation, one high-lying HOMO in combination with two low-lying degenerate unoccupied molecular orbitals, suggests a reactivity for silyliumylidenes $R\text{-}Si:^+$, **128**, that could parallel those of some early transition metal complexes. In addition, the specific nature of their frontier orbitals provides three triggers for the design of silyliumylidenes and for control of their reactivity. It is clear, however, that the preparation of silyliumylidenes or their



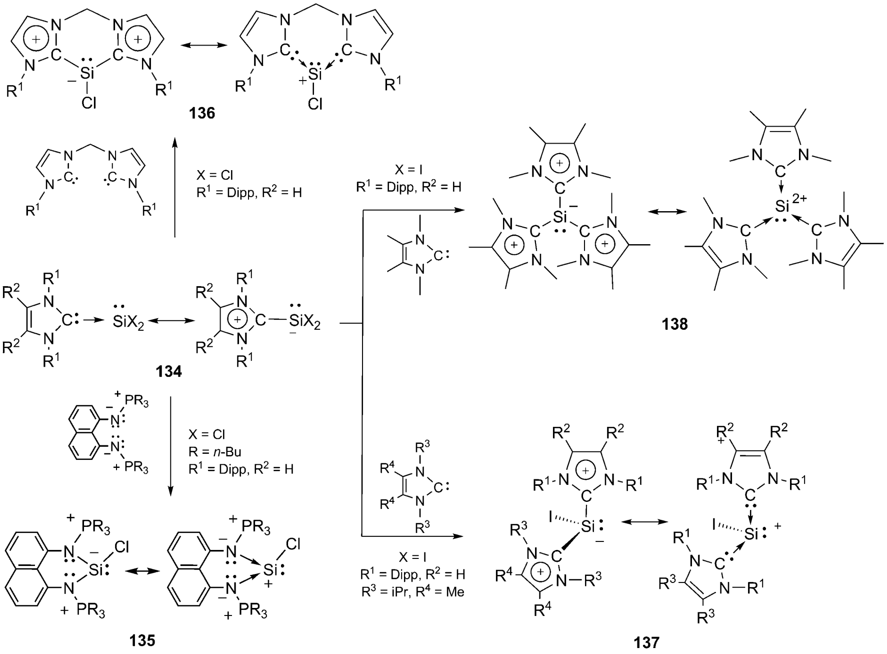
133 **132** **72**

Scheme 45 Attempts to synthesize terphenyl-substituted silyliumylidene **132** (anions are omitted) [76]

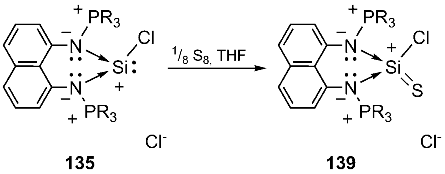
stabilized variants is a challenge for both, for the creativity of silicon chemists and for the synthetic methodology.

Several groups met this challenge: Already 2004 Jutzi and coworkers reported the synthesis of the *nido*-type silicon cluster cations **129** and demonstrated that, from a synthetic point of view, cations **129** can be regarded as resting states for cyclopentadienyl-substituted silyliumylidenes **130** [121]. Later, Driess and colleagues reported on the preparation of silyliumylidene **131**, stabilized by donor acceptor interaction with the ligand and reported on its unique chemistry [122]. The strongly stabilizing substituents that are needed to placate the electron demand of the silicon atom in cations **129** and **131**, however, significantly influence the chemical behavior of the silicon(II) cation and mask their reactivity to a certain extent. On the other hand, silyliumylidenes with more innocent substituents such as the terphenyl group are too reactive to be isolated. For example, the generation of terphenyl-substituted silyliumylidene **132** by α-elimination from 7-silanorbornadienyl cation **133** results in the isolation of diphenyl-substituted silylium ion **72** (Scheme 45). The reaction of cation **132** with the solvent benzene to give silylium ion **72** highlights its exceptional reactivity [76].

The ingenious use of N-heterocyclic carbenes (NHC) to stabilize low-coordinated silicon compounds as shown by the landmark contributions of the Robinson [123], Roesky [55], and Filippou [54] groups triggered also the chemistry of silicon(II) cations. Using NHC-stabilized silylene halides **134** and strongly donating supporter ligands several groups reported the synthesis of stabilized silyliumylidenes **135**–**137** and even the preparation of the NHC-stabilized Si(II) cation **138** was reported (Scheme 46)[124–126]. Clearly, in all these cations, the silicon center attains noble gas configuration and they can be written in several extreme Lewis representations in which the formal charge at silicon changes from +I to –I. Indeed, as far as reactivity is concerned, cations such as the stabilized silyliumylidene **136** behave as expected from a silicon(II) anion or from the isoelectronic phosphane (Scheme 47) [124]. Nevertheless these compounds are important steps forward into the direction of cationic silicon(II) chemistry and already at this stage it is fair to say that with these achievements completely new facets of silicon chemistry should emerge.



Scheme 46 Preparation silicon monocations **135–137** and dication **138** (anions are omitted) [124–126]



Scheme 47 Oxidation of silicon(II) monocation **135** to give chlorosilathionium cation **139** [124]

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Oligosilanes

Christoph Marschner

Abstract The chemistry of oligosilanes has made numerous advances since the beginning of the new millennium. While during the time from the 1960s to the 1990s research has concentrated on comparably simple systems, more recent studies have introduced much complexity into oligosilane chemistry. In the course of studies on compounds with one or several multiple bonds between silicon atoms a rich precursor and derivatization chemistry of these compounds was developed. In addition numerous functionalized oligosilanes have been prepared so that today a fairly elaborate repertoire for the synthesis of these compounds exists. Another factor which has strongly contributed to the development of oligosilane chemistry is that oligosilanes are increasingly being applied as reagents as well as activating, protecting, and stereodirecting groups in organic synthesis.

Keywords Cyclosilanes · Dendrimers · Electron delocalization · Oligosilanes · Transition metals

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Abbreviations

Ac	Acetyl
Ar	Aryl
Bu	Butyl
cat	Catalyst
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
DIBALH	Diisobutylaluminum hydride
DME	1,2-Dimethoxyethane
dmpe	Bis(dimethylphosphino)ethane
E	Electrophile
equiv	Equivalent(s)
Et	Ethyl
Fp	$CpFe(CO)_2$
i-Bu	Isobutyl
i-Pr	Isopropyl
LDA	Lithium diisopropylamide
LiNp	Lithium napthalenide
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl (not methanesulfonyl)
NBS	*N*-bromosuccinimide

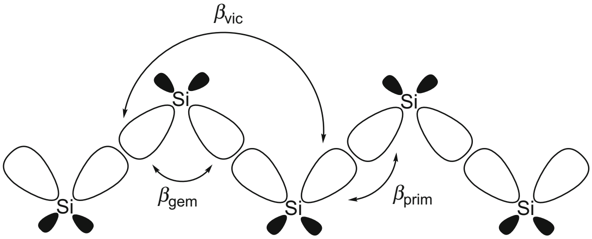
Nu	Nucleophile
Ph	Phenyl
Pr	Propyl
Pz	Pyrazolyl
s-Bu	*Sec*-butyl
t-Bu	*Tert*-butyl
Tf	Trifluoromethanesulfonyl (triflyl)
THF	Tetrahydrofuran
TMEDA	*N,N,N′,N′*-tetramethyl- 1,2-ethylenediamine
TMS	Trimethylsilyl
Tol	4-Methylphenyl
XRD	X-ray diffraction

1 Introduction

Oligosilanes are a class of small molecules containing Si–Si bonds. They are the higher congeners of alkanes and can thus be either functionalized or non-functionalized. However, as the Si–H bond is quite reactive, the expression non-functionalized usually does not refer to polyhydrogenated oligosilanes but rather to polyalkylated or –arylated ones. In terms of reactivity polyalkylated or –arylated oligosilanes can therefore be compared to alkanes, whereas polyhydrogenated oligosilanes are extremly reactive compounds. The current account attempts to give an overview about polyalkylated and –arylated oligosilanes in addition to functionalized examples of this class of compounds. While it is the main intention of the review to cover work reported after the year 2000 several seminal achievements are mentioned in the context. The field has been reviewed several times before [1–8]. Oligosilanes lacking organic substituents were reviewed most recently [9] and are therefore not covered extensively here.

The first examples of oligosilanes date back to the pioneering work of Kipping who reacted dichlorodiphenylsilane with sodium to obtain three different compounds of the molecular composition $(Ph_2Si)_n$ which he named products A, B, and C [10, 11]. It took almost 40 years until in 1963 Gilman and coworkers eventually unequivocally identified these products as the cyclosilanes $(Ph_2Si)_4$ (A), $(Ph_2Si)_5$ (B), and $(Ph_2Si)_6$ (C) [12]. In 1947 a review counted the number of known organopolysilanes (i.e., compounds containing Si–Si bond) as 16, of which six were disilanes with hexamethyldisilane being the only methylated compound [13]. A more systematic investigation of the field started with the first report of a permethylated cyclosilane [14] and in particular with the discovery of unusual UV spectroscopic properties which suggested that Si–Si bonds of polysilanes act as chromophores [15, 16]. Much of the work on oligosilanes in the 1960s, 1970s, and 1980s is associated with the research groups of Gilman, Kumada, West, and Hengge.

Fig. 1 Orbitals and resonance integrals included in the Ladder C model



2 Physical and Chemical Properties

Originally the main interest concerning preparation and reactivity of compounds with Si–Si bonds was associated with their electronic properties. In recent years, however, oligo- and polysilanes have also acquired a reputation as interesting reagents in organic synthesis and as bulky and electron-donating ligands for transition metal complexes and unsaturated main-group compounds.

2.1 *σ-Bond Electron Delocalization*

σ-Bond electron delocalization is a phenomenon that is strongly associated with polysilanes. Alkanes are of course isoelectronic to polysilanes but σ-bond electron delocalization is not well studied for them because of unsuitably high orbital energies. Nevertheless, the theoretical foundations for the electronic description of σ-bond electron delocalization were worked out for alkanes [17]. Although often compared to the more familiar π-bond electron delocalization, it needs to be taken into account that the latter requires only one orbital to be considered whereas all four valence orbitals are relevant for σ-bond electron delocalization. In order to obtain an intuitive and qualitatively correct description the Ladder C model [18] is frequently applied. This model uses simplified Hückel theory and considers essentially three types of orbital interaction. These are the primary σ-interaction (β_{prim}) between orbitals on neighboring atoms pointing at each other, the geminal interaction of orbitals on the same atoms (β_{gem}) and the vicinal interaction (β_{vic}) between orbitals on neighboring atoms pointing away from each other (Fig. 1). It is this vicinal interaction which is responsible for the conformational dependence of the delocalization efficiency. In correlation with actual measurements (*vide infra*) the model predicts that conjugation is more effective for *transoid*-conformations of chains than for *cisoid*-turns.

In an excellent account by Michl und Bande [19] it was shown that in particular for slightly longer oligosilane chains, the intuitive semi-empirical Ladder C model is in excellent agreement in its predictions with more complicated models.

2.2 Synthetically Useful Oligosilanes

It is an exciting development in recent years that oligosilanes have secured themselves a spot in the toolbox of the organic chemist. This is of course not a very general statement but rather specific for a few compounds that have gained reagent character. The most important one is certainly $(Me_3Si)_3SiH$, which has been popularized by Chatgilialoglu and coworkers as an environmentally benign alternative to Bu_3SnH. This chemistry has been reviewed several times [20–26] and shall thus not be treated here further. Another recent development concerns the use of the $(Me_3Si)_3Si$ moiety as protecting and/or directing group [27]. The advantages of this group include a substantial steric bulk, which can lead to decent selectivities in diastereoselective aldol and cascade reactions, and the possibility of removal using irradiation with UV light [28, 29]. The use of oligosilanes in organic synthesis has been reviewed recently [6]. Developments to exploit unsaturated organosilicon compounds such as silenes, disilenes, silylenes, and silyl cations are emerging currently [30, 31]. Frequently oligosilanes serve as reagents to generate these species.

Oligosilanyl groups and in particular the tris(trimethylsilyl)silyl fragment have also earned a reputation as a strong electron-donating yet sterically demanding groups for the attachment to main group elements with unusual electronic situations, transition metals, and clusters.

3 Synthetic Methods

Compared to the rich synthetic repertoire of organic chemistry to form C–C bonds, only a very limited number of ways to form Si–Si bonds exist. However, recent years have shown a transition from brute force methods, often suffering from harsh conditions, poor yields, and lacking selectivity to a synthetic methodology which is quite selective and allows the straightforward construction of molecules of astonishing structural complexity.

Still the most often used reaction to form Si–Si bonds is the Wurtz-type coupling of silyl halides in the presence of alkali metals. This method is particularly useful for the synthesis of disilanes and cyclosilanes, where it usually proceeds with good selectivity and moderate to high yields. It also represents a convenient method for the preparation of some important oligosilanes, most notably $Si(SiMe_3)_4$. Besides the use of harsh reaction conditions the most serious disadvantage of the Wurtz-type coupling is its inherent confinement to give only symmetric molecules. The logical solution of this dilemma is to separate the two silyl units to be connected in nucleophilic and electrophilic ones. Similar to organic chemistry electrophilic silanes are easily available as silyl halides or triflates, whereas silyl anions cannot be seen in such a close analogy. In organic synthesis the most convenient way to prepare carbanions is deprotonation of CH acidic compounds. As silicon is more

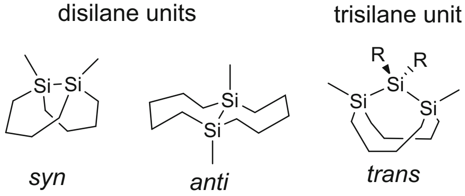


Fig. 2 Di-and trisilane units used as building blocks for oligosilanes with defined conformations

electropositive than hydrogen this cannot be done with the same ease as in organic chemistry. Therefore formation of silyl anions generally involves other synthetic procedures such as reductive cleavage of Si–Si bonds. Examples and methods for this can be found in several reviews [32–37] and a separate chapter of this volume. In any case the salt elimination of silyl anions with suitable electrophiles is currently the most versatile method to prepare more complex oligosilanes.

A fair number of other synthetically useful ways to form Si–Si bonds exists. An incomplete list comprises electrochemical methods, dehydrocoupling of hydrosilanes, cycloaddition reactions, rearrangement reactions, silylene insertion, and radical recombination. Most of these will be shown or described in the following sections outlining the formation and reactivity of different types of oligosilanes.

Methods to attach oligosilanyl unity to other organic or inorganic molecular entities are mostly confined to reactions of silyl anions or halides depending on the nucleophilic or electrophilic nature of the other fragment. Especially for addition reactions to unsaturated molecules also silyl radicals or silyl hydrides are common reagents.

4 Oligomeric Chains

From a conceptual point of view much of the early work on polysilanes was done on systems with a structural relationship to alkanes. The discovery of the UV absorption behavior of polysilanes was achieved mainly with permethylated chains and rings. While it is not a recognized synthetic challenge to prepare linear alkanes because they are abundant in natural oil, synthetic access to linear alkylated oligosilanes is still not trivial. These compounds can be prepared utilizing Wurtz-type coupling reaction conditions but not in a selective way. At a time when theoretical concepts of the relationship between conformation and UV absorption behavior of polysilanes were already well understood a bona-fide confirmation of these concepts was only achieved in the landmark studies by Tsuji and Tamao, who prepared di- and trisilane units with conformations frozen in bicyclic alkylene backbones (Fig. 2) [38–43]. Using these as building blocks larger oligosilanes with defined conformational properties could be obtained. The UV absorption properties of these molecules were in exact accordance with predictions. It was shown that a *cisoid* turn is associated with a rupture of conjugation in an oligosilane chain [39].

