

Substituted Polyhedral Silicon and Germanium Clusters

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Abstract Chemistry of polyhedral silicon and germanium clusters is summarized. Historical background, synthesis, structure, physical properties, and reactions are described in detail.

Keywords Hexasilaprismane · Octasilacubane · Polysilane · Steric protection · Strained molecules · Tetrasilatetrahedrane

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Abbreviations

<i>t</i> -Bu	<i>Tert</i> -Butyl
18-Cr-6	18-Crown-6
cat	Catalyst
d	Day(s)
DEP	2,6-Diethylphenyl
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
equiv	Equivalent(s)
e.g.	For example
Et	Ethyl
exc.	Excess
h	Hour(s)
HMPA	Hexamethylphosphoric triamide
LiNapht	Lithium naphthalenide
<i>m</i> -CPBA	<i>m</i> -Chloroperoxybenzoic acid
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl
MS	Mass spectrometry
min	Minute(s)
mol	Mole(s)
NBS	<i>N</i> -Bromosuccinimide
NCS	<i>N</i> -Chlorosuccinimide
Nu	Nucleophile
Ph	Phenyl
Pr	Propyl
<i>i</i> -Pr	Isopropyl
py	Pyridine
rt	Room temperature
s	Second(s)
SCE	Saturated calomel electrode
TBAF	Tetrabutylammonium fluoride
TBDMS	<i>Tert</i> -butyldimethylsilyl
TBDPS	<i>Tert</i> -butyldiphenylsilyl
Tf	Trifluoromethanesulfonyl (triflyl)
TFA	Trifluoroacetic acid
TGA	Thermogravimetric
thexyl	1,1,2-Trimethylpropyl
THF	Tetrahydrofuran
TEP	2,4,6-Triethylphenyl
TIP	2,4,6-Triisopropylphenyl
TIPS	Triisopropylsilyl

TMEDA	<i>N,N,N',N'</i> -tetramethyl-1,2-ethylenediamine
TMS	Trimethylsilyl
Tol	4-Methylphenyl
trityl	Triphenylmethyl

1 Introduction

Synthesis of organic compounds that possess platonic solid geometries allured many chemists because of their aesthetic appeal and synthetic challenge. Before the middle of the 1980s, except for icosahedral and octahedral molecules that could not be accessed in the case of carbon, tetrahedrane, cubane, and dodecahedrane were prepared by multistep synthesis, which are globally referred to as platonic hydrocarbons [1, 2].

With the development of the higher group-14 element chemistry, heavier platonic hydrocarbon counterparts were the next logical synthetic targets. Unlike platonic hydrocarbons that are basically stable in the air, polyhedral silicon and germanium compounds are inherently unstable towards oxidation. This prohibited the successful synthesis of cage compounds of silicon and germanium until 1988, about quarter century later than the synthesis of cubane, when octasilacubane was first isolated [3]. The kinetic instability was overcome by the use of sterically shielding substituents; many other examples of the family have been prepared since then. This review will therefore focus on cage compounds with substituents and does not aim to include the rather extensive chemistry of polyhedral Zintl anions in the solid state and – since recently – also in solution, which are covered elsewhere in this volume. In addition to the platonic compounds, other substituted silicon or germanium clusters were prepared. In Table 1, platonic hydrocarbons and heavier group 14 element congeners are summarized.

Compared to carbon clusters, silicon and germanium clusters show quite different physical properties and reactivities, due to the σ -conjugation that makes low ionization potentials [4]. In this review, synthesis, structure, properties, and reactivities of silicon and germanium clusters are described in detail.

2 Synthesis, Structures, and Properties

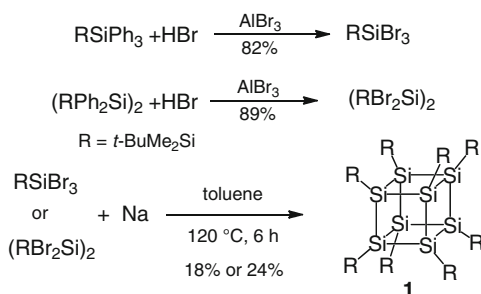
2.1 Octasilacubanes and Octagermacubanes

In contrast to the carbon analogs that demanded a multistep synthesis, octasilacubanes were obtained in a very facile single-step reaction. From the mid-1980s, the Matsumoto and Nagai group at Gunma University was interested in the chemistry of silyl-substituted silicon compounds. The introduction of bulky organic groups for steric protection often encounters with low reactivity or necessitates longer reaction

Table 1 List of Group-14 polyhedranes

	Tetrahedrane	Hexaprismane	Cubane	Pentaprismane	Dodecahedrane
C	G. Maier (1978)	T. J. Katz (1973)	P. E. Eaton (1964)	P. E. Eaton (1981)	L. A. Paquette (1982)
Si	N. Wiberg (1993)	A. Sekiguchi and H. Sakurai (1993)	H. Matsumoto and Y. Nagai (1988)		
Ge	N. Wiberg (1996)	A. Sekiguchi and H. Sakurai (1989)	A. Sekiguchi and H. Sakurai (1992)		
Sn		N. Wiberg (1999)	L. R. Sita and I. Kinoshita (1990)	L. R. Sita and I. Kinoshita (1990)	

Carbon compounds listed are hydrogen substituted

**Scheme 1** Synthesis of octasilacubane **1**

times. On the other hand, silyl substituents are introduced easily by simple usage of Grignard or lithium reagents. Longer Si–Si or Si–C bond lengths compared to C–C bond are also effective for the introduction of bulky substituents. This advantage made it possible to access to the precursors of silicon clusters, and silyl-substituted octasilacubane **1**, that is the first example of a silicon polyhedral compound, was obtained in 18% from tribromomonosilane and 24% from 1,1,2,2-tetrabromodisilane [3] (Scheme 1).

Octasilacubane **1** forms yellow crystals as shown in Fig. 1. This compound is stable in a sealed tube, but gradually decomposed in air to give a white solid. The cage structure of octasilacubane **1** is responsible for the unique UV–vis absorption up to 470 nm. A cyclic voltamogram revealed the oxidation potential to be 0.40 V, and this value is much lower than the usual cyclic polysilanes.

Because of its relative instability, X-ray crystallographic analysis was not successful in 1988 because the compound gradually decomposed under exposure of X-ray

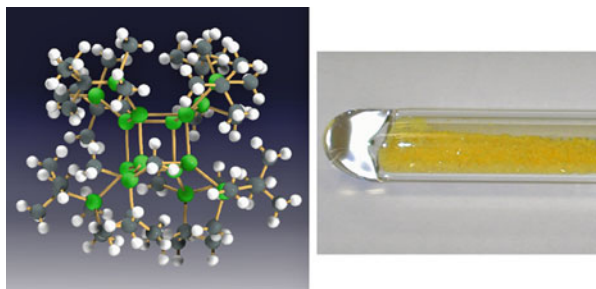
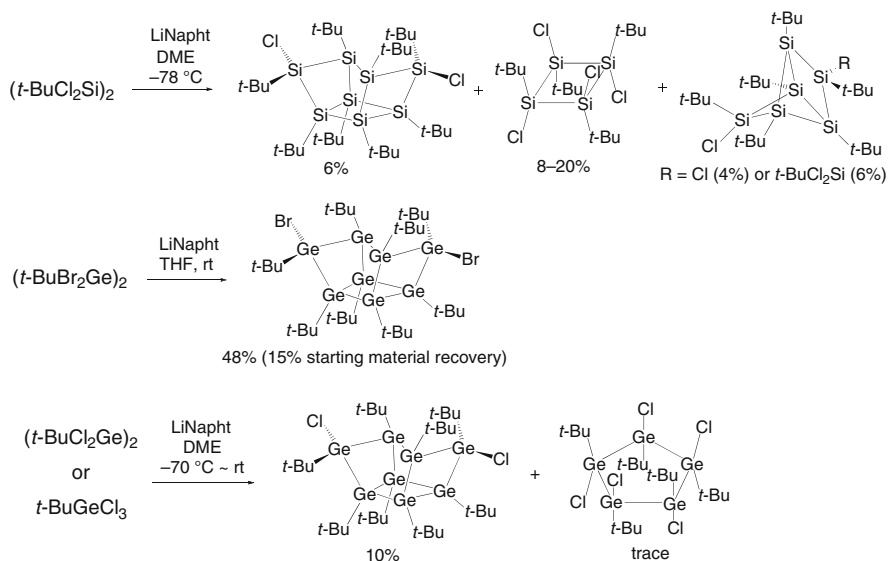


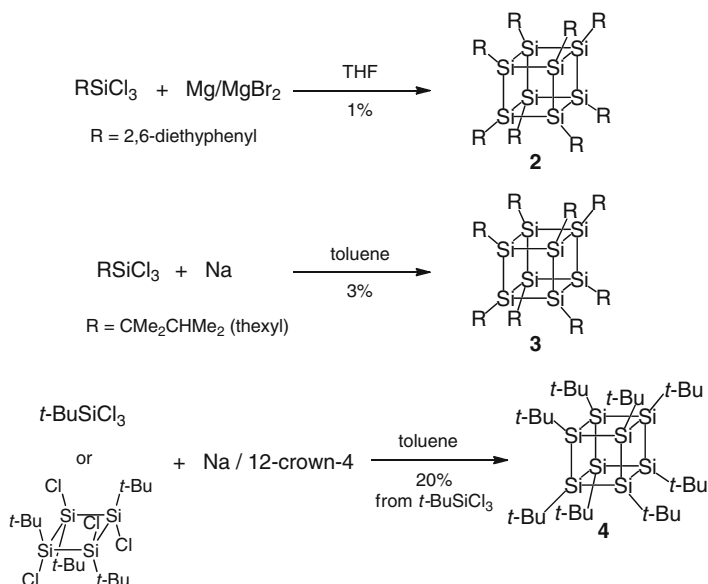
Fig. 1 Molecular structure and crystals of octasilacubane **1**



Scheme 2 Other approaches to octasilacubane and octagermacubane

even in a sealed tube. The structure analysis was possible 15 years later by rapid X-ray measurement system [5]. The structure is shown in Fig. 1. The cubic framework is well protected by bulky Si substituents to avoid oxidation. Average framework bond length was 2.412 Å and slightly longer than the usual Si–Si single bond. Framework Si–Si–Si bond angles varied from 88.0 to 91.8°, nicely approximating a cubic structure.

It is noteworthy that three independent groups published similar reactions at the same time. As shown in Scheme 2, the reactions of di(*tert*-butyl)tetrachlorodisilane and di(*tert*-butyl)tetrahalodigermane with lithium naphthalenide at low temperatures gave Si₈ and Ge₈ partial cage compounds, respectively, with two halogen atoms remaining [6–8]. Our later investigation of the reactions from octasilacubane showed that construction of strained cubic structure requires high temperatures (described below in detail).



