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Homocyclic Silanes

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Contents

I. Preface

The last general review about cyclosilanes was written in the early 1980s. Before this time, older investigations have been repeatedly summarized.[1,2,3,4] In this review the results will be reported from that point on.

The content of this article will be organized by ring size. Results about three-membered rings and their reaction products are not included, a special article about this topic has been written by M. Weidenbruch in this issue.

First there is a general introduction of the properties of cyclosilanes as a function of the ring size where important properties like spectroscopic values are discussed. New results about large rings (>7) are included in this section.

The following section covers the theoretical aspects of cyclosilanes and the results of theoretical calculations. This part is written by R. Janoschek.

After these general surveys the formation and properties of four-, five- and six-membered rings are reported. A special section deals with rotanes. The last section summarizes the results on polycyclic silanes where particularly new and interesting results have been obtained in the last few years.

This article cannot cover all the details we hope the most important results are included. The large number of papers in this field only allows brief information. For detailed results the reader should refer to the original literature.

II. General Properties of Cyclosilanes

1. Introduction

Today cyclosilanes are well known but still very interesting compounds. The general behavior is different from their carbon analogs. In contrast to the latter cyclosilanes exhibit electron delocalization effects which are similar to aromatic organic rings.[5] However this similarity should be not overrated, because in the silicon case the corresponding properties can be interpreted by σ-delocalization rather than by a π-bonding system like in aromatic organic rings. Other unusual properties are the formation of charge-

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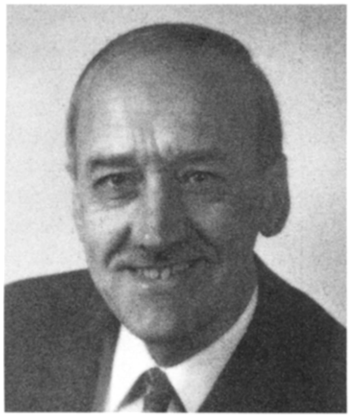
Edwin Hengge was born in Vienna. He received his Doctor degree in Chemistry from the Graz University of Technology in 1957. From 1957 to 1962 he was one of Professor Kautsky's assistants at the University of Marburg, Germany. His "Hablitiation" was in 1962. From 1964 to 1966 he was a Professor of Inorganic and Analytical Chemistry at the Technical University in Aachen, Germany. Since 1966 he has been a Full Professor and the head of the Institute of Inorganic Chemistry of the Graz University of Technology in Austria. He received many awards and is a member of several Academies of Science. His research work is focused on silicon chemistry, in particular on the chemistry of compounds with Si–Si bonds. Siloxene, high polymer polysilanes, and cyclosilanes are his major points of interest. He has published more than 200 publications in this field.



Rudolf Janoschek received his Doctor degree in theoretical physics from the Justus-Liebig-University at Giessen in 1967. He was Assistant at the Institute of Biochemistry, University of Giessen, scientific co-worker at the Max-Planck-Institute of Astrophysics, München, and Assistant at the Institute for theoretical chemistry, University of Stuttgart. Since 1978 he has been a Professor of Theoretical Chemistry and head of the Institute for Theoretical Chemistry, Karl-Franzens-University of Graz, Austria. His research work and continuing interests are in theoretical chemistry as well as in quantum chemical calculations of molecular properties. Among other topics he is author of more than 20 publications on silicon compounds. In 1994 he was a guest editor of the *Journal of Molecular Structure (Theochem)* with a special issue on "Recent Advances in Computational Silicon Chemistry".

transfer complexes and electronically delocalized anion and cation radicals. These delocalization effects are particularly evident in four-, five-, and six-membered rings. In larger rings these effects become smaller and the properties are more similar to long silicon chains. The three-membered ring has a very high ring strain and is stable only with large and bulky substituents. A review of three-membered rings can be found in the article by Weidenbruch in this issue.

Table 1. Sum of Cartledge Parameters E_s(Si): Values for Two Substituents on Silicon and Ring Size in Cyclopolysilanes

Substituents			
R^1	R^2	ring size	ΣE_s(Si)
Me	Me	7	0.00
Me	Me	6	0.00
Pr	Me	6	−0.216
i-Bu	*i*-Bu	5	−0.810
i-Pr	Me	5	−0.556
i-Pr	Me	5	−0.556
Et	Et	5	−0.298
i-Bu	Me	5	−0.405
Pr	Pr	5	−0.432
Bu	Bu	5	−0.450
i-Pr	*i*-Pr	4	−1.112
Me	*t*-Bu	4 (all-trans)	−1.46
i-Pr	*t*-Bu	4	−2.016
c-C$_6$H$_{11}$	*t*-Bu	4	−2.48
Pr	*t*-Bu	4	−1.676
i-Pr	*t*-Bu	3	−2.016
c-C$_6$H$_{11}$	*t*-Bu	3	−2.48
t-Bu	*t*-Bu	3	−2.92

2. General Properties as a Function of the Ring Sizes

Some studies were carried out investigating the influence of the bulk of substituents on ring strain, size, and stability. A set of parameters E_s(Si) defined for alkyl groups from rates of acid-catalyzed hydrolysis of SiH compounds was found by Cartledge[6] to be quite useful for the interpretation of steric effects in a wide range of reactions taking place at Si. These steric parameters are also useful to estimate the preferred ring size as a function of the substituents. Some calculated parameters for cyclosilanes with different ring sizes are given in Table 1.[101,7,8]

Generally large substituents favor the formation of small rings, small substituents favor the formation of larger rings, especially five- and six-membered rings. Weidenbruch[100] has shown, however, these parameters sometimes cannot be applied without difficulties.

Smaller rings with high ring strain are more reactive. This was visualized, for example, by the ring-opening reaction with iodine, where the rate constants were measured and the activation parameters were calculated. The measured values are listed in Table 2. As demonstrated in this table, the oxidation potentials and the longest wavelength UV absorptions of cyclopolysilanes also strongly depend on the ring size.[9]

Sometimes the formation of particular cyclosilanes is kinetically preferred followed by later rearrangements forming the thermodynamically most stable ring (also compare older reviews). The equilibria among the cyclic compounds $(\mathrm{SiMe_2})_n$ with $n = 5$, 6, and 7 were studied between 30 and 58 °C. The measured enthalpies indicate that the stabilities of the rings increase in the order $(\mathrm{Me_2\ Si})_5 < (\mathrm{Me_2\ Si})_7 < (\mathrm{Me_2\ Si})_6$. The values for the redistribution reactions between pairs of compounds are as follows: $n = 5{-}6$, $\Delta H = -18$kcal/mol, $\Delta S = -20$ cal/(deg mol); $n = 7{-}6$, $\Delta H = -3$, $\Delta S = +33$; $n = 7{-}5$, $\Delta H = +18$, $\Delta S = +51$.[10]

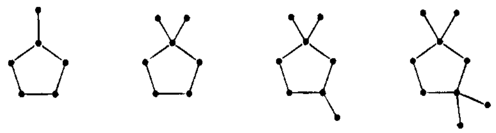
Rearrangements also occur during mass spectroscopic investigations. It is remarkable that the mass fragmentations for the permethylated cyclosilanes

Table 2. Activation Parameters for the Ring-Opening Reactions and Values of Oxidation Potential (E_{pa}) and Longest Absorption Wavelength (λ_{max}) for the Cyclopolysilanes

compound	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}_{293}$, cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{293}$, kcal mol^{-1}	E_{pa},[a] V vs SCE	λ_{max},[b] nm
$[(t\text{-BuCH}_2)_2\text{Si}]_3$	c	c	c	+0.44	310sh
$[t\text{-BuMeSi}]_4$	5.29	−34.6	16.1	+0.94	300
$[t\text{-Pr}_2\text{Si}]_4$	6.56	−38.9	16.1	+1.00	290sh
$[sec\text{-Bu}_2\text{Si}]_4$	6.00	−39.3	16.9	+1.10	290sh
$[n\text{-Bu}_2\text{Si}]_5$	7.49	−37.4	17.9	+1.40	262
$[n\text{-Pr}_2\text{Si}]_5$	7.69	−37.2	18.0	+1.42	260
$[\text{Me}_2\text{Si}]_6$	10.0	−33.2	19.1	+1.45	258sh
$\text{Me}_3\text{SiSiMe}_3$	9.94	−36.8	20.1		193.5

[a] The first anodic peak potential in MeCN; see ref 47. [b] The longest wavelength absorption band in cyclohexane; see ref 8. [c] Not determined.

Scheme 1[a]



[a] ● = SiMe_{3-n}, n = 0, 1, 2.

$(\text{SiMe}_2)_n$ with n = 6−9 and for the silylsubstituted cyclopentasilanes (Scheme 1) with the same number of Si atoms are identical.

Evidently the mass spectra of isomeric branched and unbranched cyclosilanes arise from the same initially formed cation radical species. In most cases the base peak was SiMe_3^+. With unbranched cyclosilanes an unexpected rapid methyl migration and a skeletal rearrangement seems to take place.[11] Similar reactions are also well known in solution under the catalytic influence of metal halides.[12]

Large rings (n = >7) were generated mainly with small alkyl substituents like methyl or ethyl groups. West et al. isolated permethylcyclopolysilanes up to 35 SiMe_2 units, which were formed, when dimethyldichlorosilane was added dropwise to Na/K alloy in THF very slowly. The large rings were isolated by HPLC; the yield was very small (<1%). Detailed investigations about NMR, UV, and IR/Raman spectroscopical properties were done up to a ring size of $(\text{SiMe}_2)_{24}$.[12]

With ethyl groups the largest observed ring size was eight. The best yield of 6% was obtained in the reaction of Et_2SiCl_2 with 2 equiv of Li at 0 °C in THF.[13,14] Similar results were obtained, when MeEtSiCl_2 was reacted under the same conditions.[15]

The Si−Si bond distances in cyclosilanes exhibit quite normal values between 234 and 239 pm. Only very strained rings like three-membered rings showed longer distances up to 240 pm. Si−Si bond distances are listed in ref 16.

3. UV and Visible Spectra

Many papers dealing with the synthesis of cyclosilanes also include measurements of the UV or visible spectra. The corresponding data are summarized for permethylpolysilanes in ref 5, for perethylpolysilanes in ref 13 and for cyclosilanes with different substituents in refs 8 and 17. An unexpected hypsochromic shift was observed with increasing ring size. The longest wavelength absorption was found for the four-membered rings. As the ring size increases the absorption bands shift to higher energy. However, at n = 6 for the perethyl or for n = 7 for the permethyl compounds, the hypsochromic shift was reversed. Now with larger ring sizes, a bathochromic shift was observed. This is in accordance with properties of linear polysilanes, where bathochromic shifts appear with increasing chain length.

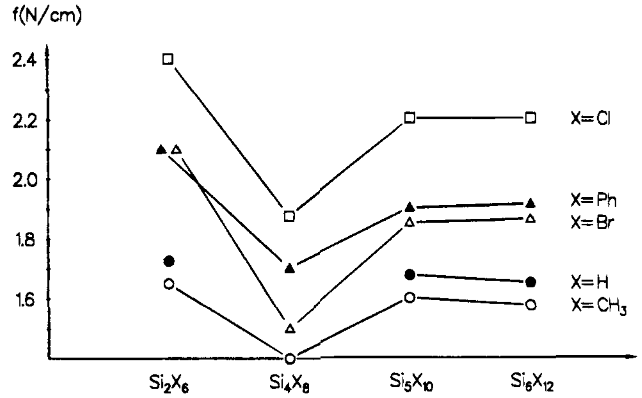


Figure 1. Si−Si Force constants of several cyclosilane derivatives.

In addition to the ring size the nature of the substituents attached to the cyclopolysilane frameworks strongly affects their UV/vis spectroscopic properties. Thus, compared to their permethyl analogs, perhalocyclopolysilanes show additional low intensity absorption bands with low absorption energies.[18] Due to these bands several perhalocyclopolysilanes even exhibit colors. The largest bathochromic shift was caused by the introduction of iodine substituents followed by bromine and chlorine. Theoretical HOMO−LUMO studies suggest that intramolecular charge transfer might be responsible for the unusual low energy of the corresponding electron transitions.[19]

4. Vibrational Spectra and Force Constants Calculations

Many IR and Raman spectra were measured to characterize the compounds. For special frequencies see the original literature. Force constants of the Si−Si bond were calculated for the halogenated cyclosilanes $(\text{SiX}_2)_n$ with n = 4, 5, and 6 and X = Cl, Br, and I,[20−22] for the hydrogenated cyclosilanes, Si_5H_{10}[23] and Si_6H_{12},[24] for the methylated cyclosilanes (including deuterated derivatives),[25] and for the perphenylated cyclosilanes (n = 4, 5, and 6).[26] The results are summarized in Figure 1.

Chlorine and phenyl substituents increased the Si−Si force constants; methyl and H gave rise to small force constants. In the four-membered ring the Si−Si force constant was lower (longer Si−Si distance, strained ring) than in the nearly unstrained five- and six-membered rings. In comparison to the force constants of disilane derivatives all values are lower.

The force constants were used for the parametrization of empirical force fields describing the structures and conformation energies of cyclosilanes.[27,28]

5. NMR Investigations

Since ^{29}Si NMR has become a routine technique in the last couple of years it turned out to be a highly valuable spectroscopic tool in organosilicon chemistry. Several characteristics, making NMR measurements of this nucleus difficult, however, require special techniques to increase the intensity of ^{29}Si signals.

For silicon nuclei directly coupled to protons, the sensitivity can be improved by polarization transfer techniques like INEPT (insensitive nuclei enhanced by polarization transfer) and DEPT (distorsionless enhancement by polarization transfer). Both of these pulse sequences and their variations transfer nuclear spin polarization from protons, which have high NMR sensitivity, to other nuclei (^{29}Si) to which the protons are coupled, so that the signal strength is increased significantly.

Since 1988 the application of ^{29}Si-double quantum coherence spectroscopy (INADEQUATE), sometimes combined with polarization transfer techniques (INEPT−INADEQUATE), provides an alternative way to determine the structure of larger polysilanes, using values of $^{29}Si-^{29}Si$ coupling constants for chemical shift assignment.[29−32,99]

Due to the large number of chemical shift values and coupling constants of cyclosilanes appearing in the literature, it is impossible to summarize all these values in this review. Except for some special results, which should be mentioned in this article, the reader must be referred to the original literature.

Permethylated cyclic polysilanes were studied in detail by ^{1}H, ^{13}C, and ^{29}Si spectroscopy. The linear relationship of the ^{29}Si shifts to the ^{13}C shifts of the carbon atoms attached to silicon, which was observed in linear permethylsilanes, did not hold for cyclosilanes. The agreement was good for large rings like $(SiMe_2)_8$ but became poorer for smaller ring sizes. Ring currents due to σ delocalization have been suggested as a possible source of an additional deshielding effect of the ^{29}Si nuclei, especially in $(SiMe_2)_5$ and $(SiMe_2)_6$. The proton-coupled ^{29}Si spectra of cyclosilanes $(SiMe_2)_n$, $n = 5-7$, are unexpectedly simple, because the ratio between the two proton−silicon spin coupling constants is close to 2/1. The spectral lines therefore all appear at multiples of the smaller coupling $^{3}J(SiH)$.[33]

The relative electron release of some cyclosilanyl groups toward the benzene ring in cyclosilanylbenzenes were calculated as σ^+ constants from ^{13}C shifts. The σ^+ constants decrease going from Me_3Si-Ph (+0.04) to $Si_6Me_{11}-Ph$ (−0.05), and Si_5Me_9-Ph (−0.07), confirming the cyclosilanyl groups to be more electron donating to benzene than Me_3Si.[34]

The first solid-state ^{29}Si and ^{13}C NMR experiments (high-power decoupling, cross polarization, and magic-angle rotation) of $(SiPh_2)_n$, $n = 4$, 5, and Si_2Ph_6 were done in 1985. The spectra revealed crystallographic inequivalences for $(SiPh_2)_5$ but not for the four-membered ring and the disilane derivative.[35] The spread of the shift tensor (called chemical shift anisotropy = CSA) provides information about the geometrical electron distribution. Tensor components are achieved by solid-state NMR. A large spread of shift tensors indicates deshielding, which might be caused besides other reasons by the low-energy difference in the transition $\sigma-\pi^*$ orbitals (HOMO's increasing, LUMO's decreasing). For instance, in double-bonded systems (C = C, Si = Si), a high value (179−140 ppm) is found.

Table 3. CSA Values of Several Cyclosilanes

$(SiMe_2)_6$	23
$[Si(CH_2)_5]_6$	35
$[Si(CH_2)_5)]_5$	52
$[(n\text{-}Pr)_2]_5$	54
$(Si\ t\text{-}BuMe)_4$	99
$Si(t\text{-}Bu_2)_3$	190
$(SiMes_2)_3$	199,217

In silicon ring systems the CSA increased with decreasing ring size. ^{29}Si CSA values for some cyclosilanes are listed in Table 3.[36,98] The ^{29}Si CSA of three-membered rings is about equal to that in disilenes. The large chemical shift anisotropies found for small silicon rings were not observed in the ^{13}C CSA for cyclic hydrocarbons, indicating that the chemical bonding must be quite different.

6. ESR Investigations

Many aryl- and alkyl-substituted cyclosilanes form radical anions. This behavior has been known since 1965.[37] The formation takes place by reduction with alkali metals or electrochemically. A summary of the older papers (until 1982) is given in ref 5. Since that time some new results have been obtained. The radical anion of the *all-trans*-1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane (see therefore also p 1503) turned out to be remarkably stable. This radical anion, formed by reaction with Na/K alloy is green-brown and stable for several days at room temperature and for several weeks at 0 °C. At 20 °C it showed a symmetrical well-resolved ESR spectrum with 30 lines, which only can be explained when interaction of the delocalized electron with the methyl and the *tert*-butyl groups is assumed. At low temperature (−50 to −70 °C) only a poorly resolved spectrum was obtained. The same was observed for the other isomers. After warming up, however, the spectra of all these isomers quickly changed to give the resolved spectrum of the *all-trans* isomer. In contrast to these results the corresponding radical anions of all isomers of the five-membered ring $(t\text{-}BuMeSi)_5$ are blue and only stable up to −50 °C. After warming up to 20 °C the color became green-brown and the ESR spectrum of the *all-trans* tetramer was observed.[38]

Many other peralkylcyclosilanes are able to form radical anions. In conclusion, the cyclopentasilanes produce blue anion radicals with only single values for α-^{13}C hfcs (hyperfine splitting constants), indicating that they are either planar or rapidly pseudorotating. Cyclotetrasilanes with small substituents like methyl or ethyl or the rotanes exhibit the same behavior. Cyclotetrasilane anions containing two bulky substituents like *sec*-Bu or *i*-Pr show two α-^{13}C hfcs and therefore appear to be bent and not rapidly interconverting (on the ESR time scale).[39,40] A detailed investigation was carried out for the radical anions of $(MeEtSi)_n$ with $n = 4$, 5, and 6.[15]

Considerations of hyperfine coupling constants (^{13}C and ^{29}Si) in the ESR spectra led to the conclusion that the singly occupied molecular orbital (SOMO) is a linear combination of Si–C σ^* and symmetry-adapted Si–Si σ^* hybrid orbitals. The unpaired electron is fully delocalized over the ring. As a result of this calculation, the odd electron density seems to be delocalized from the silicon ring to carbon and the total 2s odd electron density will increase. In case of the radical anion of perphenylcyclotetrasilane[41] odd electron delocalization onto the phenyl groups takes place. The major importance of the presence of alkyl- or aryl groups could explain why it was not possible to form a radical anion from the unsubstituted cyclosilane Si_5H_{10}.[42]

Investigation of the bis(nonamethylcyclopentasilanyl) anion radical afforded the unexpected result that the electron density of the odd electron is localized mainly in one ring although the Si–Si σ^* mixing should lead to a delocalization of the SOMO over both rings.[43]

The absorption spectra of the radical anions of cyclic polysilanes ($n = 5$, 6, and 7) formed by γ-irradiation have been recorded for rigid matrices at 77 K. A red shift was observed from 670 to 900 nm with increasing ring size. Single peaks were observed for $n = 5$ and 7, for $n = 6$ two bands occurred.[44]

A first natural abundance ^{29}Si ENDOR investigation was done with silicon-centered radicals. The results can be summarized as follows: small hyperfine anisotropies and quadrupole interactions in the case of nuclei with $I \geq 1$, large isotropic hyperfine couplings and the presence of several equivalent nuclei. The relaxation behavior of the ^{29}Si nuclei in the cyclosilanes allows the conclusion that the spin distribution around the silicon nuclei is nearly symmetrical. Investigated were $(t\text{-BuMeSi})_4$, $(Me_2Si)_5$, and $(Et_2Si)_5$.[45]

For an anion of the six-membered ring $(Si_6Me_{11}:)^-$ which is not a radical see p 1516.

7. Electrochemical Investigations

Recently, the oxidation potentials for a series of cyclosilanes were determined by cyclic voltammetry.[46,47] The study, recorded using CH_3CN and/or CH_2Cl_2 as solvent and tetrafluoroborate salts as electrolyte, showed that these compounds all exhibit at least two anodic waves which are separated by 0.2–0.4 V. Even at high scan rates a corresponding cathodic peak could not be observed. The results suggest an ECE mechanism where an electrochemical step is followed by a chemical reaction to form a new product which undergoes an electrochemical step again. In this case, after initial oxidation a cyclosilane cation radical is formed. Subsequently rapid Si–Si bond cleavage takes place followed by hydrogen or halogen abstraction to give secondary species which undergo further oxidation.