Besides the use of rigid substituent backbones, other ways have been recognized to express specific conformations of polysilanes. Marschner and coworkers have shown that bulky tris(trimethylsilyl)silyl groups connected with permethylated silanylene units force the bridging units to acquire a *transoid* (conjugating) conformation [44]. When several of these units were connected less effective conjugation between the units was observed as the connection caused a *cisoid* turn [45]. Attempts to embed oligosilane chains into bicyclic oligosilanes did not lead to improved conjugation behavior [46, 47]. Other ways to control conformational properties comprised inclusion into cyclodextrines [48] and hypercoordination of silanes [49].

Although the electronic resemblance between conjugated C–C π-bonds had been noticed a while ago it was only recently that single-molecule measurements of simple oligosilane chains were carried out which showed that the molecular conductance decreases exponentially with increasing chain length with a decay constant $\beta = 0.27 \pm 0.01$ Å^{-1}, comparable to that of conjugated π-systems [50].

5 Dendrimers

One of the reasons that polysilanes were not considered seriously as photoresists or other optoelectronic materials is that the Si–Si bond is quite sensitive. Cleavage of Si–Si bonds can alter the photophysical properties dramatically. One way to overcome this apparent problem is the incorporation of polysilanes into a dendritic architecture. Dendrimeric materials have two advantageous properties in this respect. On the one hand, the dendritic structure provides kinetic protection in a way that the core parts of the molecules cannot be easily approached by a cleaving agent. On the other hand, dendrimeric materials possess a high degree of redundancy so that cleavage of a single bond does not significantly alter the properties of the material. The first ones to implement the principle of dendrimeric architecture to oligosilane chemistry were the groups of Lambert [51–57], Sekiguchi [36, 58–60], and others [61].

More recently dendrimeric oligosilanes were mainly studied by Krempner and coworkers [62–69]. This work is covered in a recent review which besides the description of this particular class of compounds provided a very insightful analysis of the ^{29}Si NMR spectroscopic chemical shift behavior of branched oligosilanes [69].

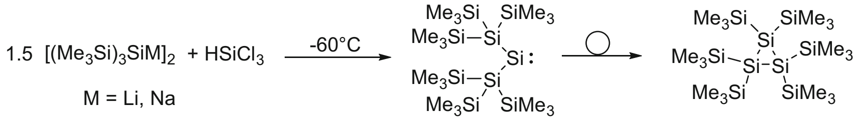
6 Cyclosilanes

Cyclosilanes have always played a prominent role in the area of oligosilanes. Several reviews document the progress in this field [70, 71]. With the recognition of the fact that σ-bond electrons in polysilanes can be delocalized in a similar way to conjugated π-systems, the question emerged whether cyclosilanes would exhibit properties similar to aromatic compounds. Several peculiar similarities between cyclosilanes and aromatic compounds were found. Oxidized or reduced cyclosilanes form radical cations or anions, respectively. They even can form charge transfer complexes with tetracyanoethylene or chloranil [72]. The UV spectroscopic properties of cyclosilanes are somewhat different from acyclic oligosilanes in a way that the smaller alkylated rings [$(R_2Si)_n$, $n = 3–7$] were found to exhibit hypsochromic shifts of the lowest energy bands with increasing ring size. With further increasing the ring size the absorption behavior starts to resemble that of linear compounds [72]. Utilizing Wurtz-type coupling methods under kinetic conditions West and coworkers have prepared, isolated, and studied homocyclic alkylated silanes with ring sized ranging from 5 to 35 [73, 74].

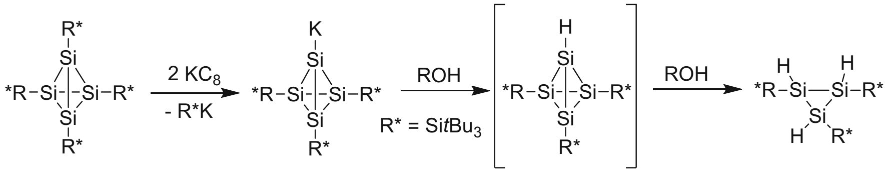
In recent years the interest in cyclosilane chemistry has somewhat shifted to more complex structural architectures and functionalized compounds.

6.1 Cyclotrisilanes

First examples of stable cyclotrisilanes were reported in the 1970s. Since then the field has been reviewed a couple of times [71, 75, 76]. In the Wurtz-type coupling approach the ring size of formed cyclosilanes is governed by the steric properties of the substituents. Cyclotrisilanes are thus obtained when larger groups such as Mes or *t*-Bu are used. The first reported cyclotrisilane was $[(2,6\text{-}Me_2C_6H_3)_2Si]_3$ generated by reaction of $(2,6\text{-}Me_2C_6H_3)_2SiCl_2$ and $Li/C_{10}H_8$ [77]. In a similar way also $(t\text{-}Bu_2Si)_3$ was prepared from $t\text{-}Bu_2SiX_2$ (X = Br, I) making use of the weaker Si–Br and Si–I bonds [78]. It needs to be pointed out that if the size of the residual groups on the silyl dihalide becomes too large cyclosilane formation is suppressed in favor of disilene formation. Reductions of 2,2-dibromotrisilanes give a good indication where the borderline between cyclosilane and disilene formation lies. Reactions of $(Et_3Si)_2SiBr_2$ with Na and of $(^iPr_2MeSi)_2SiBr_2$ and $(t\text{-}BuMe_2Si)_2SiBr_2$ with $Li/C_{10}H_8$ gave $[(Et_3Si)_2Si]_3$ [79], $[(^iPr_2MeSi)_2Si]_3$ [80], and $[(t\text{-}BuMe_2Si)_2Si]_3$ [80], respectively. In contrast to this led the $Li/C_{10}H_8$ reduction of $(^iPr_3Si)_2SiBr_2$ to the respective disilene [81]. How close the relationship between disilenes and cyclotrisilanes is, was shown by Masamune's synthesis of one of the first known disilenes, utilizing the photochemical conversion of hexa(2,6-dimethylphenyl)cyclotrisilane to the respective disilene, which included the extrusion of a silylene as the key mechanistic element [77]. One particularly interesting way to generate cyclosilanes is the isomerization of disilenes or silylenes. In an attempt to synthesize bis[tris(trimethylsilyl)silyl]silylene Klinkhammer obtained hexakis(trimethylsilyl)cyclotrisilane (Scheme 1) [82, 83]. The mechanism responsible for this rearrangement likely involves two 1,2-silyl shifts to a disilene and an isomeric silylene which inserts into an Si–Si bond. In a related reaction Hassler and coworkers obtained *E*-1-methyl-2,3,3-tris[methylbis(trimethylsilyl)silyl]-1,2-bis(trimethylsilyl)cyclotrisilane [84].



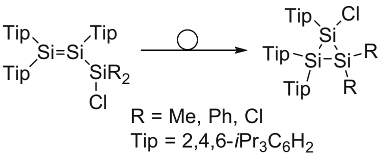
Scheme 1 Cyclotrisilane formation via a disilylsilylene intermediate and Si–Si bond insertion



Scheme 2 Silatetrahedrane anion formation, alcoholysis, and rearrangement to a cyclotrisilane

Studies by Scheschkewitz and coworkers showed that this chemistry even works with functionalized disilenes. In the reported cases the final step is likely an insertion into an Si–Cl bond (1) [85, 86].

Equation 1. Cyclotrisilane formation via a disilylsilylene intermediate and Si–Cl bond insertion.



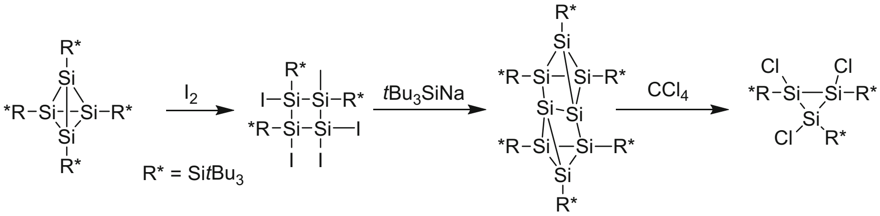
In recent years cyclotrisilane chemistry has focused strongly on functionalized compounds which can serve as starting materials for more reactive derivatives such as cyclotrisilenes and others.

In the course of the quest to obtain disilynes [87] Wiberg and coworkers prepared numerous bulky trihalosilanes $RSiX_3$ and halogenated disilenes $R(X)Si = Si(X)R$ which upon reduction were expected to give disilynes. In the course of these reactions on several occasions cyclotrisilanes were obtained [88, 89].

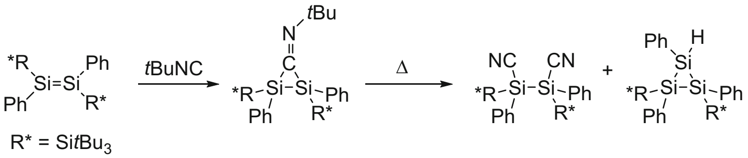
In the reaction of t-$Bu_3SiSiBr_2SiBr_2Si$$t$-$Bu_3$ with 2 t-Bu_3SiNa Wiberg and coworkers formed the first example of a silatetrahedrane (t-$Bu_3SiSi)_4$ [93]. Reaction of the latter with KC_8 gave a metalated derivative, which upon alcoholysis gave a cyclotrisilane (Scheme 2) [91].

Related chemistry also starting from silatetrahedrane (t-$Bu_3SiSi)_4$ gave an unusual cluster [94], which upon reaction with CCl_4 gave a trichlorinated cyclotrisilane (Scheme 3) [90].

Halogenated cyclotrisilanes were also found by Sekiguchi and coworkers, who reacted a cyclotrisilane with CCl_4 or $Br(CH_2)_2Br$ to form the respective dihalogenated cyclotrisilanes (2) [95].

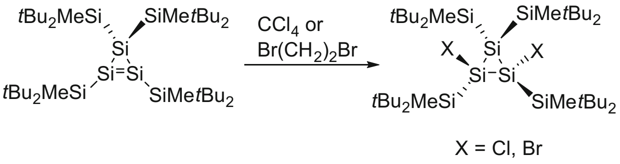


Scheme 3 Tetrasilatetrahedrane iodolysis, subsequent reductive cluster formation, and derivatization



Scheme 4 Isonitrile addition to a disilene followed by decomposition to a cyclotrisilane

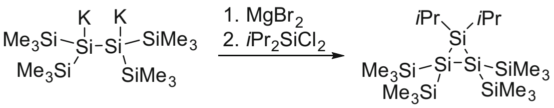
Equation 2. Halogenation of a tetrasilylcyclotrisilene.

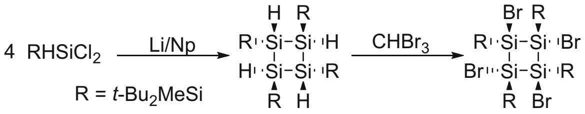


Reactivity studies of a bulky disilene with *t*-BuNC gave a disilirane, which upon heating decomposed into a cyclotrisilane and a 1,2-dicyanodisilane (Scheme 4) [92].

Also silyl anion chemistry was used to obtain cyclotrisilanes as shown by Marschner and coworkers in the reaction of a 1,2-disilanyl dianion with *i*-Pr_2SiCl_2 (3) [96].

Equation 3. Cyclotrisilane formation by reaction of 1,2-oligosilanyl dianion with *i*-Pr_2SiCl_2.



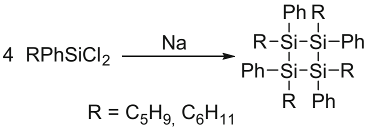


Scheme 5 Wurtz-type coupling of a tetrahydrocyclotetrasilane followed by bromination

6.2 Cyclotetrasilanes

Similar to the chemistry of cyclotrisilanes also for that of the respective four-membered rings initially mainly the Wurtz-type coupling protocol was used as the synthetic approach. For the synthesis of cycloalkyl substituted cyclotetrasilanes Roewer and coworkers were employing this strategy (4) [97].

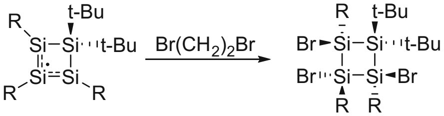
Equation 4. Wurtz-type coupling of a cyclotetrasilane.



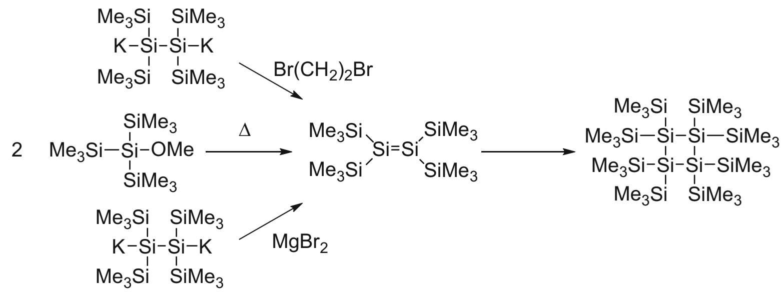
In the course of the synthetic attempts to obtain cyclosilanes with some degree of unsaturation, functionalized precursor compounds were prepared utilizing the Wurtz protocol. With bulky R groups the method can even be used to obtain four-membered rings with hydrogen substituents (Scheme 5) [98]. Subsequent bromination with bromoform set the stage for the reductive formation of an unsaturated cyclic species [98–100].

A related compound was obtained by Sekiguchi quenching an isolable cyclotetrasilenyl radical with Br(CH$_2$)$_2$Br (5) [101].

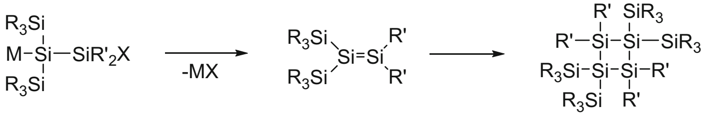
Equation 5. Bromination of a cyclotetrasilenyl radical.



Reaction of t-Bu$_2$SiCl$_2$ with lithium in THF also gave some hydrogenated cyclotetrasilanes (6) [102]. Bromination of the dihydrogenated product with NBS led to the dibromide which upon subsequent treatment with potassium gave the respective 1,3-dianionic compound [103].



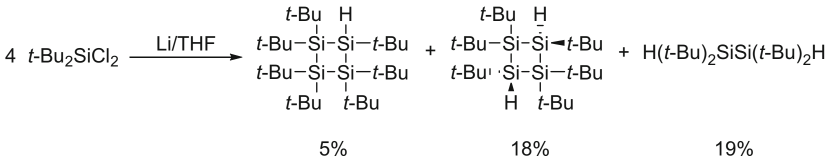
Scheme 6 Formation and dimerization of tetrakis(trimethylsilyl)disilene



M	SiR_3	R'	X
MgBr	$SiMe_2Pz$	Me	Pz
K	$SiMe_3$	*i*-Bu	Cl

Scheme 7 Formation and dimerization of asymmetric disilenes

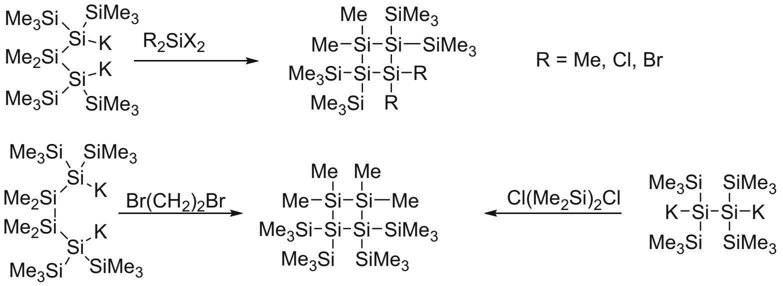
Equation 6. Wurtz-type coupling of *t*-Bu_2SiCl_2 yielding cyclotetrasilanes.