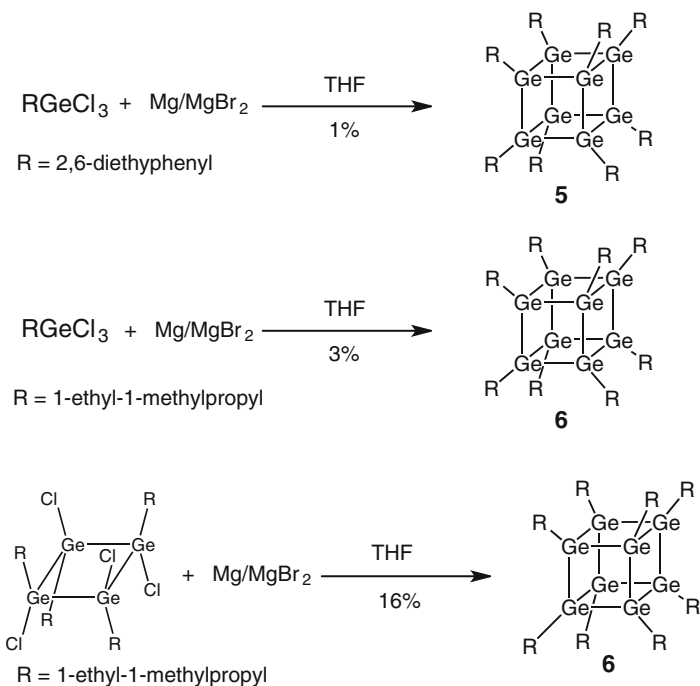
Scheme 3 Synthesis of alkyl and aryl octasilacubanes

After this work, various octasilacubanes with alkyl and aryl substituents were reported. Their syntheses are summarized in Scheme 3. Sekiguchi and Sakurai group prepared 2,6-diethylphenyl-substituted octasilacubane by the reaction with Mg/MgBr_2 [9]. The orange crystals of **2** were obtained in 1% yield. In the same year, Matsumoto group in Gunma University published the synthesis and structure of 1,1,2-trimethylpropyl (thexyl)-substituted octasilacubane **3** [10]. Independently, the synthesis of *tert*-butyl-substituted octasilacubane **4** was reported in the same year [11]. Later, the Sekiguchi and Sakurai group also reported the mesityl-substituted octasilacubane prepared in a similar manner [4]. The structures of octasilacubanes shown in Scheme 3 were determined by X-ray crystallography. Bond lengths and angles were basically independent of the substituents. Even with bulky substituents, Si–Si average bond lengths of the cubane skeleton were only slightly longer than typical Si–Si bond lengths 2.34 Å (2.412 Å for **1**, 2.399 Å for **2**, 2.421 Å for **3**, and 2.385 Å for **4**). Bond angles of the skeleton vary from 88 to 92°.

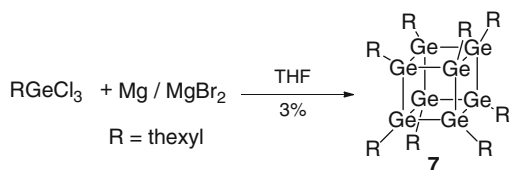
The ^{29}Si NMR chemical shift of **1** was observed at -35.03 ppm and that of aryl-substituted **2** appeared at 0.36 ppm. Alkyl-substituted **3** showed a peak at 22.24 ppm.

The reason for the successful isolation of octasilacubanes, even though the yields were poor, is their vivid color that enabled the isolation by column chromatography in a glove box. The electronic structures of octasilacubanes were intensively investigated [4] and strained polysilane systems as well as fused polycyclic structures are explained to be responsible for the unique color and reactivity.

Two octagermacubanes were introduced by Sekiguchi and Sakurai's group in 1992 [9]. The synthetic methods, similar to those of octasilacubanes, are shown in Scheme 4.



Scheme 4 Synthesis of alkyl and aryl octagermacubanes



Scheme 5 Synthesis of hexyl octagermacubane

Octagermacubane **5** with 2,6-diethyphenyl groups was obtained in 1% yield. Alkyl octagermacubane **6** was prepared by two different methods and obtained in 16% yield from cyclotetragermane or 3% from trichlorogermane.

In 2000, our group reported the synthesis, structure, and reactivity of hexyl octagermacubane. Unlike hexyl octasilacubane **3**, octagermacubane **7** was only obtained by the reaction of HexGeCl_3 with Mg/MgBr_2 . The yield was 3.3% [12] (Scheme 5).

Aryl octagermacubane **5** was reported to be stable to atmospheric oxygen and moisture, while alkyl-substituted **7** was oxidized in solution to the corresponding dioxide in a few hours (*vide infra*). Also in a solid state, **7** decomposed slowly (half life: 5 d). This is in contrast with hexyl octasilacubane **3**, which is stable in solution. The relative stability of aryl octagermacubane **5** can be attributed to the

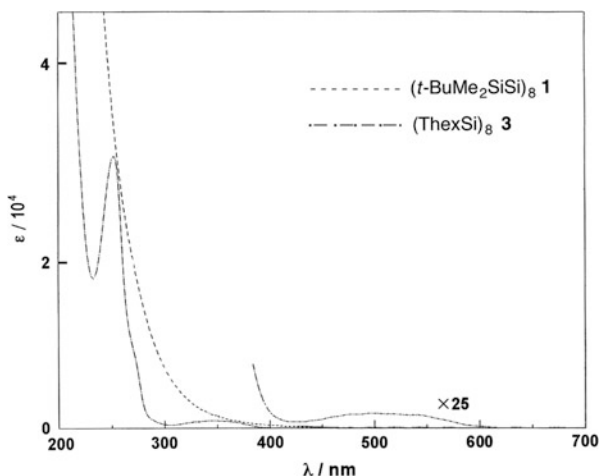


Fig. 2 UV-vis spectra of octasilacubanes **1** and **3** in hexane

electronical stabilization by aryl groups; electron is withdrawn by aryl groups from Ge_8 skeleton, diminishing the reactivity towards electrophilic reagents.

The structures of octagermacubanes are comparable to those of octasilacubane; average Ge–Ge bond lengths were 2.490 Å for **5** and 2.516 Å for **7**. Bond angles of the skeleton of **5** vary 88.9–91.1° and alkyl-substituted **7** showed wider range, 88.0–91.9°, as in the case of octasilacubanes.

All octasilacubanes are colored molecules and show absorption maxima around 500 nm in UV-vis spectra. As an example, UV-vis spectra of thexyl and silyl-substituted octasilacubane are shown in Fig. 2. The longest wavelength absorption around 500 nm for **3** was analyzed by Gaussian approximation to be a 1:5:1 mixture of 464, 508, 561 nm peaks, respectively. The absorption spectra of other octasilacubanes are summarized in the review [4, 13]. Aryl octasilacubane **2** shows much more intense absorption compared to alkyl-substituted **3**, because of the electronic perturbation by aryl groups. For example, σ – σ^* transition absorption of **2** was observed at 243 nm (ϵ 111,000), while that of **3** was detected at 252 nm (ϵ 30,800). On the other hand, the absorption at 500 nm observed for **3** was missing in the case of **2**.

Thexyl octasilacubane **3** shows thermochromism in solid state and changes its color from orange (–196°C) to bright red (200°C). The measurement of temperature-dependent UV-vis spectrum in 3-methylpentane indicated that the absorption of 561 nm decreases in intensity at lower temperature. Other peaks are basically left unchanged; therefore, slight conformational variations might be responsible for this color change. A similar feature was also observed for octagermacubane **7**, which changed its color from pale yellow (–196°C) to orange (120°C).

It is worthwhile to compare the electronic properties of octasilacubane and octagermacubane with same substituents. Figure 3 indicates the comparison of UV-vis spectra of thexyl octasilacubane **3** and octagermacubane **7**. Octagermacubane shows more intense absorption in the UV region, which tails in to the visible region around 500 nm. In contrast, aryl octasilacubane **2** and octagermacubane **5** with same

Fig. 3 UV–vis spectra of octasilacubanes **3** and octagermacubanes **7** in hexane

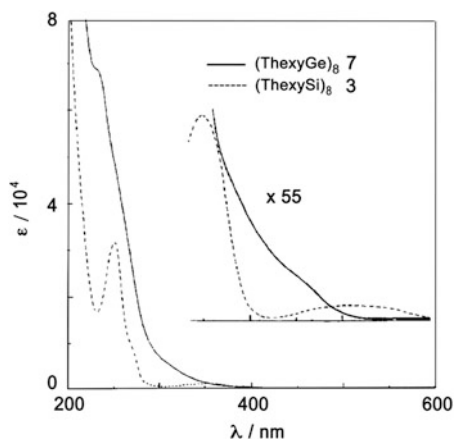
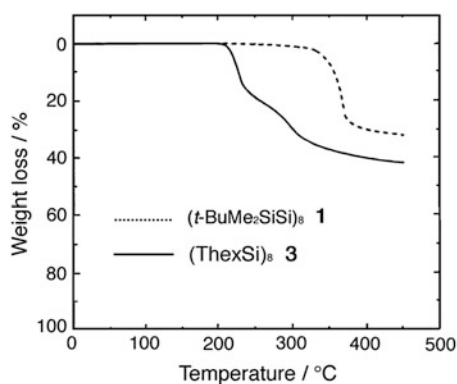


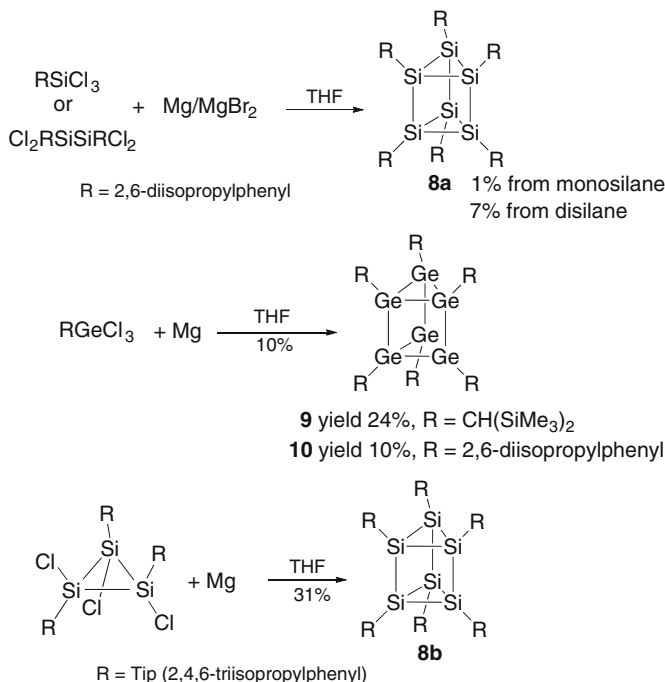
Fig. 4 TG analysis of octasilacubanes **1** and **3** in Ar atmosphere



substituents show basically similar UV–vis spectra [13]. The UV–vis spectra of alkyl octagermacubane **6** and **7** exhibit analogous features.

The high electron-donating ability of octasilacubanes is shown by the results of cyclic voltammetry. The oxidation potentials of **1** and **3** were 0.40 V and 0.43 V (in CH_2Cl_2 vs. SCE), respectively. These values are much lower than cyclic polysilanes ($i\text{-Pr}_2\text{Si}$)₄ (1.24 V, in CH_2Cl_2 vs. SCE), indicating unique electronic properties of the octasilacubane motif. Octagermacubane **7** shows even lower oxidation potential, and the value was 0.22 V (in CH_2Cl_2 vs. SCE).

The thermal properties of octasilacubane were investigated by thermogravimetric analysis (TGA). As shown in Fig. 4, silyl octasilacubane **1** shows weight decrease over 300°C, whereas thexyl-substituted **3** started to decompose from 200°C. This result was supported by the ab initio calculation indicating that silyl-substituted octasilacubane is more stable than alkyl-substituted one [14]. Octagermacubane **7** is stable up to 190°C, then starts to decompose. This temperature is slightly lower than in the case of octasilacubane **3**. The measurement of TGA-MS indicated that the weight loss is the result of the elimination of thexyl groups. The cage skeleton is thermally stable up to 500°C.