The initial oxidation potentials for the cyclosilanes depend mostly upon ring size but also on the nature of substituents on silicon. They increase going from three- to four- or higher-membered rings. In the dimethyl and diethyl series there is very little difference between the potentials of five-, six-, and seven-membered rings but in the two rotane series $[(CH_2)_{4\text{ or }5}Si]_n$ the five-membered rings are oxidized at lower potentials than their six-membered analogs. However, permethylcyclosilanes $(Me_2Si)_n$ with $n = 3$–9 exhibit significantly higher potentials than for $n > 9$.

The anodic peak potentials are well correlated with the lowest transition energies which similarly increase with increasing ring size from $n = 3$ to $n = 6$, and then decrease above $n = 9$. The determined ionization potentials also correspond with the values of the first oxidation. Si_5 and Si_6 rings show, for instance, higher ionization potentials than cyclotetrasilanes.

Since cyclopolysilanes exhibit similar properties as aromatic hydrocarbons, it is reasonable to compare their oxidation potentials with those of aromatic compounds. Electrochemical investigations on equal terms to the studies on the silanes indicated that irreversible oxidation also occurs at these species.

III. Theoretical Aspects

1. Introduction

The scope of this short section is the presentation of our recent theoretical knowledge on homocyclic silicon compounds. The basis of this review is the corresponding literature of the last two decades. Since the great success of synthetic chemistry in this field, described in this article by E. Hengge, the question for the sense of theoretical studies on silicon ring compounds is put forward. A 2-fold answer can be given to this question. On the one hand, we wish to increase not only the number of synthesized compounds, but also the understanding of their properties such as molecular structure, spectroscopy, and isomerism, which can be accomplished by means of computational methods. On the other hand, theory is not limited to the field of synthesized compounds, and therefore, computational chemistry can be successful sometimes prior to synthesis. Only one example should be mentioned. Hexasilaprismane was calculated, in 1985, to be the most stable Si_6H_6 isomer. Unfortunately, this result was in conflict with the usual belief so that publication was late in coming (1986).[85,88] In 1993, the first synthesized Si_6R_6 compound was described, and the X-ray structure of the silicon skeleton was found to be in almost perfect agreement with that of the former calculation.

In the following, numerous theoretical studies on silicon ring compounds will show how theory has formed our thoughts on these species.

2. Monocyclic Silicon Hydrides

Numerous computational treatments of small monocyclic silicon hydrides $(SiH_2)_n$, $n = 3$ and 4, can be found in the literature.[48–58] Although the parent three- and four-membered rings are still unknown, the results of interest for this series are molecular structures, harmonic vibrational frequencies, ring strain energies, as well as electronic transition energies and ionization potentials. Ab initio Hartree–Fock (HF) and also pseudopotential calculations with split valence basis sets, augmented by polarization functions (d-like functions on silicon), have been performed throughout so that the results of different authors are, as expected, in almost perfect agreement. The four-membered ring is folded with an angle of 148.8°. The barrier to planarity (D_{4h} symmetry) is found to be 0.74 kcal mol^{-1} at the HF level of theory, but electron correlation corrections (CISD

Table 4. Calculated Ring Strain Energies $E(X)$ (kcal mol^{-1}) per Strained Angle in Carbon and Silicon n-membered Ring Compounds $(XH_2)_n$ using the Homodesmic Reaction[a]

n	6	5	4	3	2
α	0	1.5	19.5	49.5	109.5
E(C)	0	1	7	10	5
E(Si)	0	1	4	12	38

[a] The angle α is the deviation of the angle between the straight atomic connection lines from the unstrained tetrahedral angle (109.5°).[55,56]

+ Davidson correction) increase the barrier to 1.75 kcal mol^{-1}.[53] A second-order saddlepoint on the energy hypersurface has been located for cyclopentasilane in D_{5h} symmetry, but the two predicted minima with C_2 and C_s symmetry have not been realized.[53] A recent ab initio MP2/6-31G* study[59] on the conformations of cyclohexasilane and their interconversion excellently confirmed molecular mechanics calculations of the older literature.[60] Molecular mechanics in the framework of MM2 force fields is still in use for structures and heats of formation of cyclic polysilanes.[61]

The most frequently discussed properties of these silicon rings are the ring strain energies defined as enthalpies of the corresponding homodesmic reactions

$$(SiH_2)_n + nSi_2H_6 \rightarrow nSi_3H_8$$

Surprisingly, cyclotrisilane has 10 kcal mol^{-1} more strain energy, and cyclotetrasilane has 10 kcal mol^{-1} less strain energy than the corresponding analogous hydrocarbon rings.[49-56,58,62] This contrasting behavior of carbon and silicon rings can be understood if, according to Baeyer, the series of strained ring compounds starts with the "two-membered" ring, i.e. $n = 2$ in the above equation.[55,56] In Table 4 the strain energy per strained angle is a function of the deviation from the unstrained angle (109.47°). Then, it becomes apparent that rehybridization in the C–H bonds in the direction $sp^3 \rightarrow sp^2$ increases the stability of small cyclic carbon compounds in contrast to the silicon analogs. In addition, the high/low π-bond strength in ethene/disilene is synonymous for low/high ring strain energy. Thus, Baeyer's theory of ring strain is only valid for the case of cyclopolysilanes. When the calculation of strain energies of cyclopolysilanes came up, it was already known that silicon is unwilling to hybridize,[63a] in contrast to carbon, due to its larger difference between the 3s and 3p orbital radii and its larger atomic size. At the same time the reluctance to form hybrids has been described generally for higher main group elements.[63b] Later, differences of X–H hybridization were commonly accepted as the key for understanding different ring strain energies for cyclopolysilanes and their carbon analogs. Consequences for the interpretation of structures of polycyclic compounds will be presented later. A more-refined analysis of ring strain energy distinguishes between different contributions from X–H bond repulsion, 1,3-repulsion, (in four-membered rings), angle strain, and X–H rehybridization.[50,53-56]

The assignment of PE and UV spectra of cyclic silicon hydrides $(SiH_2)_n$, $n = 5$ and 6, has been performed by means of ab initio calculations.[64,65] In addition, the hypothetic four-membered ring has been investigated in order to discuss trends with respect to ring size. Vertical ionization potentials as well as vertical electronic transition energies have been treated at a common level of theory applying Koopmans' theorem. Compared to linear polysilanes, cyclic polysilanes exhibit some interesting features (Table 5). The first ionization potentials as well as the lowest excitation energies increase with increasing ring size. The character of the HOMO's is σ(Si–Si)3p throughout. The excited states of the electronic transitions can be described by means of diffuse orbitals of the type σ^*(Si–Si)4s, 4p.

Table 5. Ab Initio Calculated Lowest Koopmans' Theorem Transition ΔE and Ionization Energies IP (eV) for Cyclopolysilanes $(SiH_2)_n$, $n = 4-6$[a]

	$(SiH_2)_4$	$(SiH_2)_5$	$(SiH_2)_6$
symmetry	D_{4h}	C_s	D_{3d}
ΔE	5.8	5.9 (5.7)	6.65 (6.36)
		6.3 (6.2)	
IP	8.9	9.1 (9.4)	9.4 (9.6)
	9.5	9.4	9.5

[a] Basis Set STO-3G + (s,p).[64]

Table 6. Calculated $\Delta H°$ (298 K) Values (kcal mol^{-1}) for H and H_2 (1,2) Abstraction and Si–Si Bond Dissociation in Cyclotrisilane Compared to Di- and Trisilane[68]

	abstraction		dissociation
	H	H_2(1,2)	Si–Si
Si_2H_6	89.4	48.0	76.5
Si_3H_8	86.3	44.0	74.6
Si_3H_6	83.2	44.2	26.3

The structures and stabilities of the cyclotrisilane radical cation $(Si_3H_6^+)$ and the corresponding dication $(Si_3H_6^{2+})$ have been investigated at the ab initio MP2/6-31G* level of theory.[66,67] The three-membered ring retains its triangular structure after the first ionization and is kinetically stable to fragmentation and ring opening, but the global minimum has an acyclic structure $(SiH_3SiH{=}SiH_2^+)$. Double ionization of the three-membered ring causes ring opening $(SiH_2^+SiH_2SiH_2^+)$.

Bond dissociation enthalpies for cyclotrisilane (Si_3H_6), together with a series of other small silicon hydrides, have been calculated by applying the pseudopotential MCSCF-CI procedure.[68] The comparison of calculated $\Delta H°$ (298 K) values of H and H_2 abstraction as well as Si–Si bond dissociation with well-known standard values sheds light to the bonding situation in the still hypothetic cyclotrisilane (Si_3H_6) (Table 6).

3. Monocyclic Substituted Polysilanes

The octamethylcyclotetrasilane molecule $(SiMe_2)_4$, has been investigated in order to study the effect of permethylation on the ionization and excitation energies.[64] The HOMO is destabilized by 2 eV with respect to the parent species $(SiH_2)_4$. The destabilizing interaction of the type $\pi^*[\sigma(Si{-}Si)3p{-}\sigma(CH)]$ is seen to be the reason for the effect. The bathochromic shift of the lowest electronic transition upon permethylation is calculated to be 1.2 eV (Table 7).

Ab initio PUHF studies on hyperfine coupling constants of the radical anion $(SiMe_2)_4^{\bullet-}$, have been

Table 7. Effect of Methylation on Ab Initio Calculated Koopmans' Theorem Transition ΔE and Ionization Energies IP (eV) (Experimental Values in Parentheses)[64]

	(SiH$_2$)$_4$	(SiMe$_2$)$_4$
ΔE	5.8	4.7 (4.0)
	5.9	4.9 (4.9)
	6.1	5.0 (5.4)
IP	8.9	6.9 (7.6)
	9.5	7.9 (8.1)

Table 8. Ab Initio PUHF/STO-3G+(s,p) Calculations of Hyperfine Coupling Constants of (SiMe$_2$)$_4$$^{\bullet-}$ Compared with ENDOR Experimental Results[69]

	(SiMe$_2$)$_4$$^{\bullet-}$		(SiMetBu)$_4$$^{\bullet-}$
	calcd	exp	exp
^{29}Si	+17.39		+15.15
^{13}C	+75.78	58.8	+59.07
^{1}H	−1.53	1.88	+1.45

Table 9. Semiempirical PM3 Calculations of the First Koopmans' Theorem Ionization Potentials IP (eV) of Perchlorocyclopolysilanes (Experimental Values in Parentheses)[19]

	(SiCl$_2$)$_4$	(SiCl$_2$)$_5$	(SiCl$_2$)$_6$
IP	8.85 (8.85)	9.19 (9.50)	8.98 (9.00)

performed in order to characterize the SOMO (singly occupied MO) as being composed of Rydberg-like functions σ*[π(Si−Si)4p−(C)2p].[69] This statement is based upon the useful agreement of the calculated hyperfine coupling constants with the results of ENDOR spectroscopy shown in Table 8.

A semiempirical PM3 study of perchlorocyclopolysilanes (SiCl$_2$)$_n$, $n = 4, 5$, and 6, revealed the increase of first ionization potentials near 9 eV in the order Si$_4$ < Si$_6$ < Si$_5$ (Table 9).[19] A bonding HOMO of the type σ(Si−Si)3p can be constructed only for an even number of silicon atoms in the ring. An odd number allows (Si)3s orbitals to contribute to the HOMO, which stabilizes the orbital compared to the HOMO's in the even-membered rings. The remarkably low UV absorption bands of 3−4 eV were discussed by means of the calculated HOMO−LUMO energy differences. These orbitals indicate intramolecular charge transfer from Cl to Si. The excitations are of the type π*[σ(Si−Si)3p−(Cl)3p] → σ*(Si−Si)4s.

In a series of papers the Hückel approach within the framework of the Sandorfy C formalism has been applied to cyclic permethylpolysilanes (Me$_2$Si)$_n$.[70−74] This procedure can be seen as the interpolation of experimental data from PE and UV spectra rather than a computational method. "Excellent agreement between calculated and experimental spectra" actually means for this case that the three-parameter Hückel results are properly adjusted to experimental values. The σ orbitals describing the Si−Si bonds in this model are composed of sp^3 hybrids on silicon. However, sp^3 hybrids on silicon are unrealistic and are in conflict with ab initio net atomic charges.[55,56] Moreover, ab initio calculations unequivocally have shown that excited states wave functions and photochemistry of saturated silicon compounds (and also carbon compounds) cannot be understood without the consideration of Rydberg states, i.e. the extension of the shell to 4s,4p on silicon has to be performed.[19,64,75] Silicon 4s,4p orbitals are located energetically far below the unrealistic valence σ* orbitals. Apart from the above critisicm of the meaning of adjusted results, the most discussed features of cyclic (Me$_2$Si)$_n$ compounds are summarized in the Tables 10 and 11. The data in Table 10 exhibit the stability of the six-membered ring with respect to redistribution.[70] In Table 11 the ionization potential for the five-membered ring is seen to be maximal with respect to ring size.[74]

Table 10. Adjusted (Hückel Approach) and Observed Enthalpies (kcal mol^{-1}) of Redistribution for Permethylcyclopolysilanes

	enthalpy	
redistribution	adjusted	observed
6(Me$_2$Si)$_5$ = 5(Me$_2$Si)$_6$	−16.8	−17.7
6(Me$_2$Si)$_7$ = 7(Me$_2$Si)$_6$	−16.3	−3.0
5(Me$_2$Si)$_7$ = 7(Me$_2$Si)$_5$	6.0	18.4

Table 11. Adjusted (Hückel Approach) and Observed Ionization Potentials IP (eV) and Electronic Excitation Energies ΔE (eV) for (Me$_2$Si)$_n$, n = 3−6[a]

n	3	4	5	6
IP adjusted	8.27	7.54	7.80	7.49
observed		7.60	7.94	7.79
ΔE adjusted	4.41	3.40	4.85	4.98
observed	3.99	4.08	4.51	4.51

[a] Different sets of Hückel parameters are used for ionization and excitation energies.

Conformational analysis of a series of branched cyclopentasilanes and cyclohexasilanes were performed by using the empirical force field method MM2.[61,76] In comparison with structurally similar isomers, the thermodynamically preferred isomer was usually calculated to have lower steric energy. Steric energies and equilibrium constants were used to estimate relative σ conjugation stabilizations for structurally different isomers.

4. Polycyclic Silicon Hydrides

The bicyclo[1.1.0]tetrasilane, Si$_4$H$_6$, has been a matter of controversy in the past. Two independent theoretical treatments afforded different "bond" lengths between the bridgehead atoms with 2.850[77] and 2.342 Å,[50] respectively. Additionally the reported total energy of the molecule is higher by 8.4 kcal mol^{-1} in the latter case. These inconsistent results finally could be explained by bond stretch isomerism.[78,79] This effect has been confirmed also at the GVB/3-21G* level of theory with the σ and σ* bridge bond molecular orbitals correlated in the GVB wave function.[80a] However, the energy barrier between these two structures was estimated as only 1 kcal mol^{-1} or less, so that the structure with the short bridge is not likely to be a viable isomer for Si$_4$H$_6$ itself. Indeed, it was found recently by means of pseudopotential MCSCF-CI calculations that this small barrier disappears at this level of theory.[80b] In contrast to bicyclo[1.1.0]tetrasilane, no bond stretch isomerism could be found in bicyclo[2.2.0]hexasilane, Si$_6$H$_{10}$, due to its low ring strain energy of 32.2 kcal mol^{-1}.[81] The radical cation, Si$_4$H$_6$$^+$, does not undergo bond stretch isomerism on the same energy hypersurface, unlike the case of the neutral Si$_4$H$_6$.[82] The Si−Si bridge bond does not lengthen upon ionization.

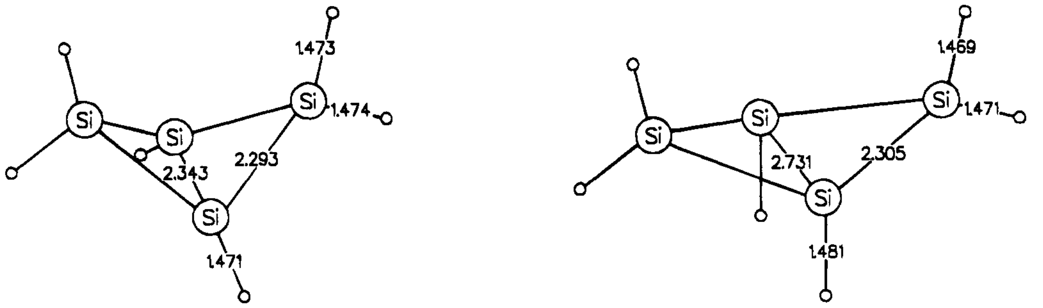


Figure 2. Two calculated bond stretch isomers of bicyclo[1.1.0]tetrasilane.[78]

Table 12. Ab Initio Calculated Strain Energies *E* (kcal mol^{-1}) of Cyclopolysilanes Obtained from Homodesmic Equations

compound		*E*	ref
cyclotrisilane	Si_3H_6	40.0	58
cyclotetrasilane	Si_4H_8	16.5	58
bicyclo[1.1.0]tetrasilane	Si_4H_6	69.7	58
bicyclo[2.2.0]hexasilane	Si_6H_{10}	32.7	81
pentasila[1.1.1]propellane	Si_5H_6	71.3	58
bicyclo[1.1.1]pentane	Si_5H_8	37.4	58
tetrasilatetrahedrane	Si_4H_4	140.9	84
hexasilaprismane	Si_6H_6	113.8	84
octasilacubane	Si_8H_8	93.5	84

The two cationic states $^2A_1$ and $^2A_2$ differ in their Si–Si bridge bond lengths of 2.777 and 2.228 Å, respectively, where the first state is more stable by about 18 kcal mol^{-1} at different correlated levels of theory (MP2/6-31G*). The occurrence of bond stretch ismerism for Si_4H_6 in earlier calculations has been explained by means of the very different ring strain energies of the three- and four-membered silicon rings (see Table 4). The four-membered ring diradical bond stretch isomer of Si_4H_6 experiences considerable strain relief in changing from the short to the long Si–Si bridge. This explanation can also be applied to the pentasila[1.1.1]propellane where a Si–Si bridge of 2.72 A has been calculated.[79,83] A comparison of calculated ring strain energies of polycyclic silicon hydrides supports the concept of bond stretch isomerism given above (Table 12).[58,84]

Interesting valence isomers of tetrasilatetrahedrane and hexasilaprismane are tetrasilacyclobutadiene and hexasilabenzene, respectively. The results of the first quantum chemical calculations (pseudopotential RHF) of the hypothetic Si_6H_6 system were presented in 1985.[85a] For hexasilabenzene the Si–Si bond length turned out to be 2.19 Å, and a "resonance" stabilization of 20.7 kcal mol^{-1} has been obtained from the homodesmic equation

$$3SiH_2SiHSiHSiH_2 \rightarrow Si_6H_6 + 3SiH_2SiH_2$$

π-Bond orders are extracted from the CI density matrix over localized molecular orbitals. These π-bond orders are nearly the same for C_6H_6 and Si_6H_6.[85b] As the most surprising result, the "aromatic" hexasilabenzene and the strained hexasilaprismane resulted to be almost isoenergetic, and the latter should be easier synthesized. Later the Si_6H_6 isomers were recalculated by other groups of authors.[86,87] The contrasting stabilities of carbon and silicon aromatic rings have been explained on the basis of hybridization.[55,56,88] The RHF/6-31G*-calculated harmonic vibrational frequencies indicate a transition structure for the planar (D_{6h} symmetry) Si_6H_6 which connects two isoenergetic chair-like structures (D_{3d} symmetry). At the MP2/6-31G*//RHF/6-31G* correlated level of theory the barrier to inversion of Si_6H_6 (D_{3d}) over the planar D_{6h} transition structure resulted to be 1.7 kcal mol^{-1}.[89] The hexasilabenzene-to-hexasilaprismane interconversion has been studied by means of the corresponding MP2/6-31G*//RHF/6-31G* calculated transition structure. The low barrier of 9.2 kcal mol^{-1} exhibits kinetic instability for the "aromatic" six-membered silicon ring.[90] At the correlated level of theory the zero point energy corrected relative energies of hexasilabenzene and hexasila-Dewar benzene are both 11 kcal mol^{-1}, referenced to hexasilaprismane.

Despite of several successful attempts of calculating tetrasilatetrahedrane Si_4H_4,[84,91-95] this utmost strained structure was finally found to be kinetically unstable.[93] The concept of bond stretch isomerism has been confirmed by calculations affording a puckered four-membered ring as the most stable valence isomer, 30 kcal mol^{-1} below tetrasilatetrahedrane.

Ab initio RHF/6-31G* calculations show that electropositive substituents such as silyl groups lead to the relief of strain energy in polycyclic silicon compounds. Persilyl substitution in tetrasilatetrahedrane, hexasilaprismane, and octasilacubane reduces ring strain energy by 26.4, 18.1, and 15.6 kcal mol^{-1}, respectively.[96]

The most stable structure of persilaspiropentane, $Si(SiH_2)_4$, is the twisted (distorted pyramidal) form, with the planar structure being higher in energy by 66.2 kcal mol^{-1} at the RHF/6-31G*//3-21G level.[97] Replacement of the central silicon atom by carbon lowers the resistance to twisting toward planarity by a factor of 2.

IV. Cyclotetrasilanes

1. Formation

The four-membered ring exhibits high ring strain compared to the five- and six-membered rings. In general the stability of such strained ring systems depends on the size of the substituents. Larger sizes increase the stability.

The usual route to form organic derivatives of cyclotetrasilane is the reductive elimination of halogen in dihalodialkyl(aryl)silanes by action of alkali metal. Yields strongly depend on the kind of alkali metal, the solvent, and the reaction conditions.