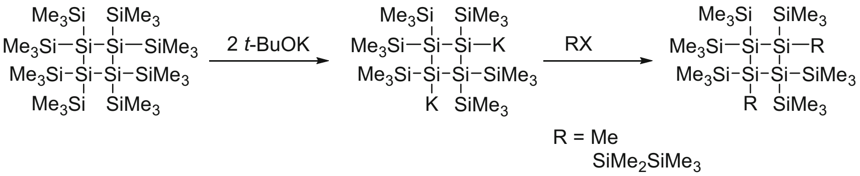
Another interesting method to obtain cyclotetrasilanes is the [2 + 2]cycloaddition of disilenes. Depending on the nature of R groups disilenes either are stable or undergo a dimerization reaction to a cyclotetrasilane. Tetrakis(trimethylsilyl)disilene, which forms either by thermolysis of methoxytris(trimethylsilyl)silane [104], by treatment of 1,2-dipotassiotetrakis(trimethylsilyl)disilane with $BrCH_2CH_2Br$ [96] or by reaction of the respective fluoride adduct with $MgBr_2$ [105], dimerizes to octakis (trimethylsilyl)cyclotetrasilane (Scheme 6).

In similar processes asymmetric disilenes, which can form from silyl anions with good leaving groups in α-position dimerized in a head-to-tail process to the respective cyclotetrasilanes (Scheme 7) [106, 107].

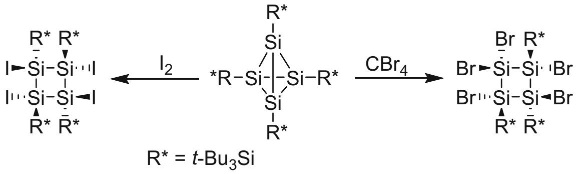
As already shown above for cyclotrisilanes, oligosilanyl dianions are convenient building blocks for the synthesis of cyclosilanes with different substitution pattern [47, 96, 108]. 1,1,2,2-Tetrakis(trimethylsilyl)tetramethylcyclotetrasilane which forms in the oxidative coupling of the 1,4-dipotassium compound (Scheme 8) can



Scheme 8 Cyclotetrasilane formation using oligosilanyl dianions as precursors



Scheme 9 Cyclotetrasilane derivatization involving dianion formation



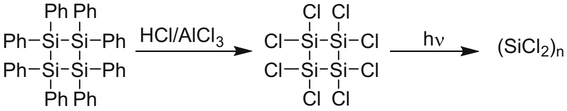
Scheme 10 Halogenating ring-opening of a silatetrahedrane to tetrahalocyclotetrasilanes

also be obtained in the course of reductive elimination of a titanacyclopentasilane (*vide infra*) [109, 110].

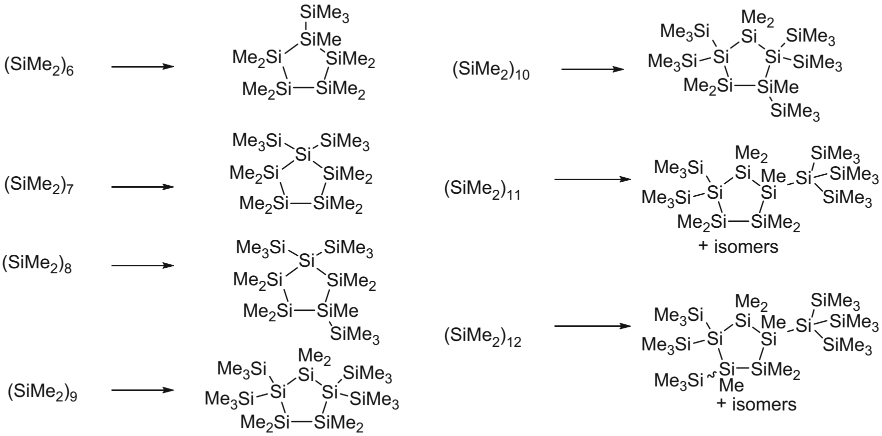
The oligosilanyl anion chemistry was also used to change the substitution pattern of a cyclotetrasilane. Reaction of tetrakis(trimethylsilyl)cyclotetrasilane with *t*-BuOK led to the respective silyl potassium compounds which further were reacted with suitable electrophiles (Scheme 9) [111].

Treatment of Wiberg's tetrahedrane with iodine led to the formation of a tetraiodinated cyclotetrasilane whereas reaction with CBr_4 gave a pentabrominated product (Scheme 10) [90, 94].

The perchlorinated cyclotetrasilane is easily available from the respective octaphenylcyclotetrasilane [112]. This compound was found to undergo a ring-opening polymerization to $(SiCl_2)_n$ in a way that the polymer retains a crystalline state and could be studied by XRD single crystal analysis (Scheme 11) [113, 114].



Scheme 11 Chlorinating dephenylation and subsequent polymerization of a cyclotetrasilane



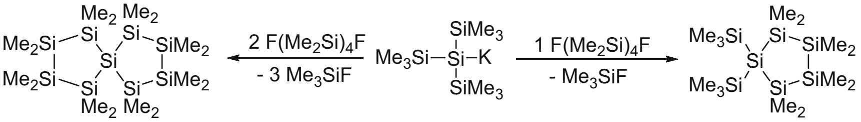
Scheme 12 Lewis acid catalyzed rearrangement processes of permethylated oligosilanes and isomers

6.3 Cyclopentasilanes

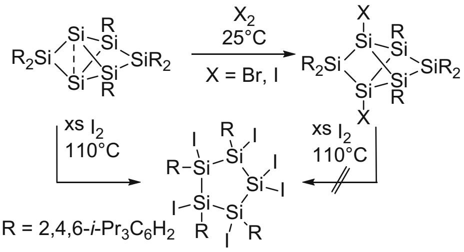
Interest in the synthesis of decaphenylcyclopentasilane has been renewed in recent times [115] as it still is the commonly used precursor for the synthesis of cyclopentasilane [116], which has become a valuable material for solution-phase processing to obtain printable devices based on elemental silicon [117].

Marschner and coworkers have used 1,3-, 1,4-, and 1,5 oligosilanyl dianions to obtain cyclopentasilanes with different substitution pattern [118–120]. Based on older work by Kumada [121] and West [122] the same group reinvestigated the $AlCl_3$ catalyzed rearrangement reaction of permethylated cyclosilanes. In contrast to an earlier report [122] it turned out that the reactions of isomers of rings with a formal ring size ranging from 5 to 14 always proceed in a way that substituted cyclopentasilanes are formed. For compounds with a formal ring size larger than ten mixtures of isomers are formed which share a common structural motif of the cyclopentasilane unit (Scheme 12) [111].

A subsequent study in this field revealed that the rearrangement of certain branched acyclic oligosilanes can also lead to the formation of substituted cyclopentasilanes, which occurs with elimination of tetramethylsilane (7) [123].

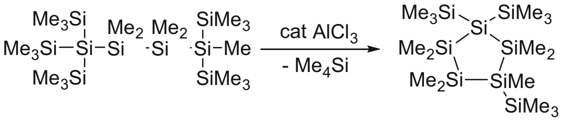


Scheme 13 Cyclization reactions of the tris(trimethylsilyl)silyl anion with $F(Me_2Si)_4F$



Scheme 14 Iodination of a stable persilapropellane to a hexaiodocyclopentasilane

Equation 7. Lewis acid catalyzed rearrangement/cyclization of an oligosilane.

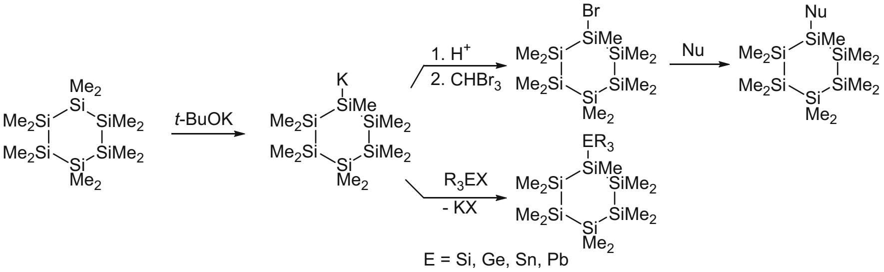


The reaction of tris(trimethylsilyl)silyl potassium with 1,4-difluorooctamethyltetrasilane also gave cyclopentasilanes [124]. Depending on the amount of fluorosilane used either 1,1-bis(trimethylsilyl)octamethylcyclopentasilane or a rare example of a spirocyclic oligosilane was formed (Scheme 13). The driving force in these reactions is the intramolecular attack of the leaving fluoride onto a trimethylsilyl group [124].

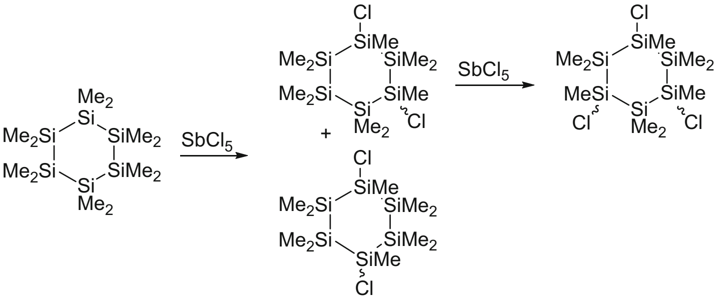
Scheschkewitz and coworkers observed the formation of a hexaiodocyclopentasilane upon iodination of a stable persilapropelane-type Si_6R_6 isomer under forcing conditions. If the reaction was carried out at ambient temperature, a simple addition product was obtained, which, however, could not be converted further to the hexaiodocyclopentasilane with excess iodine at higher temperature (Scheme 14) [125].

6.4 Cyclohexasilanes

Much of the cyclohexasilane chemistry carried out recently is based on dodecamethylcyclohexasilane. One approach in this direction employs the reaction of dodecamethylcyclohexasilane with *t*-BuOK which leads to undecamethylcyclohexasilanyl potassium [126]. Reactions of the latter provided access to several



Scheme 15 Formation and derivatization of undecamethylcyclohexasilanyl potassium



Scheme 16 Chlorination of dodecamethylcyclohexasilane with $SbCl_5$

undecamethylcyclohexasilanyl substituted silanes [127, 128], germanes, stannanes, and plumbanes [129]. The same route also provides access to an electrophilic undecamethylcyclohexasilanyl fragment by hydrolysis of the silanyl anion and subsequent bromination (Scheme 15) [127]. Reactions with nucleophiles proceeded smoothly [130, 131].

To obtain di- or trihalogenated methylated cyclohexasilanes reaction of dodecamethylcyclohexasilane with $SbCl_5$ has become an established route [132, 133]. Depending on the conditions this reaction gives mixtures of 1,3-dichloro- and 1,4-dichlorodecamethylcyclohexasilane isomers or a mixture of these in addition to isomers of 1,3,5-trichlorononamethylcyclohexasilane (Scheme 16).

These mixtures can be separated by various procedures to provide pure di- and trichlorocyclohexasilanes. Utilizing these compounds Chernyavskii and coworkers have studied the formation and properties of polymers with cyclohexasilanylene units [133–135]. Reactions of the di- and trichlorocyclohexasilanes with nitrogen [130, 136] and oxygen [132, 136–138] nucleophiles were investigated by the groups of Stüger [130, 132, 136, 139] and Chernyavskii [137, 138]. Stüger and coworkers used the 1,4-cyclohexasilanediyl fragment as a spacer between donor and acceptor units to study electron transfer through oligosilane units [131, 140]. While undecamethylcyclohexasilanes and most other cyclohexasilanes have a preference for the *chair*-conformation, the attachment of bulky groups such as 1-pyrenyl in 1,4 position can change this in a way that a *boat*-like geometry is adopted [141].

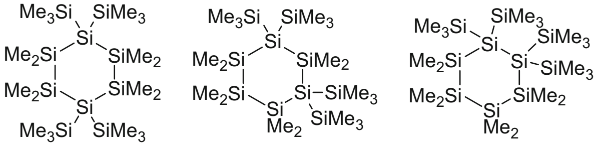


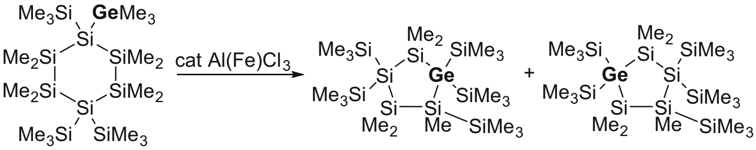
Fig. 3 Different isomers of tetrakis(trimethylsilyl) octamethylcyclohexasilane

As outlined above the use of oligosilanyl dianions allows for the selective synthesis of rings not only with a certain ring size but also with a particular substitution pattern (Fig. 3). The reaction of 1,1,4,4-tetrakis(trimethylsilyl)-1,4-dipotassio-tetramethyltetrasilane with 1,2-dichlorotetramethyldisilane gave 1,1,4,4-tetrakis (trimethylsilyl)octamethylcyclohexasilane [142]. The compound represents a rare example of a cyclohexasilane adopting a *twist*-conformation in solid state and in solution [143]. Using 1,2- or 1,5-dianions it was possible to obtain also the respective isomers with the 1,1,2,2-tetrakis(trimethylsilyl) and the 1,1,3,3-tetrakis(trimethylsilyl) substitution pattern.

The trimethylsilylated positions in these molecules were metalated by reaction with *t*-BuOK, and further manipulation of the substituent pattern was thus possible [111, 120]. This method was also used to connect cyclo- and bicyclosilanes with oligosilanylene bridges to study their σ-electron delocalization behavior [47].

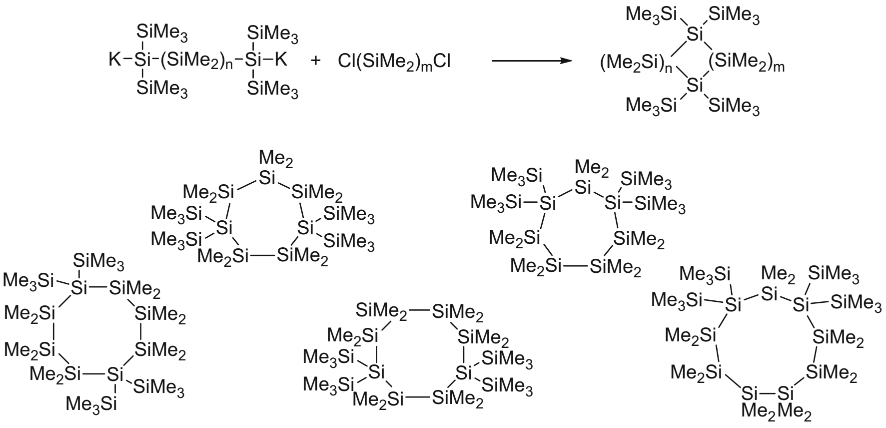
Another interesting reaction of a cyclohexasilane is the $AlCl_3$ catalyzed rearrangement of a trimethylgermylated cyclohexasilane, which led to a mixture of two structural isomers with the germanium atom shifted to a tetrasilylated position (8) [144].