Scheme 6 Synthesis of hexaprismanes

2.2 Hexasilaprismanes and Hexagermaprismanes

A hexaprismane comprising higher group-14 element was first reported in 1989 with bis(trimethylsilyl)methyl-substituted hexagermaprismane [15]. Hexasilaprismane and hexagermaprismane with 2,6-diisopropylphenyl groups were isolated in 1993 [16] both by Sekiguchi and Sakurai group. They applied bulkier substituents to obtain smaller cages, and the essentially identical method to that employed for the preparation of octasilacubanes gave the targeted hexaprismanes. One different point is reducing reagent; Mg/MgBr_2 proved too reactive for hexagermaprismanes and Mg was used instead. For hexasilaprismane **8a**, Mg/MgBr_2 gave a good result (Scheme 6). More recently, Scheschkewitz's group reported the synthesis of hexasilaprismane **8b** by reductive coupling from trichlorocyclotrisilane [17]. Their result clearly indicates that larger prebuilt fragments afford the targeted polyhedron in much higher yields.

Theoretical calculations indicated that strain energy of hexaprismanes are higher than octasilacubanes or octagermacubanes [18]. However, hexasilaprismane **6** was oxidatively stable in the solid state. The authors described that no change was observed after a couple of months in air.

Another unique point for these compounds was hindered rotation of the aryl group of **8a** and **10**. Unlike octasilacubanes, two peaks of nonequivalent *o*-isopropyl groups

were observed in ^1H NMR. The ΔG^\ddagger values for the rotation were calculated to be 16.5 kcal/mol for hexasilaprismane **8**, and 13.1 kcal for hexagermaprismane **10**, reflecting longer Ge–Ge bond length [16].

In the solid state, hexasilaprismane **8** exhibited two peaks in ^{29}Si NMR at -22.2 and -30.8 ppm with a ratio of 2:1. The authors explained this with the distorted skeleton as shown in X-ray analysis.

The crystallographic analyses of hexaprismanes **8–10** revealed their unique structures. Thus, the average bond angles for **8a** were 2.380 \AA for the three-membered ring moiety and 2.373 nm for the four-membered ring and slightly shorter than diethyphenyl-substituted octasilacubane **2**. On the other hand, the average bond lengths of hexagermaprismane **10** were 2.503 \AA for three-membered ring and 2.468 \AA for four-membered ring. Alkyl-substituted **9** shows comparatively long bond lengths: 2.580 \AA for three-membered ring and 2.522 \AA for four-membered ring, which can readily be attributed to the bulkier alkyl groups.

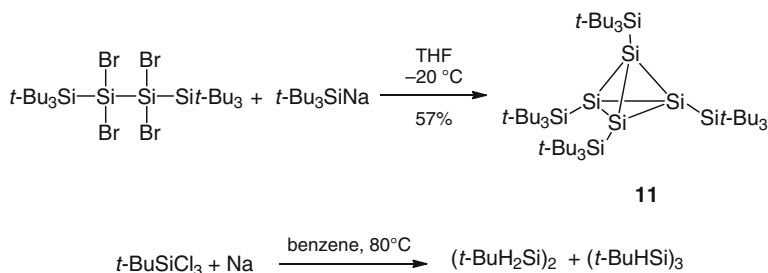
Because of the strained polysilane/polygermane structure, the polyhedral cages are all colored compounds and show UV–vis absorptions in the visible region in hexane solution. Thus, all three compounds have absorptions tailing into the visible region (500 nm). Two hexagermaprismanes **9** and **10** showed similar spectra, whereas alkyl-substituted **9** was red-shifted (280 nm, ϵ 32,000) compared to that of **10** (261 nm, ϵ 84,000). Hexasilaprismane **8** shows absorption maximum at 240 nm (ϵ 78,000) with several shoulders up to 500 nm.

2.3 Tetrasilatetrahedranes and Tetragermatetrahedranes

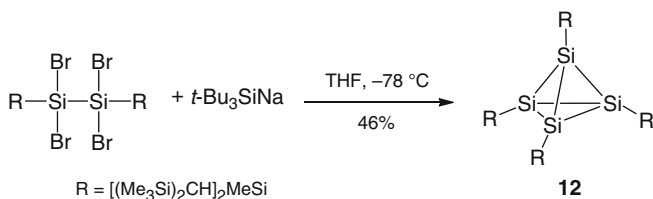
Among the polyhedral clusters, tetrahedrane is the most strained [4, 17]. The isolation of tetrasilatetrahedrane was realized in 1993, five years after the synthesis of octasilacubane. Wiberg's group applied very bulky tri-*t*-butylsilyl (*supersilyl*) groups and succeeded in the synthesis as shown in Scheme 7 [19]. Again, the choice of precursors is important; when *tert*-butyltrichlorosilane was treated with sodium, only reduced disilane and cyclotrisilane were obtained as products. In addition to using a 1,1,2,2-tetrabromodisilane precursor, *t*-Bu₃SiNa had to be employed as reducing agent instead of typical alkali metal reagents.

The tetrahedrane **11** was obtained as yellow-orange crystals and, surprisingly, stable towards water, air, and light. Because of the cage tetrasilane system, UV–vis absorptions are observed at 210 (ϵ 76,000), 235 (ϵ 71,000), 310 (ϵ 20,000), and 451 (ϵ 3,600) nm. The crystallographic analysis was possible by the co-crystallization of **1** with disilane (*t*-Bu₃Si)₂. Average skeleton Si–Si bond lengths were 2.326 \AA , and this value is slightly shorter than typical Si–Si single bond ($\sim 2.34\text{ \AA}$). The exocyclic Si–Si bonds were longer, and average bond lengths were 2.362 \AA .

In 2003, the Sekiguchi and Ichinohe group isolated the bis(trimethylsilyl) methyl-substituted tetrasilatetrahedrane as the second example [20]. They applied



Scheme 7 Synthesis of tetrasilatetrahedrane



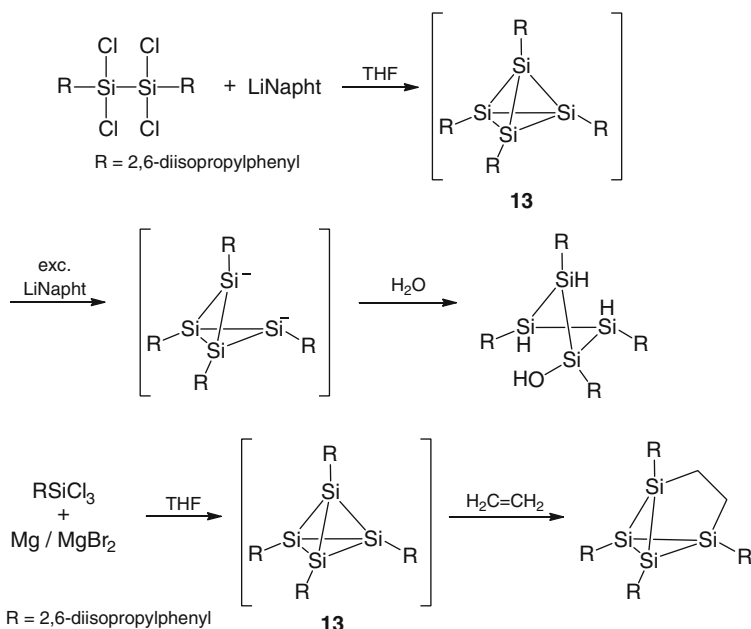
Scheme 8 Synthesis of tetrasilatetrahedrane **12**

basically identical reaction conditions and obtained the target compound in 46% yield (Scheme 8). Average Si–Si bond lengths were 2.352 Å (*endo*) and 2.409 Å (*exo*); both are slightly longer than those of **1**.

Lerner's group reported the synthesis of **12** by a one-pot procedure in 2009 [21]. Compound **12** was obtained by treatment of either HSiCl_3 , $\text{Cl}_3\text{SiSiCl}_3$, or $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ with $\text{NaSi}(\text{t-Bu})_3$. In the case of HSiCl_3 and $\text{NaSi}(\text{t-Bu})_3$, the yield was 48%.

Sekiguchi's group investigated the reaction using 2,6-diisopropylphenyl groups as substituents. As shown in Scheme 9, the reaction of tetrachlorosilane with LiNapht gave cleaved silanol after aqueous workup. When they treated substituted trichlorosilane with Mg/MgBr_2 , ethylene inserted tetrahedrane was obtained (ethylene was generated in situ by the reaction of Mg and dibromoethane) [4]. These results indicated the intermediacy of tetrahedrane **13**; isolation, however, was not possible with these aryl substituents.

The ^{29}Si NMR chemical shift of tetrahedrane **11** was reported to be 38.89 ppm, a quite different value from that of silyl-substituted octasilacubane **1** (δ –35.03 ppm). ^{29}Si NMR chemical shifts are apparently drastically affected by the polyhedral cage motif. Therefore, ^{29}Si NMR seems to be a useful tool for determination of the structures of silicon polyhedranes.



Scheme 9 Attempted synthesis of tetrasilatetrahedrane **13**

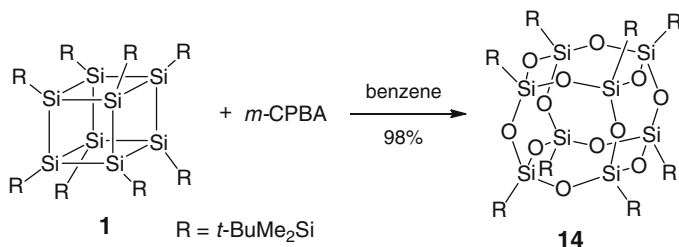
3 Reactions

3.1 From Octasilacubanes and Octagermacubanes

Although many silicon and germanium clusters were isolated, the reactions starting from them are very limited. There are several reasons:

1. With bulky steric protecting groups, reactivity of the starting compound is low.
2. Even if some reactions occurred, the stability of the products is often insufficient for separation and isolation.
3. The structure of the products are often complicated; therefore, identification by spectroscopic analyses is difficult.
4. In some cases (e.g., compounds **4** and **12**), solubility in organic solvent is too low to perform reactions.

Among all clusters listed above, thexyl-substituted octasilacubane **3** and octagermacubane **7** have unique properties. Thus, this compound can survive in the HPLC analysis with THF/MeOH eluent, and this makes it possible to isolate the products by preparative recycle-type HPLC. In addition, compounds **3** and **7** can be dissolved in many organic solvents. This is the reason why most of the known reactions are from these compounds.



Scheme 10 Oxidation of octasilacubane **1**

As mentioned in the previous chapter, octasilacubanes show low oxidation potential. Therefore reactions with electrophilic reagents can be expected. Indeed, silyl-substituted octasilacubane **1** reacted with excess amount of *m*-CPBA to give octasilsesquioxane **14** [5] (Scheme 10; the chemistry of silsesquioxanes is described in detail in a different chapter of this volume). Cage octasilsesquioxanes (T_8) are well-known compounds [22]; however, only one silyl-substituted T_8 has been known to date except **14**. In addition, if bulky substituents are applied, conventional hydrolysis-dehydration methods would not give cage products but incompletely condensed silanols. Therefore, compound **14** can be claimed to be the octasilsesquioxane with the largest substituents.

