

Review

## Silicate cages: precursors to new materials

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### 1. Background and the condensation process

Second only to carbon, silicon forms the largest number of bonds with other elements. Unlike carbon, however, where C–C, C–O, and C–H bond energies are approximately equal, the Si–O bond is considerably stronger than the Si–H bond and much stronger than the Si–Si bond. Therefore, chains of Si–O–Si–O–Si make up the skeletons of silicate chemistry. In silicates all silicon atoms exist in tetrahedral coordination by four oxygen atoms, and these are the molecular units from which naturally occurring silicates are constructed. Silicates can occur as rings, connected in chains and layers, or in the form of cages [1]. The structure of cage silicates is based on Si–O linkages forming a cage with a silicon atom at each vertex. Substituents coordinate around the silicon vertices tetrahedrally. The nature of the exo cage substituent in a compound can determine many physical properties. The number of (XSiO<sub>3</sub>) units sets the shape of the frame, which is uniquely unstrained for eight and ten units. The silicate cage compounds (RSiO<sub>1.5</sub>)<sub>n</sub>, (R = organic or inorganic group), *n* = 6 (I), *n* = 8 (II), *n* = 10 (III) or *n* = 12 (IV) (Fig. 1), represent a rather versatile class of potential three-dimensional building block units for the synthesis of new materials, and therefore they are of considerable theoretical and practical interest. Silicate cages of types II and IV are present as subunits in zeolite A (II) and zeolites type X and Y (IV) respectively (Fig. 2).

A cage structure involves several rings connected together in a finite three-dimensional molecular skeleton. These compounds are known as polyhedral silsesquioxanes [2,3]. The nomenclature most commonly used is given by a trivial systematic system. Sil-ses-quioxane, denotes that each silicon atom is connected to three oxygen atoms, (SiO<sub>3</sub>). The prefix 'oligo' is often used to indicate a small number of silsesquioxane links. Otherwise, prefixes such as 'octa-, penta-, deca-, etc.' are used to indicate a specific number of these links, e.g. (HSiO<sub>1.5</sub>)<sub>8</sub> [octasilsesquioxane or

octa(hydrosilsesquioxane)] and (CH<sub>3</sub>)<sub>7</sub>C<sub>6</sub>H<sub>5</sub>(SiO<sub>1.5</sub>)<sub>8</sub> [heptamethylphenyloctasilsesquioxane]. The general formula of polyhedral silsesquioxanes is (XSiO<sub>1.5</sub>)<sub>n</sub>, where *n* ≥ 4, and X = H, organyl, halogen, etc., which are called hydrosilsesquioxanes (also known as hydrospherosiloxanes), organylsilsesquioxanes, and halosilsesquioxanes, etc. respectively.

Oligosilsesquioxanes are generally colourless crystalline substances. With growing chain length of the alkyl group in octa(alkylsilsesquioxanes) the melting points and densities decrease, whereas volatility and solubility in organic solvents increase. Volatility of these compounds is extremely high. For the same substituent the octamers have the highest melting point and are the least volatile.

Polyhedral silsesquioxanes are potentially a very useful class of compounds. Their chemistry has, however, remained underdeveloped for a long time because of a lack of facile methods for their synthesis in useful quantities. It has taken a long time to develop suitable syntheses. The most common process now used to obtain polyhedral silicon–oxygen skeletons of oligosilsesquioxanes with R = organic group is by the hydrolytic condensation of trifunctional monomers XSiY<sub>3</sub>, where X is a chemically stable organic substituent and Y is a highly reactive substituent, such as Cl or alkoxy, and is strongly dependent on several factors including:

1. concentration of initial monomer in the solution;
2. nature of the solvent;
3. character of substituent X in the initial monomer;
4. nature of functional group Y in the initial monomer;
5. type of catalyst employed;
6. temperature;
7. rate of addition of water and quantity of water added;
8. solubility of the polyhedral oligomers formed.