Investigations of the formation of the four-membered ring in comparison to other ring sizes show, that the thermodynamic stability of the small ring

Table 13. Cyclotetrasilanes with the Same Substituents on the Ring System

compound	ref(s)	compound	ref(s)
Si_4Ph_8	102	$Si_4(\textit{sec}\text{-}Bu)_8$	8
$Si_4\textit{p}\text{-}Tol_8$	103, 105	$Si_4(\textit{i}\text{-}Bu)_8$	8
Si_4Me_8	104, 117	Si_4Cl_8	110
Si_4Et_8	13, 14	Si_4Br_8	111
$Si_4\textit{i}\text{-}Pr_8$	7, 8, 106, 147	Si_4I_8	112
$Si_4(cyclohexyl)_8$	107	$Si_4(SiMe_3)_8$	113, 114
$Si_4(\textit{t}\text{-}BuCH_2)_8$	108	$Si_4(Me_2Et)_8$	114, 115
		$Si_4(CH_2SiMe_3)_8$	109, 147

is enhanced with bulky substituents. It is known that the thermodynamic equilibrium is reached rapidly if an excess of alkali metal is used. The preferred metal is lithium and the usual solvent is THF. In the case of methyl groups the six-membered ring is the thermodynamically most stable one, in the case of the ethyl group it is the five-membered ring. With large substituents like phenyl-, trimethylsilyl-, or *t*-Bu- groups, the four-membered ring becomes more stable.

Cartledge proposed a series of steric parameters for various groups attached to silicon.[6] The most favored ring size depends on the sum of these parameters on one ring. The larger the substituents the smaller the favored ring size. With isopropyl and cyclohexyl groups the four-membered ring seems to be thermodynamically preferred.[100] For a comparison with other ring sizes and the values of the Cartledge parameters see the general part.

The oldest known compound of this class is the phenylated derivative $(Ph_2Si)_4$. It was synthesized first by Kipping in 1921.[101] Properties and reactions have been summarized in several articles (see section I).

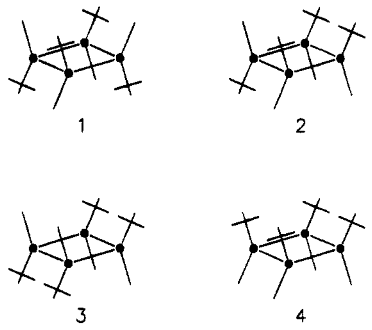
Known four-membered rings substituted with only one kind of substituents are listed in Table 13.

Si_4H_8 is unknown so far, it seems to be very unstable. As one can see in the table, not only are organic substituted derivatives known, but also halogenated rings. These are formed in the reaction of octaphenylcyclotetrasilane with hydrogen halides in the presence of the corresponding aluminum halides as a catalyst. The high reactivity of the Si–halogen bond causes these compounds to be important starting materials for the preparation of other derivatives like octamethylcyclotetrasilane. This compound was found by Kumada for the first time[104] but the yield was very low. He irradiated dodecamethylcyclohexasilane which formed silylene radicals in a first step. This was confirmed by a later investigation.[116] On the other hand methylation of Si_4Cl_8 with dimethylzinc or trimethylaluminum gives octamethylcyclotetrasilane in high yield.[117]

A similar way is to start with corresponding disilane derivatives. 1,2-Dichlorodisilane derivatives react with Li to four-membered rings in good yields.[7]

Reductive elimination of halides also takes place in an electrochemical reduction. Diphenyldichlorsilane reacts at the cathode to form octaphenylcyclotetrasilane, in addition to some polymeric material. No other rings were observed.[118] A recent investigation afforded similar results.[119] This electrochemical method opens the possibility to form cyclotetrasilane bearing flourine-containing organic groups like octakis(*p*-fluorophenyl)cyclotetrasilane. Such derivatives cannot be formed in the usual Wurtz-type reaction.

Scheme 2



At the anode, the halogen, mainly chlorine, is caught by sacrificial anodes (Mg, Al, Hg), by stable anodes (SiC) or by a new type of hydrogen anode, forming HCl.[120] To understand the reaction mechanism of these electrochemical reactions, some investigations were done using cyclic voltammetry. The values of the oxidation and reduction potentials are similar for all derivatives of the four-membered ring, but different for other ring sizes.[47,46] (See section II.7.)

Other methods to form cyclotetrasilanes are ring extension reactions, starting from the three-membered ring. For these reactions see the article by Weidenbruch in this issue.

More interesting are derivatives with different substituents giving rise to the formation of several isomers. Many examples are known. One of the best studied systems are *tert*-butylmethylcyclotetrasilanes. The first syntheses were reviewed earlier. New syntheses were made to investigate the properties.[8] The four possible steric isomers are shown in Scheme 2. It should be noted, that these rings are folded and not planar. Therefore the pictures can only show the position of the substituents in the different isomers.

A mixture of all isomers was formed from *tert*-butylmethyldichlorosilane with an excess of Li in THF in an overall yield of 85%. The isomeric distribution at these reaction conditions was 9:49:29:13 (isomers **1**–**4**, see Scheme 2), close to the statistical distribution. Isomer **2** could be isolated by recrystallization from the supernatant liquid; isomer **3** could be isolated by further recrystallization. Isomer **4** was only isolated as a 3:2 mixture of isomers **3** and **4**. The isomers were identified by ^1H and ^{13}C NMR spectroscopy.[38]

Photolysis (300 nm, 30 min) of the pure isomers **1** or **2** (Scheme 2) or of mixtures of both afforded an isomeric distribution of 44:37:19:0 for **1** to **4**. The resulting ratio was independent from the composition of the starting mixture of the isomers. The reaction mechanism seems to be working via *tert*-butylmethylsilylenes. This could confirmed by trapping the silylene with Et_3SiH giving $Et_3Si\text{-}\textit{t}\text{-}BuMeSiH$. Longer exposure times destroyed the ring.[38]

The four-membered ring with the small methyl and ethyl groups is not a thermodynamically preferred system, as is the five-membered ring. Therefore in the reaction of methylethyldichlorosilane with an excess of Li in THF no four-membered ring is formed.

Four-membered rings with small substituents are only obtained in a nonequilibrium state by kinetic preference. With sodium in toluene a mixture of all possible isomers of tetramethyltetraethylcyclotetrasilane was formed in a yield of 19%. This was suggested by ^{13}C and ^{1}H NMR investigations. A better route to this cycle is the photolysis of the five-membered ring. It is known from the chemistry of other cyclosilanes that photolysis leads to an elimination of a silylene and contraction to the next smaller ring. This is also valid in this case. The best yield was obtained after an irradiation time (254 nm, isooctane as solvents) of 1 h; longer reaction times split the initially formed ring and a linear trisilane $H(SiMeEt)_3H$ was the major volatile product.[15]

A special synthesis was necessary for 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. Starting with Si_4Ph_8 one phenyl group of each silicon atom was substituted by a triflate group. These triflate groups were exchanged subsequently by use of methylmagnesium bromide by methyl groups. The dominating isomer resulting from this synthesis possesses an *all-trans* structure and can be isolated in up to 95% purity. The *trans,cis,trans,cis* and the *trans,trans,cis,cis* isomers were obtained in smaller yields. The *all-cis* isomer has not been detected. The structures were assigned by ^{1}J(C−Si), ^{2}J(C−Si), and ^{3}J(C−Si) values of the three isomers with ^{13}C-labeled methyl groups.[150,153] ^{19}F NMR studies of the triflates have been carried out earlier.[151,152] Dearylation of another phenyl group in 1,2,3,4-tetramethyltetraphenylcyclotetrasilane by triflic acid followed by methylation afforded 1,1,2,3,4-pentamethyltriphenylcyclotetrasilane.[150]

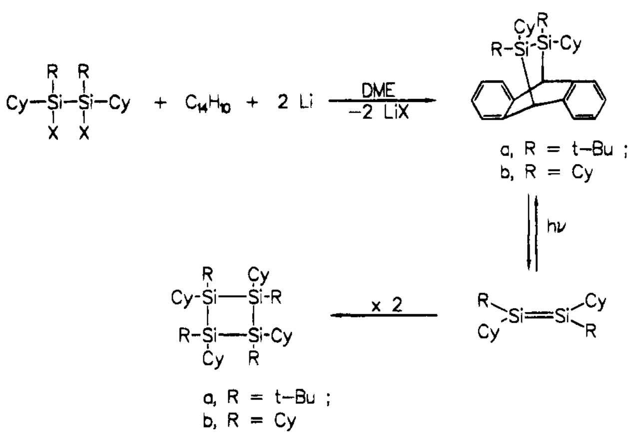
Similar other cyclotetrasilanes with two different kinds of substituents are known. 1,2,3,4-Tetra-*tert*-butyltetraphenylcyclotetrasilane and 1,2,3,4-neopentyl-tetraphenylcyclotetrasilane were prepared by the usual way with Li, starting from the corresponding monosilane or the disilane. All possible isomers were observed but not isolated.[122] (t-Bu-n-PrSi)$_4$ has also been described.[8]

The synthesis of *all-trans*-(t-BuClSi)$_4$ via chlorodephenylation of (t-BuPhSi)$_4$ with $HCl/AlCl_3$ was also accomplished. The phenyl derivative was made by the usual dechlorination of dichloro-*tert*-butylphenylsilane. Three isomers were formed: *cis,cis,trans*, *cis,trans,cis* and *all-trans*. In the dephenylation reaction only the *all-trans* product was found.[123] Another synthesis of this compound started from 1,2-di-*tert*-butyl-1,1,2,2-tetrachlorodisilane.[124]

An interesting type of synthesis was achieved by the use of anthracene. 1,2-Di-*tert*-butyl-1,2-dicyclohexyl-1,2-dichlorodisilane reacted with an excess of lithium in the presence of anthracene via the disilabicyclo derivative (see Scheme 3) and a photochemical formation of the disilene derivative in a [2 + 2] cyclodimerization to the four-membered ring.[125]

Interesting derivatives of the four-membered ring with Si−H groups were investigated by Masamune et al.[126] 1,1,2-Trichloro-1-(2,6-diisopropyl-4-*tert*-butylphenyl)-2,2-diisopropyldisilane reacted with 5 equiv of lithium naphthalenide in DME at low temperature to a red solution which was assumed to contain the intermediates shown in Scheme 4. Work up with water yielded a four-membered cyclosilane with two Si−H bonds (A). Similar work up with methyl iodide yielded the corresponding dimethyl derivative (B).

Scheme 3



The use of 3.5 equiv of the Li reagent led, upon aqueous work up, to the formation of two isomers (4:1 mixture) with hydroxy groups (C + D).

A reaction mechanism was postulated involving tetrasilabicyclo[1.1.0]butane and dianionic cyclotetrasilane intermediates. In this connection see also ref 127.

The treatment of 1,1,2-trichloro-1,2-bis(2,6-diisopropylphenyl)disilane with Li led to four-membered rings with one Si−H bond on each silicon atom. NMR investigations suggested that three isomers in a mixture of 4:2:1 (A:B:C in Scheme 5) were formed. The *all-cis* stereoisomer (D) was not observed.[126] Also in this reaction the intermediate seems to be a dianion which is shown in Scheme 5.

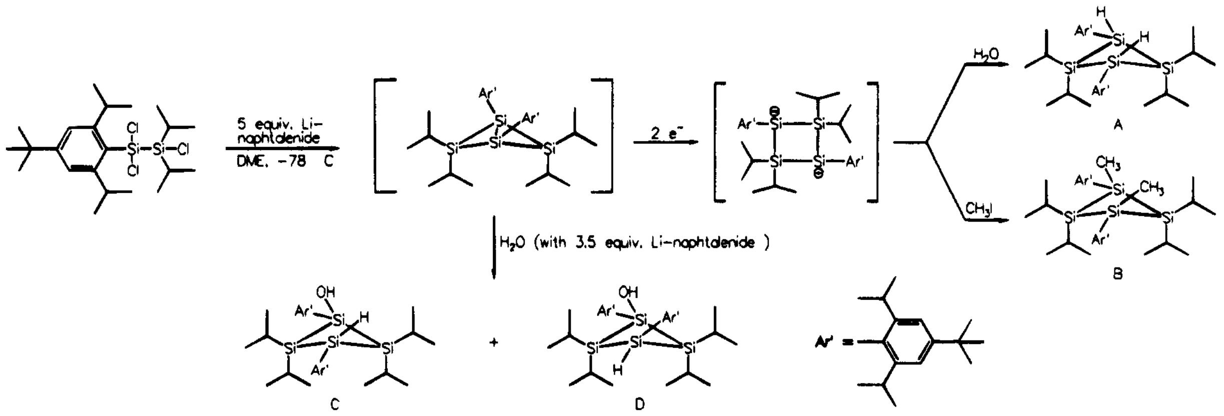
Cocondensation of two molecules of 1,2-dichlorotetraalkyldisilanes bearing different alkyl groups resulted in the formation of peralkylcyclotetrasilanes of the type $(R^1R^2Si)_2(R^3R^4Si)_2$ with $R^1 = R^2 = t$-$BuCH_2$, R^3 and $R^4 = i$-Pr or $R^1 = R^2 = t$-$BuCH_2$, $R^3 = t$-Bu and R^4 = Me, respectively. Formation of the symmetric products also took place and the yield of the asymmetric product generally was low.[128]

It is interesting that in some cases the course of the reductive dehalogenation reactions depends on the kind of halogen. The larger halogens Br and I in di-*tert*-butyldihalosilane led to the three-membered ring (see section on three-membered rings). However di-*tert*-butyldichlorosilane yielded trans-1,1,2,3,3,4-hexa-*tert*-butylcyclotetrasilane in a yield of 15% along with tetra-*tert*-butyldisilane.[129]

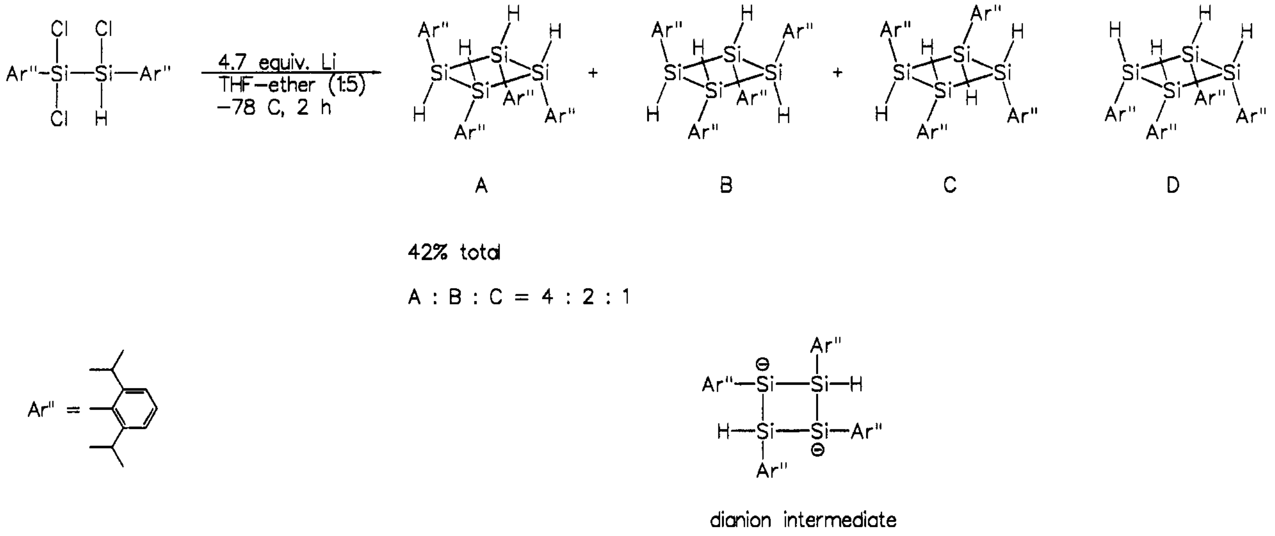
2. Chemical Reactivity

Ring-opening reactions are quite generally observed for the rather strained cyclotetrasilane systems. Permethylated,[130] perphenylated (see many old papers in former reviews), and perethylated[131] rings, for instance, afford the corresponding α,ω-dihalotetrasilane derivatives upon treatment with Cl_2, Br_2, or I_2. Ring-opening reactions of octaphenylcyclotetrasilane with halogens (X = Cl, Br, I) or PX_5 (X = Cl, Br) in the presence of HX/AlX_3 yield perhalogenated tetrasilanes Si_4X_{10} (X = Cl, Br, I)[22] which otherwise are very difficult to prepare. A ring cleavage reaction of octaphenylcyclotetrasilane with lithium is also possible and leads to dilithiumoctaphenyltetrasilane which crystallizes with THF

Scheme 4



Scheme 5



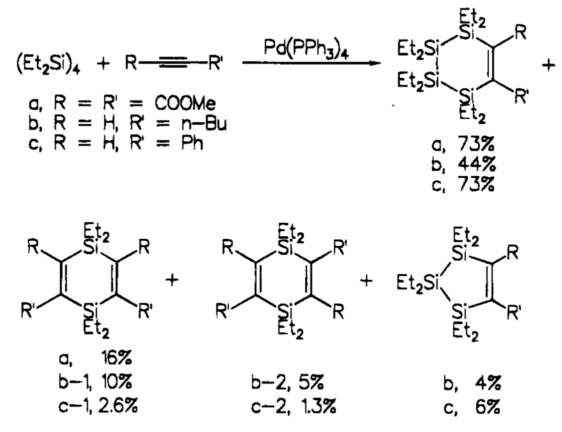
molecules.[132] Reaction with diluted sulfuric acid followed by the usual splitting of the Si−phenyl bonds with HCl/$AlCl_3$ yielded $H(SiCl_2)_4H$.[133] The dilithium octaphenyltetrasilane reacts with many compounds forming heterocycles. Most of these reactions are described in former reviews.

Some cleavage reactions were done with octakisisopropylcyclotetrasilane. Reaction with HCl yielded the α,ω-dihydrogen derivative; MeCOCl/$AlCl_3$ or iodine split the ring system to the corresponding α,ω-dihalogenated derivatives. Removal of the isopropyl group from the ring was not observed.[106] A kinetic study of the cleavage reaction with iodine showed second order. Comparison of the rate constants show that the four-membered ring reacts faster than the larger rings (see also section II.2).[9]

Ring extension reactions are also possible. Sulfur and selenium in the elementary state reacted with octamethylcyclotetrasilane upon heating with insertion of one or two S or Se atoms to the corresponding five- and six-membered heterocycles.[134,135] In case of the disulfur derivatives the 1,4 isomer seems to be preferred. This is in contrast to results with octaethylcyclotetrasilane, where a mixture of the 1,3- and the 1,4-dithiacyclohexasilane was found.[136] Presumably, these differences are caused by the different size of the substituents but also by the different reaction conditions applied.

Insertion of alkynes into Si_4Et_8 in the presence of a palladium catalyst led to six-membered heterocycles (Scheme 6) along with small amounts of other ring systems. After insertion of the first ethine molecule further splitting of Si−Si bonds seems to take place.[131] The 1,4-disilacyclohexadienes, without any Si−Si bonds, appear to be the stable end products of these catalytic reactions.

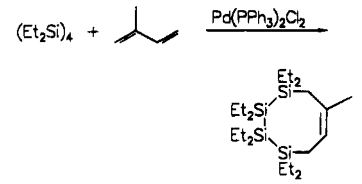
Scheme 6



Insertion of isoprene was also possible; however, only one Si−Si bond was split in this case and some starting material was recovered after the reaction. The newly formed compounds are depicted in Scheme 7.