Interestingly, compound **14** exhibits relatively intense absorption in the UV region [5]. Against the fact that the silsesquioxane framework usually does not show UV–vis absorption, the lowest transition-energy absorption of **14** in cyclohexane occurs at 285 nm (ϵ 4,900) (Fig. 5). The reason of this intriguing observation is unclear as yet, however, spatial interaction of Si–Si σ bonds is most plausible because similar spectrum was obtained with trimethylsilyl- T_8 , but not with 2-trimethylsilylethyl- T_8 .

Reflecting the stability in the air, oxidation of hexyl-substituted octasilacubane **3** demanded harsher conditions. Oxidation of **3** with *m*-CPBA resulted in the mixture of $\text{Thex}_8\text{Si}_8\text{O}_n$. During the investigation of photoreaction of **3**, we found that oxidized octasilacubanes were often observed. We therefore tried the photoreaction of **3** in the presence of DMSO as an oxidant, and mono- and di-oxidized compounds were obtained in good yields (Scheme 11). Thanks to the stability of **3** as described above, all the products including residual starting material **3** were isolated by recycle-type HPLC (ODS, eluent MeOH/THF) [23].

Although many isomers for dioxide **16** are possible, only the single isomer with diagonally opposing SiOSi bridges was obtained. We also tried the oxidation of **15** in a similar manner, and again, only **16** was obtained (Scheme 11). This interesting reactivity was explained by the X-ray crystal analysis of **15**. Because of the insertion of the first oxygen atom, the hexyl groups were pushed back, and the opposing Si–Si bond was elongated (2.559 Å; other bonds were 2.423–2.463 Å). This elongation made the reactivity of this bond higher, resulted in the sole generation of **16** (Scheme 12).

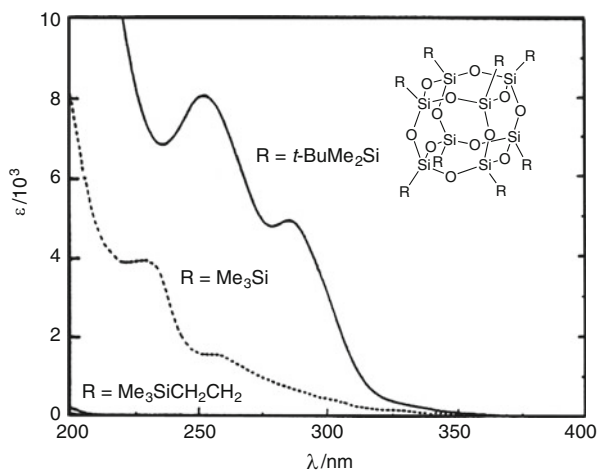
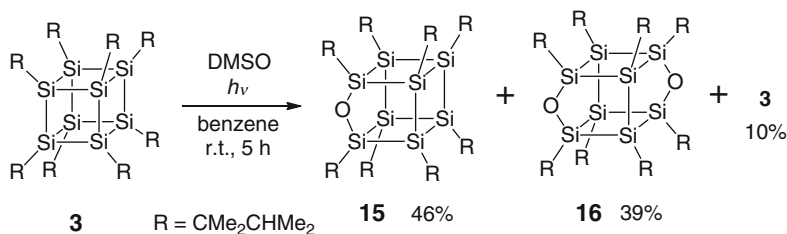
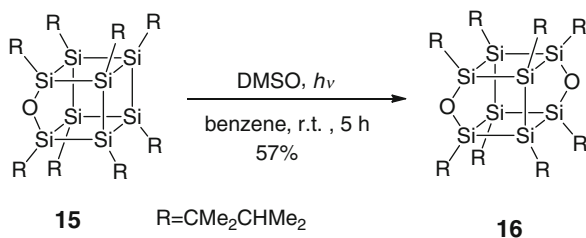


Fig. 5 UV-vis absorption of octasilsesquioxane **14** in cyclohexane

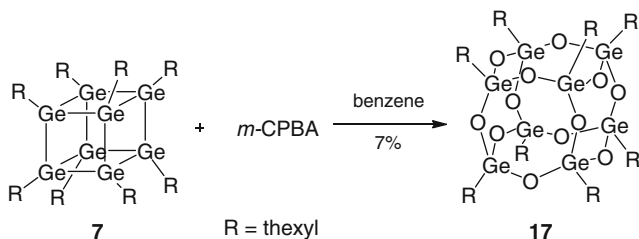


Scheme 11 Oxidation of octasilacubane **3**



Scheme 12 Oxidation of oxaoctasilacubane **15**

For octagermacubanes **7**, oxidation reaction occurred with *m*-CPBA, and octagermsesquioxane **17** was obtained in 7% yield (Scheme 13). Probably because of the longer Ge–Ge bonds, **7** is more easily oxidized compared to the silicon analog. When **7** was stirred in hexane for 12 h with oxygen, dioxide (ThexGe)₈O₂ was obtained as yellow crystals in 7% yield. The position of the two oxygens was not clear because crystallographic analysis could not be performed in this case.



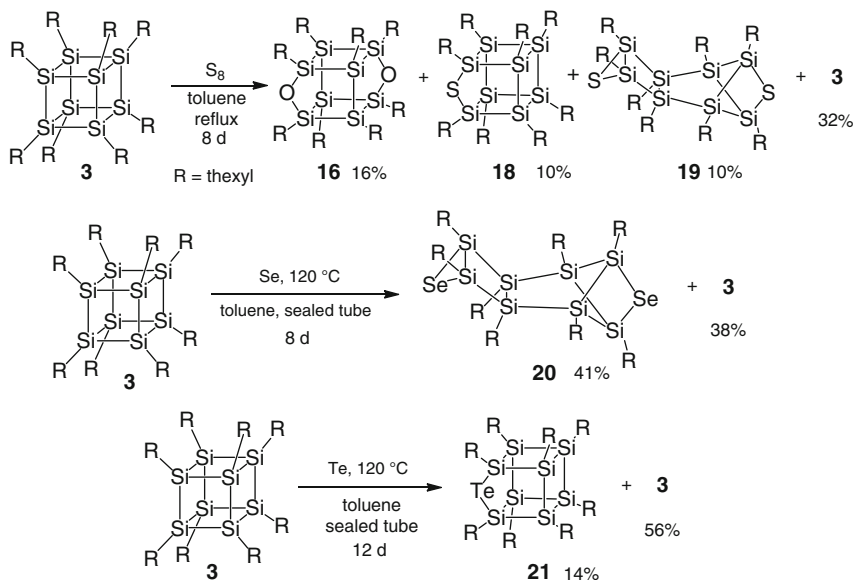
Scheme 13 Oxidation of octagermacubane **7**

The reaction of octasilacubane with sulfur, selenium, or tellurium proceeded by thermal reaction [24]. When octathexyloctasilacubane **3** was heated with sulfur under toluene reflux condition for 8 days, the HPLC chart of the reaction mixture showed the generation of three products in addition to the starting octasilacubane. Separation with recycle-type HPLC revealed that two of the products were dioxaoctasilabishomocubane **16** and monothiaoctasilabishomocubane **18**, the former probably resulting from contamination of the reaction mixture with dioxygen. Both compounds were identified by X-ray crystallographic analysis. Another product was not identified, but the reaction of **3** with selenium in a sealed tube gave a similar ring-opening compound **20** whose structure was determined crystallographically. On the basis of similar ^{29}Si NMR data, the product was determined to be **19**. In the case of tellurium, the thermal reaction of the octasilacubane resulted in the formation of a tellurium-inserted compound **21**, which decomposed in solution to give the octasilacubane and tellurium. The whole reaction is summarized in Scheme 14.

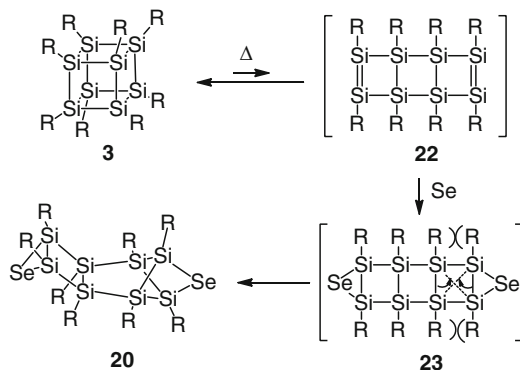
The mechanism of the formation of **19** or **20** is not clear, but it can plausibly be explained with the reaction sequence shown in Scheme 15. Usually [2,2] ring opening is thermally prohibited; however, a transiently generated ladder intermediate **22** may promptly react with selenium to give **23**. Because of the severe steric hindrance of bulky hexyl groups in **23**, skeletal rearrangement might occur to give product **20**. Similar ring-opening reaction of hexasilaprismane was also suggested by photoreaction (described below).

Octasilacubane **3** also readily reacts with halogenating reagents [25]. Simple one-bond cleaved dihalides had been anticipated, but the products obtained were all skeletal rearranged dihalides. As shown in Scheme 16, when **3** was allowed to react with halogenating reagents, three stereoisomers were obtained in good yields. All products were isolated with recycle-type HPLC (ODS, MeOH/THF), and the structures were unequivocally determined by X-ray crystallographic analyses. Usually iodosilanes are unstable to moisture; however, the diiodo compounds obtained in this reaction were stable, thanks to the steric protection by hexyl groups, and isolated without problems by HPLC.

The reason of the skeletal rearrangement is explained by the release of the strain of octasilacubane. Thus, electrophilic attack by halogenating reagent resulted in the Si–Si bond cleavage and generation of silyl cation. In this stage, skeletal rearrangement occurred before the second atom attacks to give the rearranged dihalides.

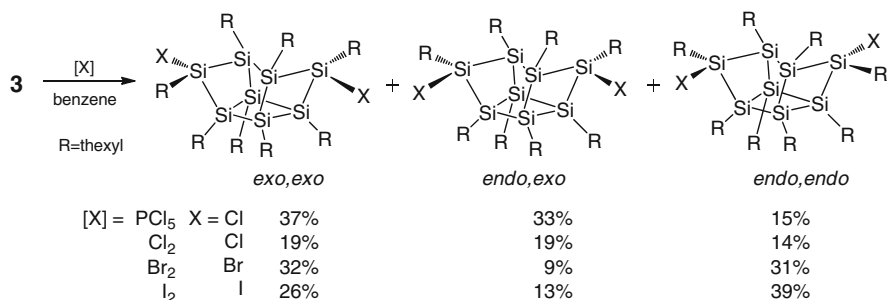


Scheme 14 Reaction of octasilacubane **3** with sulfur, selenium, and tellurium

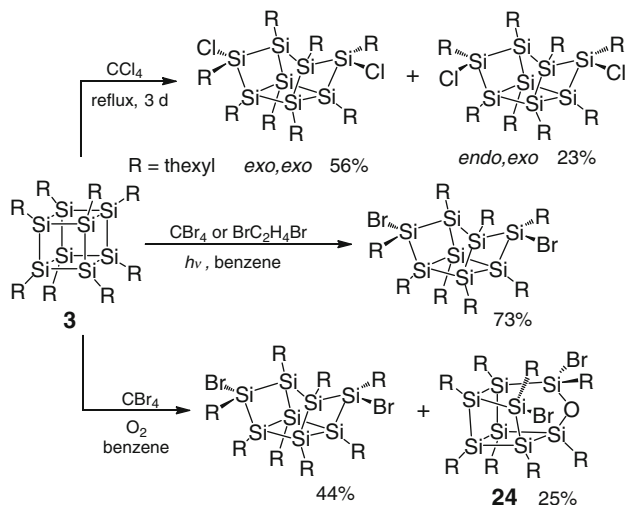


Scheme 15 Plausible reaction mechanism for the generation of **20**

The described halogenation reaction proceeds via an ionic pathway, but radical halogenation is also possible [26]. When octasilacubane **3** was heated in CCl_4 , similar products were obtained. In this reaction, no *endo,endo*-isomer was obtained. The reaction of **3** with CBr_4 or dibromoethane demanded photo-irradiation, and the *exo,exo*-isomer was obtained as the only product. For these reactions, carefully degassed solvent was used; however, when the reaction with CBr_4 was performed in the presence of oxygen, oxahomocubane **24** in addition to the *exo,exo*-isomer were obtained. All the reactions are summarized in Scheme 17. It is noteworthy that the framework of the rearranged compounds was previously known as shown in Scheme 2.