Equation 8. Lewis acid catalyzed rearrangement of a trimethylgermylated oligosilane with formal germanium migration.



6.5 Larger Cyclosilanes

With respect to cyclosilanes with ring sizes larger than six not much is known. In seminal studies West and coworkers have investigated the Wurtz-type coupling of Me_2SiCl_2 under kinetic conditions. It was possible to separate the reaction products which consisted of permethylated cyclosilanes with ring sizes up to $n = 35$ [73, 145]. Of particular interest in this connection were the optical absorption properties.



Scheme 17 Formation of medium ring size cyclosilanes and the formed products

For the two compounds with ring sizes 13 and 16 XRD crystal structure analyses revealed conformations quite different from the analogous cycloalkanes with the same ring sizes [146]. The only recent contribution to medium ring sized cyclosilanes was by Marschner and coworkers who utilized their approach of reacting oligosilanyl dianions with α,ω-dihalooligosilanes to obtain seven-, eight-, and nine-membered rings (Scheme 17) [120, 143]. The UV-spectroscopic analysis of the obtained trimethylsilylated cyclosilanes revealed that the lowest energy absorption bands correspond to open chain molecules of the same chain length. Given the generally accepted opinion that effective σ-bond electron delocalization in linear chains is more effective in an *all-transoid* conformation, which cannot be adopted in a cyclic system the behavior of these cyclosilanes is not fully understood yet.

6.6 Bi- and Tricyclosilanes

While synthetic access to cyclosilanes utilizing the Wurtz-type coupling protocol gives acceptable yields for small ring sizes the same procedure does not work well when used to obtain bicyclic compounds by cross coupling of di- and trihalogen-organosilanes. Utilizing oligosilanyl dianion chemistry also various bicyclosilanes could be obtained (Fig. 4) [120, 142, 143].

Kira and coworkers reported the lithium-mediated Wurtz-type coupling of $MeSi(SiMe_2Cl)_3$ to tetradecamethylbicyclo[2.2.2]octasilane, which was further functionalized [147, 148]. A rare example of a tricyclic oligosilane was obtained when a [2.2.1]bicyclosilane connected to a cyclohexasilanyl unit was subjected to $AlCl_3$ catalyzed rearrangement conditions to give a persila-adamantane (Scheme 18) [149].

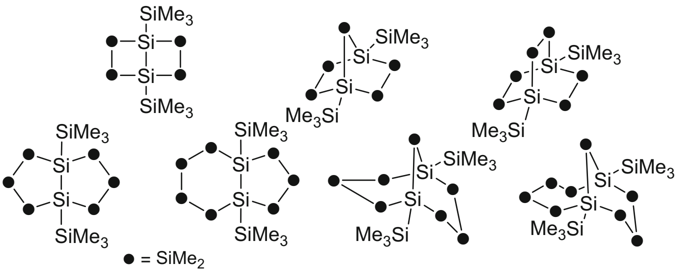
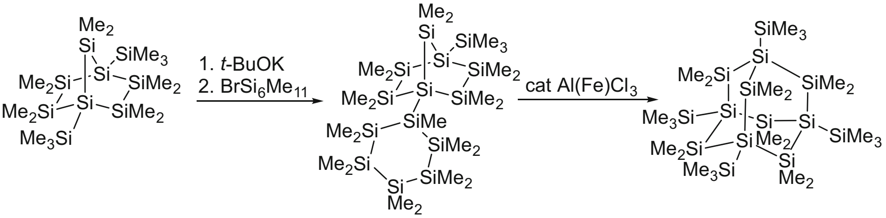


Fig. 4 Bicyclosilanes obtained using oligosilanyl dianion chemistry



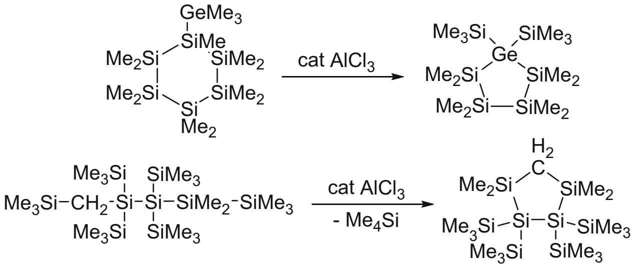
Scheme 18 Synthesis of the precursor and subsequent rearrangement to a persilaadamantane molecule

Breher and coworkers reported the synthesis of the pentasilapropellane Si_5Mes_6, which features two ligand-free, "inverted tetrahedral" bridge-head silicon atoms [150]. A related molecule, with two blades of the propellane being bridged by an additional silylene unit (Scheme 14), was obtained by Scheschkewitz and colleagues during their studies on stable isomers of persilabenzenes Si_6R_6 [151].

6.7 *Heterocyclosilanes*

In addition to the numerous homocyclic oligosilanes described above also a fair number of heterooligosilanes have been prepared and studied. Most of these compounds were synthesized by one of the two complementary strategies. Reaction of either α,ω-dielectrophilic or α,ω-dinucleophilic chains with respective dinucleophiles or dielectrophiles usually leads to cyclic compounds.

Numerous four- and five-membered heterocyclosilanes with N and O as heteroelements were prepared by Watanabe et al. in the reactions of $Cl(R_2Si)_nCl$ ($R = i\text{-Pr}, t\text{-BuCH}_2$; $n = 3,4$) with LiHNR ($R = \text{Pr}, C_6H_{11}$) and water [152]. In a similar way oxacyclosilanes with 2,3,4,5-tetracycloalkyl-2,3,4,5-tetraphenyl substitution pattern were obtained from the reaction of the respective 1,4-dibromotetrasilanes with water [97].



Scheme 19 Germanium and carbon containing heterocyclosilanes obtained by acid catalyzed rearrangement reactions

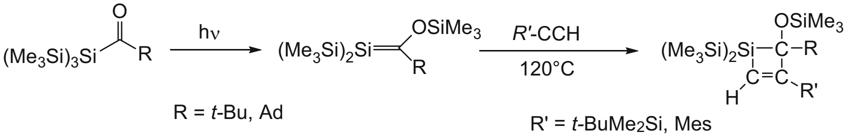
Marschner and coworkers demonstrated the use of 1,1,4,4-tetrakis (trimethylsilyl)-1,4-dipotassio-tetramethyltetrasilane for heterocyclosilane formation. Reaction of this compound with diorganogermanium- and –tindihalides gave five-membered rings with Ge and Sn atoms incorporated [118, 119, 153]. Reaction with amino-substituted boron and phosphorus dichlorides gave tetrasilaborolanes [154] and -phospholanes [154, 155]. In a similar way In [156], Ga [156], Zn [157], and Mg [158] were incorporated into five-membered rings. The reaction was even used to obtain heterocyclosilanes with transition metal atoms incorporated as shown for group 4 metals (*vide infra*) [109, 110, 118, 119].

Most recently Li, Lai, and coworkers have shown that reaction of a 1,4-oligosilanylenyl dianion with elemental S, Se, and Te leads to the formation of the respective chalcogenacyclosilanes [159]. Heterocyclosilanes with carbon [123] and germanium [144] heteroatoms were obtained in the $AlCl_3$ catalyzed rearrangement of suitable precursors (Scheme 19).

7 Functionalized Oligosilanes: Alkynes, Olefins, Hydrides, Halides, Radicals

While much of the oligosilane research until the 1990s was concentrating on structural issues with mainly alkyl and aryl groups as substituents, the more recent period has experienced a development of functionalized oligosilanes. The expression functionalized here covers not only the attachment of organic functional groups but also unique silicon-based functionality such as anions, cations, radicals, silylenoids, disilenes, disilynes, and silylenes.

The current chapter will neither cover perhydrogenated nor perhalogenated oligosilanes which have been the topic of a recent overview [9]. It will also omit compounds with multiple bonds between Si-atoms, silylenes, silylenium cations, silyl anions, and silylenoids. All these will be treated in other chapters of this volume.



Scheme 20 Addition of alkynes to silenes

7.1 Alkynyl and Vinylsilanes

Alkynyl groups can easily be attached to silanes by reaction of acetylides with silyl halides or similar electrophilic species. A substantial number of alkynyl substituted disilanes have been prepared and studied. Among these are several examples of multiply alkynylated di-and oligosilanes [160–162]. Even the resolution of optically active 1,2-ethynyldisilanes was reported [163]. Di- and oligosilane formation by coupling of alkynylated silanes was also possible [164, 165]. Incorporation of alkynylated disilane units into medium-sized rings [166, 167] and polymers [168–172] has been studied. These polymers and also some model compounds were further studied with respect to electron transfer [173, 174], hole-mobility [170], and use in organic solar cells [172]. Also a number of oligosilanylalkynyl substituted hexa- and heptacenes [175, 176] have been reported. Several examples of larger oligosilanes with alkynyl units have been prepared [119, 177–180]. An interesting aspect of the reactivity of these compounds is their strongly facilitated silyl anion formation behavior [119, 177, 178, 181]. The coordination of oligosilanyl alkynes to transition metals in particular to cobalt [166, 167, 180] and to group 4 metals [109, 179, 182] has been studied. The photochemical rearrangement behavior of disilanyl alkynes, which involves intermediate silirene formation has been the subject of several reports [183–186].

Ishikawa and coworkers studied addition reactions to silenes with substituted acetylenes which give [2 + 2]-addition products frequently followed by a complex ring-opening chemistry (Scheme 20) [187, 188].

A major development in recent oligosilane chemistry is concerned with the tris (trimethylsilyl)silyl group in organic synthesis. One way to introduce this fragment is the use of tris(trimethylsilyl)silane as a source for silyl radicals. This way the formation of tris(trimethylsilyl)vinylsilanes is easily possible by hydrosilylating alkynes.

7.2 Silyl Hydrides

The number of reported oligosilanyl hydrides is too large to allow a detailed discussion. Silyl hydrides are a very important functional group. Frequently they serve as precursors for the generation of silyl radicals. Much of the importance of $(Me_3Si)_3SiH$ as a reagent is based on this valuable reaction. The same property also allows facile radical-type halogenation by reaction with CX_4 or CHX_3 (X = Cl, Br, I). Alternatively, direct halogenation of the Si–H bond with X_2 even in the presence of Si–Si bonds has also been reported. The Si–H bond is also important with respect to the facile oxidative addition of transition metals, which renders the metal-catalyzed hydrosilylation as one of the most important reactions for Si–C bond formation. In some cases Si–H bonds can be subjected to deprotonation and thus serve as starting materials for silyl anions [189].

Formation of silyl hydrides is mainly achieved either by hydrolysis of silyl anions or be the treatment of silyl halides with hydride donors (especially $LiAlH_4$ and DIBALH are well suited). Also addition reactions of HX to unsaturated silicon compounds such as disilenes or silylenes can lead to Si–H bond formation.

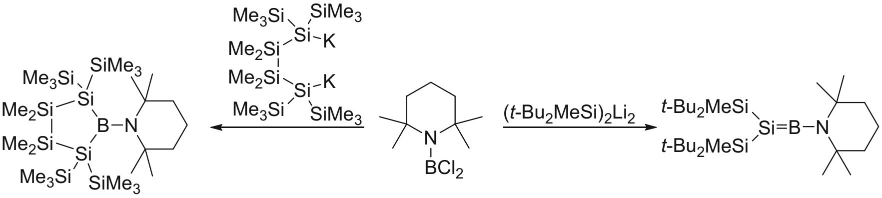
7.3 Silyl Halides

Oligosilanyl halides are also very abundant and their treatment as a separate compound class would thus be too exhaustive. Silyl halides are of major importance for the generation of numerous silicon species. By reaction with nucleophiles including lithium alkyls, silyl anions, amines, amides, alcohols, and alkoxides, Si–X bonds are easily formed. They also serve as starting materials for Si–Si bond formation by Wurtz coupling or for the generation of unsaturated compounds such as disilenes, disilynes, or silylenes.

The formation of silyl halides occurs either in the direct process as known for major industrial silyl halides such as Me_2SiCl_2 or by a number of synthetically viable procedures. Of major importance in this connection is the treatment of arylsilanes with HX (sometimes in the presence of AlX_3) to cleave off aromatic substituents in a protodesilylation reaction. Other preparative pathways involve cleavage of Si–H or Si–Si bonds with X_2 or treatment of Si–NR_2 bonds with HX.

7.4 Heterosubstituted Oligosilanes

Over the last years numerous compounds with oligosilanyl groups attached to main group elements have been reported. One of the reasons for this is that oligosilanyl groups in general and the tris(trimethylsilyl)silyl group [7] in particular have gained a reputation as ligands for kinetic stabilization. The fact that the group can easily be introduced as nucleo- or electrophile or even as a radical has certainly contributed to its popularity. As a consequence of this, several of the compounds described in the following sections feature the oligosilanyl group less in a leading but more in a supporting role for interesting bonding situations.



Scheme 21 Reactions of an aminodichloroborane with oligosilanyl dianions

7.4.1 Group 13

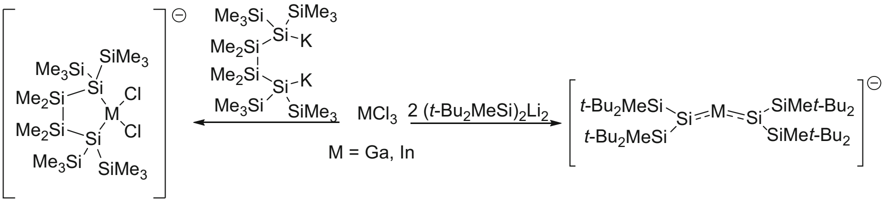
Some work by Braunschweig and coworkers utilizing oligosilanyl moieties involved $(Me_3Si)_3SiBCl_2$ which upon reaction with $Na_2[Cr(CO)_5]$ converted to the borylene complex $(Me_3Si)_3SiB = Cr(CO)_5$ [190, 191]. Reactions with other metalates led to oligosilanylated chloroboryl complexes of iron and manganese [192]. Reaction of dichloro(2,2,6,6-tetramethylpiperidino)borane with tris (trimethylsilyl)silylpotassium was found to give the silylated chloroborane [154]. A similar compound with a diisopropylamino group was obtained by Nöth and coworkers and subsequently treated with $LiPPh_2$ to give $(Me_3Si)_3SiB(N\textit{i}\text{-}Pr_2)PPh_2$ [193].

Reactions of an aminodichloroborane with 1,4-oligosilanyl dianions gave mono- or bicyclic disilylated boranes [154], whereas reaction with the geminal dianion $(t\text{-}Bu_2MeSi)_2SiLi_2$ led to a stable silaborene (Scheme 21) [194].

It is interesting to note that until recently no stable silylated hydroboranes were known. After the formation of $K[(Me_3Si)_3SiBH_3]$ by reaction of $(Me_3Si)_3SiK$ with $BH_3{\cdot}NEt_3$, this borate was treated with $B(C_6F_5)_3$ to abstract a hydride. The resulting $(Me_3Si)_3SiBH_2$ was dimeric in solution and in the solid state [195].