Oxidation of $(Et_2Si)_4$ is possible, slowly in air, rapidly with m-chloroperbenzoic acid. Depending on

Scheme 7



the equivalents of *m*-chloroperbenzoic acid used rings with one (five-membered ring), two (1,3- and 1,4-dioxacyclohexasilanes), three (seven-membered ring), and four (cyclotetrasiloxane) endocyclic oxygen atoms were obtained.[131]

The general reactivity is dependent on the size and the position of the substituents, protecting the sensitive strained ring. This was demonstrated, for example, by the oxidation reactions of the four isomers of $(t\text{-BuMeSi})_4$. They are unreactive toward air and toward concentrated H_2SO_4 but react with *m*-chloroperbenzoic acid to give the oxygen insertion products $(t\text{-BuMeSi})_4O_n$ (n = 1, 2, and 4). The reactions are stereospecific and regioselective. The oxidation is preferred in the *cis* isomers in strained rings adjacent to endocyclic oxygen atoms.[141]

Anionic ring-opening polymerization is another interesting reaction of cyclotetrasilanes. It is known that octamethylcyclotetrasilane slowly polymerizes at room temperature. However, octaethylcyclotetrasilane seems to be stable for longer periods under these conditions. Octaphenylcyclotetrasilane only rearranges to decaphenylcyclopentasilane. Catalyzed by silylpotassium or butyllithium as initiators polymerization of 1,2,3,4-tetraphenyl-1,2,3,4-tetramethylcyclotetrasilane took place. Polymers were formed with molecular weights up to 100 000.[142,154] Recently silylcuprates were used for this ring opening polymerization of the *all*-trans isomer of 1,2,3,4-tetramethyltetraphenylcyclotetrasilane forming methylphenylpolysilane with defined stereochemical structures. From ^{29}Si NMR data one can see that 25% isotactic and 75% heterotactic triads were formed. The polymer was defect free, linear, with molecular weights up to 50 000. The polymerization proceeded with nearly quantitative conversion (>98%) to polymer and no depolymerization via a backbiting process to cyclic products was observed. The polydispersities of the resulting polymers were in the range of $M_w/M_n \approx 1.5$.[155,156] It also has been published that dicyanohexaphenylcyclotetrasilane polymerizes anionically and octamethoxycyclotetrasilane polymerizes cationically.[143]

3. Photochemical Reactivity

The usual photochemical reaction upon irradiation of cyclosilanes is ring contraction and the formation of a silylene which takes place easier in case of the ethyl derivative compared to the methyl derivative. The smallest ring which can be obtained by this reaction is the four-membered ring, starting from all other larger ring sizes and using small substituents. The formation of the silylene Et_2Si was confirmed by trapping experiments with Et_3SiH to give the corresponding disilane and trisilane derivatives.[13]

With larger substituents, the end product is the three-membered ring (see paper by Weidenbruch). The four-membered ring is suitable as a starting material; however, the reaction seems to take place only with bent cyclotetrasilanes. In case of the flat silylated four-membered rings like $Si_4(SiMe_3)_8$ or $Si_4(SiMe_2Et)_8$, photolysis at 410 nm (293 K) or 415 nm (77 K) resulted in the formation of disilene via the three-membered ring.[137,138]

Scheme 8

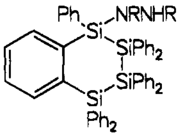


Table 14. Dihedral Angles of Some Four-Membered Rings

compound	angle, deg	ref
octaphenylcyclotetrasilane	12.8	145
1,2,3,4-tetramethyl-1,2,3,4-tetra-*tert*-butylcyclotetrasilane	36.8	146
octakis[(trimethylsilyl)methyl]cyclotetrasilane	36.6	147
1,1,2,2-tetraneopentyl-3,3,4,4-tetraisopropylcyclotetrasilane	39.39	128
octaneopentylcyclotetrasilane	38.8	108
octaisopropylcyclotetrasilane	37	147
octacyclohexylcyclotetrasilane	27.6	107
cis,cis,trans-1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetracyclohexylcyclotetrasilane	34	100
octakis(trimethylsilyl)cyclotetrasilane	0	113

Irradiation (>390 nm) of cyclotetrasilanes $(R^1R^2Si)_4$ in a solvent mixture ($EtOH/MeCN/C_6H_{12}$) with 9,10 dicyanoanthracene as a sensitizer yielded the corresponding 1-ethoxy-4-hydrotetrasilanes. The reaction started with a ring-opening step (see also paper on three-membered rings by Weidenbruch).[139]

The photochemical reaction of octaphenylcyclotetrasilane with azobenzene (or 4,4′-dimethylazobenzene) led to an addition of the two nitrogen atoms and ring extension by employing one of the phenyl groups[140] as shown in Scheme 8.

4. Structure and Special Physical Properties

4.1. Structure

The four-membered ring is a strained system. The ring can be flat or bent. Compared to carbon atoms the bond angles at silicon atoms generally are more flexible. As a result of this, the dihedral angle is strongly dependent on the size of the substituents but also dependent on the state of the compound. It is interesting, that the permethylated four-membered ring is flat in the solid crystalline state,[144] but folded with an angle of 29.4° in the gaseous state.[149] In Si_4Cl_8 and Si_4Br_8 selection rules in vibrational spectra point toward a nonplanarity.[20] As already has been shown in the general section on cyclosilanes, radical anions of the four-membered cyclosilane derivatives are generally planar or rapidly interconverting. Exceptions are the radical anions of octaisopropylcyclotetrasilane and octa-*sec*-butylcyclotetrasilane where ESR spectra indicated bent structures.[40]

Some selected dihedral angles of further cyclotetrasilanes are given in Table 14.

4.2. UV Investigations

The longest wavelength absorption maxima of four-membered rings generally are shifted bathochromically compared to larger ring systems. They usually appear around 300 nm. It is remarkable that such very low energy transitions occur at about 300 nm also for the silylated cyclotetrasilanes [(Si(SiMe$_3$)$_2$]$_4$ (ϵ = 1300) and [Si(SiMe$_2$Et)$_2$]$_4$ (ϵ = 1900). This demonstrates that silylated cyclotetrasilanes are intense chromophores.[114] However, the perhalogenated rings show absorption bands at longer wavelenlengths (Si$_4$Cl$_8$, 394 nm; Si$_4$Br$_8$, 402 nm; and Si$_4$I$_8$, 424 nm) with very low extinctions.[18]

Further details of the UV absorption of cyclotetrasilanes in comparison to other ring sizes are included in the general section on cyclic silanes.

Fluorescence spectra have been observed with an extremly large Stokes shift (up to 13 700 cm^{-1}) in rigid glass at 77 K.[148]

4.3. CT Complexes

Compounds with Si–Si bonds form CT complexes with the π acceptor tetracyanoethylene (TCNE). The position of the first CT band in cyclosilanes depends on the ring size and the kind of substituents. The measured values are listed in ref 8. The lowest energy transition was observed for tetrakis(neopentyl)cyclotetrasilane at 600 nm (in CH$_2$Cl$_2$).[108]

4.4. Electrochemical Properties and ESR Investigations

Some electrochemical properties are known including some cyclovoltammetric investigations. These results, however, are discussed in connection to the results on cyclic compounds with other ring sizes. The same is true for the results of ESR investigations. See therefore, the general section on cyclosilanes.

V. Cyclopentasilanes

1. Formation

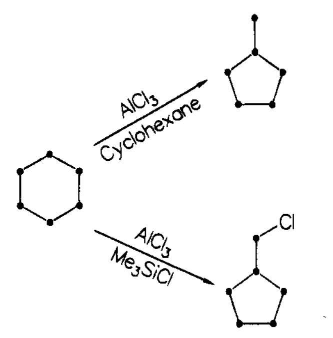
Several derivatives of cyclopentasilanes are known. The unsubstituted hydrogen containing ring Si$_5$H$_{10}$ is also known and well characterized.[157] It is used for chemical vapor deposition of silicon.[158]

The oldest known derivative is the perphenylated five-membered ring, discovered by Kipping in 1921. Many investigations have been done since then and have already been reviewed. This perphenylated compound is remarkably stable. It is stable toward air and melts at about 464 °C without decomposition. This stability seems to be caused by its low ring strain and the very good steric protection of the Si skeleton by the phenyl groups.

Inorganic derivatives like the perhalogenated cyclopentasilanes are accessible by dephenylation of decaphenylcyclopentasilane with HX/AlX$_3$ (X = Cl, Br, I).[22,112] Si$_5$H$_{10}$ could be obtained from these derivatives by hydrogenation with LiAlH$_4$. The perfluorinated cyclopentasilane is unknown so far.

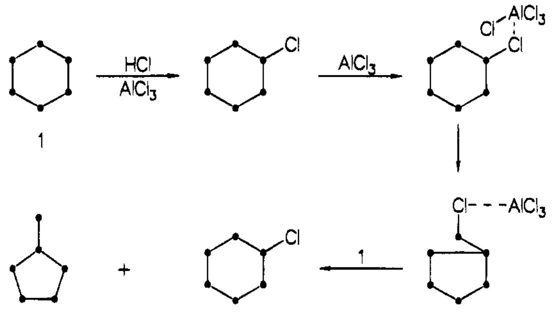
Many organic derivatives are known. The thermodynamically most preferred compound in the case of the methyl derivatives is the six-membered ring,[10] as outlined also in the general section (II.2). Therefore, the yield of decamethylcyclopentasilane in the usual reaction of dimethyldichlorosilane with Li in THF is very low.[12] The oxygen-containing solvent THF gives rise to the formation of siloxanes at higher reaction temperatures which further lowers the yield of cyclosilanes.[159]

Scheme 9



● = SiMe$_{3-n}$ n = 0, 1, 2

Scheme 10



● = SiMe$_{3-n}$ n = 0, 1, 2

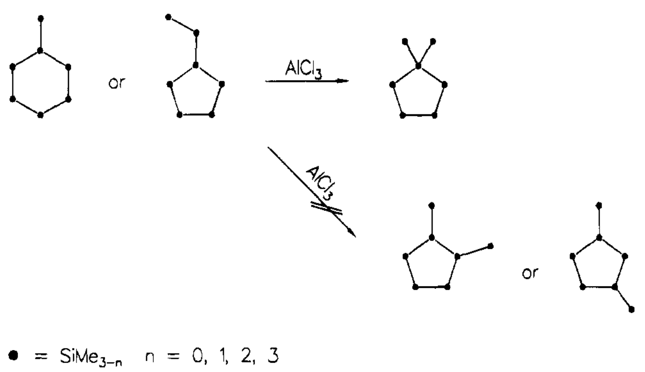
However, irradiation of dodecamethylcyclohexasilane at 254 nm yielded the decamethylcyclopentasilane in very high yields. To optimize the yield it was necessary to trap the byproduct dimethylsilylene. Otherwise insoluble white polysilane was formed which made the photolysis difficult. To avoid the formation of polysilanes, triethylsilane was used as a trapping reagent and the volatile 1,1,1-triethyl-2,2-dimethyldisilane was formed.[160] A similar rearrangement from the six-membered to the five-membered ring could also be induced by γ-irradiation (^{60}Co scource).[161]

Another synthesis for decamethylcyclopentasilane was achieved by the methylation of (SiCl$_2$)$_5$ with dimethylzinc or trimethylaluminum.[117] Decamethylcyclopentasilane was also formed in the thermal decomposition of polydimethylsilane.[162,163]

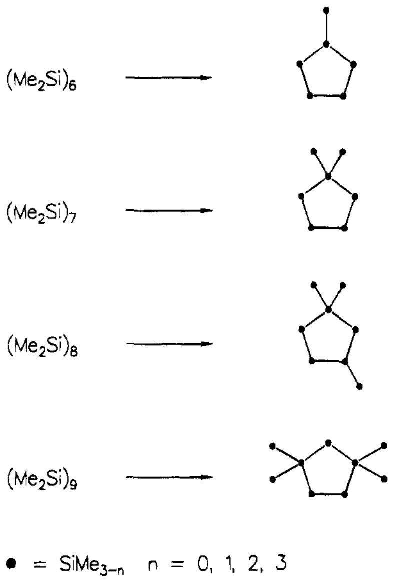
A special method for the synthesis of five-membered rings is the ring contraction by use of AlCl$_3$. Dodecamethylcyclohexasilane reacted with AlCl$_3$ to 1-(trimethylsilyl)nonamethylcyclopentasilane.[164] In the presence of trimethylchlorosilane the dimethylchlorosilyl-substituted derivative was obtained[165] (Scheme 9).

The reaction mechanism shown in Scheme 10 was proposed by Ishikawa and Kumada. It seems to be that AlCl$_3$ is the catalyst for the ring contraction reaction forming an intermediate addition product. As the first step the chlorination of the six-membered ring was postulated, which subsequently is followed by the rearrangement. The formed 1-(chlorodimethylsilyl)nonamethylcyclopentasilane again reacts with dodecamethylcyclohexasilane via a methyl/chlorine rearrangement catalyzed by AlCl$_3$.[164]

Scheme 11



Scheme 12



This reaction mechanism seemed to be proved by the similar rearrangement of 1-chloroundecamethylcyclohexasilane in the presence of $AlCl_3/Me_3SiCl$ to 1-(chlorodimethylsilyl)nonamethylcyclopentasilane in nearly quantitative yield.

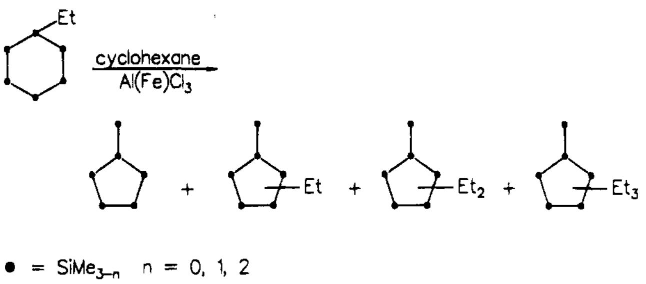
Starting with 1-(trimethylsilyl)undecamethylcyclohexasilane or 1-(pentamethyldisilanyl)nonamethylcyclopentasilane $AlCl_3$ catalyzed the rearrangement in boiling benzene to 1,1-bis(trimethylsilyl)octamethylcyclopentasilane. 1,2 or 1,3 substitution were never observed (Scheme 11).

Another reaction mechanism has been postulated by West et al.[166] In a detailed investigation they showed, that the catalyst $AlCl_3$ needed to contain some Fe as $FeCl_3$ or a complex like $AlFeCl_6$. The structure of this compound $AlCl_3$/ $FeCl_3$ is unknown. It is interesting that a mixture of pure $AlCl_3$ and $FeCl_3$ did not catalyze cyclosilane rearrangements. After cosublimation of both chlorides the mixture became active as a catalyst. By use of this catalyst five-membered ring systems were formed by rearrangement of six- to nine-membered permethylated cyclosilanes (Scheme 12).

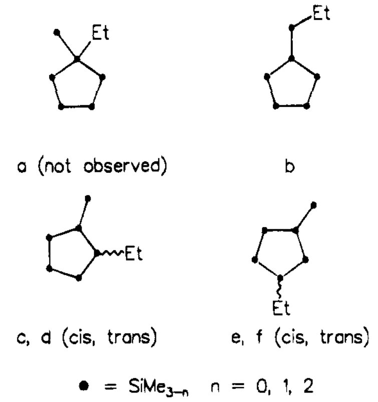
The yielded five-membered ring did not rearrange further under these reaction conditions. It is remarkable that only one product was formed in these rearrangement reactions; no isomers or other reaction products were observed.

With decaethylcyclopentasilane no reaction was found in refluxing cyclohexane, while complete decomposition occurred in refluxing benzene.

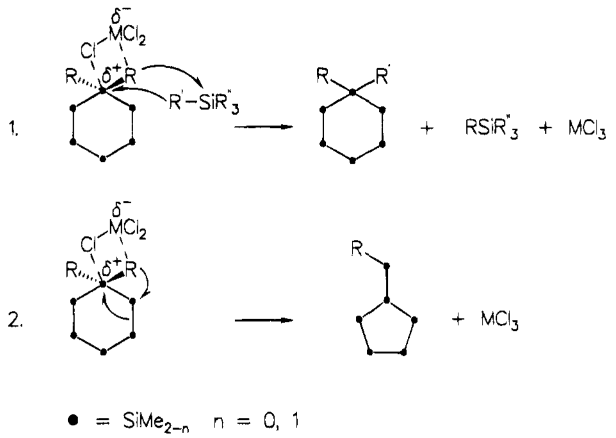
Scheme 13



Scheme 14



Scheme 15



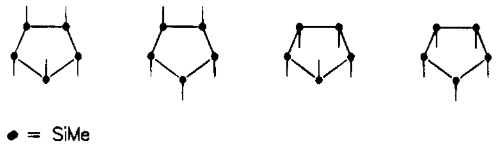
1-Ethylundecamethylcyclohexasilane reacted with the catalyst under the usual reaction conditions to four trialkylsilylcyclopentasilanes with one, two, and three ethyl groups in different positions and (trimethylsilyl)nonamethylcyclopentasilane (see Scheme 13).

NMR investigations showed only five of the six possible isomers of the monoethyl derivative (see Scheme 14). 1-Ethyl-1-(trimethylsilyl)octamethylcyclopentasilane could not be observed.

From the results of this investigation a reaction mechanism different from that postulated by Kumada and Ishikawa could be derived. West et al. postulated a pentacoordinated intermediate as shown in Scheme 15. This intermediate either exchanges alkyl groups with uncomplexed cyclosilane (way 1) or rearranges via intramolecular 1,2 silicon−silicon and silicon−carbon shifts to give branched cyclosilanes (way 2).

Decaethylcyclopentasilane is also a known and well-investigated derivative. Formation was achieved with diethyldichlorosilane and potassium. The yield

Scheme 16



of the five-membered ring depended upon the reaction conditions. An excess of potassium led to a high yield. Other ring sizes were formed in small yields. The five-membered ring very likely is the most stable one in the case of the ethyl derivative in contrast to the methyl derivative. Although the methyl and ethyl groups are very similar electronically, the steric bulk of the ethyl group is significantly greater. Therefore, its size seems to be responsible for the different behavior.[14,13]

Decaethylcyclopentasilane was also obtained in an isolated yield of about 50% with diethyldichlorosilane and Li in THF. Other derivatives (Pr, Bu, i-Bu) were synthesized very similarly.[8,167,168]

Several examples of cyclopentasilanes are known with two different kinds of substituents. 1,2,3,4,5-Pentaethylpentamethylcyclopentasilane has been described. In the reaction of methylethyldichlorosilane with Li in THF the five-membered ring is the preferred ring size. Other ring sizes (4, 6, 7, 8), however, were also obtained. The best yield of the five-membered ring was obtained with 10% excess of Li in THF at 65 °C.[15] Four stereoisomers are possible. The formation of three isomers was observed by means of ^{13}C NMR. Similar to other derivatives photolysis led to abstraction of a silylene and to the formation of a smaller ring:

$$(SiEtMe)_n \xrightarrow{h\nu} (SiMeEt)_{n-1} + SiMeEt$$

Other examples of mixed substituted cyclopentasilanes are 1,2,3,4,5-pentaisobutylpentamethylcyclopentasilane (all four possible isomers in a statistical distribution were found)[38] and 1,2,3,4,5-pentamethylpentapropylcyclopentasilane.[8] These derivatives were obtained by normal reductive dehalogenation. A more detailed investigation was done with 1,2,3,4,5-pentamethylpentaphenylcyclopentasilane. The four possible isomers are depicted in Scheme 16. Three of the four isomers (1−3) were found by NMR investigations, only the *all-cis* isomer seemed to be absent.[169]

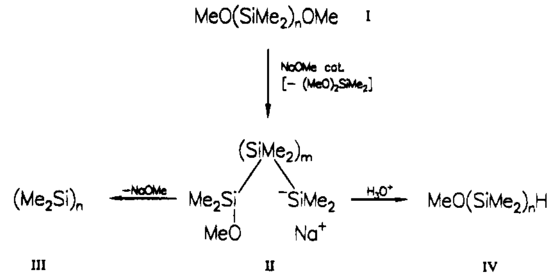
In the presence of ultrasound the formation of cyclic products seems to be preferred compared to linear products.[170] The presence of trimethyltriphenyldisilane or hexaphenyldisilane as an equilibrating catalyst seemed to be advantageous.[169,171]

Dehalogenative coupling of mixtures of di- and trichloromethylsilane led to five-membered rings with trimethylsilyl and pentamethyldisilanyl side chains along with other ring systems.[172]

Cocondensation of 4 equiv of dimethyldichlorosilane and 1 equiv of $R^1R^2SiCl_2$ (R^1, R^2 = CH_3, Ph, *t*-Bu) afforded 1,1-$R^1R^2Si\ (SiMe_2)_4$ in small yields.[17]

Small amounts of 1,2,3,4,5-penta-*n*-butylcyclopentasilane (SiH-*n*-Bu)$_5$ were obtained by the known dehydrogenative catalytic reaction of monosilanes (in this case *n*-$BuSiH_3$) with Cp_2MCl_2/2*n*-BuLi (M = Zr, Ti).[173,174]

Scheme 17



An alternative route to cyclopentasilanes is the use of disilane derivatives instead of monosilanes as the starting material. $R^1R^2SiCl{-}SiClR^1R^2$ with R^1 = *i*-Pr, R^2 = Me and R^1 = Me_3SiCH_2, R^2 = Me yielded the corresponding five-membered rings.[7]

In the presence of a catalytic amount of sodium methoxide, *sym*-dimethoxytetramethyldisilane was converted into cyclic polysilanes (n = 5−7). The maximum yield of the cyclopentasilane was reached after 1 h and then decreased gradually to attain a constant value of ca. 12%. An investigation of the reaction mechanism showed the formation of α,ω-dimethoxypolydimethylsilane (I in Scheme 17) in a first step followed by the formation of a sodium-containing intermediate (II). In the final stage, the polysilyl anions undergo intramolecular nucleophilic substitution to give the cyclic polysilanes (III) and NaOMe. Since α-hydro-ω-methoxypermethylpolysilanes (IV) were formed after hydrolysis of the reaction mixture, it is evident, that the polysilyl anions were formed by Si−Si bond cleavage of I by NaOMe[175] (Scheme 17).

The dehydrogenative polymerization of phenylmonosilane $PhSiH_3$ by use of zirconocene derivatives as a catalyst led to five- and six-membered rings beside polymeric material.[193,196] Also mono-*n*-butyl- and mono-*n*-hexylmonosilane were investigated and afforded five- and six-membered rings.[173,174]

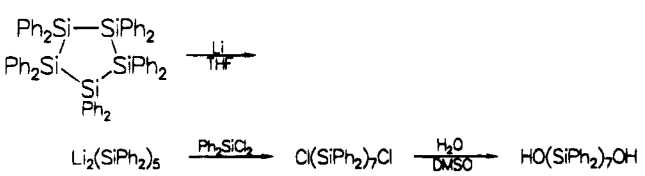
2. Chemical Reactivity

2.1. Ring Cleavage Reactions

Ring cleavage reactions are possible with several reagents. Cleavage by halogens has been known for a long time and also takes place on the five-membered ring system. With more reactive halogens like bromine or chlorine smaller chain length fragments were formed as side products, therefore, the use of iodine is recommended. Decamethylcyclopentasilane reacted with iodine in hexane in high yield to give 1,5-diiododecamethylpentasilane.[130] A kinetic study of the cleavage with iodine was made with *n*-butyl- and *n*-propylcyclopentasilane derivatives. A comparison to other ring sizes showed that smaller rings are cleaved faster (see general section, II.2) and ref 9.

Cleavage of the phenylated cyclopentasilane is also possible with lithium. The reaction is strongly dependent on the reaction conditions, smaller dilithio silicon chains have also been observed. The formed 1,5-dilithio compound was suitable as a starting material for several derivatives of pentasilanes, for example $H(SiCl_2)_5H$[133] or 1,5-diallyldecaphenylpentasilane.[176] Chain elongations by reaction with chlo-

Scheme 18



rosilanes and hydrolysis led to the perphenylated 1,7-dihydroxyheptasilane[177] (Scheme 18).