Scheme 16 Halogenation of octasilacubane **3**

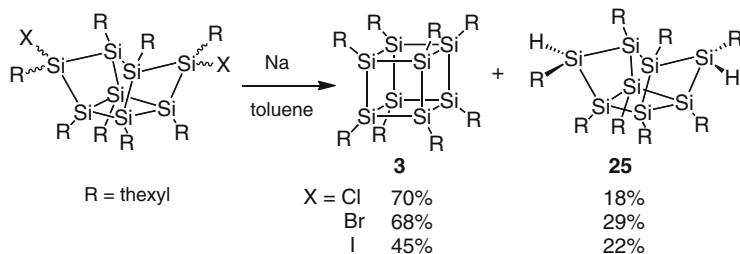
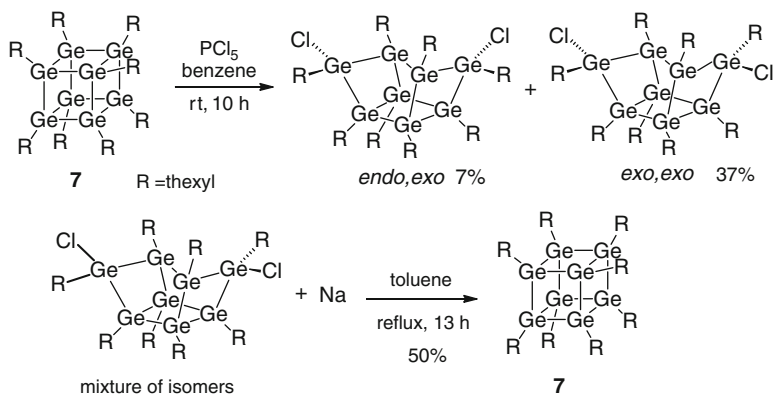


Scheme 17 Radical halogenation of octasilacubane **3**

Kabe and Masamune's group examined the further reaction of obtained *exo,exo*-dichloride with LiNapht, but dihydride **24** was the only product instead of the anticipated cage motif [6]. Considering the strained structure of octasilacubane, conversion of rearranged dihalides to octasilacubane seemed to be impossible.

Against this expectation, we succeeded in the regeneration of octasilacubane by applying similar reaction condition to the synthesis of octasilacubane [27]. As shown in Scheme 18, all isomers of dihalides could be transferred to octasilacubane by the reaction with sodium in refluxed toluene. Reduced dihydride (only *exo,exo*-isomer) was the by-product. From this result as well as the similar reaction of octagermacubanes described below, it can be concluded that generation of cubane skeleton usually requires elevated temperatures.

Similar halogenation and regeneration was also observed for octagermacubane [12]. As depicted in Scheme 19, chlorination occurred in the reaction with PCl₅, and two isomers were obtained. The identification of *exo,exo*-isomer was accomplished

**Scheme 18** Regeneration of octasilacubane **3****Scheme 19** Reaction of octagermacubane **7**

by comparing NMR spectrum with that of silicon analog of *exo,exo*-isomer. The unsymmetrical structure of *endo,exo*-isomer made it possible to identify this compound by NMR spectra. Although octagermacubane was synthesized by the reaction with Mg/MgBr_2 , no reaction occurred from the rearranged dichloride. Instead, reaction with sodium in toluene gave the octagermacubane in 50% yield. Again in this reaction, the higher stability of hexyl-substituted octagermacubane is one of the reasons for the generation of octagermacubane, while the regeneration of more strained cubane skeletons demands high reaction temperature.

Photoreaction of octasilacubane **3** was investigated soon after its isolation. Irradiation of **3** at 77 K in 3-methylpentane gave intense absorptions around 450 and 700 nm in UV–vis spectrum. As shown in Fig. 6, new absorptions at 345, 471, and 714 nm increased their intensity by time. The species were stable at least for several hours at that temperature; however, starting octasilacubane was recovered when the solution was warmed to room temperature.

We first presumed that the species responsible for these absorptions include unsaturated Si–Si bonds and tried trapping experiments with diene, alcohol, or water. However, no trapped products were obtained and only octasilacubane was recovered. The absorption at 714 nm is red-shifted compared to those of most

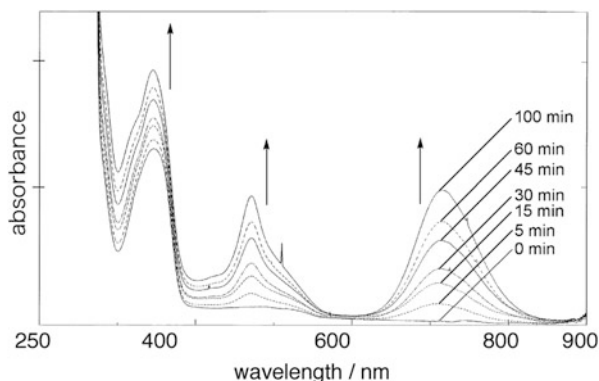
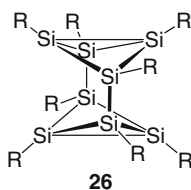


Fig. 6 UV spectra of **3** irradiated in 3-methylpentane at 77 K



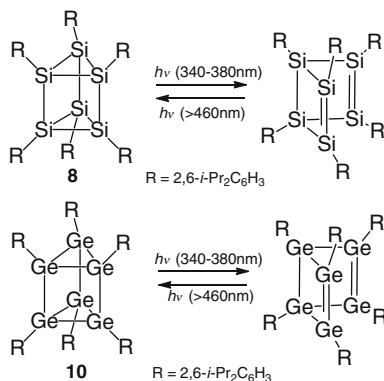
Scheme 20 Suggested intermediate of the photoreaction of octasilacubane **3**

unsaturated silicon compounds, and consequently the generation of different species had to be considered. With a collaborative work with Horiuchi and Hiratsuka photochemistry group, we could suggest the structure of the product of photoreaction [28]. From the result of INDO/S-CI calculation it was concluded that the structure of the photo-rearranged product corresponded to the saturated, but highly strained molecule **26** (Scheme 20). This compound matches well to the UV-vis spectrum as well as the inertness towards alcohol or diene. In addition, generation of the dioxaoctasilacubane **16** in the photooxidation of octasilacubane can readily be explained by the insertion of oxygen atom to top and bottom Si-Si bonds of **26**.

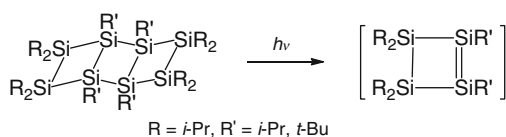
3.2 From Hexasilaprismane and Hexagermaprismane

Photoisomerization was also reported for hexasilaprismane and hexagermaprismane. The irradiation of **8** at -50°C or in a glass matrix at 77 K, new absorption bands appeared at 335, 455, and 500 nm. With a result of a HF/6-31G* level energy calculation [4], Sekiguchi and Sakurai suggested the generation of hexasila-Dewar benzene **27**. With irradiation of longer wavelength light, this species regenerated hexaprismanes (Scheme 21) [4, 13].

Similar photoreaction was observed with ladder polysilanes. In this case, generated cyclobutene was trapped by various reagents (Scheme 22) [29].



Scheme 21 Photoisomerization of hexaprismanes



Scheme 22 Photoreaction of ladder polysilane

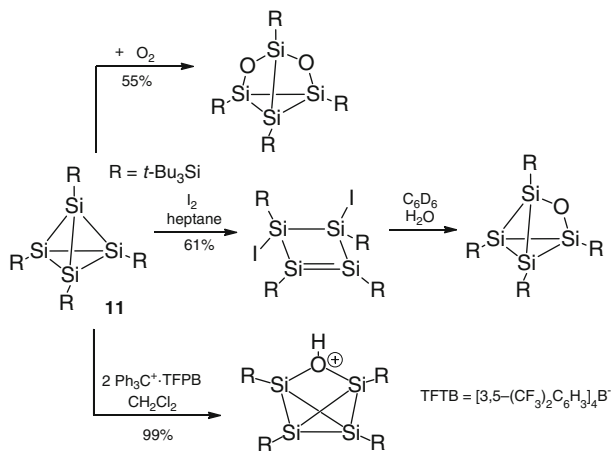
3.3 From Tetrahedranes

Tetrasilatetrahedranes are thermally of considerable stability, but a broad variety of reports on their rich reactivity have appeared up to now. Partial oxidation occurred with reaction of oxygen in solution [30]. With iodine, diido tetrasilacyclobutene is obtained [31]. When **11** was treated with trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate protonated monoxide was obtained, probably formed under involvement of water contamination [32] (Scheme 23).

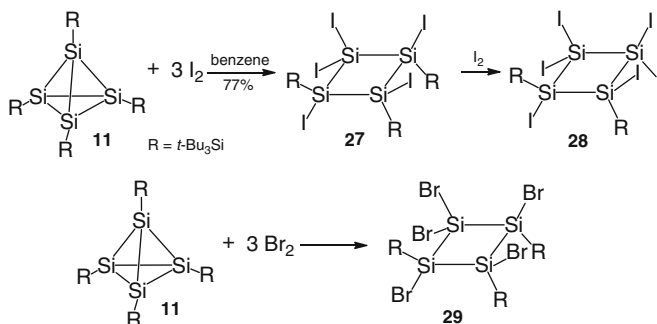
Additional halogenation reactions were also reported. With excess amount of iodine [33, 34] or bromine [35], tetrahedrane **11** underwent a substitution-addition reaction to give pentahalogenated products (Scheme 24).

From the thus obtained pentaiodide **27**, novel cage octasilane **30** was afforded by treatment with $\text{NaSi}(t\text{-Bu})_3$ (Scheme 25). The neutral cluster **30** exhibits the rare structural feature of hemispheroidally coordinated unsubstituted vertices (see Sect. 4.1).