The polycondensation process is very difficult to understand because of strong mutual effects of the above-mentioned factors. However, by an examination

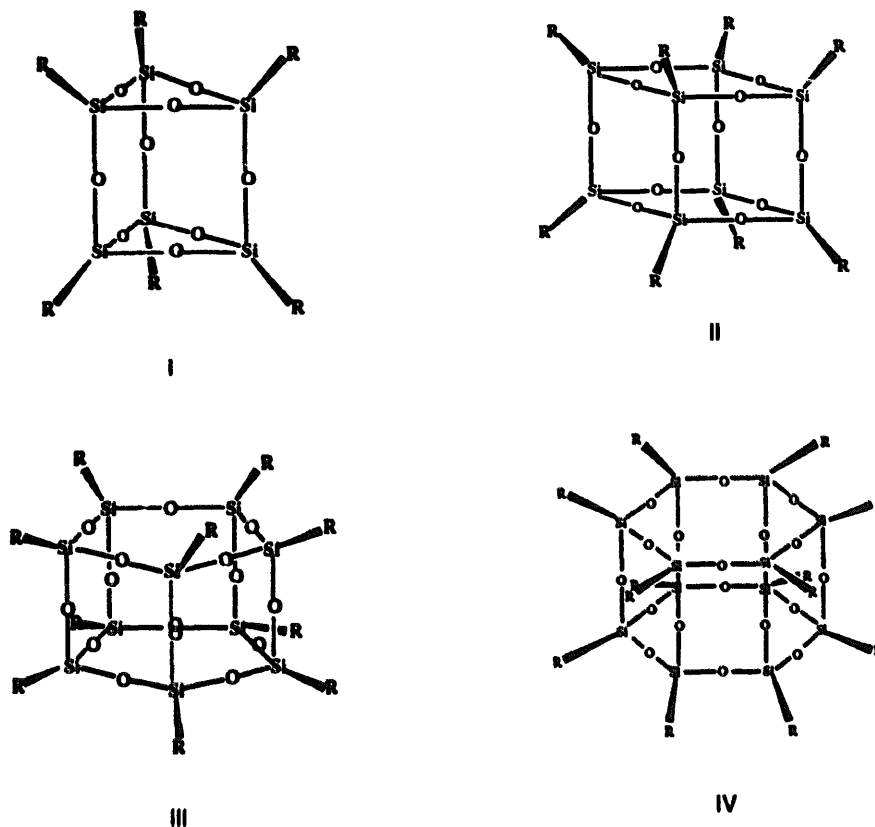


Fig. 1. Representations of  $[\text{RSiO}_{3/2}]_n$  cage structures where  $n = 6$  (I),  $n = 8$  (II),  $n = 10$  (III), and  $n = 12$  (IV). (These are idealized representations; the SiO angles in the real structures are very close to tetrahedral angles. The Si-O-Si angle is opened to ca.  $150^\circ$ ).

of each individual factor itself, qualitative trends can be deduced. Increase in temperature results in the formation of highly condensed polymers. Hence the temperature should be kept low, at room temperature or preferably subambient. Slow, careful addition of water will keep the concentration of silanol groups formed low. On the other hand, the choice of a suitable solvent such as an alcohol or ether can stabilize silanol groups by hydrogen-bonding of the Si-OH to the alcohol or ether function as well as to the remaining silalkoxy groups. The nature of the functional group Y in the initial monomer can also have an effect. For  $Y = \text{Cl}$  the hydrolysis is very rapid compared to when  $Y = \text{OEt}$ ,  $\text{OMe}$  or  $\text{CH}_3\text{COO}$ , and the reaction becomes autocatalytic with the formation of  $\text{HCl}$ . The character of the substituent X in the initial monomer plays a role due to

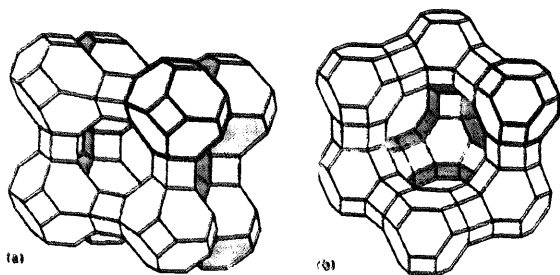
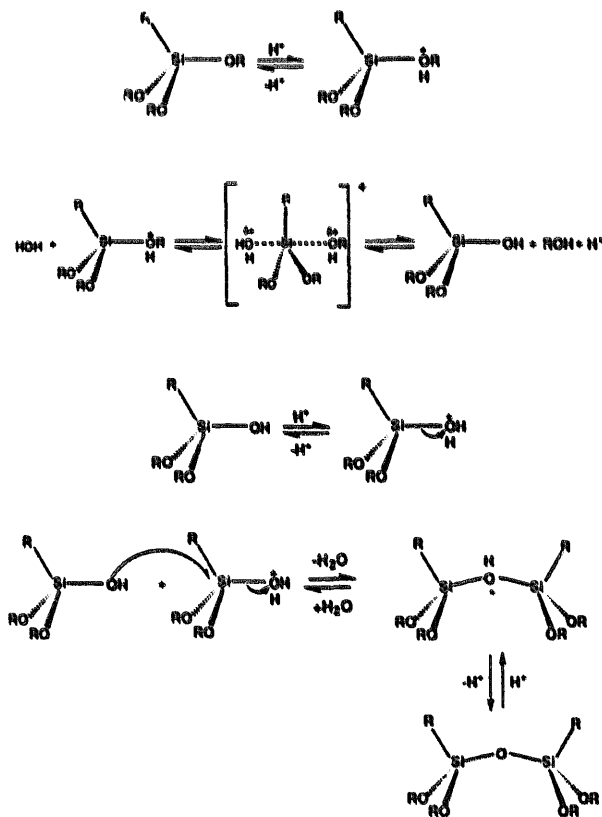
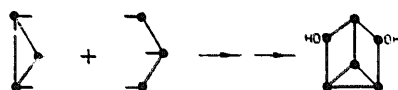