Cleavage with iodine, followed by dephenylation with HI/AlI$_3$ affords Si$_5$I$_{12}$.[22]

An alternative way is the cleavage reaction with halides. PCl$_5$ split the permethylated ring specifically to 1,5-dichlorodecamethylpentasilane. No methyl exchange to a chlorinated ring and no cleavage to smaller chains were observed. The reaction was strongly dependent on the solvents; CCl$_4$ seemed to be most suitable.[178] A similar reaction took place with decaphenylcyclopentasilane. The 1,5-dichlorodecaphenylpentasilane formed was the starting material for many reactions like the formation of heterocyclic rings with oxygen or 1,5 diaminopentasilane.[179] SnCl$_4$ split the five-membered ring (methylated) faster than the six-membered ring. The ethyl derivative also reacted, but slower than the methylated one. With increasing amounts of SnCl$_4$ the yield of lower chloropermethylpolysilanes increased. TiCl$_4$ gave similar results.[180] A cleavage reaction was also possible with SOCl$_2$ or S$_2$Cl$_2$ affording 1,5-dichlorodecamethylpentasilane selectively, even at room temperature. The product readily decomposed at reflux temperature to give 1,3-dichlorohexamethyltrisilane and 1,2-dichlorotetramethyldisilane.[181]

Ring splitting occurred also by electrochemical oxidation. Deca-*n*-propylcyclopentasilane reacted anodically in the presence of Et$_4$NBF$_4$ in CH$_2$Cl$_2$/MeCN. After working up in aqueous solution F(SiMe$_2$)$_n$F (n = 2, 3, 4, 5) beside some other products like F(SiMe$_2$)$_n$OH (n = 3,5) or F(SiMe$_3$)F were obtained.[198]

2.2. Exchange of Substituents

Alkyl and aryl groups only offer small possibilities for reactions on the ring system. Therefore, an exchange against groups with enhanced reactivity is of interest.

Halides are valuable reagents to split methyl groups from the ring. One of the best-investigated compounds is SbCl$_5$. It is a strong Lewis acid and reacts with most solvents forming a 1:1 adduct. Only CCl$_4$ does not form an adduct. Therefore the reaction is strongly dependent on the solvent and on the reaction conditions. SbCl$_5$ in most solvents including CCl$_4$ at higher temperatures split the five-membered permethylated ring forming α,ω-dichloromethylpolysilanes Cl(SiMe$_2$)$_n$Cl with $n = 2-5$. In the reaction of SbCl$_5$ in CCl$_4$ at room temperature, 1-chlorononamethylcyclopentasilane was formed in a yield of about 50%. No higher chlorinated ring derivatives were observed; only linear cleavage products were formed as byproducts in small yields.

AlCl$_3$ reacts similarly. A series of the reactivity of several halogenating reagents has been found to be ZnCl$_2$ < FeCl$_3$ < SbCl$_5$ < AlCl$_3$.

The reaction with iron chloride was especially effective, only monochlorononamethylcyclopentasilane was formed (~50%) and no cleavage products were observed.[178]

All these halogenating reactions require decamethylcyclopentasilane as the starting material. As already has been shown, the preparation of larger amounts of this compound is troublesome. It is easier to start with the permethylated six-membered ring and, by the described rearrangement, a five-membered ring with a trimethylsilyl or a chlorodimethylsilyl side chain can be obtained (see section on formation). This side chain could be split from the ring by action of sodium ethoxide/ethanol. It is remarkable that this splitting reaction was easier with the trimethylsilyl group than with the phenyldimethylsilyl group.[165] In both cases 1-ethoxynonamethylcyclopentasilane was formed. The ethoxy group could be substituted by chlorine with acetyl chloride affording 1-chlorononamethylcyclopentasilane. In the reaction with AlCl$_3$/Me$_3$SiCl small amounts of 1-(chlorodimethylsilyl)-2-chloro- and 1-(chlorodimethylsilyl)-3-chlorooctamethylcyclopentasilane were formed. These disubstituted products could be separated after phenylation via distillation.

These reactive partly halogenated five-membered ring systems opened the possibility to form other derivatives by exchange of the halogen, which is demonstrated by several reactions depicted in Scheme 19.[165,192]

An exchange of phenyl groups in decaphenylcyclopentasilane is also possible with trifluoromethanesulfonic acid. Only one or two phenyl groups can be exchanged (Scheme 20). In case of the exchange of two phenyl groups, NMR investigations led to the conclusion, that a 1,3-triflate derivative was formed. These triflate derivatives opened the possibility of formation of several other derivatives.[188,190,191,197]

Some transition metal-containing five-membered rings were prepared by exchange reactions. The first example with five-membered cyclosilanes was reported with sodium dicarbonylcyclopentadienyliron[194] and 1-(chlorodimethylsilyl)nonamethylcyclopentasilane. In addition a compound with two iron groups was synthesized (Scheme 21). The crystal structure showed the ring in an envelope form.

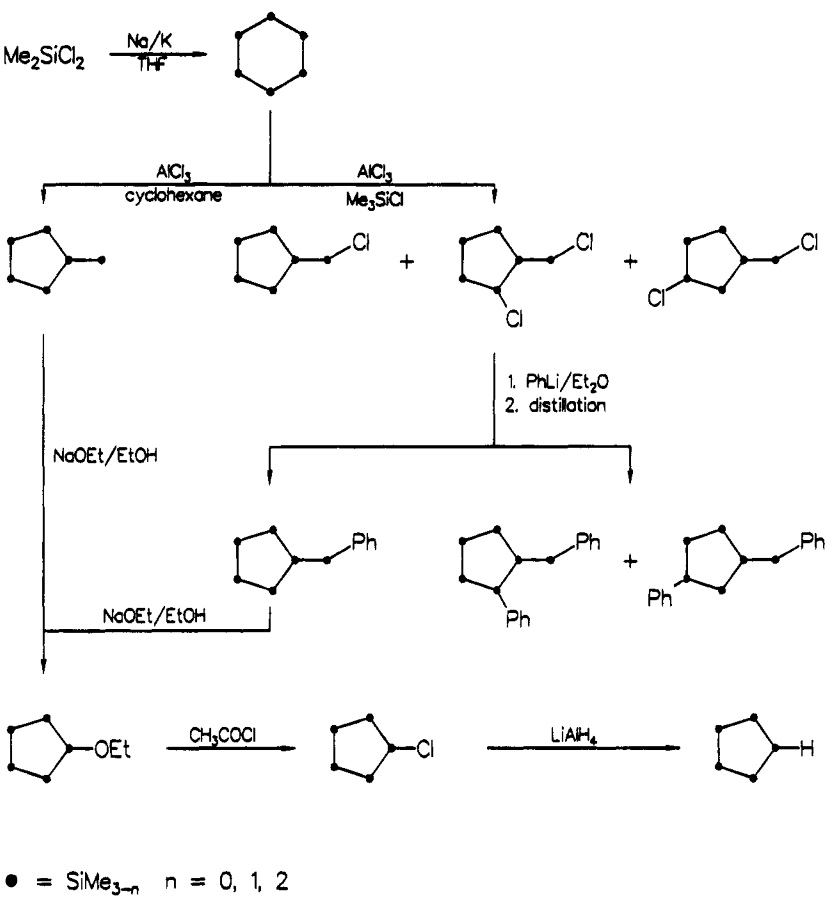
In a recent investigation (1-dicarbonylcyclopentdienyl)iron nonamethylcyclopentasilane and the corresponding cobalt derivative were synthesized. The starting materials in case of the Co derivative were the triflate derivative and K[Co(CO)$_3$PPh$_3$] (Scheme 22). The presence of the triphenylphosphane group in the Co complex increased the nucleophilic character of the compound and makes the reaction possible.[195]

2.3. Insertion Reactions

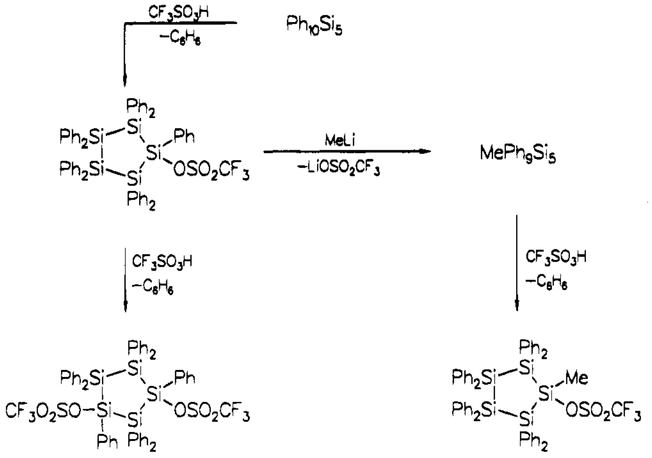
Ring insertion reactions on five-membered ring systems are possible, but in general they are much slower than in the strained four-membered rings. Sulfur inserted into decaethylcyclopentasilane to give decaethyl-1-thiacyclohexasilane in 48% yield. The reaction required 4 days at 190 °C.[136]

Decamethylcyclopentasilane reacted with 1 equiv of sulfur to decamethyl-1-thiacyclohexasilane, higher amounts of sulfur led to insertion of a second sulfur atom into the ring. The postulated instable intermediate decamethyl-1,3-dithiacycloheptasilane sub-

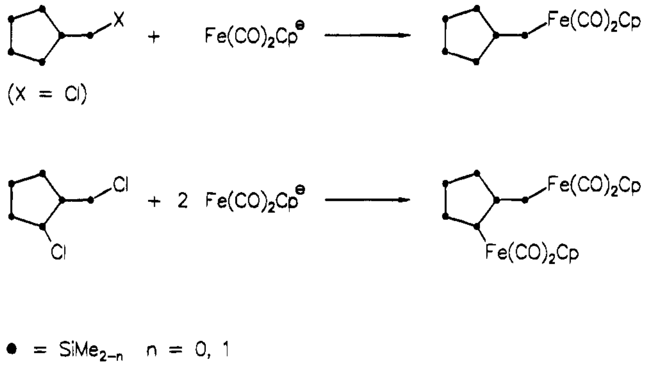
Scheme 19



Scheme 20



Scheme 21



sequently decomposed to the stable octamethyl-1-thiacyclopentasilane and silanethione (Scheme 23).

A reaction mechanism was postulated for the insertion reaction of sulfur into dodecamethylcyclohexasilane (see section VI.2.2). The same mechanism seems to be valid for the five-membered ring.[182,183]

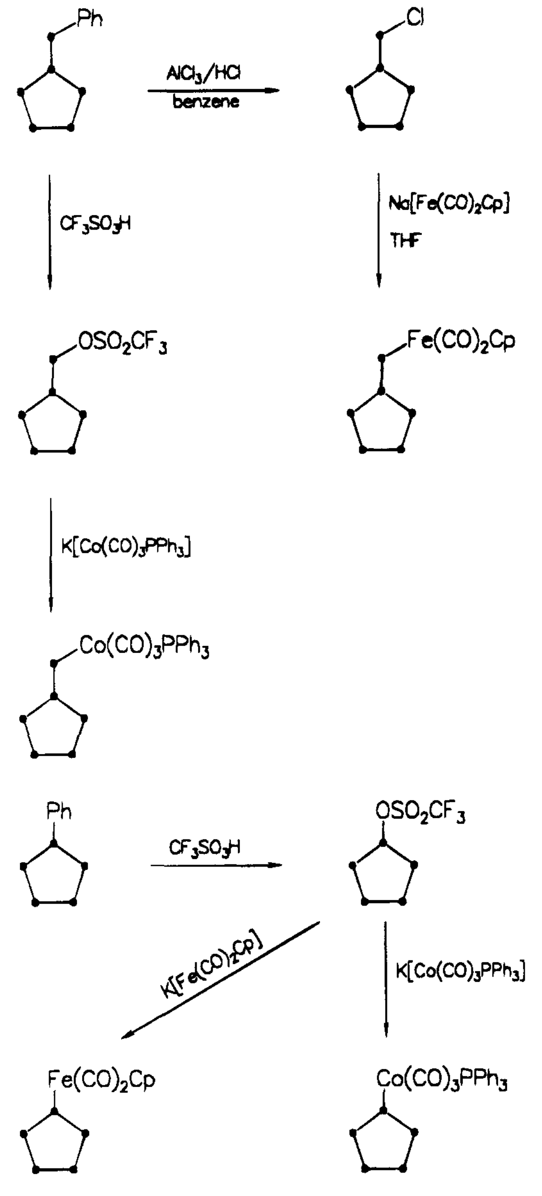
3. Physicochemical Properties

3.1. Structures

Only a few papers describe structures of five-membered ring systems. An older paper reported the structure of Si_5Ph_{10}.[184] Electron diffraction measurements were done for Si_5H_{10}.[185] A structure investigation of crystals of Si_5I_{10} (at room temperature (RT) and at low temperature (LT), −196 °C) and Si_5Br_{10} showed that the five-membered ring is not flat but adopts conformations which are intermediate between the envelope and the twist form. This result is in agreement with older investigations. Bond lengths within the Si_5 ring are between the values reported for cyclopentasilane in the gas phase (234.3(3) pm) and the crystalline Si_5Ph_{10} (239.6(8) pm). Deviations from the average length of the five bonds are as follows: RT Si_5I_{10} 236.2(10); LT Si_5I_{10} 236.6(10); LT Si_5Br_{10} 235.3(8) pm. The three structures Si_5X_{10} (X = iodine LT and RT, and bromine, LT) are closer to the envelope than to the twist form. While the puckering amplitudes are the same for these compounds, the Si_5 ring of the perphenylated derivative is significantly more puckered.[186]

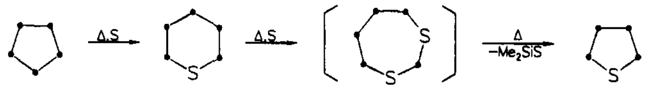
A solid-state transition to a plastic crystalline phase takes place at 234 K for Si_5Me_{10}. Molecular motion in the brittle and plastic phase was studied by using proton NMR relaxation data. Similar

Scheme 22



● = $SiMe_{3-n}$ n = 0, 1, 2

Scheme 23



● = $SiMe_2$

investigations were done on the permethylated six-membered ring (see section VI.3).[187]

3.2. NMR Investigations

General trends of NMR data (chemical shifts and coupling constants) are summerized in the general part together with the comparison to other ring sizes.

A special comparison was made on five-membered ring systems with or without a $SiMe_2X$ side chain. The structure and ^{29}Si chemical shifts of the (halodimethylsilyl)nonamethylcyclopentasilanes Si_5Me_9-$SiMe_2X$ and the halononamethylcyclopentasilanes Si_5Me_9X (X = F, Cl, Br, I) were assigned using ^1J(Si−Si) and ^2J(Si−Si) coupling constants derived from ^{29}Si-INADEQUATE and ^{29}Si-INEPT-INADEQUATE NMR spectra. The compounds exhibited good correlations between chemical shift, ^1J(Si−Si) and Pauling electronegativities. The value of the coupling constant over one bond is strongly dependent on the electron density of the nucleus. Therefore, an estimation of the s or σ^* character became possible. The higher the value of ^1J the lower the σ^* character. This value in the Si ring is significantly higher in comparison to the exocyclic Si−Si bond.[32]

VI. Cyclohexasilanes

1. Formation

Inorganic derivatives are known as perhalogenated six-membered rings Si_6Cl_{12},[199,200] Si_6Br_{12}, and Si_6I_{12}.[112] All these derivatives were formed by dephenylation of Si_6Ph_{12} with HX/AlX_3. About their spectroscopic properties in comparison to other ring sizes see section II.2. Hydrogenation with $LiAlH_4$ yielded Si_6H_{12}.[199]

The oldest known derivative is the perphenylated ring. It was discovered in 1921 by Kipping, but the first proposed structure was wrong. Later Gilman and others were able to assign the correct structure. Investigations of this compound are complicated because of its very low solubility in the most common solvents. Since 1980 no investigations have been done about this perphenylated cyclohexasilane. However, the structure was determined. It was found to be a centrosymmetric Si_6 chair with six axial and six equatorial phenyl substituents, respectively. The Si−Si distance is 239.3(3) pm.[244]

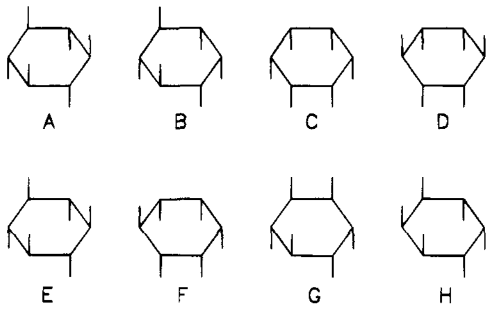
The most investigated six-membered cyclosilane is the permethylated derivative. It is a key substance for the synthesis of other cyclic silanes and of linear silanes. The usual route is the dehalogenating reduction starting with dimethyldichlorosilane. In the first preparation in 1949 the yield was only 2%. Since this paper many other investigations have been done and the actual yield is now nearly 100%. A convenient synthesis used Li in THF as the reducing agent and the yield is about 80%. 1,1,1-Trimethyltriphenyldisilane can be used as a catalyst for this reaction. This compound forms silyllithium compounds in situ, which work as a catalyst.[160]

The use of ultrasound makes the heterogeneous reaction more effective.[201]

Another study reported on the equilibrium between $(Me_2Si)_5$, $(Me_2Si)_6$, and $(Me_2Si)_7$ in a temperature range from 30 to 58 °C. THF (dried) was used as the solvent and to the starting cyclosilane ($n = 5$ or 6) was added Na/K alloy (see section II.1 for details). The thermodynamic data indicated that the stabilities of the rings increase in the order $(Me_2Si)_5 < (Me_2Si)_7 < (Me_2Si)_6$. The six-membered ring is the most stable ring after the equilibrium has been reached. Longer reaction times and higher temperatures cause decomposition of the cyclic structures.[10] In the equilibrium state the yield of the six-membered ring is about 90%. Most of the dodecamethylcyclohexasilane is produced from depolymerization of the polymer which is the initial product. Higher ring sizes are also formed[12] (see section II.1).

Instead of dimethyldichlorosilane the starting material can also be dimethylchlorosilane Me_2SiHCl. This method should be simpler and safer.[202]

Scheme 24



In case of the ethyl derivative the six-membered ring does not appear to be the preferred ring size. Similar to dodecamethylcyclohexasilane dodecaethylcyclohexasilane can be formed in a dehalogenating coupling reaction of diethyldichlorosilane. The products formed in this reaction depended upon the alkali metal and the conditions. The six-membered ring was obtained in the highest yield of 15% with 2 equiv of lithium at −40 °C in THF. Higher temperatures or other alkali metals decreased the yield. Another way to the perethylated six-membered cyclosilane is photolysis. Starting from the seven-membered ring the six-membered ring was formed after irradiation at 254 nm for 15 min. Diethylsilylene was the second product which could be trapped by triethylsilane.[13,14]

Several examples of mixed substituted hexasilanes are known. Cocondensation of 5 equiv of dimethyldichlorosilane with 1 equiv of a dialkyldichlorosilane $R^1R^2SiCl_2$ with Li in THF provided the five- and six-membered rings $R^1R^2Si(SiMe_2)_4$ and $R^1R^2Si(SiMe_2)_5$. In the case of R^1 = Me and R^2 = Ph the main product was 1-phenylundecamethylcyclohexasilane. A yield of 44% was reported. Dephenylation with NH_4Cl/H_2SO_4 yielded the monochloroundecamethylcyclohexasilane. Other examples are known with R^1, R^2 = Ph, Ph; Me, *t*-Bu; and *t*-Bu, *t*-Bu and the corresponding five- and six-membered rings were obtained. UV and NMR investigations were carried out with all these derivatives.[17]

$(n\text{-PrMeSi})_6$ was prepared by the dehalogenation of $n\text{-PrMeSiCl}_2$ with Li in THF.[17] In the reaction of methylethyldichlorosilane with Li in THF, the best yield was obtained with a 10% excess of Li and a reaction temperature of 0 °C. It was speculated that redistribution of the first-formed, kinetically produced rings (5 and 8) or polymer takes place, which finally produces the six-membered ring as the main rearrangement product.[15]

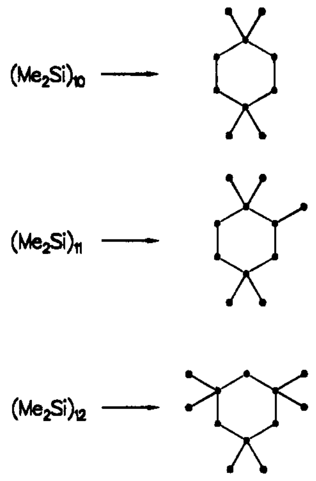
The reaction of $PhMeSiCl_2$ with Li in THF in the presence of $Me_3SiSiPh_3$ as a catalyst produced a mixture of 62% of five isomers of $(MePhSi)_6$ besides some five-membered derivatives.[169,203] Theoretically eight isomers are possible, which are depicted in Scheme 24. The X-ray diffraction of the *all-trans* isomer (A in Scheme 24), which seems to be the most favored isomer, showed a cyclohexane chair formation. Separated were the isomers A and B (by fractional crystallization and HPLC); NMR investigations showed the presence of isomers A to E.