As part of Schnöckl's work on subvalent group 13 halides reactions of AlX (X = Cl, Br) with $(Me_3Si)_3SiLi$ gave $Al_2Cl_2\{Si(SiMe_3)_3\}_2{\cdot}(THF)_2$ [196], $(Me_3Si)_3SiAlBr_2{\cdot}THF$ [196] $Li[\{(Me_3Si)_3Si\}_2AlBr_2]$ [197] and the tetrasilylated aluminum tetrahedrane $\{(Me_3Si)_3Si)\}_4Al_4$ [197]. Related silylated aluminum dihalides were also obtained from the reactions of $(Me_3Si)_3SiK$ with AlX_3 (X = Cl, Br, I) [198]. A number of other tris(trimethylsilyl)silylated aluminum, gallium, and indium compounds were obtained by reactions of $(Me_3Si)_3SiM$ (M = Li, Na, K) with R_2AlCl (R = Me, Et), Me_2GaR (R = Cl, Me), and $InCl_3$ [199]. The reaction with Me_3Ga gave $Li[(Me_3Si)_3SiGaMe_3]$ whereas $\{(Me_3Si)_3Si\}_2InIn\{Si(SiMe_3)_3\}_2$ was produced in the reaction with $InCl_3$ [199]. Reacting $MeAlCl_2$ with $(Me_3Si)_3SiLi$ two $(Me_3Si)_3Si$ groups were attached to aluminum [200].

Reaction of $GaCl_3$ with base-free $(Me_3Si)_3SiLi$ gave the trisilylated $\{(Me_3Si)_3Si\}_3Ga$ [201]. Reactions of $(Me_3Si)_3SiM$ (M = Li, K) with subvalent gallium halides gave depending on reaction conditions and stoichiometry gallium clusters like $\{(Me_3Si)_3Si\}_6Ga_{10}$ [202], silylated gallium halides [202], or an anionic 1,3,2,4-di-siladigalletane-derivative $K[\{(Me_3Si)_3SiGaSi(SiMe_3)_2\}_2H]$ [203]. Slight variations in the structure of the silanide such as the use of $(Me_3Si)_2MeSiLi$ gave



Scheme 22 Reactions of oligosilanyl dianions with group 13 trichlorides

clusters such as $[Ga_6\{SiMe(SiMe_3)_2\}_6]$ in which Ga forms an octahedron substituted with oligosilanyl groups [204]. In a way similar to the formation of the stable silaborene described above, reactions of $(t\text{-}Bu_2MeSi)_2SiLi_2$ with $GaCl_3$ and $InCl_3$ led to 1,3-disila-2-gallata- and -indataallenic anions (Scheme 22) [205]. In the same sense reactions of a 1,4-dianionic oligosilane with MCl_3 (M = Ga, In) gave heterocyclic metalates (Scheme 22) [156].

Formation of a tetrasilylated indium tetrahedrane was reported by the reaction of Cp*In with $(Me_3Si)_3SiLi$ [206].

7.4.2 Group 14

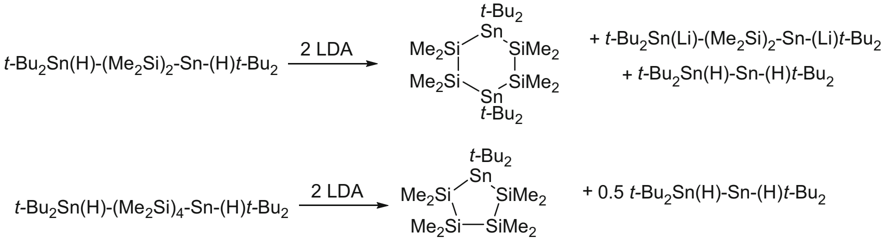
Oligosilanes with bonds to heavier group 14 elements are quite abundant. Typically these bonds are formed using the same methods that are also used for generating Si–Si bonds.

Group 14 Germyl Oligosilanes

Reacting silanyl anions with germyl halides is probably the most common method to obtain germylated silanes. This was shown on several occasions to form $Me_3GeSi_6Me_{11}$ [129], $[(Me_3Si)_3Si]_2GeMe_2$ [207], $[(Me_3Ge)(Me_3Si)_2SiMe_2Si]_2$ [144], and some others [153]. The inverse polarized reaction with germyl anions works equally well [208]. Reductive coupling of $Cl\textit{i}\text{-}Pr_2GeSi\textit{i}\text{-}Pr_2Cl$ with sodium gave octaisopropyl-1,2-disiladigermacyclobutane [209].

The germasilene $(t\text{-}BuMe_2Si)_2GeSi(SiMe_2t\text{-}Bu)_2$ was synthesized by coupling of $(t\text{-}BuMe_2Si)_2Ge(H)Li$ with $t\text{-}BuMe_2Si)_2Si(H)Cl$, subsequent bromination of the Si–H and Ge–H bonds and treatment of the dibromide with sodium [210]. Using $[(Me_3Si)_3Si]_2Mg$ Castel and coworkers have prepared oligosilanyl substituted Ge(II) compounds by reaction with Ge(II) chlorides [211, 212].

Schnepf and coworkers have studied reactions of subvalent Ge(I) halides with $(Me_3Si)_3SiLi$ and obtained tris(trimethylsilyl)silated clusters such as $[Ge_9\{Si(SiMe_3)_3\}_3]^-$ [213–215]. The use of these clusters as ligands to transition metal fragments has also been investigated in some detail [216–220]. Schnepf's chemistry is complemented by recent studies by Sevov and coworkers who obtained quite similar oligosilylated cluster compounds, which, however, were derived from the reaction of $(Me_3Si)_3SiCl$ with the Zintl anions K_4Ge_9 [221, 222].



Scheme 23 Metallation of oligosilanylated hydrostannanes leading to stannacyclosilanes

Tilley and coworkers have studied oligosilylated germoles as ligands for ferrocene-type complexes [223]. Mochida and coworkers reacted $HPh_2Ge(SiMe_2)_nGePh_2H$ (n = 0–3) with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ to obtain initially the hydrido(germyl)platinum complex *cis*-$Pt(H)[GePh_2\text{-}(SiMe_2)_nGePh_2H](PPh_3)_2$, followed by the formation of the cyclic bis(germyl)platinum complex $Pt[GePh_2\text{-}(SiMe_2)_nGePh_2](PPh_3)_2$ [224].

In a series of papers Sekiguchi and Lee have investigated the chemistry of disilagermirenes and related compounds. These studies have likely led to the highest number of germanium containing oligosilanes [95, 225–236]. Related chemistry from the same group concerning heavy cyclobutadienes was also studied with germanium incorporation into the cyclobutadiene analogs and the respective precursor molecules [99, 237, 238].

Group 14 Stannyl Oligosilanes

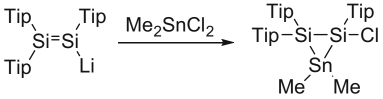
Uhlig and coworkers reported the reactions of undecamethylcyclohexasilanyl potassium with a number of different tin halides to obtain compounds with either one, two, or three attached cyclohexasilanyl groups [129]. The reactions of 1,4-dihalogen substituted decamethylcyclohexasilanes (X = F, Cl) with R_2SnCl_2 (R = Me, Ph) in the presence of magnesium gave 1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octanes [239]. Attempts to lithiate oligosilanylene bridged distannylhydrido compounds gave beside the expected dilithiated compounds stannacyclosilanes (Scheme 23) [240].

A number of branched tri(stannyl)tetrasilanes $MeSi(SiMe_2SnR_2R')_3$ ($R = R' =$ Ph; $R = R' =$ Me; $R = t$-Bu, $R' =$ H) were obtained using reactions of alkali metal tri- or diorganostannides with $MeSi(SiMe_2X)_3$ (X = F, Cl) or by reacting triphenylchlorostannane with $MeSi(SiMe_2F)_3$ in the presence of magnesium. $MeSi(SiMe_2Sn\textit{t}\text{-}Bu_2H)_3$ was halogenated by treatment with $CHCl_3$ or $CHBr_3$. Reaction of $MeSi(SiMe_2Sn\textit{t}\text{-}Bu_2H)_3$ with 3 equiv. LDA led to the formation of 2-dimethylsilyl-1,1,2,3,3-pentamethyl-4,4,5,5-tetra-*tert*-butyl-1,2,3-trisila-4,5-distannacyclopentane with a bridging distannylene unit [241].

The trimethylsilylated branched group 14 compounds $(Me_3Si)_3SiSn(SiMe_3)_3$ and $(Me_3Si)_3SiSn\textit{i}\text{-}Pr_3$ were prepared by salt elimination reactions [242]. As mentioned above stannacyclosilanes were prepared by reaction of α,ω-oligosilanyl dianions with diorganodichlorostannanes [118, 119, 242]. In a similar way also cyclic disilylated stannylene phosphine adducts were obtained from the same α,ω-oligosilanyl dianions in the reaction with $SnCl_2{\cdot}PEt_3$ or $Sn[N(SiMe_3)_2]_2/PEt_3$ [243, 244]. Related acyclic oligosilanylated stannylenes have also been prepared [211, 245].

In a comparable way as outlined below for lead, Klinkhammer and coworkers obtained a number of oligosilanylated stannyl anions and radicals by reaction of oligosilanyl anions with diamino and diaryloxy stannylenes [246]. Scheschkewitz and coworkers found that the reaction of a disilenyl lithium species with Me_2SnCl_2 gave a chlorinated disilastanniranes (9) [247].

Equation 9. Disilastannirane formation by reaction of a lithium disilenide with Me_2SnCl_2.

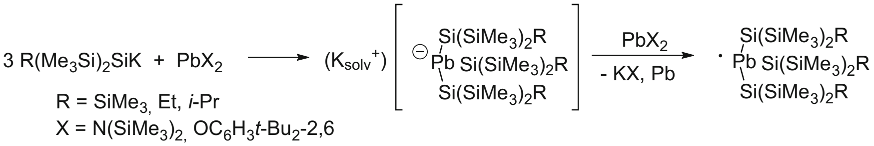


Tip = 2,4,6-iPr$_3$C$_6$H$_2$

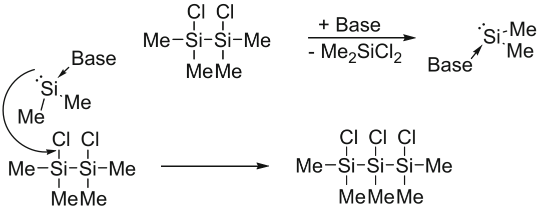
In a similar way as mentioned above for subvalent Ge(I) halides Schnepf and coworkers have also reported several reactions of Sn(I) halides with silyl anions which gave silylated Zintl-type clusters Sn_9 and Sn_{10} [248–251]. In addition to these clusters smaller units such as the stannyl anion $[\{(Me_3Si)_3Si\}_3Sn]^-$, the cyclotristannene $[\{(Me_3Si)_3Si\}_4Sn_3]$, and the novel cluster $[\{(Me_3Si)_3Si\}_4(Me_3Si)_2SiSn_4]$ formed in the course of these reactions [252, 253].

Group 14 Plumbyl Oligosilanes

Surprisingly, only few silyl-lead compounds are known with Pb in the oxidation state +4. One of these is $Ph_3PbSi_6Me_{11}$ obtained by reaction of undecamethylcyclohexasilanyl potassium with Ph_3PbCl [129]. Most of the recent oligosilanyl lead chemistry has been investigated by Klinkhammer and coworkers. Starting out from the preparation of bis[tris(trimethylsilyl)silyl]lead [254] studies of its addition chemistry led to a few derivatives [245]. A related silyl substituted plumbylene, $Pb\{Si(SiMe_3)_3\}C_6H_3$-2,6-(2,4,6-i-Pr_3-C_6H_2)$_2$, was synthesized by the reaction of the respective aryl plumbylene bromide with 1 equiv. of $(Me_3Si)_3SiLi$ [255]. The reaction of $[(Me_3Si)_3Si]_2Pb$ with PH_3 and $[\{HCuPPh_3\}_6]$ led to the formation of tris(trimethylsilyl)silylated Pb-clusters consisting of 9 and 10 Pb atoms, respectively [256]. More recent work showed the formation of plumbyl anions from the reaction of 3 equiv. of silyl anions with PbX_2 ($X = N(SiMe_3)_2$, OC_6H_3t-Bu_2-2,6). By reaction with oxidating agents such as PbX_2 the anions were converted to (stable) radicals (Scheme 24) [246, 257].



Scheme 24 Formation of silanylated plumbyl anions and radicals



Scheme 25 Oligosilane formation by silylene insertion into Si–Cl bonds

Marschner and coworkers obtained a cyclic disilylated plumbylene which was only of limited stability in solution but was stable as a PEt_3 adduct [258]. Reactions of this adduct with Cp_2MCl_2 (M = Ti, Zr, Hf) in the presence of magnesium gave plumbylene metallocene complexes [244].

7.4.3 Group 15

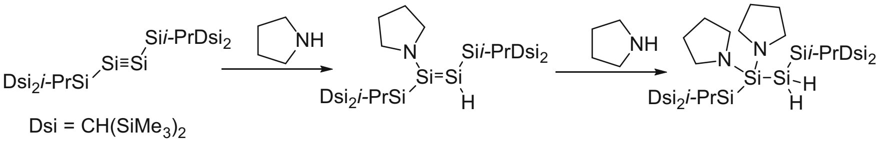
Oligosilanes with group 15 substituents consist mainly of aminosilanes but heavier analogs have gained more and more ground recently.

Group 15 Amino Oligosilanes

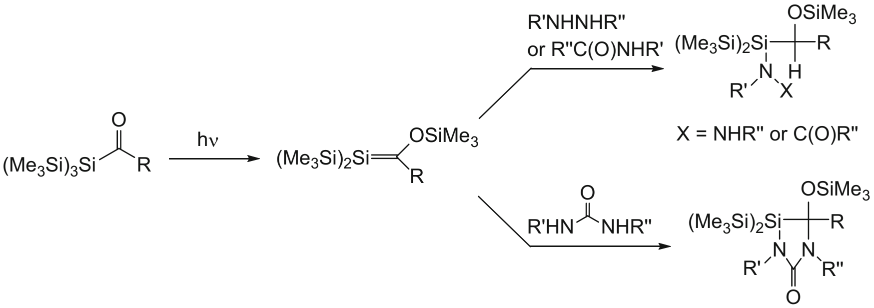
The base catalyzed disproportionation of chlorinated disilanes was studied and found to give oligosilanes with up to five silicon atoms. The reaction is believed to involve base stabilized silylenes which insert into Si–Cl bonds (Scheme 25) [259].

$Et_2NSi(SiMe_3)_3$ was obtained from the respective bromide and then converted to the silylenoid $Et_2N(Me_3Si)_2SiK$ which was used to obtain a number of derivatives [260]. Stüger and coworkers prepared and studied amino-substituted cyclosilanes with $N(SiR_3)_2$ and NH_2 substituents. The latter were found to give polysilazane in the presence of catalytic amounts of acid [130, 132, 261].

In the course of the studies of *N*-heterocyclic silylenes Gehrhus and coworkers observed Si–Si coupling either to disilanyl or to cyclotetrasilanyl units. With the preservation of the *N*-heterocyclic substitution pattern these compounds can be regarded as amino-substituted oligosilanes [262–265]. Related chemistry was also observed by West and coworkers [266, 267].