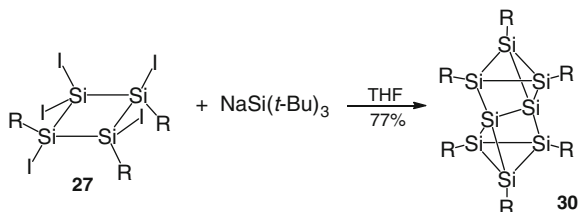
In 2003, the first silicon cage anion was reported by Ichinohe and Sekiguchi group. They reduced tetrasilatetrahedrane **12** with KC_8 in ether to obtain the anion [20]. The structure of the product was determined by X-ray crystallography. The skeletal bond lengths are similar to that of **12** (average 2.322 Å) except one bond that connected to the anionic silicon center (2.7288 Å). They also measured the ^{29}Si NMR, and single peak of tetrahedrane skeleton was observed at -153.6 ppm. Even at lower temperature (-73°C), no peak broadening or splitting manifested



Scheme 23 Reactions of tetrasilatetrahedrane with oxygen, iodine, and a trityl borate



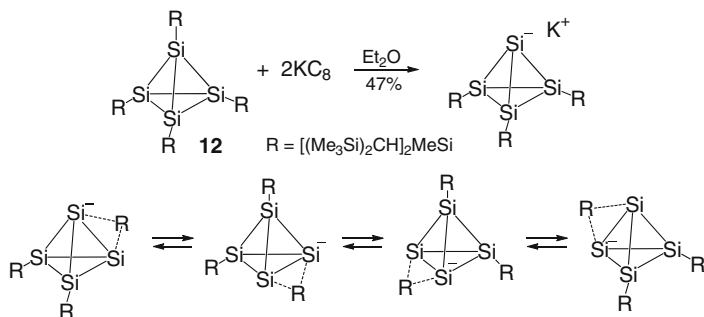
Scheme 24 Reaction of tetrasilatetrahedrane with excess iodine or bromine



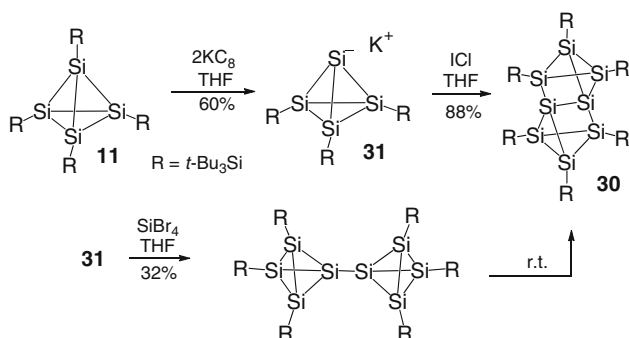
Scheme 25 Synthesis of cage octasilane

itself. The authors explained this observation with the rapid migration of the three substituents over the Si_4 skeleton (Scheme 26).

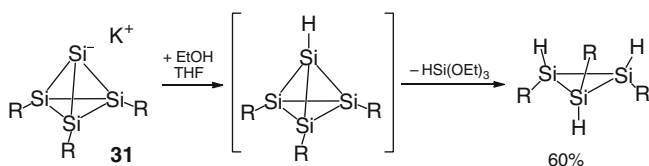
More recently, Klapötke's group in Munich reported further reactions starting from tetrahedrane **11** [36] (Scheme 27). They performed KC_8 reduction and obtained potassium salt of tetrahedrane anion **31**. This anion is a stable orange



Scheme 26 Synthesis of potassium tetrasilatetrahedranide and substituents migration in solution



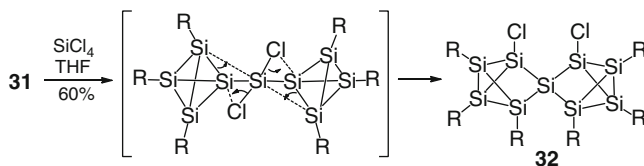
Scheme 27 Generation and reactions of potassium salt of tetrahedrane



Scheme 28 Reactions of potassium salt of tetrasilatetrahedranide **31** with alcohol

red solid at rt but decomposes in solution. The reaction of **31** with SiBr₄ resulted in the formation of cage octasilane **30** via ditetrahdranyl (R₃Si₄–Si₄R₃). Compound **30** could also be prepared in 88% yield from **31** by reaction with ICl.

When potassium salt **31** was treated with methanol or ethanol at rt, cyclotrisilane was obtained. Without bulky supersilyl groups, tetrahedrane framework could not survive to give eliminated product (Scheme 28). Although the tetrasilatetrahedranide salt **31** is not stable in solution at rt, the corresponding complex with 18-crown-6 is stable in solution, which was obtained in 56% yield by simply adding 18-crown-6 to a heptane solution of **31**. It is noteworthy that the same reaction in THF gave a product in which an Si–Si bond of **31** inserted into the 18-crown-6 ring [36].



Scheme 29 Reactions of potassium salt of tetrasilatetrahedranide **31** with SiCl_4

The reaction of **31** with SiBr_4 resulted in a formation of octasilane **30** as shown above; however, reaction with SiCl_4 gave a different product. Thus, treatment of **31** with SiCl_4 in THF at -78°C after filtration and recrystallization gave a pink-red solid. The crystallographic analysis revealed that the product was the novel spiro compound, dichlorononasilane **32** [37]. The reaction mechanism is shown in Scheme 29; the release of the strain of tetrahedrane is again a driving force.

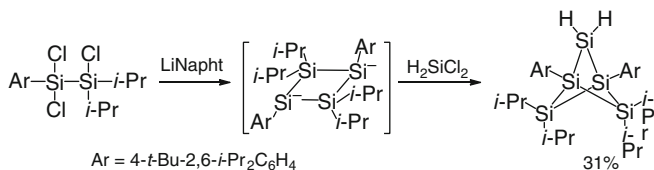
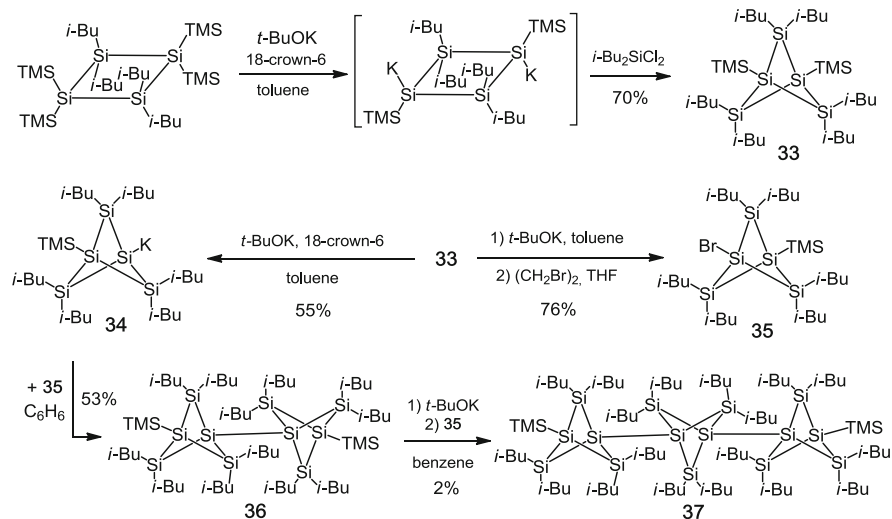
4 Other Polyhedral Clusters

As seen from the results shown above, thanks to the recent development of rapid crystallographic analysis and possible handling of unstable species in an inert atmosphere, the number of isolated strained molecules and polysilicon cage compounds drastically increased in recent years.

4.1 Strained Cage Molecules

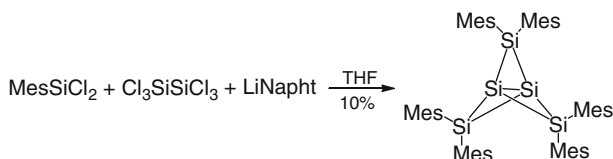
Synthesis of bicyclo[1.1.1]pentasilane was first synthesized by Kabe and Masamune's group in 1990. The reductive coupling of bulky aryl-substituted trichlorodisilane followed by treatment with dichlorosilane gave the target compound in 31% yield [38] (Scheme 30). After more than 20 years, Iwamoto's group in Sendai prepared silyl-substituted bicyclo[1.1.1]pentasilane **33** as air-stable colorless crystals. By application of a synthetic protocol (cleavage of silyl groups with KO^tBu) initially developed by Marschner et al. for oligosilanes, pentasila[*n*]staffanes **36** and **37** were obtained (catenated bicyclo[1.1.1]pentasilanes) [39] (Scheme 31).

All the compounds show very short nonbonding distances between bridgehead silicon atoms (e.g., 2.9768 Å for **33**). This value is much shorter than the sum of van der Waals radii of silicon atoms (4.20 Å). The bond lengths between bridgehead silicon atoms in **36** and **37** are similar to that of Si–TMS bond in spite of a catenated structure. Just like polysilanes, UV–vis spectra of pentasila[*n*]staffanes showed bathochromic shifts with increasing number of repeat units *n*, indicating the expansion of the σ -conjugated system. The ^{29}Si NMR peak for the bridgehead silicon atoms was observed at -99.7 ppm for **33**. This value is close to that of previously reported bicyclo[1.1.1]pentasilanes (-89.9 to -96.5 ppm) [38]. More recently, Breher's group reported the alkynyl-bridged bicyclo[1.1.1]pentane comprising silicon and tin [40].

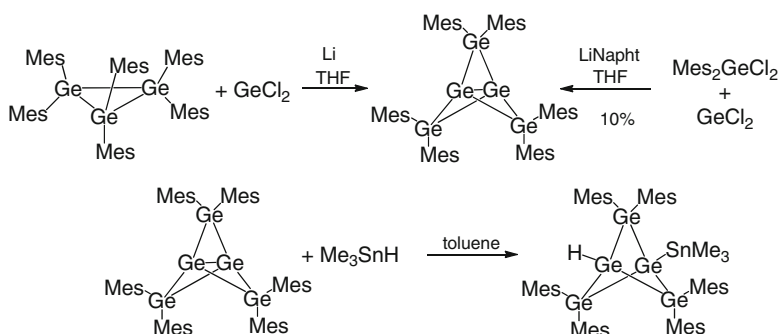
**Scheme 30** Synthesis of bicyclo[1.1.1]pentasilane**Scheme 31** Synthesis of pentasila[n]staffanes

Propellanes comprising heavier group 14 elements were identified as a central synthetic challenge in an article by Masamune in 1991 [41], and numerous synthetic experimental and theoretical approaches have been investigated since then. Although propellanes containing Sn were prepared by Kinoshita and Sita relatively early on [42], the syntheses of silicon or germanium homologues were only realized in 2009. Breher's group in Karlsruhe isolated first pentasila[1.1.1]propellane by the reaction of $\text{Mes}_2\text{SiCl}_2$ and hexachlorodisilane with LiNapht. The target compound was obtained as yellow crystals and found to be extremely sensitive to air and moisture [43]. The distance of two bridgehead silicon atoms was 2.636 Å and 13% longer than typical Si–Si single bond. On the other hand, the Si–Si bond length of $t\text{-Bu}_3\text{Si-Si}(t\text{-Bu})_3$ was reported to be 2.697 Å [44]; therefore, the authors concluded that there exists a weak stretched bond between the bridgehead atoms. The ^{29}Si NMR peak of bridgehead atom was observed at -273.2 ppm and thus very high field reflecting the strained structure. Several reactions of this propellane were examined: H_2O , PhSH , PhOH , and Me_3SnH are readily added across the bridge as judged from preliminary reactions on NMR scale.