A coupling between $PhMeSiCl_2$ and Me_2SiCl_2 with Na/K alloy resulted, in addition to several unidentified phenylated permethylcyclohexasilanes in the formation of trans 1,4-diphenyldecamethylcyclohexasilane. Only this derivative could be isolated by repeated recrystallizations. The structure was determined by X-ray structure determination and NMR data.[246]

Scheme 25

$$MeO(SiMe_2)_2OMe \xrightarrow{Na} 1/6\ (SiMe_2)_6 + Me_2Si(OMe)_2$$

Scheme 26



● = $SiMe_{3-n}$ n = 0, 1, 2, 3

In an investigation by a Chinese group $(p\text{-MeC}_6H_4\text{SiMe})_6$, $(o\text{-MeC}_6H_4\text{SiMe})_6$, $(PhCH_2SiMe)_6$, $(PhEtSi)_6$, and $(PhSiCH_2CH{:}CH_2)_6$ were synthesized by the usual dehalogenation of the dichlorides with Li and characterized by NMR, IR, MS, and UV.[171]

In presence of a catalytic amount of sodium methoxide, 1,2-dimethoxytetramethyldisilane was converted into cyclic polysilanes $(SiMe_2)_n$ ($n = 5-7$). The best yield of about 60% of the six-membered ring was observed after a reaction time of 4 h at room temperature.[175] A proposed reaction mechanism is described in section V.1. The reaction takes place also with sodium metal[204] (Scheme 25).

It seems to be that the sodium forms sodium silyl compounds as intermediates, similar to the reaction with sodium methoxide.

By use of $AlCl_3/FeCl_3$ as a catalyst large permethylated cyclosilanes ($n = 10-12$) undergo a rearrangement to six-membered rings with side chains (Scheme 26).[166] A proposed reaction mechanism is discussed in section V.1.

Formation of cyclosilanes by dehydrogenation with zirconocene derivatives was possible with monophenylsilane. $(HSiPh)_6$ was formed[193,196] besides other rings. $n\text{-BuSiH}_3$ and n-hexyl-SiH_3 were also used, and six-membered rings were formed.[173,174]

2. Chemical Reactions

2.1. Exchange of Substituents

The synthesis of new derivatives is possible by exchange of substituents. One of the usual reactions is the dephenylation by several agents like HX or triflic acid. 1,2,3,4,5,6-Hexamethylhexaphenylcyclohexasilane was the starting material to form derivatives like $Si_6Me_6X_6$ (X = Cl, Br, F, or OMe). The dephenylation was achieved with $HCl/AlCl_3$ or with $HBr/AlBr_3$. Substitution of the halogen atoms with

ZnF_2 to the fluorinated derivative or methoxylation with methanol were the ways to the other products.[205]

By use of triflic acid hexamethylhexaphenylcyclohexasilane reacted with substitution of two phenyl groups in 1,4-position. With KF 1,4 difluorotetraphenylhexamethylcyclohexasilane was yielded.[206]

Monohalo-substituted permethylated six-membered rings are important starting materials for the preparation of other derivatives and polycyclic silanes. Several methods for their preparation are possible. One way is the cocondensation of dimethyldichlorosilane with phenylmethyldichlorosilane, followed by dephenylation using NH_4Cl/H_2SO_4 or HX. These reactions are described in section VI.1.[17]

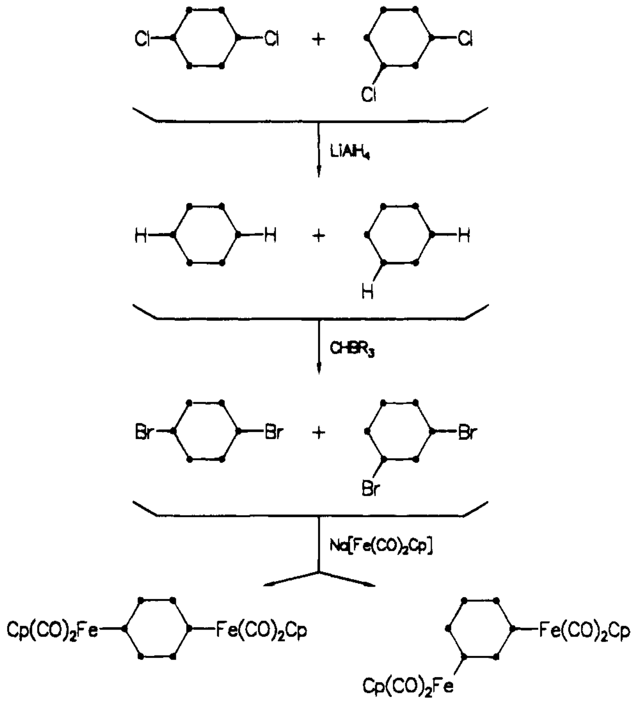
Another way is the exchange of one methyl group. This was possible with $HCl/AlCl_3$ but rearrangements to the five-membered ring (see section V.1) make the isolation troublesome. For isolation a phenylation was necessary followed by distillation of the monophenylated derivative. Dephenylation with $HCl/AlCl_3$ afforded pure monochloroundecamethylcyclohexasilane.[207]

Better is the use of antimony pentachloride. The reaction was described first by Carberry et al.[208] and was used for the preparation of 1,4-dichlorodecamethylcyclohexasilane by Wojnovski.[180,209] More detailed investigation about this reaction showed that depending on the stoichiometric ratio $SbCl_5$/cyclosilane mono- or dichloro derivatives were formed. 1,3- and 1,4-dichloro derivatives were formed simultaneously. The separation of the isomers was only possible by derivatization. 1,4-Dichlorodecamethylcyclohexasilane was isolable through reaction with H_2S. A 1,4-sulfur-bridged cyclosilane was formed which could be separated from the other products.[209] The 1,3-dichloro product afforded polymeric products. Cleavage of the S bridge by HCl yielded pure 1,4-dichlorodecamethylcyclohexasilane. The isolation of the 1,3-dichloro product was more difficult. It was possible via the iron derivatives, as it is depicted in Scheme 27. The bromine derivatives were required for the reaction with $Na[Fe(CO)_2Cp]$. The two iron-containing derivatives could be separated by the better solubility of the 1,3 isomer in benzene. Reaction with HBr afforded the pure dibromo derivatives.

The availability of these mono- and dihalodecamethylcyclohexasilanes opened the possibility of the formation of many new derivatives. Starting from the monohalo compounds other derivatives of the type $Si_6Me_{10}X$ (with X = H, Cl, Br, I, F, OH, OMe, OLi, SH, ONa) were synthesized and characterized. Difunctional groups afforded the formation of molecules with two cyclohexasilanyl units: $Si_6Me_{11}-S-Si_6Me_{11}$ or $Si_6Me_{11}-PPh-Si_6Me_{11}$. It is interesting that it was not possible to form the corresponding siloxane. Only polymeric material was observed. The reason seems to be that the OH group in the silanol is very basic, which can be seen by the chemical shift. Therefore, this OH group is able to split a Si–Si bond of a second molecule and polymerization occurs[210] (Scheme 28).

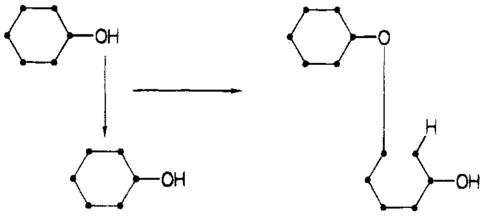
$Si_6Me_{11}H$ reacted with di-*tert*-butylmercury to form $(Si_6Me_{11})-Hg-(Si_6Me_{11})$. This compound reacted with K/Na alloy forming $Si_6Me_{11}K$ which is a valuable starting material for the formation of other derivatives and polycyclic silanes[207] (see section VIII.2).

Scheme 27



● = $SiMe_{2-n}$ n = 0, 1

Scheme 28



● = $SiMe_{2-n}$ n = 0, 1

Some derivatives with transition element substituents are known. The 1,3- and 1,4-bis(cyclopentadienyldicarbonylferrio)decamethylcyclohexasilanes have been mentioned above.[211] The structure of these isomers was assured by NMR (^{29}Si-INADEQUATE) and by X-ray diffraction. The structure of the 1,4 derivative is depicted in Figure 3.[212]

The monosubstituted derivatives $Si_6Me_{11}[Fe(CO)_2Cp]$ and $Si_6Me_{11}[Mo(CO)_3Cp$ were also described.[213]

$Si_6Me_{11}[Fe(CO)_2Cp]$ underwent a photochemical rearrangement to a five-membered ring with a side chain[214] (Scheme 29).

The Mo-derivative could be synthesized only from the monotriflylcyclohexasilane, which could be easily prepared by action of triflic acid with $Si_6Me_{11}Ph$.[215] A Mn–cyclosilane derivative $Si_6Me_{11}(Mn(CO)_5$ was synthesized also by salt elimination but the starting material was the potassium undecamethylcyclohexasilane which reacted with $Cl(Mn(CO)_5$.[216] A first example of a mixed transition metal (with Fe and Co complexes) cyclosilane derivative was obtained by use of 1-hydro-4-bromodecamethylcyclohexasilane. The latter compound was not isolated, it was a mixture with the 1,4-dibromo derivative. Separation was possible via the iron derivatives[215] (different solubility) (Scheme 30).

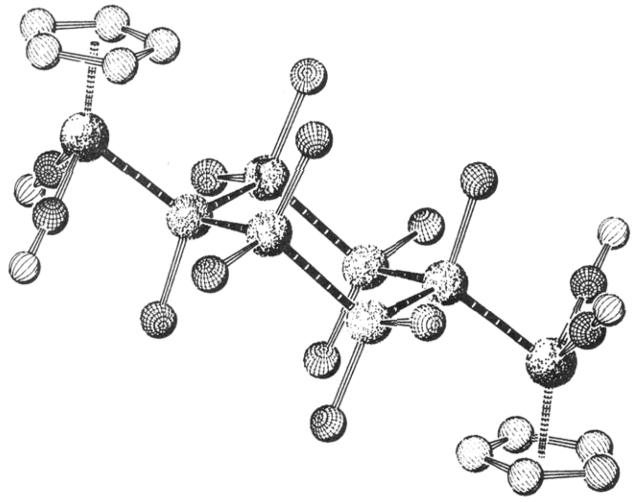


Figure 3. 1,4-Bis(dicarbonylcyclopentadienylferrio)decamethylcyclohexasilane.

Scheme 29

● = $SiMe_{2-n}$ n = 0, 1

Mono- and dicobalt derivatives were formed with $Na[Co(CO)_3PPh_3]$. The presence of the triphenylphosphane group increased the nucleophilicity of the corresponding transition metal anion[215] (Scheme 31).

Recently the first tungsten cyclohexasilane derivative was synthesized. Monochloroundecamethylcyclohexasilane reacted with $K[W(CO)_3Cp]$[217] (Scheme 32).

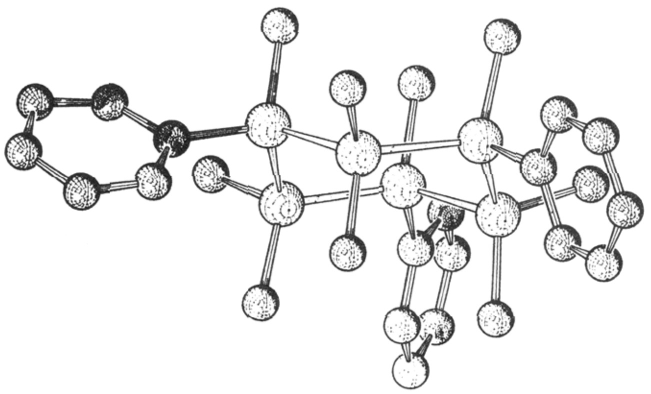
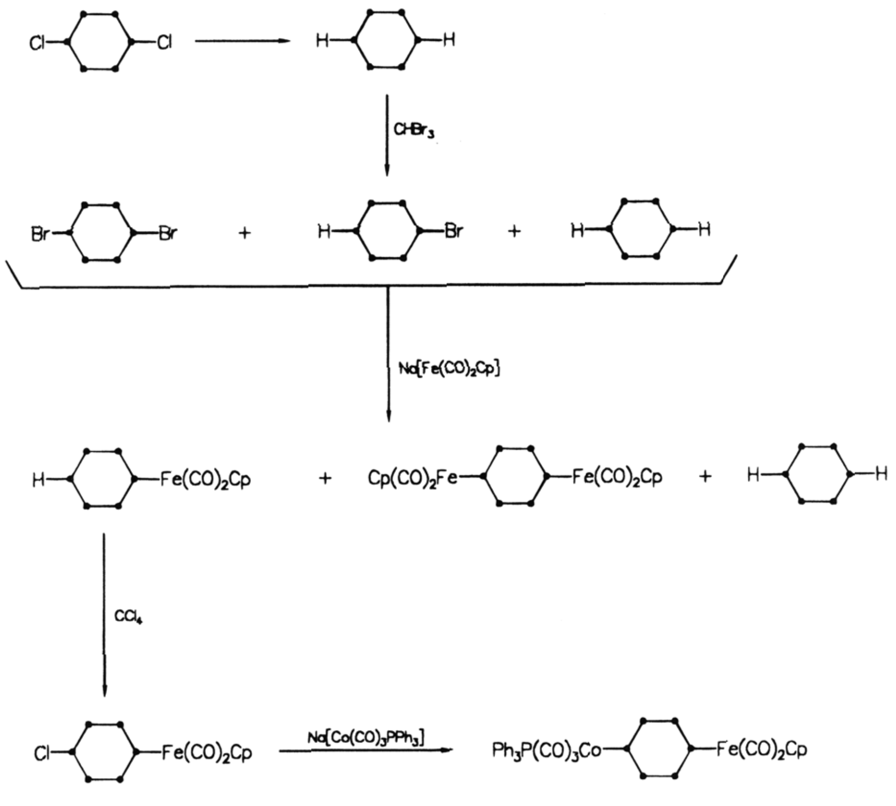


Figure 4. 1,3,5-Triphenylnonamethylcyclohexasilane.

An interesting rearrangement was observed with dicarbonyl(η^5-indenyl)(undecamethylcyclohexasilanyl)iron. This compound was synthesized by normal salt elimination. With i-Pr_2NLi, an intermediate salt was formed and after treatment with methyl iodide migration of the cyclosilanyl group to the 2-position of the indenyl has been observed[218] (Scheme 33).

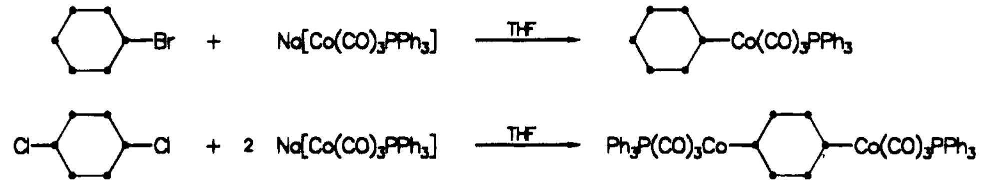
$SbCl_5$ reacted with Si_6Me_{12} under forced reaction conditions to 1,3,5-trichlorononamethylcyclohexasilane. The isolation of the pure compound was possible via phenylation with phenyllithium and distillation of the phenyl derivative. Bromination with HBr, hydrogenation by $LiAlH_4$, and chlorination with CCl_4 led to the pure 1,3,5-trichlorocyclohexasilane. In addition the fluorination of the bromo derivative was possible with ZnF_2. Only the symmetrical 1,3,5 derivatives were formed (Scheme 34), but four configurations are possible. The X-ray structure of the 1,3,5-triphenylnonamethylcyclohexasilane (Figure 4) shows an all-equatorial stereoiso-

Scheme 30



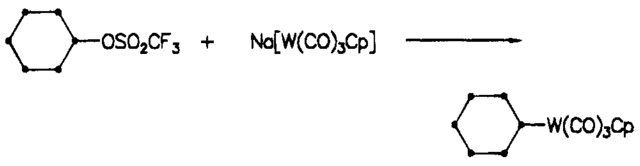
● = $SiMe_{2-n}$ n = 0, 1

Scheme 31



• = $SiMe_{2-n}$ n = 0, 1

Scheme 32



• = $SiMe_{2-n}$ n = 0, 1

mer. On the other hand NMR investigations of 1,3,5-trifluorononamethylcyclohexasilane showed the presence of an all-equatorial and an all-axial conformer as the main products.[219]

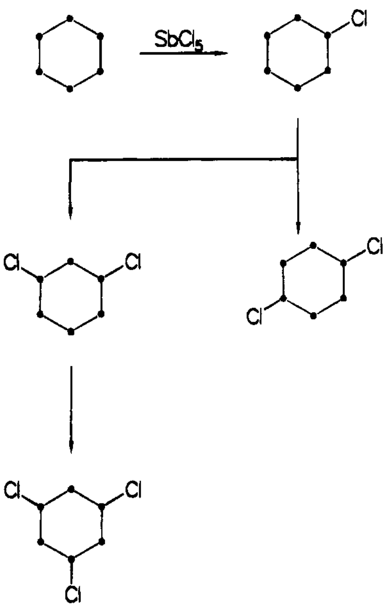
A special method by a stepwise formation of the cyclohexasilane with different substituents was used by Uhlig.[220] This way allowed the formation of 1,2 substituted permethylcyclohexasilanes. The synthesis started with a disilane derivative (Scheme 35). Dephenylation was achieved by action of triflic acid and after addition of a (phenylsilyl)lithium compound a tetrasilane was formed. Repetition of the sequence yielded a hexasilane which could be cyclized by Li.

Irradiation of dodecamethylcyclohexasilane in CCl_4/CH_2Cl_2 in the presence of 9,10-dicyanoanthracene afforded 1,6-dichlorododecamethylhexasilane.[221]

Photochemical decomposition of dodecamethylcyclohexasilane to the corresponding cyclopentasilane and dimethylsilylene is one of the standard methods to generate the silylene. Many trapping experiments were carried out. The chemistry of silylenes is not part of this article. Therefore only some references in this field should be given.[116,161,222-229]

The formation of an undecamethylcyclohexasilyl anion $(Si_6Me_{11})^-$ was observed in the reaction of Si_6Me_{12} with electron transfer reagents like methyllithium, alkali metals, or trimethylsilyl anion in the presence of either hexamethylphosphoramide or of 18-crown-6 in etheral solvents (Scheme 36). The anion can also be produced electrochemically. In HMPA solution the anion is red and stable at room temperature in the absence of water and air. It is a useful intermediate that can be derivatized with a variety of electrophiles.[230]

Scheme 34

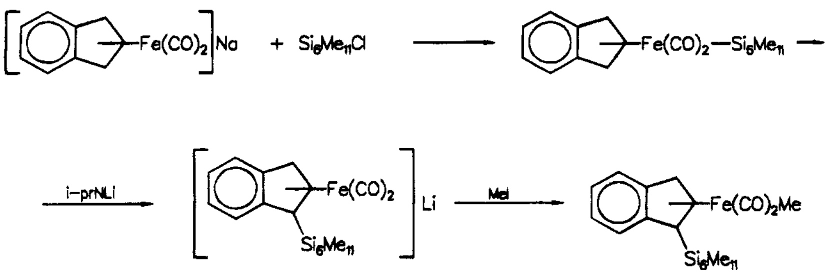


• = $SiMe_{2-n}$ n = 0, 1

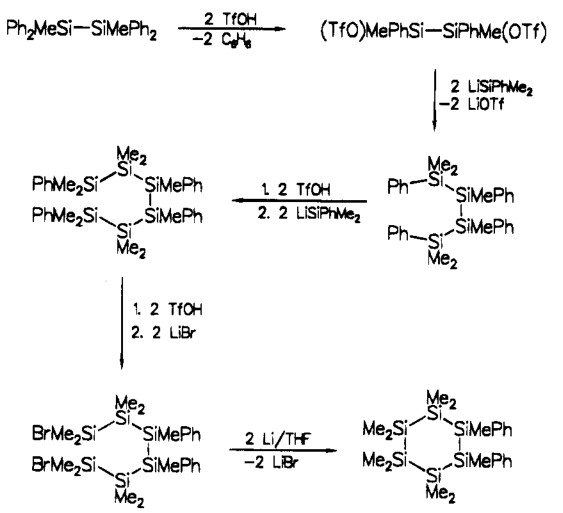
2.2. Insertion Reactions

Dodecamethylcyclohexasilane reacted with sulfur, but slower than cyclopentasilane or other more strained rings (see section V.2.3). The first step between the cyclosilane and sulfur seems to be the formation of a charge transfer complex (polysilane as a donor), followed by an insertion of one sulfur atom with formation of a sulfurane-like transition state, which after rearrangement at the central sulfur atom dissociates to thiacycloheptasilane and an another sulfur molecule. With an excess of sulfur, a second sulfur atom inserted to 1,3-dithiaoctacyclosilane. This was not stable, the Me_2SiS fragment was split from this molecule and monothiacyclohexasilane was formed. This last product was formed also in the insertion reaction of sulfur into decamethylcyclopentasilane (see section V.2.3). Many other smaller sulfur-containing cyclosilanes were observed

Scheme 33



Scheme 35

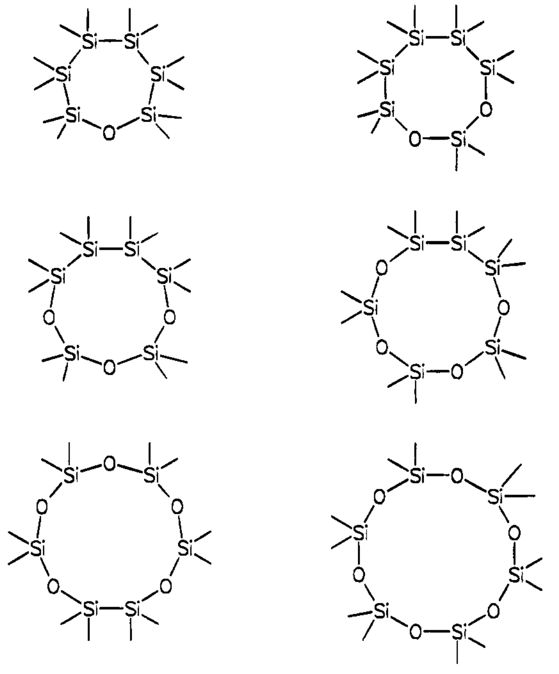


Scheme 36

$$\mathrm{Si_6Me_{12}} \xrightarrow{\mathrm{Na}} \mathrm{Si_6Me_{11}^-} \xrightarrow{\mathrm{Y{-}Hal}} \mathrm{Si_6Me_{11}Y}$$

$$\mathrm{Y = -C_2H_5, -C_3H_7, -CH(CH_3)_2, -CH_2Si(CH_3)_3}$$

Scheme 37



upon heating the starting reaction mixture of sulfur and the cyclosilane.[182,183]

Dodecamethylcyclohexasilane was oxidized by peroxybenzoic acid to form 1,4-dioxacyclohexasilane. The reaction was faster than with open chains. With an excess of peroxybenzoic acid more oxygen inserted and finally dodecamethylcyclotetrasiloxane was formed.[231] Oxidation with *m*-chloroperbenzoic acid led to six oxidation products with one, two, three, four, five, and finally six oxygen atoms in the ring. Only one isomer for each oxidation level was formed. All six silicon atoms are present in the siloxane rings.[232] The formed products are depicted in Scheme 37.