Scheme 26 Pyrolidine addition reactions to a disilylated disilyne



Scheme 27 Addition reactions of nitrogen nucleophiles to silenes

Reaction of $(Me_3Si)_3SiN(SiMe_3)PCl_2$ with $GaCl_3$ and Me_3SiN_3 resulted in the formation of a cyclo-2-phospha-4-sila-1,3-diazenium tetrachlorogallate [268]. Reaction of $(Me_3Si)_3SiN(H)PCl_2$ with Et_3N gave *cis*-1,3-dichloro-2,4-bis-tris(trimethylsilyl)silyl-cyclo-diphosphadiazane [269], which proved to be an interesting starting material for further derivatization [270, 271].

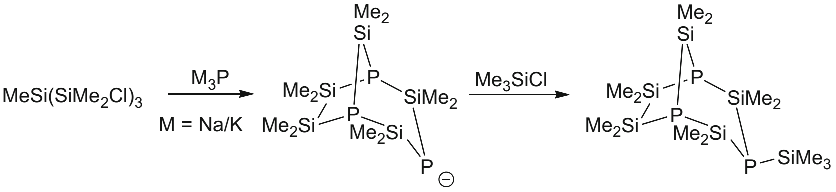
The lithium amide $(Me_3Si)_3SiN(Li)SiMe_3$ was formed by deprotonation of the respective amine with *n*-BuLi [272]. The related amide $(Me_3Si)_3SiN(Li)Ar$ was obtained from the reaction of ArN_3 (Ar = Ph, p-MeC_6H_4, 1-naphthyl) with $(Me_3Si)_3SiLi$ [273]. Analogously a bis[tris(trimethylsilyl)silylated] dilithium diamide was formed in the reaction of *o*-phenylene diazide with 2 equiv. $(Me_3Si)_3SiLi$ [273].

Addition reactions to unsaturated silicon compounds (silenes, disilenes, disilynes) offer opportunities to form aminooligosilanes. An example is the reaction of Sekiguchi's disilyne with pyrrolidine, which gave the silicon version of an enamine. Further addition gave a geminal diaminotetrasilane (Scheme 26) [274].

Addition of hydrazines and amides to silenes occurred selectively to form amino- [275] or amidosilanes [276], whereas addition of ureas gave 1-sila-2,4-diaza-3-oxocyclopentanes (Scheme 27) [275].

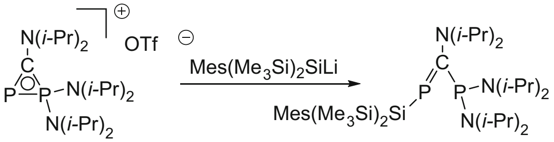
Group 15 Oligosilanyl Phosphines

Reactions of silyl anions with electrophilic organophosphorus compounds constitute a popular access to silylated phosphines. Reaction of a diphosphirenium salt with $Mes(Me_3Si)_2SiLi$ gave the corresponding P-silylated phosphaalkene (10) [277].



Scheme 28 Formation of a tetrasila-1-phosphanido-3,5-di-phosphabicyclo[3.2.1]octane

Equation 10. Phosphaalkene formation by silyl anion addition to a diphosphirenium salt.



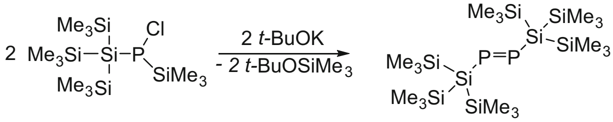
Reactions of mono- or dianionic oligosilanyl potassium or magnesium compounds with Et_2NPCl_2 gave $(Me_3Si)_3SiP(X)NEt_2$ (X = Cl, Br) [154] and a number of cyclic disilylated aminophosphines [154, 155].

Haenisch and coworkers studied reactions of chlorosilanes with phosphides. The 1,2-diphosphanyldisilanes $[Me_4Si_2(PH_2)_2]$ and $[Me_4Si_2(PHMe)_2]$ as well as the cyclic silaphosphine $[(Me_4Si_2)_2(PMe)_2]$ were obtained from reactions of $[Me_4Si_2Cl_2]$ with $[LiAl(PH_2)_4]$ and $[LiAl(PHMe)_4]$, respectively [278]. In a similar way cyclic tetrasilaphosphines $(i\text{-}Pr_2Si)_3PH$ and $(i\text{-}Pr_2Si)_4PH$ formed in reactions of the respective α,ω-dichlorotri- and tetrasilanes with $[Li(DME)PH_2]$. Both compounds were lithiated and coupled to diphosphines $[(i\text{-}Pr_2Si)_3P]_2$ and $[(i\text{-}Pr_2Si)_4P]_2$ [279, 280].

Hassler and coworkers have studied the chemistry of oligosilylated phosphorus compounds extensively. From the reaction of $MeSi(SiMe_2Cl)_3$ with excess of Na_3P/K_3P they obtained the anionic hexamethyltetrasila-1-phosphanido-3,5-di-phosphabicyclo[3.2.1]octane, which was converted to its trimethylsilylated derivative with Me_3SiCl (Scheme 28) [281].

In the reaction of $(Me_3Si)_3SiP(SiMe_3)Cl$ with t-BuOK the bis[tris(trimethylsilyl)silyl]diphosphene was formed in excellent yields (11) [282].

Equation 11. Synthesis of bis[tris(trimethylsilyl)silyl]diphosphene.

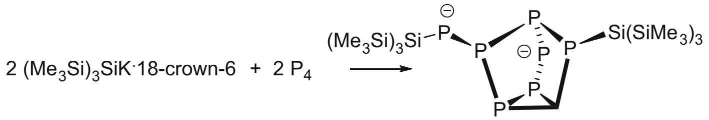


The synthesis of $(Me_3Si)_3SiPH_2$ was accomplished either by reaction of $(Me_3Si)_3SiOTf$ with PH_3 or, alternatively, by reaction of $NaPH_2$ with $(Me_3Si)_3SiCl$ which also gave $[(Me_3Si)_3Si]_2PH$. $(Me_3Si)_3SiPH(SiMe_3)$ and $(Me_3Si)_3SiP(SiMe_3)_2$

were used to prepare $(Me_3Si)_3SiPHK$ and $(Me_3Si)_3SiP(SiMe_3)K$, respectively, by reaction with *t*-BuOK. By reaction of $(Me_3Si)_3SiP(SiMe_3)_2$ with *t*-BuOK. Reaction of $(Me_3Si)_3SiPH_2$ with *n*-BuLi gave $(Me_3Si)_3SiPLi_2$. Also the halogenated compounds $(Me_3Si)_3SiPX_2$ and $(Me_3Si)_3SiPX(SiMe_3)$ (X = Cl, Br) were synthesized [283]. By reaction of $[(Me_3Si)_2MeSi]_2SiCl_2$ with LiPHR [R = C_6H_2-2,4,6-*t*-Bu_3, $Si(SiMe_3)_3$] the respective silylphosphines $[(Me_3Si)_2MeSi]_2Si(Cl)PHR$ were prepared. Although reactions of both compounds with *t*-BuLi indicated formation of phosphasilenes unfortunately, their isolation was not possible. In the same study $(Me_3Si)_3SiP(SiMe_3)SiCl_3$ was obtained from the reaction of $(Me_3Si)_3SiP(SiMe_3)K$ with $SiCl_4$ [284].

Hassler and coworkers have also studied the reactivity of silylated Zintl P_7^{3-} cluster molecules, which were prepared from the reaction of red phosphorus with Na/K alloy followed by the addition of 3 equiv. of a silyl halide. This way several compounds of the type $P_7(SiR_3)_3$ (SiR_3 = $Si(SiMe_3)_3$, $Si(SiMe_3)_2Me$, $Si(SiMe_3)_2Ph$, Si_6Me_{11}) were obtained [285]. Further attempts to generate silyl anions by reaction with *t*-BuOK led to a rich rearrangement and Si-P cleavage chemistry [285]. Another entry into this type of chemistry was possible by silyl exchange reaction which gave $[(Me_3Si)_3Si]_2P_7SiMe_3$ from the reaction of $P_7(SiMe_3)_3$ with $(Me_3Si)_3SiCl$ [286]. It was even possible to connect two silylated P_7 clusters with a disilanylene bridge [286]. It is interesting to note that the reaction of $(Me_3Si)_3SiK$ with white phosphorus also led to the typical P_7 nortricyclene cluster. The additional phosphorus atom from the condensation was attached to as a substituent giving the P_8 cluster dianion: $[P_8\{Si(SiMe_3)_3\}_2]^{2-}$ (12) [287].

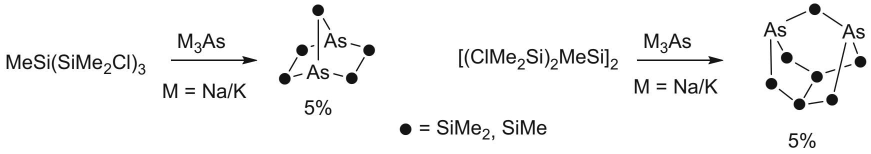
Equation 12. Reaction of $(Me_3Si)_3SiK$ with white phosphorus to a P_8-cluster dianion.



Group 15 Oligosilanyl Derivatives of the Heavier Elements

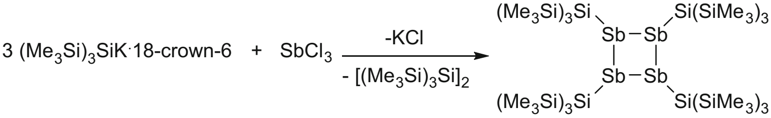
While there is a considerable number of amino and phosphino substituted oligosilanes the heavier group 15 elements did not receive much attention. From the reactions of $MeSi(SiMe_2Cl)_3$ and $[(ClMe_2Si)_2MeSi]_2$ with Na_3As/K_3As Hassler and coworkers isolated decamethylpentasila-1,4-diarsabicyclo[2.2.1]heptane and dodecamethylheptasila-1,5-diarsatricyclo[3.3.1.0^{3,7}]nonane (Scheme 29) [281].

The reaction of $(Me_3Si)_3SiK$ with $SbCl_3$ in the presence of crown ether gave a tetrasilylated cyclotetrastibine (13) [288].



Scheme 29 Formation reactions of As and Si containing cage molecules

Equation 13. Formation of a tetrasilylated cyclotetrastibine.



Analogous chemistry with bismuth was reported earlier by Linti and coworkers, who found that in the reaction of $(Me_3Si)_3SiLi$ with $BiBr_3$ 77% of $[(Me_3Si)_3SiBi]_4$ were formed [289]. The use of $BiCl_3$ in this reaction led to the formation of the bismuthide $[(Me_3Si)_3Si]_2BiLi$ [290].

7.4.4 Group 16

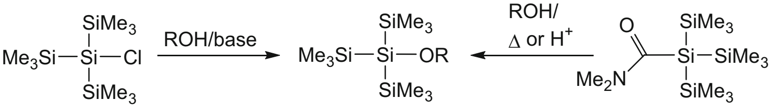
Group 16 Alkoxy and Silyloxy Oligosilanes

Of the considerable number of oxygen substituted oligosilanes that have been reported after the year 2000 most contain the tris(trimethylsilyl)silyl unit. Three reasons are mainly responsible for this: The first one is the introduction of the residue as a protecting group with attractive cleavage conditions (UV light irradiation). The second reason is an increasing popularity of tris(trimethylsilyl)silane as a reagent in radical chemistry. And finally, in connection to its use as a protective group the tris(trimethylsilyl)silyl unit has also gained a reputation as a large stereodirecting group suitable for selective cascade aldol and similar other reactions.

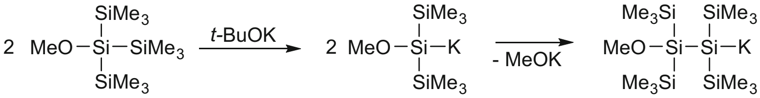
The foundation for the use of the tris(trimethylsilyl)silyl protecting group was laid by Brook and coworkers, who reported protocols for the introduction and removal of this group [291, 292]. While reactions of alcohols with tris(trimethylsilyl)silyl halides in the presence of a base are most commonly employed, Ottosson and coworkers provided an interesting acid catalyzed protocol (Scheme 30) [293].

How the steric bulk of the group can be advantageously used for inducing stereoselectivity in C–C coupling reactions was demonstrated by Yamamoto and coworkers in a series of papers [294–302].

Most recently siloxides have become attractive ligands for highly reactive metal fragments [303]. Krempner and coworkers have developed an approach to bidentate siloxides using hydrolysis of oligosilanyl dihalides [62, 304–316]. Reactions of the



Scheme 30 Introduction of the tris(trimethylsilyl)silyl unit as protecting group



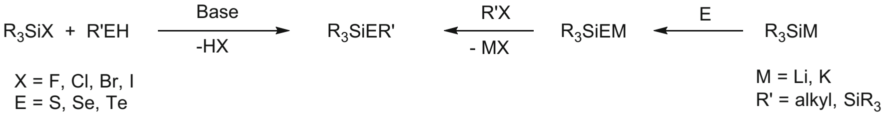
Scheme 31 Formation and dimerization of a methoxy silylenoid

thus obtained oligosilane diols with a number of metal complexes were studied [304–316].

In a series of papers Baines and coworkers studied addition reactions of carbonyl compounds to tetramesityldisilene [276, 317–319]. Although the mechanistic picture observed in these reactions is quite diverse, they share the common feature of the formation of alkoxy substituted disilanes. Similar reactivity was observed by Wiberg and coworkers [92] as well as by Sekiguchi and coworkers in reactions with cyclic disilenes [226, 230]. In the course of their continued studies of the addition chemistry of silenes Ishikawa and coworkers obtained a substantial number of complex oxygen substituted oligosilanes [229, 320–328]. Oehme and coworkers found that the cationic rearrangement of (3-hydroxy-1-propenyl)tris (trimethylsilyl)silanes leads to (1-trimethylsilyl-2-propenyl)bis(trimethylsilyl) silanols [329]. Sekiguchi and coworkers also found that addition of methanol to a number of reactive unsaturated compounds gave methoxyoligosilanes. Reaction with a disilaquinodimethane gave the 1,6-adduct [330]. With a boryl substituted disilene a 1-boryl-2-methoxydisilane was formed [331] and with a tetrasilylated trisilaallene 3,3-dimethoxypentasilane derivatives were obtained [332]. Oxygen substituted oligosilanes were also derived from the addition of elemental oxygen to Wiberg's silatetrahedrane [88] and disilyne [333]. A methoxy substituted silyl anion was found to exhibit silylenoid character, which led to dimerization (Scheme 31) [334].

Group 15 Oligosilanyl Sulfides, Selenides, and Tellurides

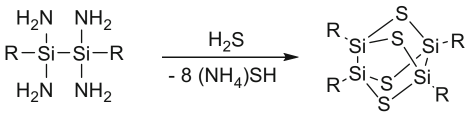
The chemistry of heavier oligosilanyl chalcogen derivatives was studied in much detail by Herzog and coworkers [335–353]. Their major strategies to obtain these compounds were either reactions of silyl halides with the respective REH (E = S, Se, Te) species in the presence of base or, alternatively, reaction of alkali metal silyls with elemental chalcogenes, which causes an insertion reaction of the respective chalcogen into the Si–metal bond (Scheme 32).