Fig. 2. The structures of zeolite A (a) and zeolites X and Y (b).



Scheme 1. Proposed mechanism for the hydrolytic condensation of  $\text{RSi}(\text{OR})_3$ .



Scheme 2.

both steric as well as +I-inductive effects. For example, in the alkylchlorosilane series, the hydrolysis rate is known to slow down with increasing hydrocarbon substituent length [4]. When  $X = \text{CH}=\text{CH}_2$ ,  $d\pi-p\pi$  effects have consequences for the stability of the five-coordinated silicon intermediate. Therefore, in most cases, the mechanism of polycondensation of trifunctional monomers  $\text{XSiY}_3$  bearing a different substituent X is also different. Also, it is not surprising that the size of the silicon atom is of great importance, and for the heavier Group 14 elements germanium and tin such cubic sesquioxane structures typical for silicon are not known. A close look at the condensation and hydrolysis equilibria involved in the dimerization of silanols (Scheme 1) shows how complex the mechanisms are, and will give an initial idea for a qualitative interpretation of the above-mentioned factors. As seen in Scheme 1, a five-coordinated silicon complex is proposed to be involved as an intermediate.

The formation of oligosilsesquioxanes in the course of hydrolytic polycondensation of  $\text{XSiY}_3$  monomers in dilute solvents can be represented by the overall equation

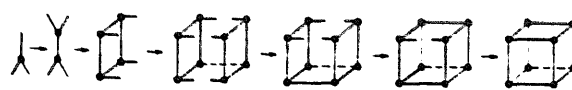


However, it is in reality a multistep and rather complicated process. Sprung and Guenther [5] were the first to postulate that the hydrolysis of organonyltrifunctional monomers  $\text{XSiY}_3$  involves the formation consecutively of linear, cyclic, polycyclic, and finally polyhedral siloxanes, and assumed the chain growth to be of a random character. This hypothesis was further developed by Brown and coworkers, who studied the hydrolysis of cyclohexyl- [6] and phenyltrichlorosilane [7] and suggested the formation of polyhedral silsesquioxanes and their homo derivatives occurred as a result of consecutive stepwise polycondensation of cyclic macromolecules, as illustrated in Schemes 2 and 3 respectively.

On the basis of the polycondensation intermediates observed, cyclization at the initial step of the reaction and simultaneous formation of linear and cyclic oligosiloxanes were proposed to occur. Co-condensation of the latter was believed to lead to polycyclosiloxanes [7] which are inert to further intermolecular polyconden-



Scheme 3.



Scheme 4.

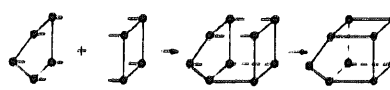
sation (Schemes 4 and 5). Interestingly, the polycondensation of  ${}^1\text{BuSi}(\text{OH})_3$  has been reported to give a unique example of the fully condensed, tetranuclear silsesquioxane,  $[{}^1\text{BuSiO}]_4$ , which could be isolated in 94% yield [8]. In this case, the compound which results from the first step,  $[{}^1\text{BuSi}(\text{OH})_2]_2\text{O}$ , comprises hydrogen-bonded sheets in the solid state [9].