Pentagerma[1.1.1]propellane was prepared by the reaction from hexamethylcyclotrigermane with lithium and GeCl_2 -dioxane [45]. Better yields were realized



Scheme 32 Synthesis and reaction of pentasila[1,1,1]propellane

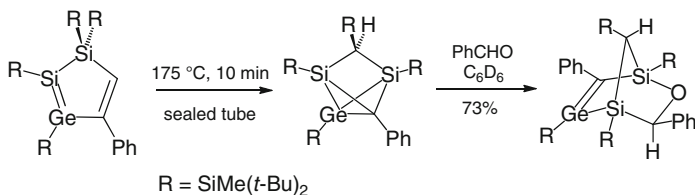
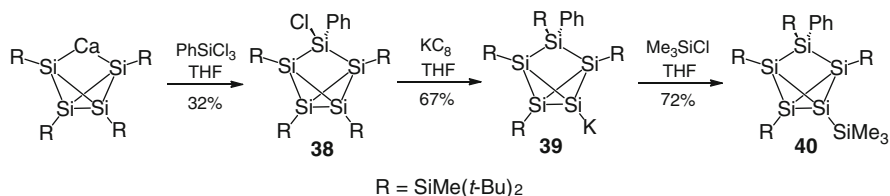
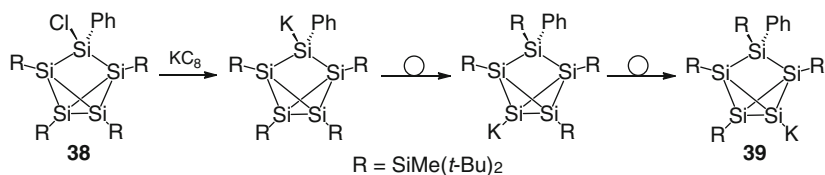


Scheme 33 Synthesis and reaction of pentagerma[1,1,1]propellane

by the reaction of $\text{Mes}_2\text{GeCl}_2$ with LiNapht in the presence of $\text{GeCl}_2 \cdot \text{dioxane}$ (Scheme 32). This propellane was obtained as orange crystals and sensitive to air, but stable towards degassed water. The distance of two bridgehead atoms was 2.869 Å, and that was much longer than usual Ge–Ge bond (2.40 Å). The reaction with Me_3SnH was examined, and an addition product across the bridgehead atoms was obtained (Scheme 33).

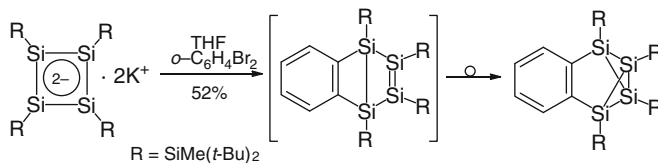
Another strained cage molecule is tricyclo[2.1.0.0^{2,5}]pentane, or “expanded tetrahedrane.” Lee and Sekiguchi group isolated the first example of such a compound with heavier group 14 elements. As shown in Scheme 34, thermal reaction starting from substituted silole homolog [46] gave 2,4-disila-1-germatricyclo[2.1.0.0^{2,5}]pentane quantitatively as air-sensitive yellow crystals. The structure of this unique “mixed cage” was established unequivocally by X-ray crystallography, and a very long Ge–C bond (2.242 Å, 15% longer than normal value) was observed. The reaction with benzaldehyde resulted in the formation of norbornene-type adduct.

Later, the same group reported simpler cases [47]. The first pentasilatricyclo[2.1.0.0^{2,5}]pentane was obtained by the reaction starting from calcium salt of tetrasilabicyclo[1.1.0]butane dianion prepared readily from tetrasilacyclobutadiene dianion $[(t\text{-Bu}_2\text{MeSi})_4\text{Si}_4]_2 \cdot 2\text{K}^+$. Monochloride **38** was obtained in 32% yield as yellow crystals. This monochloride served as a good precursor for the potassium salt **39**. This compound could be further transferred to silyl derivative **40** by the reaction with Me_3SiCl (Scheme 35). In the generation of potassium salt **39**, a 1,3-migration of silyl groups occurred from the anticipated anion, then further 1,2-migration afforded the final product **39** (Scheme 36). This reaction pathway

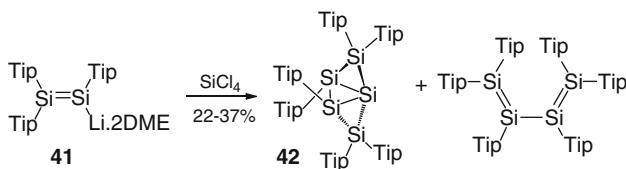
**Scheme 34** Synthesis and reaction of 2,4-disila-1-germatricyclo[2.1.0.0^{2,5}]pentane**Scheme 35** Synthesis of pentasilatricyclo[2.1.0.0^{2,5}]pentane**Scheme 36** Migration of silyl groups

was confirmed by theoretical calculations. The isomerization was thought to be driven by the tendency that anionic charge is favorably located at cage atoms with greater s-character. The ²⁹Si NMR peaks of bridgehead atoms were observed at −222.4 and −217.1 ppm for **38**, −253.9 ppm for **39**, and −182.3 and −178.6 ppm for **40**. The structure of **39** was determined by X-ray analysis. In the crystals, **39** exists as a contact ion pair, and the potassium cation shows interaction with the π-system of phenyl substituent. This unique structure can also explain the silyl-groups migration in the synthesis of **39**. The distance between the bridgehead atoms was determined to be 2.3801 Å, a normal value for an Si–Si single bond.

The first synthesis of tetrasilabenzobenzvalene was reported in 2007 [48]. Starting from the same tetrasilacyclobutadiene dianion [(*t*-Bu₂MeSi)₄Si₄]^{2−}·2K⁺ as above, the reaction with *o*-dibromobenzene gave the target compound as air- and moisture-sensitive yellow crystals (Scheme 37). X-ray crystallographic analysis revealed that all Si–Si bond lengths are within a normal range. For instance, the bridgehead Si–Si bond length was determined to be 2.3462 Å. The chemical shift of bridgehead silicon in ²⁹Si NMR was observed at −130.4 ppm in the expected high field region. The authors suggested the reaction mechanism as shown in Scheme 37. Thus, a transient Dewar-benzene would first be generated by [2+2] cycloaddition, then fast isomerization to give thermodynamically more stable benzvalene isomer would occur.



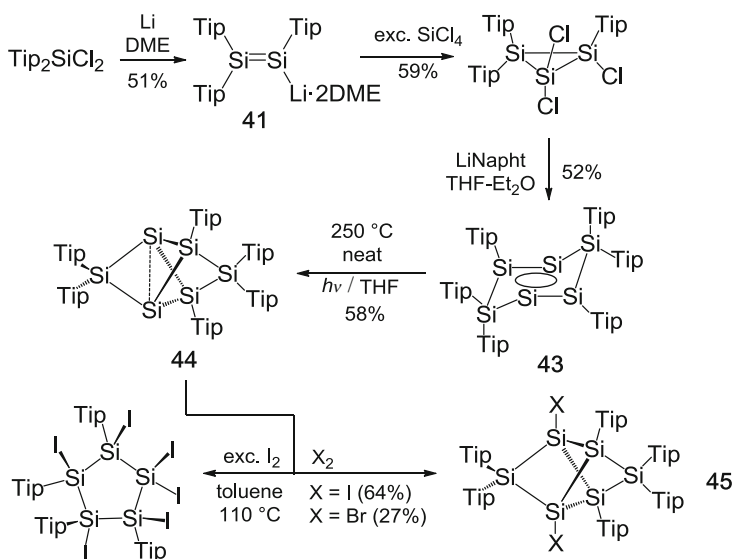
Scheme 37 Synthesis and reaction mechanism of tetrasilabenzobenzvalene



Scheme 38 Synthesis of first silicon cluster with unsubstituted vertex

In recent years, Scheschkewitz's group has reported many silicon clusters taking advantage of a reactive disilene as a starting compound. Their isolation of Tip-substituted disilene anion **41** [49], silicon analog of vinyl anion, was expected to serve as a precursor for many unusual compounds. First result appeared in 2005. As shown in Scheme 38, reaction of **41** with SiCl_4 serendipitously gave **42**, an Si_5 cluster with “naked” vertex silicon atom [50]. The yield was optimized up to 22–37%, varying because of the tedious separation from the systematically formed oxidation product of **41**. The result of ^{29}Si NMR supported that the structure of **42** was maintained in solution. Three peaks were observed at 7.4, -108.4 , -124.8 ppm; non-substituted silicon's chemical shift was assigned to be -124.8 ppm by the measurement of 2D NMR spectrum. This compound forms red block crystals, and its UV–vis spectra show absorptions at 365 and 540 nm. The result of X-ray analysis indicated that the Si–Si bond between mono-tip silicon (2.306 \AA) was shorter than the normal value, whereas other bonds were within normal range. The most astonishing point of this compound is that **42** represents the first example of an unsubstituted vertex silicon atom.

In 2010, Scheschkewitz's group introduced a tricyclic aromatic isomer of the elusive hexasilabenzene **43** [50]. The aromaticity of this compound was examined in detail by DFT-calculations. On the basis of the strongly negative NICS values and the pronounced stability of inversion-symmetric **43**, it was concluded that despite the presence of silicon atoms in the formal oxidation states of +II, +I and 0 compound **43** should be aromatic. The isomerism to hexasilabenzene (with a uniform formal oxidation state of +I) prompted the authors to coin the term “dimutational aromaticity.” One year later, Scheschkewitz et al. also reported the thermal isomerization of **43** to hexasilane (bridged propellane) **44** [51] (Scheme 39). From the result of X-ray crystallographic analysis of **44**, several intriguing points were observed. Thus, the distance of bridgehead atoms was 2.7076 \AA , and this value is much longer than previously reported untethered propellane [43] (2.636 \AA ,

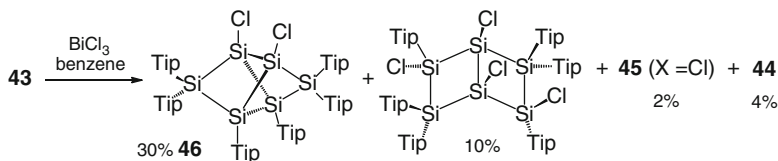


Scheme 39 Synthesis and reaction of bridged propellane

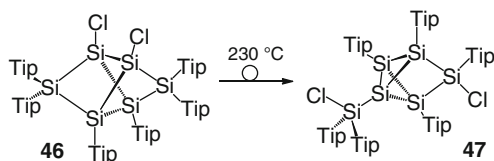
Scheme 32). All the other bond lengths are within the typical range. Because the two “propeller blades” were connected by additional silicon atom, the angle of these blades was smaller than other two angles. The ^{29}Si NMR chemical shift of bridgehead silicon was -274.2 ppm, similar to that of Mes_6Si_5 propellane. The low-field resonance at 174.6 ppm was assigned to the untethered blade silicon atom, an exceedingly unusual value for a tetracoordinate silicon atom.

Treatment of **44** with Cl_2 or Br_2 afforded dihalo compounds showing similar reactivity to Si–Si single bonds. Interestingly, the bridgehead distance was only slightly shortened; 2.6810 Å for dichloride, and 2.6547 Å for dibromide. Similarly, reaction with iodine gave diiodo compound. On the other hand, the reaction with excess iodine in refluxing toluene resulted in the quantitative formation of a hexaiodocyclopentasilane and therefore in the contraction of the silicon scaffold [17].