Scheme 32 Methods for the formation of Si-heavy group 16 element bonds

The reaction of the tetraaminodisilane $R_2Si_2(NH_2)_4$ [R = $CH(SiMe_3)_2$] with H_2S led to the formation of an $R_4S_4Si_4$ cage (14) [338].

Equation 14. S_4Si_4-cluster formation by reaction of a tetraaminodisilane with H_2S.



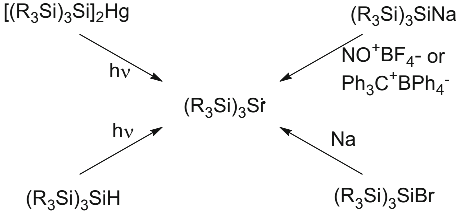
Rosenberg and coworkers reported the formation of several 1,2-dithiolated disilanes from the $B(C_6F_5)_3$ catalyzed reaction of $R_2HSiSiHR_2$ (R = Me, Ph) with thiols or thioketones [354, 355]. Reactions of phosphoryldithioacetates with the bulky $(Me_3Si)_3Si$ radical gave the respective spin adducts, which were studied using EPR spectroscopy [356, 357].

The trithiaheptasilaadamantane $MeSi(SiMe_2SiMeS)_3$ was prepared by reaction of $MeSi(SiMe_2SiMeBr_2)_3$ with H_2S [61]. Addition of carbon disulfide to disilenes gave a transient *S*-heterocyclic carbene with a disilane backbone that was characterized as its cycloaddition product with C_{60} [92, 358]. Reaction of a tetrasilylated cyclotrisilene with elemental sulfur was reported to give a sulfur adduct which rearranges to a thiacyclotetrasilene [359].

Reactions of $(Me_3Si)_3SiTeSiMe_3$ [360] with $RBiCl_2$ (R = $(Me_3Si)_3C$, $(Me_3Si)_2HC$) and $SnCl_2$ were found to give $RBi[TeSi(SiMe_3)_3]_2$ [361] and the unusual cluster $[\{(Me_3Si)_3SiTe\}_4Te_2Sn_4]$ [362].

7.5 Silyl Radicals

Recent years have seen a remarkable development of the preparation, isolation, and characterization of stable silyl radicals. Among these $(Me_3Si)_3Si$ has gained particular prominence as a popular reagent in organic synthesis [20–26]. In this connection related radicals have been studied to some extent. Following seminal contributions by Matsumoto and coworkers [363–365] key achievements in this development have been made by Sekiguchi and coworkers, which were reviewed only recently [8, 366, 367]. Most stable silyl radicals are trisilylated ones and are commonly prepared either from the respective hydrosilanes, from silyl mercury compounds, by oxidation of silyl anions, or by reduction of silyl halides (Scheme 33) [8].



Scheme 33 Methods for the formation of trisilylated silyl radicals

8 Oligosilanyl Ligands for Transition Metals

Numerous transition metal complexes are known containing silyl groups as ligands [368, 369]. The number of complexes containing oligosilanyl groups is considerably smaller but still substantial. The following overview is classified by transition metal groups.

8.1 Group 4

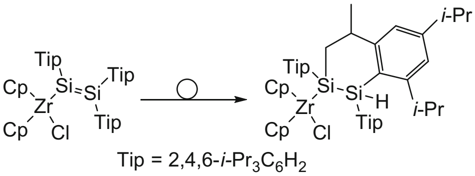
The chemistry of group 4 silyl compounds is closely associated with the dehydrogenating coupling of hydrosilanes. This reaction was discovered by Harrod and coworkers who converted $PhSiH_3$ with a catalytic amount of Cp_2TiMe_2 to $H(PhSiH)_nH$ [370]. Later Tilley and coworkers showed that if zirconocene and hafnocene complexes are used in the reaction a catalytic cycle is involved which consists of σ-bond metathesis steps [371]. To enhance σ-bond metathesis reactivity with Si–H and C–H bonds $Cp_2Hf(Me)Si(SiMe_3)_3$ and related compounds were treated with $B(C_6F_5)_3$ to obtain cationic Hf complexes [372].

Marschner and coworkers prepared a number of zirconocene and hafnocene complexes with different oligosilanyl groups usually by reaction of a silyl potassium species with Cp_2MCl_2 (M = Zr, Hf). It was shown that in the reaction of $(Me_3Si)_3SiK$ with Cp_2MCl_2 (M = Zr, Hf) either one [373] or two [374] tris(trimethylsilyl)silyl groups can be attached to the metal. Also the generation of a zirconocene with an amino-substituted oligosilanyl group was possible this way [260]. Using oligosilanyl dianions metallaheterocyclosilanes can be obtained [118, 119, 155]. If the used dianion is a 1,2-dianion, disilene complexes were obtained [375, 376], whereas the reaction of a geminal dianion with Cp'_2HfCl_2 ($Cp' = C_5H_4Me$) led to a Schrock-type hafnocene silylene complex [377].

One of the peculiarities of the dehydrogenating coupling reaction is that it was initially discovered for titanium but details of the σ-bond metathesis reaction steps were worked out for Zr and Hf. The reason that this had not been done for Ti was the difficulty to generate suitable precursor compounds such as $Cp_2Ti(Cl)Si(SiMe_3)_3$. Recent studies have shown that the Si–Ti bond is much weaker than the corresponding bonds to Zr and Hf [110]. As a consequence reductive elimination of silylated titanocenes is a facile process. The thus formed Ti(II) species can comproportionate with Ti(IV) to give Ti(III) compounds [109, 110] which seem to be the catalytically active compounds in the Ti catalyzed dehydrogenating coupling reaction. Based on this mechanistic insight it was possible to obtain titanaheterocyclosilanes with Ti(III). The paramagnetic Ti(III) center which is incorporated into a cyclosilane renders these compounds as heterocyclic analogs of cyclosilane radical anions [110].

Non-metallocene oligosilanylated group 4 compounds have received much less attention. Xue and coworkers have reacted Zr and Hf amides with silyl anions (including $(Me_3Si)_3SiLi$ and other oligosilanyl anions) to study ligand exchange processes [378–381]. Reaction of oligosilanyl anions with MCl_4 (M = Ti, Zr, Hf) in ethereal solvents leads to ether cleavage caused by the strong Lewis acidic character of the metal halides. Reaction in a non-coordinating solvent in the presence of TMEDA gave mono- or disilylated octahedral TMEDA metal adducts [382, 383]. Zr and Ti complexes containing a chelating triamido ligand with a tris (trimethylsilyl)silyl substituent were obtained by reaction of the respective chloride with $(Me_3Si)_3SiK$ [384]. An oligosilylated Hf imido complex was prepared by reaction of $(2,6\text{-}i\text{-}Pr_2C_6H_3)NHf(THF)_2Cl_2$ with $(Me_3Si)_3SiK$ [385]. A disilanyl zirconocene chloride was found to form in the course of an intramolecular C–H addition of an isopropyl group across the Si=Si double bond of a disilenyl zirconocene chloride (15) [386].

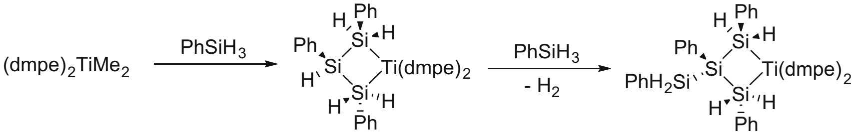
Equation 15. Intramolecular C–H bond addition to the Si=Si bond of a disilenyl complex.



In studies of the reaction of $TiMe_2(dmpe)_2$ with $PhSiH_3$ Girolami and coworkers could isolate two interesting oligosilane titanium complexes (Scheme 34) which can be considered as intermediates in a dehydrocoupling polymerization process [387].

8.2 Group 5

Much less activity is concerned with oligosilylated group 5 compounds. Xue and coworkers have studied the reactivity and exchange processes of silylated Ta amido complexes such as $(Me_2N)_4TaSi(SiMe_3)_3$ [379, 388]. The synthesis and rich reactivity of $Cp^*(2,6\text{-}i\text{-}Pr_2C_6H_3N)Ta(H)Si(SiMe_3)_3$ and related compounds was studied by Tilley and coworkers [389–391].



Scheme 34 Stepwise build-up of oligosilanyl titanium complexes

8.3 Group 6

Reaction of (2,6-*i*-$Pr_2C_6H_3N)_2MoCl_2(DME)$ with $LiNMe_2$ and $(Me_3Si)_3SiLi$ was reported to give the Mo imide amide silyl complex ((2,6-*i*-$Pr_2C_6H_3N)_2Mo(NMe_2)Si(SiMe_3)_3$ [392]. Reactions of a number of different oligosilanyl potassium compounds with group 6 metal hexacarbonyls or group 6 halogen pentacarbonyl metalates gave the corresponding oligosilylated pentacarbonyl metalate derivatives [155, 393]. In a related reaction, as part of their recent studies of oligosilanyl anions with pendant polydonor groups, Krempner and coworkers have obtained tungstenates by reaction with $W(CO)_6$ [106, 394]. Synthesis and reactivity of di- and trisilanylene-bridged *ansa* half-sandwich complexes of Mo and W was reported by Braunschweig and coworkers [395, 396].

8.4 Group 7

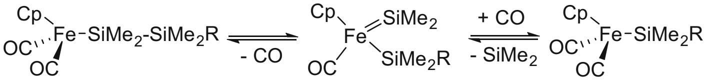
The reaction of $(Me_3Si)_3SiLi$ with $MnCl_2$ was found to give $[Li(THF)_3]\{Mn[Si(SiMe_3)_3]_2Cl\}$ [397] which after treatment with Me_3SiOTf gave the neutral complex $[Mn[Si(SiMe_3)_3]\cdot(THF)_2$ which exchanges THF as base easily [398].

8.5 Group 8

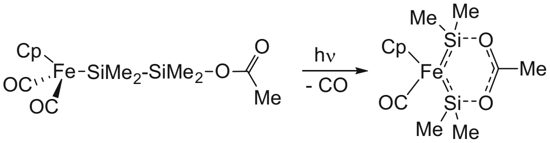
Oligosilanyl compounds of group 8 are a fairly well-studied class of compounds. In a series of papers Pannell and coworkers have continued their studies of the photochemistry of oligosilanyl Fp compounds [399–408]. The typical rearrangement behavior of these compounds involves formation of silyl silylene complexes followed by extrusion of a silylene (Scheme 35). The reversibility of these reactions can also cause rearrangements of the attached oligosilanyl groups.

Related work concerning base stabilized iron and ruthenium silyl silylene complexes was also carried out by Ogino, Tobita, and coworkers (Scheme 36) [409–411].

They could demonstrate the facile bromodemethylation of $Cp^*(CO)_2FeSiMe_2SiMe_3$ with BBr_3 selectively at the α-silicon atom to produce $Cp^*(CO)_2FeSiBrMeSiMe_3$, and subsequently to $Cp^*(CO)_2FeSiBr_2SiMe_3$ [412]. Similar activation had previously been observed by Malisch et al. in the reaction of $Cp^*(CO)_2FeSiH_2SiH_3$, which was chlorinated selectively in α-position [413].



Scheme 35 Oligosilyl-silyl/silylene iron complex rearrangement reaction



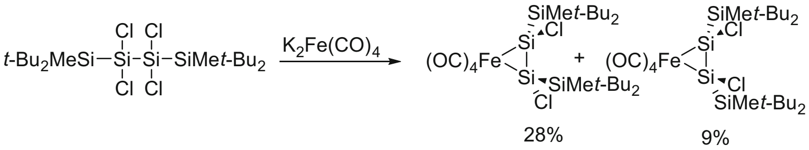
Scheme 36 Formation of a stabilized silyl/silylene iron complex

The electron transfer behavior from Fp and analogous Ru fragments via silanylene bridges was studied by Stüger and coworkers [414, 415]. In the course of these studies also the electrochemical formation of oligosilanyl Fp complexes was investigated [416].

In a similar way to $[Mn[Si(SiMe_3)_3]\cdot(THF)_2$, Tilley and coworkers prepared $[Fe[Si(SiMe_3)_3]\cdot(THF)$ [398]. Reaction of the anionic, tripodal phosphine ligand $[PhB(CH_2P\textit{i}\text{-}Pr_2)_3]^-$ with $FeBr_2$ and subsequently with $(Me_3Si)_3SiK$ provided a zwitterionic paramagnetic tris(trimethylsilyl)silyl iron complex [417]. In the context of the development of new hydrosilylation catalysts, formation of the Os complex $Cp^*(\textit{i}\text{-}Pr_3P)Os(H)(Br)SiH_2Si(SiMe_3)_3$ and related complexes was achieved by oxidative addition of H_3SiSiR_3 to $Cp^*(\textit{i}\text{-}Pr_3P)OsBr$ [418]. The related Ru complex $Cp^*(\textit{i}\text{-}Pr_3P)Ru(H)_2SiH(OTf)Si(SiMe_3)_3$ was formed starting from $Cp^*(\textit{i}\text{-}Pr_3P)RuOTf$ [419].

By reaction of a 2,2,3,3-tetrachlorotetrasilane with $K_2Fe(CO)_4$ Kira and coworkers obtained a mixture of two isomers, which represent the first examples of halogenated disilene transition metal complexes (16) [420].

Equation 16. Halogenated disilene iron complexes.

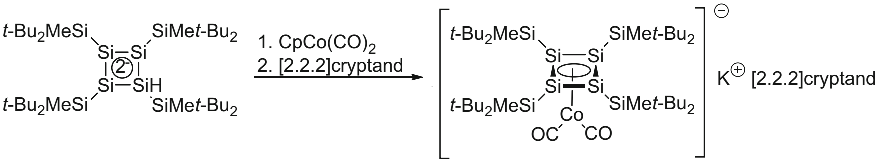


Although not strictly concerning oligosilanyl iron complexes with Si–Fe σ-bonds, the work of Sekiguchi and coworkers about silylated cyclotetrasiladienes and related ligands of iron and ruthenium should be mentioned here [100, 421–424].

8.6 Group 9

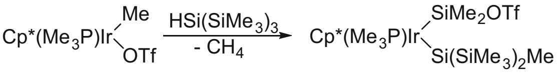
Sekiguchi's work concerning the use of silylated cyclotetrasiladienes and related ligands covered also several cobalt (17) and rhodium complexes [237, 422, 425]. Related work on a monosila cyclobutadiene complex was reported by Kira and coworkers [426].

Equation 17. Formation of a silylated cyclotetrasiladiene cobalt complex.



An interesting rearrangement reaction involving an oligosilanyl iridium complex was reported by Tilley [427]. Reaction of Cp*(Me$_3$P)Ir(Me)OTf with (Me$_3$Si)$_3$SiH gave a bissilylated iridium complex (18).

Equation 18. Formation of a stabilized silyl/silylene iridium complex.



8.7 Group 10

Several research groups made contributions to group 10 oligosilanyl chemistry. Some exciting work by Kira and coworkers studied coordinated tetrasilylated disilenes to platinum and palladium. These complexes were obtained by reaction of 1,2-oligosilanyl dianions with L$_2$MCl$_2$ (M = Pt, Pd). By careful choice of the phosphine ligand at Pd they showed that 16-electron complexes with two phosphine ligands are of the metallacyclopropane type whereas a 14-electron complex with one phosphine can be regarded as a π-complex (Fig. 5) [428–431]. Similar palladium complexes of disilenes with aryl, alkyl, and phosphinyl substituents were studied by Kira [432] and Scheschkewitz [433]. A related platinum silene complex was reported by Apeloig and coworkers as the product of the reaction of a stable silene with (Cy$_3$P)$_2$Pt (Fig. 5) [434].