The mechanism by which oligo(ethylsilsesquioxanes) are formed in the hydrolysis of ethyltrichlorosilane [10,11] and ethyldichlorosilane [12] has been established by GC-mass spectrometry. The formation of oligoethylsilsesquioxanes through hydrolysis of  $\text{C}_2\text{H}_5\text{SiCl}_3$  in aqueous butanol is shown in Scheme 6. Investigation of the hydrolysis of  $\text{C}_2\text{H}_5\text{SiCl}_3$  in aqueous butanol by GC-mass spectrometry [13] shows the influence of the substituent X, and is shown in Scheme 7.

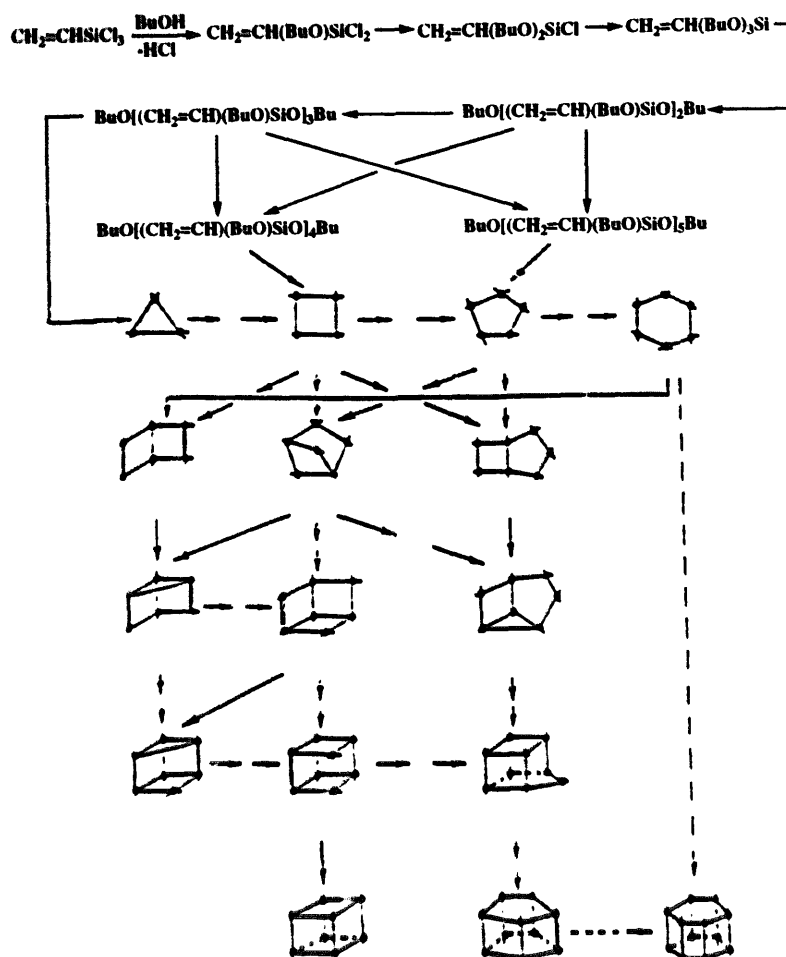
## 2. Trigonal prismatic $\{\text{Si}_6\text{O}_9\}$ cages

The first double three ring (D3R) silicate (type I, see Section 1) compounds,  $(\text{CH}_3)_6\text{Si}_6\text{O}_9$  and  $(\text{C}_2\text{H}_5)_6\text{Si}_6\text{O}_9$ , were first synthesized in 1955 by Sprung and Guenther [5,10,14]. The homologous compounds  $(\text{C}_7\text{H}_{15})_6\text{Si}_6\text{O}_9$  [15,16],  $(\text{C}_8\text{H}_{17})_6\text{Si}_6\text{O}_9$  [15–17],  $(i\text{-C}_9\text{H}_{19})_6\text{Si}_6\text{O}_9$  [15,16],  $(\text{C}_6\text{H}_{11})_6\text{Si}_6\text{O}_9$  [6,18] and  $(\text{C}_6\text{H}_5)_6\text{Si}_6\text{O}_9$  [19,20] were also successfully synthesized in the following years by hydrolysis of their corresponding  $\text{RSiX}_3$  monomers where  $X = \text{Cl}$  or alkoxy. In 1970, Smolin [21] was able to synthesize and determine the structure of the D3R silicate (type I with  $\text{R} = \text{O}^-$ ) by reacting an ethylenediamine solution of nickel hydroxide with a 2.5% solution of silica in ethylenediamine. The structure of the crystals obtained exhibits two  $\{\text{Si}_6\text{O}_{15}^{6-}\}$  cage anions surrounded by three  $[\text{Ni}(\text{en})_3]^{2+}$  cations (en = ethylenediamine). In between the anions and cations are situated hydrogen-bonded water molecules (Fig. 3). Compared to the idealized structure I (see Section 1) the crystal structure of  $\{\text{Si}_6\text{O}_{15}^{6-}\}$  is very distorted so that most of the  $\text{O}-\text{Si}-\text{O}$  angles are close to the tetrahedral angle whereby the D3R system is stabilized.