2.3. Ring Opening Reactions

Dodecamethylcyclohexasilane undergoes a long-known ring size reduction reaction with $AlCl_3$. This reaction is described in former reviews and on the formation reactions of five-membered rings[164] (see therefore section V.1).

Halogens like chlorine, bromine, and iodine split the permethylated six-membered ring forming 1,6-dihalododecamethylhexasilanes.[130] A kinetic study of the cleavage rates of iodine with dodecamethylcyclohexasilane showed that the reaction is slower than with more strained rings[9] (see section II.1).

Ring opening was also possible with $SOCl_2$ to the linear 1,6-dichlorododecamethylhexasilane.[233] A quantitative regeneration to the six-membered ring was described with orthoformic acid trimethyl ester[234] and with other agents (alcohols, water, AcOH),[235] but these reports were not found to be reproducible.[181]

Many other halides are able to split the cyclohexasilane forming not only six-membered chains but also shorter chain lengths with halogens on the ends. This was effected with $SbCl_5$, $SnCl_4$, $TiCl_4$, $GaCl_3$, etc.[180]

Cleavage of dodecamethylcyclohexasilane to α,ω-dihydrocarbyl-substituted compounds (allyl, vinyl, tolyl, etc.) was also possible.[236]

Ring-opening reaction occurred also by electrochemical oxidation. Dodecamethylcyclohexasilane, $(SiMe_2)_6$, reacted anodically in the presence of Et_4NBF_4. After working up in aqueous solution $F-(SiMe_2)_n-F$ with $n = 1-6$ and $F-(SiMe_2)_n-OH$ with $n = 2$, 3, or 5 were obtained.[198]

2.4. Other Reactions

Thermolysis of Si_6Me_{12} at 450 °C (50 h, autoclave, final pressure 12 bar) led to polycarbosilanes and about 20% of gaseous products. These gases contain mainly Me_2SiH_2 (72%), hydrogen (14.4%), and methane (9%). Small amounts of $MeSiH_3$ and Me_3SiH were also observed.[237]

A film of Si_6Me_{12} is forming a polycrystalline β-SiC deposit at heating the film at more than 1000 °C. Smooth thin films of β-SiC with good adhesion to the substrate were also obtained by H-PECVD at temperatures higher than 1273 °C.[238] It has been reported, that a preceramic polymer with a molecular weight of more than 1000 could be formed in the reaction of dichlorodecamethylcyclohexasilane with an alkali metal.[240]

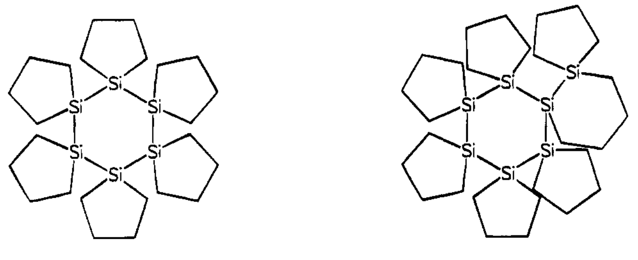
Another report showed that Si_6Me_{12} together with $W(CO)_6$ was an effective cocatalyst of photoinitiated metathesis of hexene (general α-olefins) with a high degree of selectivity. The initial formation of a tungsten−silylene complex was postulated.[241]

3. Physicochemical Properties

In many investigations about the synthesis of cyclohexasilane derivatives vibrational spectra are included. The reader is referred to the original literature for papers dealing with vibrational spectroscopy. Recently an investigation was done with $(R^1R^2Si)_6$ From the observed vibrational spectra it appears the $\sigma-\pi$ hyperconjugation between the phenyl groups and Si atoms in the SiR^1R^2 fragments decreased in the order R^1/R^2 = Ph/Ph, Ph/H (*all-trans*), CH_2PhH (*all trans*).[245]

A solid-state transition of Si_6Me_{12} to a plastic−crystalline phase took place at 350 K. From proton NMR relaxation data methyl reorientation and aniso-

Scheme 38



I II

tropic molecular reorientation were observed in the brittle phase. Anisotropic reorientation appeared to occur simultanously with inversion of the chair-form cyclohexasilane ring. In the plastic phase, isotropic reorientation and translational diffusion were observed.[187]

Motion in the crystalline and plastic phases of Si_6Me_{12} was analyzed by cross-polarization solid-state ^{13}C and ^{29}Si NMR (CP MAS NMR). Even below the transition temperature to the plastic-crystalline state, a large-scale motion became possible without increase in disorder. This motion could be described as a jumplike rotoreptation.[242]

An electron diffraction study of cyclohexasilane Si_6H_{12} was carried out at 130 °C. The molecule is predominantly in a chair form but the other possible forms, the twist and the boat form, seem to exist also in the equilibrium state. The energy barriers are very small between the three forms. The Si–Si distance is 234.2 pm and the Si–Si–Si angle in the chair conformation is 110.3°.[243]

VII. Organosilicon Rotanes

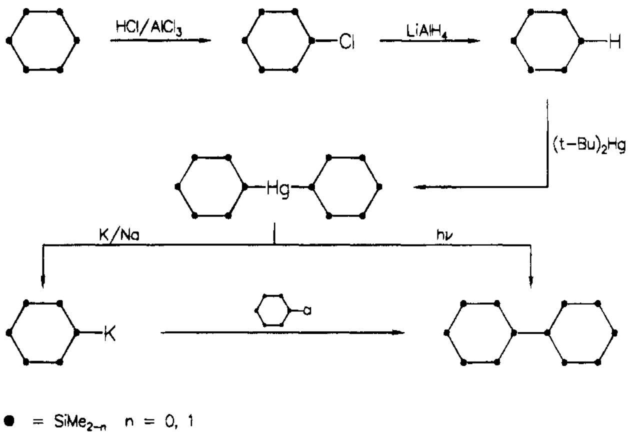
Polyspirocyclopolysilanes $[(CH_2)_4Si]_n$ with $n = 5-12$ and $[(CH_2)_5Si]_n$ with $n = 4-7$, called rotanes, were synthesized by West and co-workers.[247,248] They used cyclotetramethylenedichlorosilane or cyclopentamethylenedichlorosilane, respectively, and alkali metal (Li or K/Na alloy) in THF. When cyclotetramethylenedichlorosilane was used the main product was the thermodynamically most stable six-membered ring (see formula I in Scheme 38) with a yield of 28%. The other ring sizes were formed as kinetic products under nonequilibrium conditions in smaller yields.

A special product in this synthesis was a cyclosilane shown in formula II in Scheme 38 which was observed in a yield of 12%. The structure was assigned mainly by ^{29}Si NMR investigation. This rearrangement is not known on simple alkylcyclosilanes.

In the case of the cyclopentamethylene silicon rotanes, the best yields were obtained with an excess of potassium in THF. The main product was the thermodynamically most stable five-membered ring $[(CH_2)_5Si]_5$.

The rotanes are air stable. Their reactivity generally appears to be higher than for other alkylcyclosilanes, which is propably caused by the smaller steric protection of the cyclosilane skeleton. Crystal structures were determined from the main products. The six-membered ring exhibited a chair conformation, the five-membered ring adopted a variety of conformations.

Scheme 39



The UV spectra of the cyclotetramethylenecyclopolysilanes showed regular changes up to $n = 10$. The last compound exhibited an unusual intense band at 268 nm (similar to $(Me_2Si)_{10}$). This special property may be caused by a sharp conformational change.

Photolysis of $[(CH_2)_5Si]_5$ and $[(CH_2)_4Si]_6$ led to loss of a cyclic silylene and formation of the next smaller ring. The smallest ring, which was observed was the four-membered ring. Photolysis in triethylsilane as trapping agent was very useful for this ring contraction.[160]

Photolysis in 3-methylpentane glass at 77 K splits the ring-forming silylene, showing a wavelength of the longest electronic transition at 436 nm for $[(CH_2)_4Si]_6$ and 449 nm for $[(CH_2)_5Si]_5$. Upon annealing of the glass, the silylene absorption was lost and new absorption bands appear assigned to disilenes formed by dimerization of the silylenes.[226]

VIII. Polycyclic Silanes

1. General Remarks

This section will summarize the current knowledge about directly connected cyclosilanes. Not included are cyclosilanes linked by heteroatoms. Examples of this last group of cyclosilanes are given on page 1514. Publications before 1980 are not included.

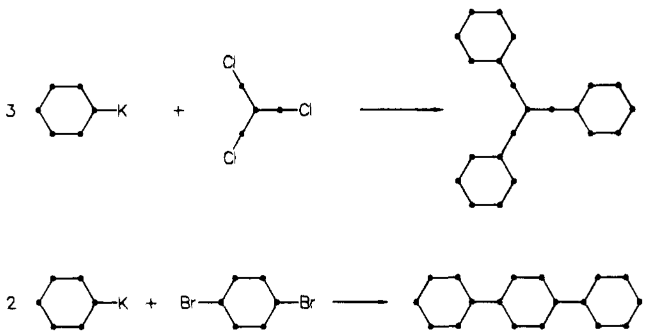
Two general possibilities are given to connect cyclosilanes together. Either the cyclosilanes are linked linear over one Si atom, or the cyclosilanes share one or more Si atoms forming annelated cyclosilanes or cages.

2. Linearly Connected Polycyclic Silanes

The availability of alkali metal cyclosilane derivatives provided the possibility to form bi(cyclohexasilanyl). Potassium undecamethylcyclohexasilane could be formed from bi(cyclohexasilanyl)mercury with Na/K alloy. The mercury compound was synthesized from the monohydroundecamethylcyclohexasilane with di(*tert*-butyl)mercury. Bi(cyclohexasilanyl) was formed in the reaction of the potassium compound with monochloroundecamethylcyclohexasilane. Another way to this bicycle was the decomposition of the mercury compound by light[207] (Scheme 39).

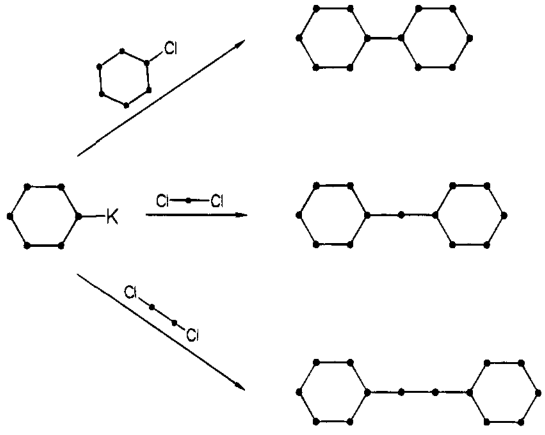
It was reported in a short communication that this compound was also formed in the reaction of undecamethylcyclohexasilane by action of di-*tert*-butyl peroxide.[249]

Scheme 40



● = $SiMe_{2-n}$ n = 0, 1

Scheme 41



● = $SiMe_{2-n}$ n = 0, 1

The structure of the bicycle exhibited a longer Si–Si distance (237.8(3) pm) for the exocyclic Si–Si bond. In a normal coordinate analysis, based on vibrational spectra, the Si–Si force constant of this exocyclic Si–Si bond was calculated to be 155 N/m.[250] Therefore, it is understandable that this bond can be split very easily.

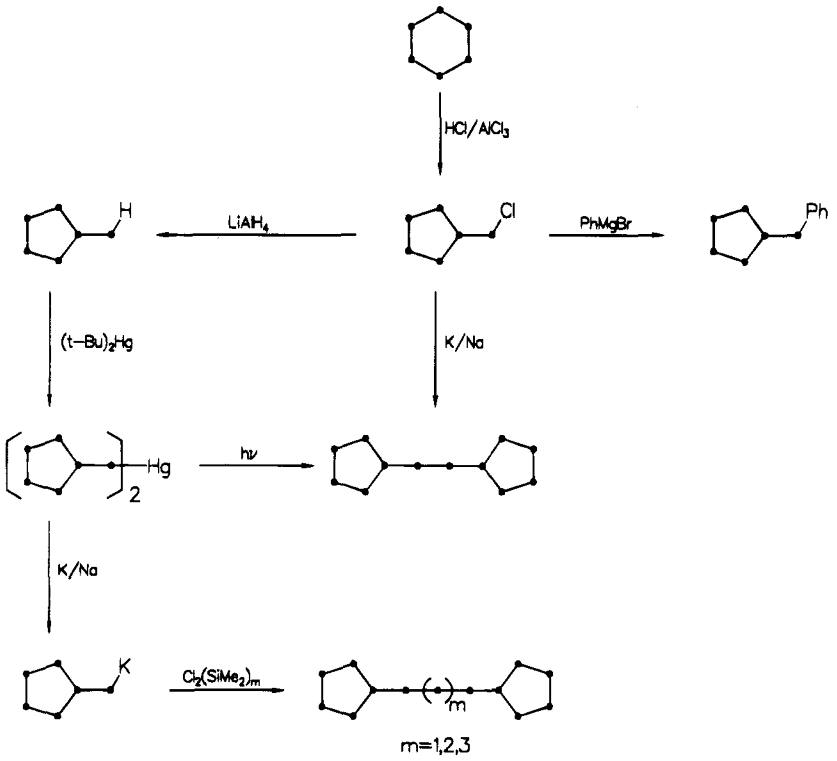
Starting from potassium undecamethylcyclohexasilane other polycyclic silanes could be synthesized. Some examples are given in Scheme 40. The reaction with 1,4-dibromodecamethylcyclosilane, for instance, led to a tricyclic silane and the reaction with 1,3,4 trichloroisotetrasilane afforded a tricyclic cyclosilane with 22 Si atoms.[251]

When potassium undecamethylcyclohexasilane was reacted with dichlorodimethylsilane or α,ω-dichloropermethyloligosilanes bicyclic silanes with the two rings connected by one or more $SiMe_2$ units were formed[207] (Scheme 41).

This was also possible with five-membered ring systems employing a very similar reaction pathway, which is depicted in Scheme 42.[252]

Dehalogenative reduction of monochlorononamethylcyclopentasilane with Na/K alloy was used to synthesize bi(cyclopentasilanyl) Si_5Me_9–Si_5Me_9.[164] Although some conformers of the two rings are possible ^{29}Si NMR INEPT-INADEQUATE investigations showed that only one conformer seemed to be present. By use of ^1J and ^2J coupling constants exact assignment of single atoms and an evaluation of the structures were achieved. No additional ^2J(Si1–Si2′) couplings, indicating the presence of other conformers, were found at the given resolution.[254] The application of the INADEQUATE pulse sequence (both in one-dimensional and two-dimensional cases) was extended to study such silicon frameworks. This was shown at the bicyclic six-membered ring Si_6-

Scheme 42



● = $SiMe_{2-n}$ n = 0, 1

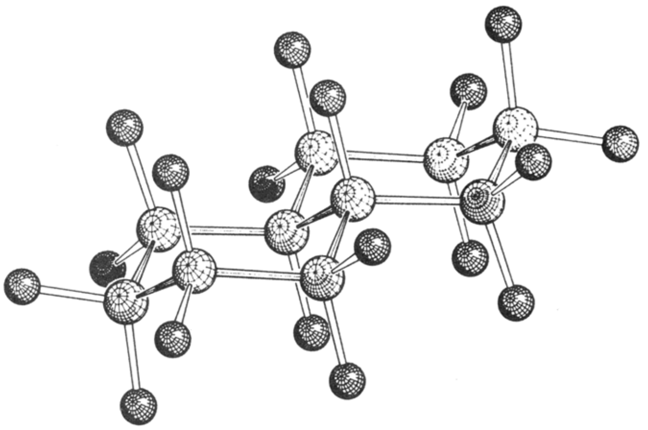
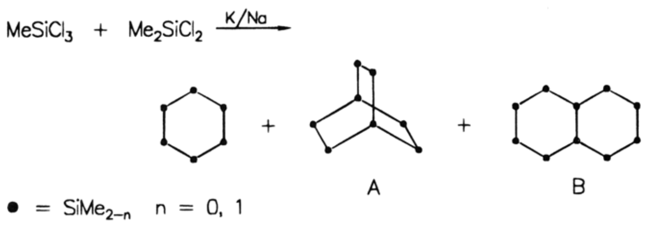


Figure 5. Structure of octadecamethylbicyclo[4.4.0]decasilane.

Scheme 43



$Me_{11}-Si_6Me_{11}$ and at a bicyclic ring with a connecting $SiMe_2$ group $Si_6Me_{11}-SiMe_2-Si_6Me_{11}$.[30]

Interesting are the UV spectra of these linearly connected polysilanes. The Si_5 ring generally is more shifting than the Si_6 ring. The longest wavelength absorption was shifted bathochromically, when the connecting $SiMe_2$ chain became longer. An exception was the directly connected rings exhibiting a strong bathochromic shift which makes increased electronic interactions in these systems very likely.[253]

3. Annelated Silicon Ring Systems

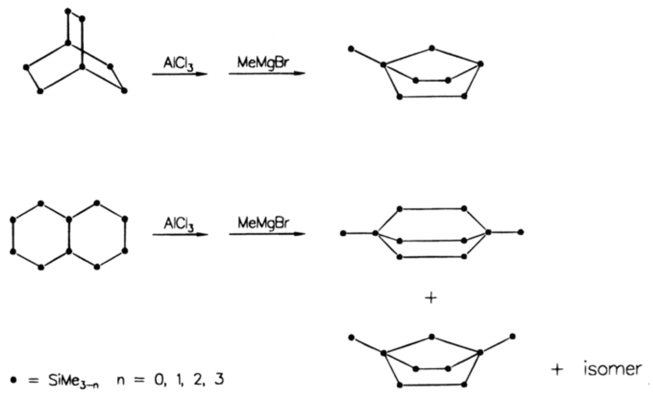
The action of Na/K alloy upon a mixture of methyltrichlorosilane and dimethyldichlorosilane was used to synthesize polycyclic silanes with annelated rings. Two compounds (A and B in Scheme 43) were isolated. Other linear and cyclic silanes were found in small yields.

Rearrangements took place with $AlCl_3$. The products formed were treated with MeMgBr and the methylated derivatives were identified. The result is depicted in Scheme 44.[164]

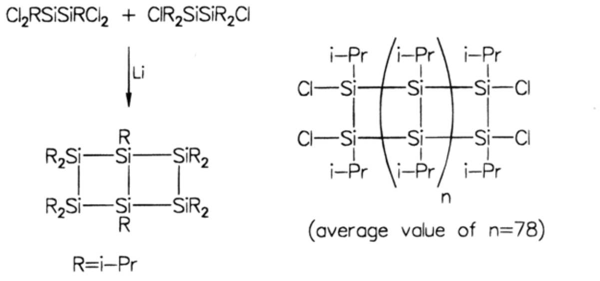
Recently the synthesis of B (Scheme 43) was reinvestigated and the reaction mixture was worked up by use of chromatographic methods (reversed-phase HPLC and MPLC).[172] The X-ray structure of B is depicted in Figure 5. It is interesting that in the crystal used for the structure determination only the "trans" form was present, which adopted a regular chair formation.[254]

Chemically the bicycle B proved to be very sensitive. Irradiation with light resulted in decomposition to monocyclic rings and polymers. $AlCl_3$ split the system to chlorinated oligosilanes. However, the stability was high enough to form a radical anion $Si_{10}Me_{18}^-$ by action of Na/K alloy in a mixture of diethyl ether/glyme at 130 K. The radical anion is stable only at low temperatures for a short time. It rearranged to the known radical anion of the monocyclic five-membered ring[254] (see section II.6).

Scheme 44



Scheme 45



A first bicyclo[2.2.0]hexasilane was synthesized by reacting a mixture of 1,1,2,2-tetraisopropyldichlorodisilane and 1,2-diisopropyltetrachlorodisilane with Li.[255] Decaisopropylhexasilabicyclo[2.2.0]hexane (Scheme 45) was formed in very small yield of about 3%. It is stable to atmospheric oxygen and water. The bicyclic skeleton is twisted and exhibits C_2 symmetry. The puckering of each four-membered ring is 21.8°.[269] With an increasing amount of tetrachlorodisilane in the ratio of the two starting components, polymeric ladder polysilanes (Scheme 45) were formed.[270]

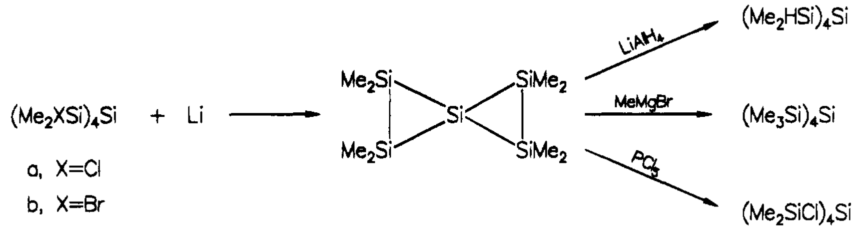
Octamethylspiropentasilane (Scheme 46) was synthesized from tetrakis(dimethylbromosilyl)silane or the corresponding chloride with Li. The compound was not isolated but seemed to be stable in solution for several days at room temperature. The rather strained system underwent splitting reactions to tetrasilanes with $LiAlH_4$, Grignard compounds, or PCl_5[271] (Scheme 46).