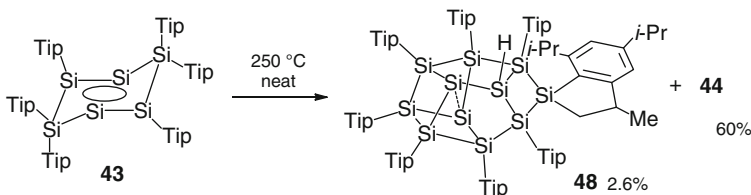
Many other reactions were reported in an article in 2012 [17]. Unlike bridged propellane **44**, compound **43** afforded complex mixture in the reaction of halogens. The authors utilized BiCl_3 as milder halogenation reagent, and a mixture of three halogenated compounds and **44** was obtained and separated. The main product **46** is the 1,2- Cl_2 -isomer of the halogenation products of **44** (30%), a ladder-type tetrachloride and **45** were obtained in 10 and 2% isolated yield, respectively (Scheme 40). The structures of all products were determined unequivocally by X-ray crystallographic analysis. The generation of tetrachloride is explained by the reaction of **46** with additional chlorine at the longest Si–Si bond although isolated **46** did not react with excess BiCl_3 .



Scheme 40 Halogenation of **43**



Scheme 41 Thermal rearrangement of **46**



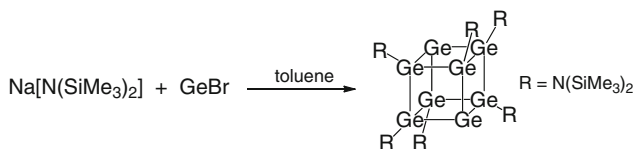
Scheme 42 Thermal reaction of **43**

Heating of dichloride **46** to 230°C until completely melted resulted in clean isomerization to afford **47** (Scheme 41). All these halogenated compounds should be excellent precursors of further complicated (or simple) silicon clusters.

In the thermal reaction from **43**, shown in Scheme 39, a side product was obtained in a small quantity. Isolation and structure determination revealed that the product was core-expanded Si_{11} cluster **48** (Scheme 42). Again in this case, two vertices consist of unsubstituted silicon atoms with shorter bond distance (2.4976 \AA) compared to those of **45** (2.7076 \AA) or pentasilapropellane (2.66 \AA). The reaction mechanism to form this complex compound is not clear yet.

4.2 Polysilicon and Polygermane Cage Molecules

Synthesis of polysilicon and polygermane clusters was a difficult task because separation and identification are much more difficult than smaller clusters. Nonetheless, recent development of rapid crystallographic analysis and handling unstable species made it possible to isolate a considerable number of those intriguing compounds. In this last chapter, recent reports of polysilicon and polygermane clusters are summarized.



Scheme 43 Synthesis of R_6Ge_8 cluster

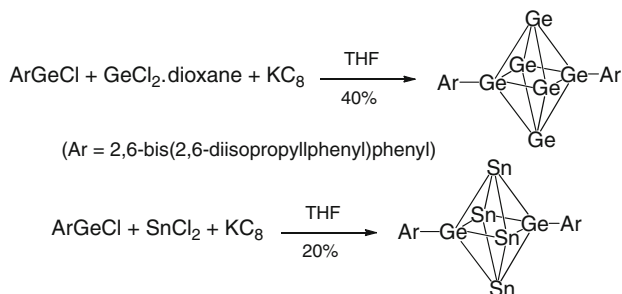
In early 2003, Schnepf and Köppe in Karlsruhe reported Ge_8 cubic cluster with different approach [52]. They noticed that solid Ge(I) bromide would be a good source for the clusters, because this compound disproportionates above 90°C to produce germanium and germanium tetrabromide. Indeed, treatment of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ with GeCl afforded $\text{Ge}_8[\text{N}(\text{SiMe}_3)_2]_6$ cluster as dark red crystals. The crystallographic analysis showed that this cluster consists of a cubane skeleton with two naked germanium atoms. Two different $\text{Ge}-\text{Ge}$ bond lengths were observed; 2.67 \AA for $\text{Ge(R)}-\text{Ge(R)}$ and 2.50 \AA for $\text{Ge(R)}-\text{Ge}$. In the crystal, two parallel toluene molecules are located above naked Ge atoms, bridging two cluster molecules in a manner (Scheme 43).

Later in the same year, Power's group in California reported the synthesis of unique octahedral clusters [53]. As shown in Scheme 44, treatment of bulky terphenyl-substituted chlorogermane and GeCl_2 -dioxane with KC_8 in THF gave hexagermaoctahedrane with only two substituents. Similar reaction with SnCl_2 also afforded Sn_4Ge_2 cluster. The unsubstituted Ge_4 or Sn_4 moieties comprise perfectly square arrays. Spectral data (^1H and ^{13}C NMR, and UV-vis spectra) showed no unusual features. The solution ^{119}Sn NMR displayed a signal at $1,583 \text{ ppm}$, showing a significant downfield shift.

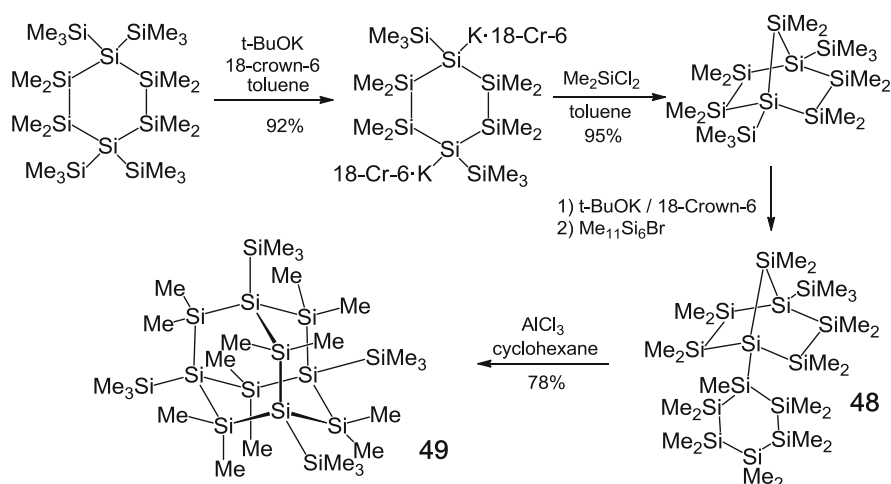
Decasiladamantane represents a part of the bulk silicon lattice and has been a synthetic target for silicon chemists for a long time. In 2005, Marschner's group in Graz finally succeeded the synthesis [54]. They employed a rearrangement reaction with AlCl_3 , not like the previously examined step-by-step synthesis and obtained the target compound in 78% yield (Scheme 45). The synthesis began with bicyclo[2.2.1]heptasilane [55], and treatment with *t*-BuOK and following cyclohexasilanyl bromide afforded the precursor **48**. Rearrangement with catalytic AlCl_3 of **48** gave the target **49**. In solution, the ^{29}Si NMR spectrum showed three peaks at -4.8 , -26.0 , and -118.6 ppm , and these resonances were considerably downfield-shifted compared to $(\text{Me}_3\text{Si})_4\text{Si}$ or $(\text{Me}_2\text{Si})_6$. This cage polysilane showed strong absorption at 222 nm (ϵ 120,000) in UV-vis spectrum. As expected all the bond lengths and angles were within normal range.

Bicyclo[2.2.1]heptasilane, appears in Scheme 45, and bicyclo[2.2.2]octasilane are also cage compounds. Without much strain, these compounds were already prepared in 1970s [56] and have been studied since then.

In 2013, Ishida and Kyushin group in Gunma reported the synthesis of Si_{16} cluster containing octasilacuneane core, an isomer of octasilacubane [57]. Reduction of tetrachlorotetra-*t*-butylcyclotetrasilane, readily available in two steps from dichlorodi-*t*-butyldiphenyldisilane, with sodium afforded the silicon cluster **50** in



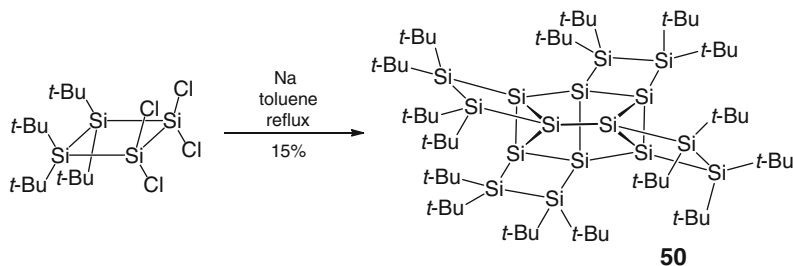
Scheme 44 Synthesis of R_2Ge_6 and $\text{R}_2\text{Sn}_4\text{Ge}_2$ cluster



Scheme 45 Synthesis of decasilaadamantane **49**

15% yield as air-sensitive orange crystals. Coincidentally, this reaction condition is exactly same as that of octasilacubanes **1** and **3**. No other isomers of **50** were observed in the reaction mixture. Apparently, only intractable polymers were generated as side products (Scheme 46).

The crystallographic analysis revealed a structure with C_2 symmetry axis. This compound contained many substructures like [3.2.1]propellane, [3.2.2]propellane, spiro[3.3]oligosilane, and spiro[4.3]oligosilane; all are previously unknown structures comprising silicon atoms. Interestingly, the bond lengths between unsubstituted bridgehead silicon atoms of [3.2.1]propellane structure were determined to be 2.384 and 2.361 Å and thus within the normal values. This feature is quite different from [1.1.1]propellane or related silicon clusters described above, all showing very long bridgehead distance. Four bridgehead atoms ([3.2.1]- and [3.2.2]propellanes) are included in this compound, and all these atoms adopted unusual trigonal monopyramidal structure. Each bridgehead silicon atom has a planar structure with



Scheme 46 Synthesis of Si_{16} cluster containing octasilacuneane core

three connected silicon atoms, and the fourth bond was almost perpendicular ([3.2.2] propellane part) or about 60° angle ([3.2.1] propellane part) to these planes. The result of ^{29}Si CP-MAS NMR shows the expected eight signals. Among them, bridgehead signals were observed at -56.6 , -62.4 , and -71.8 ppm for those contained in cyclo-trisilane rings, and the resonance of the fourth one contained in cyclotetrasilanes ring was observed between 25.0 and 39.0 ppm (unassigned). These features clearly show the difference of this larger-ring propellanes from smaller-ring propellanes. The absorption of **50** does not show clear band above 250 nm and tails into 570 nm with several shoulders at 345 and 380 nm. With many possible oligosilyl structures, the energy levels of this molecular are probably close with a small band gap, making a broad spectrum without distinct peaks.

5 Summary, Conclusions, Outlook

In this field, most intensive research activities appears to be accumulated in 1988–1993, first 5 years from the isolation of octasilacubane. Nonetheless, just after quarter century from the beginning, it seems that we are facing a turning point with a growing numbers of new clusters.

As a matter of fact, Table 1, shown in the introduction in this article, lacks two more platonic solid compounds: octahedrane and icosahedrane. This is because those compounds comprising group-14 elements were thought to be impossible to be prepared. Obviously, Scheschkewitz's result as well as Power's octahedrane opened a gate towards octahedranes. And for icosahedranes? Yes, silicon and higher group-14 elements can adopt pentacoordinated and hexacoordinated structure!

It is noteworthy that recent approaches often adopt reactions with mixing ligands and core-atom molecules which make the syntheses simple. This development is expected to continue from now on in attempt to bridge the evident analytical gap between silicon molecules and bulk silicon.

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Low Oxidation States

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