Mochida and coworkers studied the oxidative addition and rearrangement chemistry of hydrogenated di- and trisilanes with Pt(0) complexes. Dinuclear platinum complexes with silylene or silanylene bridges were frequently formed in the course of these reactions (Scheme 37) [435–438].

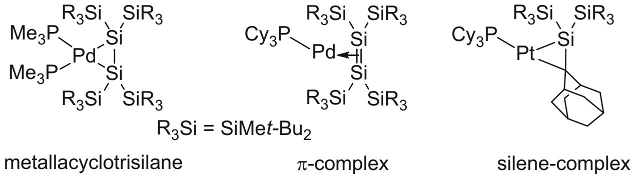
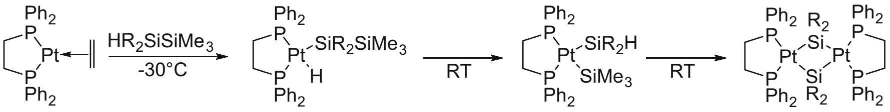


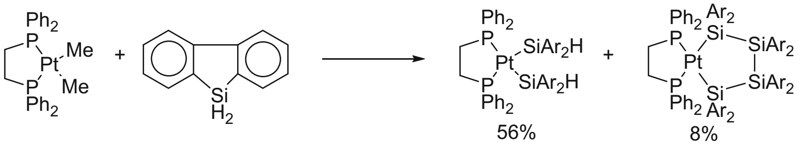
Fig. 5 Different types of silylated disilene and silene complexes of palladium and platinum



Scheme 37 Rearrangement of a disilanyl platinum complex to a disilyl complex and further to a dinuclear disilylene complex

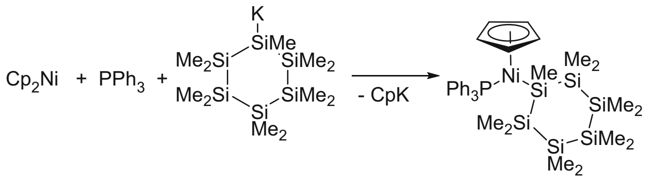
Reactions of 1,2-bishydrosilylated benzenes with Ni, Pd, and Pt were studied by the Tanaka [439–442] and Tessier [443] groups. In the course of the formation of dinuclear complexes ligand rearrangement with concurrent Si–Si bond formation was observed on several occasions. An interesting platinacyclopentasilane was obtained by Braddock-Wilking and coworkers by reaction of a dimethylplatinum complex with 9,9-dihydridosilafluorene (19) [444].

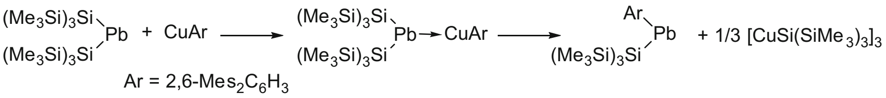
Equation 19. Formation of a platinacyclopentasilane.



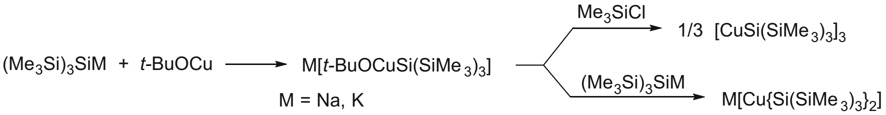
An undecamethylcyclohexasilanyl nickel complex was formed in the reaction of Cp_2Ni with undecamethylcyclohexasilanyl potassium (20) [445].

Equation 20. Formation of a cyclohexasilanyl nickel complex.





Scheme 38 Coordination of a disilylated plumbylene to copper



Scheme 39 Formation of oligosilanyl copper clusters and cuprates

8.8 Group 11

Despite the fact that silyl cuprates are an established area of research, not much is known about oligosilylated group 11 compounds. Recent results were reported almost exclusively by Klinkhammer and coworkers [446–449]. Trimeric tris(trimethylsilyl)silylcopper was obtained in a metathesis reaction of bis[tris(trimethylsilyl)silyl]lead and an arylcopper compound (Scheme 38) [446].

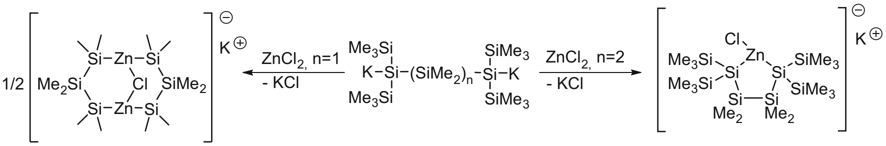
Reaction of $[CuSi(SiMe_3)_3]_3$ with $(Me_3Si)_3SiLi$ gave the cuprate $Li[\{(Me_3Si)_3Si\}_3Cu_2]$ [447]. The related mixed cuprates $M[t\text{-}BuOCuSi(SiMe_3)_3]$ were formed in the reaction of $(Me_3Si)_3SiM$ (M = Na, K, Cs) with *t*-BuOCu (Scheme 39) [448]. The mixed cuprates $M[t\text{-}BuOCuSi(SiMe_3)_3]$ (M = Na, K) served as a source for $M[\{(Me_3Si)_3Si\}_2Cu]$ and $[CuSi(SiMe_3)_3]_3$ by reaction with $(Me_3Si)_3SiM$ and Me_3SiCl, respectively (Scheme 39) [448].

Similar chemistry starting with AuI was also shown for gold with structures of $K[Au\{Si(SiMe_3)_3\}_2]$ and $K[Au_2\{Si(SiMe_3)_3\}_3]$ and some other interesting gold clusters [449].

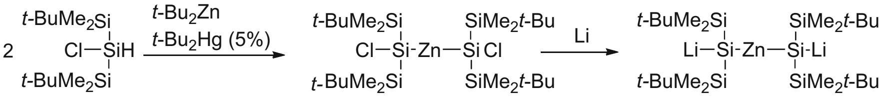
8.9 Group 12

While recent oligosilanyl zinc chemistry was studied by several research groups not much has been done with respect to cadmium. In contrast to this a large variety of oligosilanyl mercury compounds were studied almost exclusively by Apeloig and coworkers, who utilized the unique properties of Si–Hg compounds for the generation of silyl radicals or anions.

Using the bulky oligosilanylanion $(t\text{-}Bu_3Si)_2HSiNa$ reactions with $ZnCl_2$, CdI_2, and $HgCl_2$ gave the respective disilylated metal compounds [450]. Reaction of $(Me_3Si)_3SiK$ and more bulky oligosilanyl anions with $ZnCl_2$ gave the related disilylated compounds of the type $[R_3Si(Me_3Si)_2Si]_2Zn$ [157]. Reactions of sterically less demanding oligosilanyl anions such as $(Me_3Si)_2MeSiK$ were found to give zincates such as $K[\{(Me_3Si)_2MeSi\}_3Zn]$ [157, 451]. Reactions with



Scheme 40 Reaction of oligosilanyl dianions with $ZnCl_2$ to oligosilanyl zincates



Scheme 41 Reaction of silylhydrochloride with t-Bu_2Zn to dioligosilanyl zinc compounds

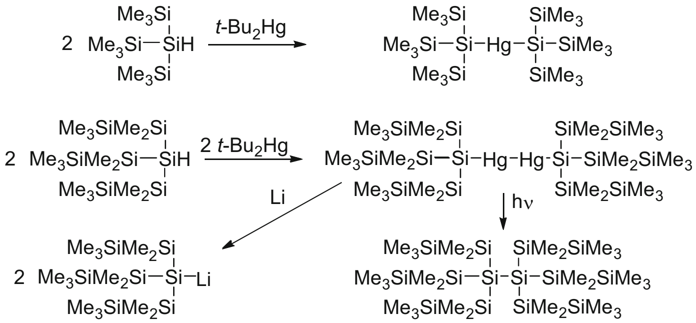
oligosilanyl dianions were also shown to give zincates either with halides or ether molecules as bases (Scheme 40) [155, 157]. Zincate formation was also observed in the reaction of $R(Me_3Si)_2SiLi$ (R = $SiMe_3$, Ph) with $ZnCl_2$ giving $R(Me_3Si)_2SiZn$ (THF)Cl which is dimeric in the solid state. Zn atoms are bridged by chlorides and are tetrahedrally coordinated by an additional THF molecule [452].

In recent work on oligosilanyl anions with pendant polydonor groups Krempner and coworkers showed that reaction of $[Si(SiMe_2OCH_2CH_2OMe)_3M]$ (M = Li, K) with $ZnCl_2$, ZnI_2, and $ZnMe_2$ gave the respective zincates with no substitution or salt elimination occurring [453]. Only recently Apeloig and coworkers reported that reactions of silylhydrides such as $(Me_3Si)_3SiH$ with *t*-Bu_2Zn represent an interesting synthetic alternative to the use of silyl anions [454]. The reaction most likely follows a radical mechanism and can even be used for the preparation of halogen substituted zinc silyls, which can further be converted to geminal heterodimetalated oligosilanes (Scheme 41) [454].

Oligosilanyl mercury compounds are a well known group of compounds. The reason for this is not that these compounds are very easy to prepare. In fact they are synthetically challenging and quite sensitive. The Si–Hg bond is, however, unique and provides access to a number of highly interesting reactive species. In particular radicals can be obtained by homolytic cleavage of the Si–Hg bond and also metalated silanes can be prepared, for instance, by reaction with lithium. The elaboration of this highly useful chemistry is closely associated with the names Apeloig and Bravo-Zhivotovskii [454–464].

The preparation of silyl mercury compounds can be achieved in a straightforward way by reaction of silyl hydrides with *t*-Bu_2Hg. Its photolysis gives the corresponding radical [465], while reaction with lithium leads to the corresponding lithium silyls. In an attempt to subject a very bulky silyhydride to the reaction it was shown that in cases where the silanyl group is too bulky to allow one mercury atom to bind to both fragments, these will be bridged by two mercury atoms (Scheme 42).

The Apeloig group's most exciting work with silyl mercurials is associated with functionalized silyl anions and will thus be treated in the respective chapter about this class of compounds.



Scheme 42 Formation and derivatization of oligosilanyl mercury compounds

8.10 Rare Earths and Lanthanides

While the chemistry of rare earths and lanthanides with silylated alkyl complexes is a fairly well-investigated field results about silylated examples are scarce. The few reports concerning oligosilylated compounds so far originate mainly from Tilley's group [466–473]. The most recent example concerns scandium chemistry and the formation of $Cp^*{}_2ScSi(SiMe_3)_3$ (21), which was found to be a catalyst precursor for catalytic processes of the dehydrogenative silylation of hydrocarbons (including methane, isobutene, and cyclopropane) with Ph_2SiH_2 via σ-bond metathesis [473].

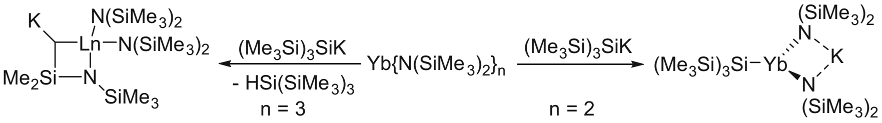
Equation 21. Metathesis reaction of a scandium methyl complex to an oligosilanyl complex.

$$Cp^*{}_2ScMe \;+\; HSi(SiMe_3)_3 \xrightarrow[\text{- CH}_4]{} Cp^*{}_2ScSi(SiMe_3)_3$$

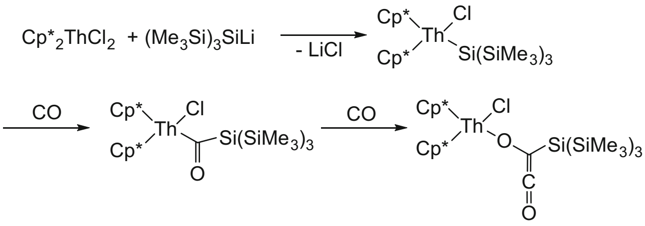
Niemeyer studied the reactions of Y and Yb amides with $(Me_3Si)_3SiK$ [474]. While a silylated Yb complex could be obtained from $Yb\{N(SiMe_3)_2\}_2$, reaction of $Ln\{N(SiMe_3)_2\}_3$ (Ln = Y, Yb) with $(Me_3Si)_3SiK$ led to deprotonation of a methyl group (Scheme 43).

8.11 Actinides

As for actinide silyl complexes in general not much is known about oligosilanyl actinide complexes. Only three examples at all have been reported so far. The groups of Marks [475] and Cummins [476] showed that reactions of uranium (IV) halides with $(Me_3Si)_3SiLi$ give the respective tris(trimethylsilyl)silylated complexes (22).

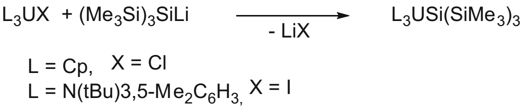


Scheme 43 Reactions of ytterbium amides with tris(trimethylsilyl)silyl potassium



Scheme 44 Formation and derivatization of a tris(trimethylsilyl)silylated thorium complex

Equation 22. Formation of oligosilanyl actinide complexes.



$$L_3UX + (Me_3Si)_3SiLi \xrightarrow[-\,LiX]{} L_3USi(SiMe_3)_3$$

$L = Cp,\ X = Cl$

$L = N(tBu)3{,}5\text{-}Me_2C_6H_3,\ X = I$

In a similar way Tilley and coworkers [477] obtained $Cp^*{}_2Th(Cl)Si(SiMe_3)_3$ from $Cp^*{}_2ThCl_2$ and $(Me_3Si)_3SiLi$. The complex was not stable but could be trapped with CO, which twice inserted into the Th–ligand bond to give a metalloxy ketene complex, which was structurally characterized (Scheme 44).

9 Summary, Conclusions, Outlook

The systematic study of oligosilanes has started in the 1960s and since then the field has experienced a remarkable development. While the first years of investigation were very much dedicated to the synthesis and study of non-functionalized oligosilanes with a major attention to structural variety, the last some 20 years have shown a trend to the synthesis of oligosilanes with a variety of functional groups. This includes not only compounds with organic groups or heteroatoms attached to the oligosilanyl moiety but also functionality unique to silicon such as silenes, disilenes, disilynes, silylenes, silyl cations and anions, silylenoids, and silyl radicals. Stable examples of all these compounds have been reported in the meantime. As for saturated oligosilanes also a much wider structural and functional variety has emerged. Many of these compounds were either prepared to serve as precursors for the generation of unsaturated compounds or formed in derivatization reactions of unsaturated compounds. The comparably huge number of compounds that we know today clearly shows that the field has become a mature area of research. The initial leitmotif to figure out whether silicon is capable to mimic all the bonding situations of carbon has made way to a deeper understanding of how unique silicon as an element is.

Currently a number of exciting developments in oligosilane chemistry are in progress. One of these is the chemistry of small silicon clusters. These compounds can be regarded as intermediates between ordinary oligosilane molecules and small pieces of elemental silicon. Other flourishing areas include compounds with conjugated Si–Si multiple bonds, compounds with Si–metal multiple bonds, silylenes as agents for small molecule activation, to name just a few.

Oligosilane chemistry has come a long way but my personal impression is that it has never been so exciting as today. There are marvelous developments to expect and I look forward to be participating in these.

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