The inverse structure, two three-membered rings sharing a Si−Si bond is the tetrasila[1.1.0]butane system. As a first example 1,3-di-*tert*-butyl-2,2,4,4-tetrakis-(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]-butane was synthesized as shown in Scheme 47.[127,256] The central Si−Si bond was found to be readily susceptible to a variety of external attacks and the puckered ring system itself undergoes rapid inversion. The central Si−Si bond is relatively short, 237.3(3) pm. The dihedral angle is 121°.[257] Some reactions, leading to derivatives of the four-membered ring, are depicted in Scheme 48.[127]

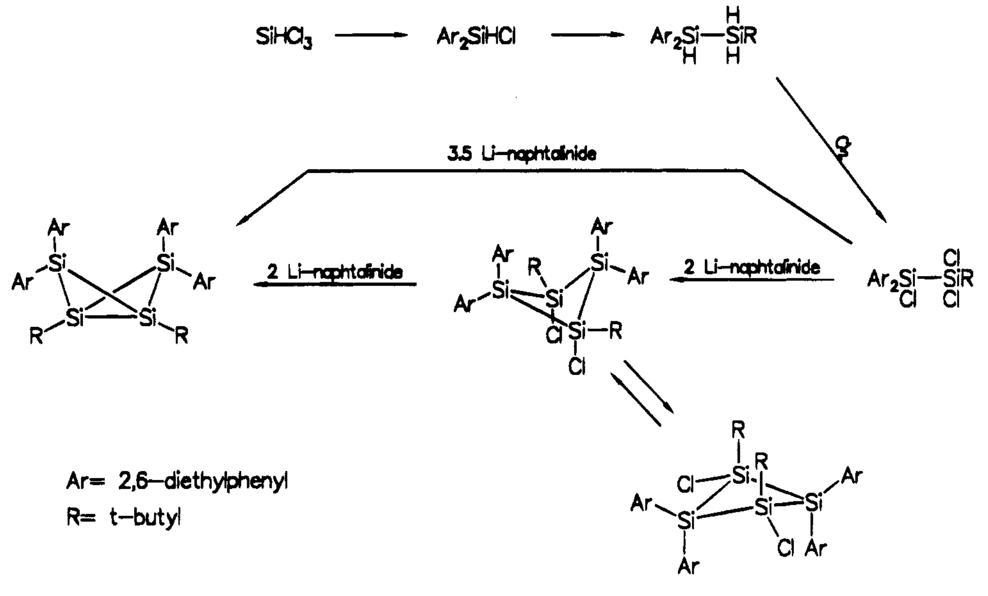
This ring system has also been postulated as an intermediate in the formation of some cyclotetrasilane derivatives[126] (compare with section IV.1).

First investigations of the reductive oligomerization of 1,2-di(*tert*-butyl)-1,1,2,2-tetrachlorodisilane led to the formation of unexpected tricyclo[$2.2.0.0^{2,5}$]hexa-

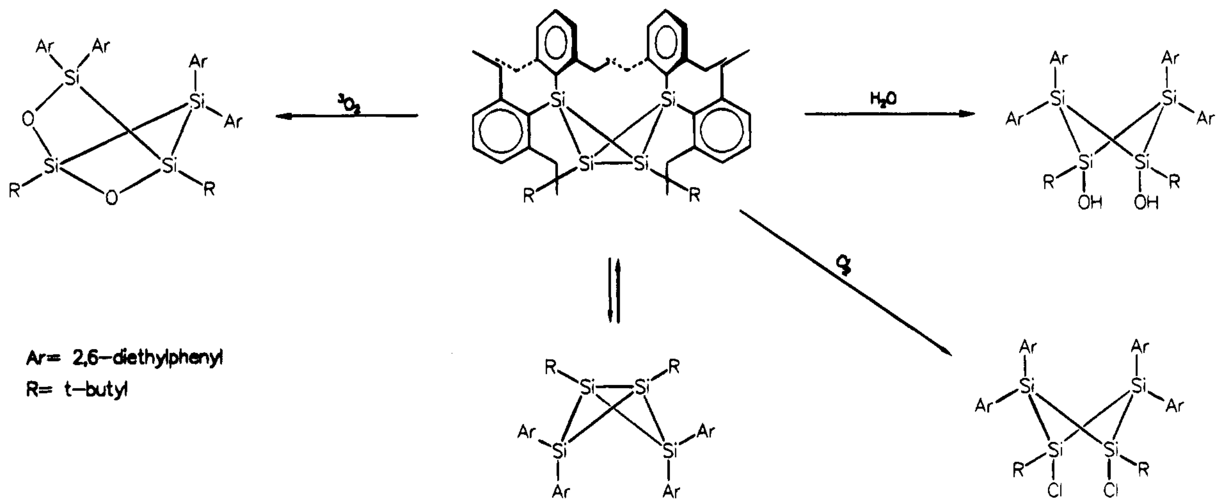
Scheme 46



Scheme 47



Scheme 48



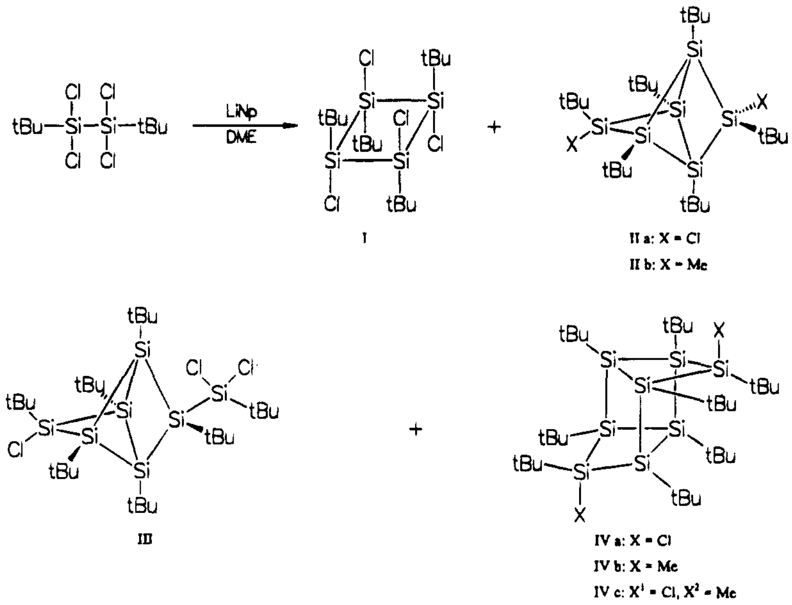
silane and tetracyclo[3.3.0.0^{2,7}.0^{3,6}]octasilane derivatives.[124] The reduction took place with LiNp in DME, whereby the resulting product distribution depended on the amount of LiNp in relation to (t-BuSiCl$_2$)$_2$. Using the relation LiNp/(t-BuSiCl$_2$)$_2$ = 2.5:1 the products I, IIa, III, and IVa were formed and identified after fractional recrystallization by NMR[258] and X-ray diffraction. With the ratio LiNp/(t-BuSiCl$_2$)$_2$ = 5:1, the compounds IIb, IVb, and IVc were formed and identified after chromatographic separation (Scheme 49).

The methyl groups in IVb and IVc could be substituted by chloride quantitatively by a Benkeser reaction, using H_2PtCl_6/ $HSiCl_3$.

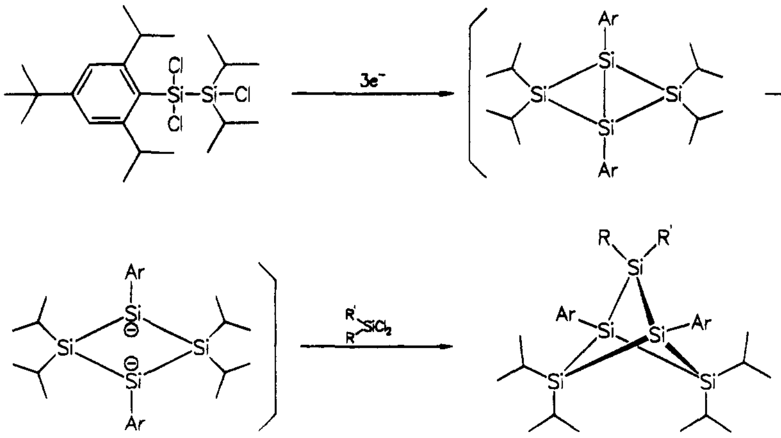
In 1990 a study on bicyclo[1.1.1]pentasilane derivatives was published.[259] 1,3-Bis(4-*tert*-butyl-2,6-diisopropylphenyl)-2,2,4,4-tetraisopropylbicyclo[1.1.1]pentasilane and similar derivatives were formed in the reaction of 1,1,2-trichloro-1-(4-*tert*-butyl-2,6-diisopropylphenyl)-2,2-diisopropyldisilane and 5 equiv of LiNp with RR′SiCl$_2$ (R = R′ = H or R = Me, R′ = H or R = Ph, R′ = H) (Scheme 50). The structure of the compounds exhibited high homology to the corresponding carbon analogs. These analogs can be used for a quick estimation of “nonbonding” Si–Si distances in unknown compounds. The structure was determined by NMR and by X-ray diffraction.

An interesting group of compounds among the polycyclic octasilanes are the octasilacubanes. The first success in synthesizing these strained cage structures was achieved by using *tert*-butyldimethylsilyl groups as bulky substituents, which confer kinetic stability on the cubic silicon skeleton.

Scheme 49



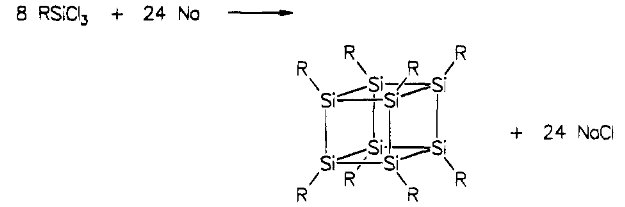
Scheme 50



The reaction was carried out by condensation of $RSiBr_2{-}SiBr_2R$ or $RSiBr_3$ ($R = t\text{-}BuMe_2Si$) with sodium in toluene. After recrystallization from methylcyclohexane the product formed bright yellow prisms, which were air-sensitive, but indefinitely stable in an inert atmosphere. The compound was moderately soluble in aliphatic and aromatic solvents.[260] The structure was determined by the simplicity of the ^{29}Si NMR spectra which showed only two signals. An X-ray structure determination of this derivative also was performed.[261]

Structure determinations were also done for other derivatives. Ab initio calculations (HF/6-31G*) gave rise to the assumption, that alkyl-substituted structures might be more strained compared to the corresponding silyl derivatives. Therefore, a second derivative was made with $R = CMe_2CHMe_2$.[262] The synthesis was carried out with the monosilane and sodium (Scheme 51). This derivative formed orange prismatic crystals which were stable on air and moderately soluble in organic solvents. The cubic structure (Figure 6) was slightly distorted from the regular cube, due to the size of the substituents. These substituents seem to be excellent protecting groups, providing high kinetic stability to the compound. The thermodynamic stability also seemed to be very high; the compound was stable up to 200 °C.

Scheme 51



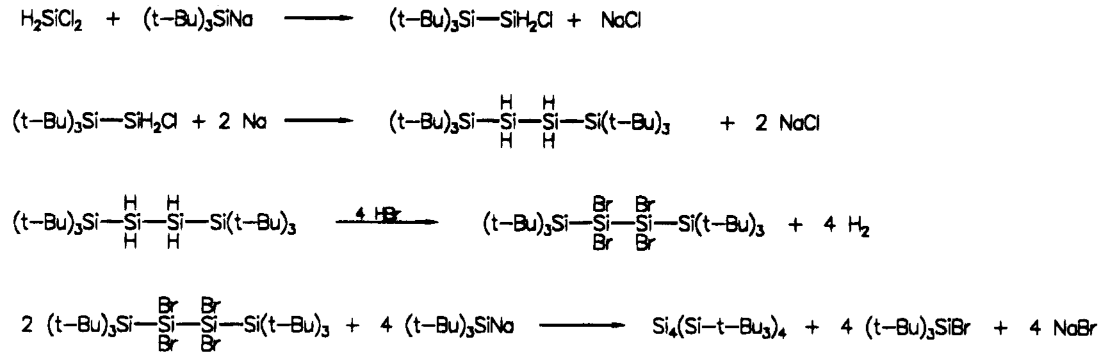
Another derivative with R = 2,6-diethylphenyl was synthesized using $Mg/MgBr_2$ in THF.[263] In this case the X-ray structure indicated an almost perfect cubic structure of the framework.

A derivative with R = *t*-Bu groups was also described.[264]

In 1993 the first hexasilaprismane was prepared by reductive coupling in the same way which was reported for the octasilacubanes[265] (Scheme 51). $Mg/MgBr_2$ was used because alkali metals sometimes caused cleavage of Si–Si bonds. The resulting hexakis(2,6-diisopropylphenyl)tetracyclo[$2.2.0.0^{2,6}0^{3,5}$]hexasilane formed orange crystals which were stable on air. The structure showed that the skeleton is slightly distorted from the regular prismane structure (Figure 7).

According to ab initio studies the strain energy of $(SiH)_n$ polyhedrons increases with the number of

Scheme 52



$$H_2SiCl_2 + (t\text{-}Bu)_3SiNa \longrightarrow (t\text{-}Bu)_3Si{-}SiH_2Cl + NaCl$$

$$(t\text{-}Bu)_3Si{-}SiH_2Cl + 2\ Na \longrightarrow (t\text{-}Bu)_3Si{-}\overset{H}{\underset{H}{Si}}{-}\overset{H}{\underset{H}{Si}}{-}Si(t\text{-}Bu)_3 + 2\ NaCl$$

$$(t\text{-}Bu)_3Si{-}\overset{H}{\underset{H}{Si}}{-}\overset{H}{\underset{H}{Si}}{-}Si(t\text{-}Bu)_3 \xrightarrow{4\ HBr} (t\text{-}Bu)_3Si{-}\overset{Br}{\underset{Br}{Si}}{-}\overset{Br}{\underset{Br}{Si}}{-}Si(t\text{-}Bu)_3 + 4\ H_2$$

$$2\ (t\text{-}Bu)_3Si{-}\overset{Br}{\underset{Br}{Si}}{-}\overset{Br}{\underset{Br}{Si}}{-}Si(t\text{-}Bu)_3 + 4\ (t\text{-}Bu)_3SiNa \longrightarrow Si_4(Si{-}t\text{-}Bu_3)_4 + 4\ (t\text{-}Bu)_3SiBr + 4\ NaBr$$

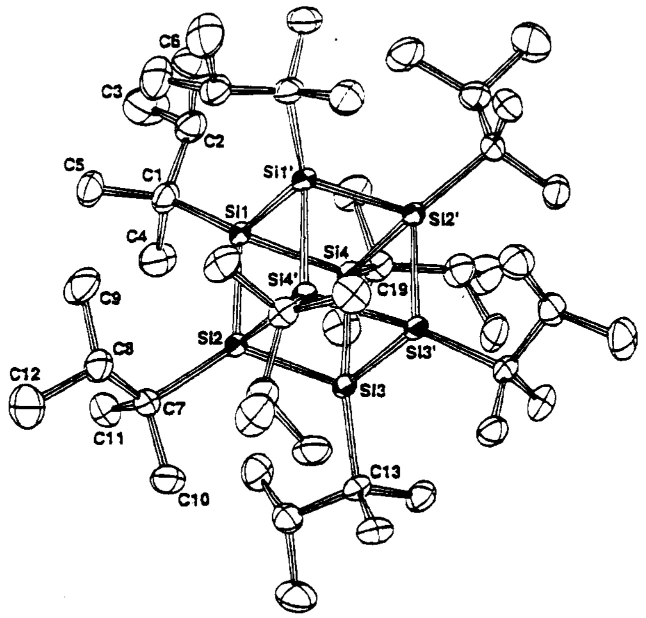


Figure 6. Structure of octakis(1,1,2-trimethylpropyl)-octasilacubane. (Reprinted from ref 262. Copyright 1992 VCH Weinheim, Germany.)

triangular rings in the skeleton. That causes increasing difficulties in synthesizing smaller polyhedrons. Very bulky substituents should make the tetrahedrotetrasilane more stable.

Recently it was possible to synthesize such a tetrahedro-tetrasilane with "supersilyl" groups (= tris-*tert*-butylsilyl group). The first step was the synthesis of 1,1,1-tris-*tert*-butyl-2-chlorodisilane. This disilane derivative was coupled to form 1,1,1,4,4,4-hexa-*tert*-butyltetrasilane by action of sodium. After bromination with HBr a coupling to the tetrahedrotetrasilane derivative was possible by use of sodiumsupersilyl^{266} (Scheme 52).

The product formed intensively colored yellow-orange crystals, which underwent reversible color change to dark red on heating. The crystals were highly temperature and photolytically stable and also insensitive to water and air. The compound could not be reduced with sodium in the presence of 18-crown-6 and benzene, but underwent a reaction with oxidizing agents as tetracycanoethylene or bromine.^{266}

Pure crystals of Si_4R_4 have not been obtained so far, but crystallization together with $(t\text{-}Bu_3Si)_2$ ("Superdisilane") in C_6D_6 gave yellow-orange squares of the composition $2Si_4R_4{\cdot}(t\text{-}Bu_3Si)_2{\cdot}C_6D_6$ whose structure has been be determined by X-ray investigation (Figure 8).

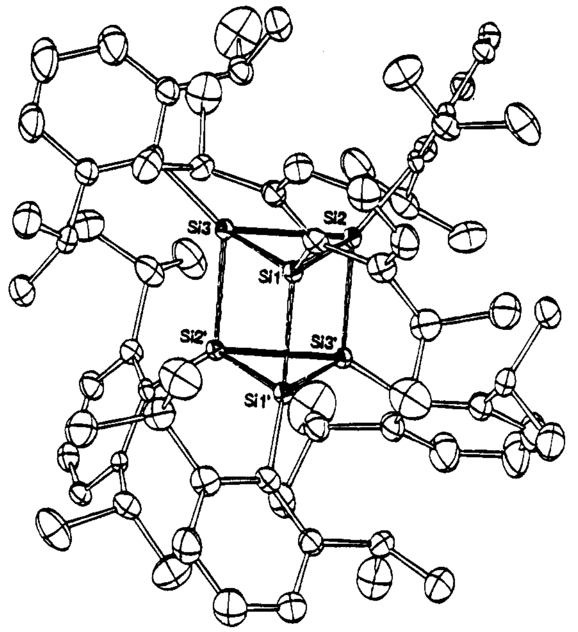


Figure 7. Structure of hexakis(2,6-diisopropylphenyl)-tetracyclo[2.2.0.0.^{2,6}0^{3,5}]hexasilane. (Reprinted from ref 265. Copyright 1993 American Chemical Society.)

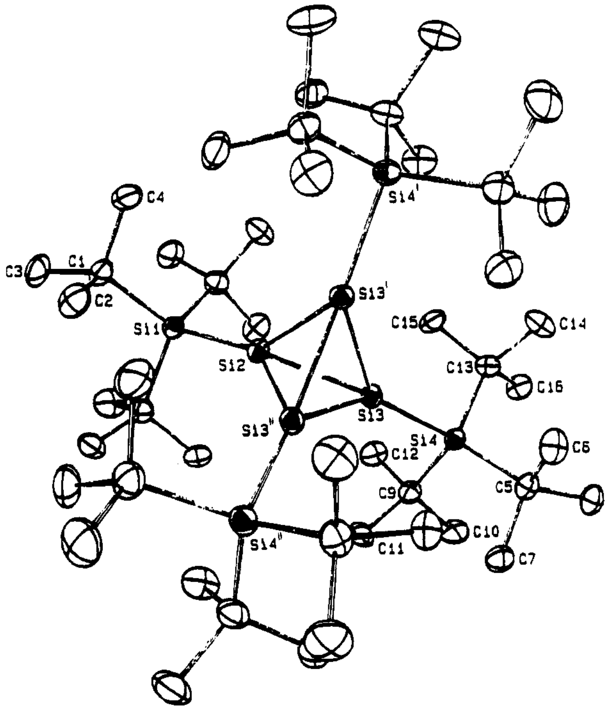


Figure 8. Structure of $(t\text{-}Bu_3Si)_4Si_4$. (Reprinted from ref 2. Copyright 1993 VCH Weinheim, Germany.)

Organic derivatives of Si clusters and cages are not the only ones known. Several silicides also contain such Si frameworks in the structure. A Si_4^{4-} ion with a tetrahedron structure is included in M_4Si_4 (M = Na, K, Rb, Cs).[272] An investigation of the IR spectra showed tetrahedron symmetry and very small force constants of the Si–Si bond ($\approx$ 1.05 N/m).[268] Very large clusters with 46 Si atoms were found in K_8Si_{46} with the Si atoms forming a dodecaeder.[267] Several other cluster structures in inorganic compounds are known.

IX. Acknowledgments

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X. Literature

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