In the 1970s many investigations of acidified sodium monosilicate solutions by  ${}^{29}\text{Si}$  NMR gave evidence that D3R silicates are also present in these systems [22–28].



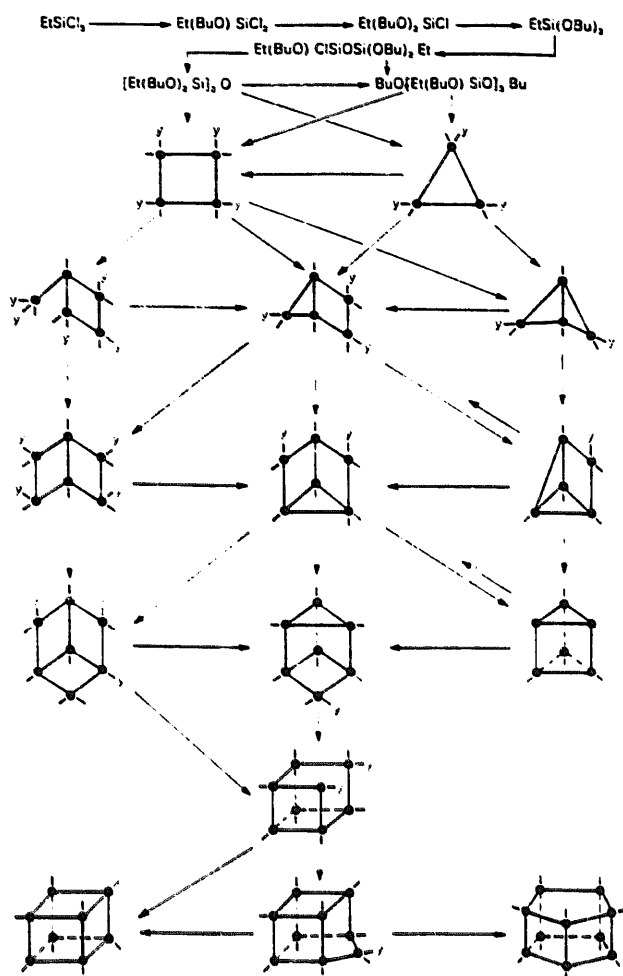
Scheme 5.



Subsequent investigations of silicate solutions with tetraethylammonium (TEA) as the cation showed that this cation had a stabilizing effect on the D3R silicate system [29–33]. It was found that using TEA as the cation in a silicate solution favoured the formation of D3R silicates to more than 95% if the optimum concentration range of Si and the optimum Si:NEt<sub>4</sub><sup>+</sup> ratio was chosen [29]. <sup>29</sup>Si NMR of solutions of various Si concentrations and different Si:NEt<sub>4</sub><sup>+</sup> ratios are shown in Fig. 4. For a concentration of 0.9 M SiO<sub>2</sub> and a ratio of TEA:Si = 3.7 there is a resonance at ca. -88 ppm for the D3R silicate (Si<sub>6</sub>O<sub>13</sub><sup>6-</sup>). In addition, small signals at ca. -82 ppm and ca. -70 ppm are present which are due to traces of disilicate and monosilicate respectively. At an SiO<sub>2</sub> concentration of 3.07 M and a ratio of TEA:Si = 0.81, several changes are observable in the spectrum. Besides the strong signal at ca. -88 ppm for the D3R silicate, many small signals are seen around that peak as well as many other small peaks in the disilicate and silicate three- and four-ring region at around ca. -80 ppm and in the double four ring (D4R) silicate region around ca. -98 ppm. At a SiO<sub>2</sub> concentration of 3.95 M and a ratio of TEA:Si = 0.62 there are

major changes in the spectrum. In addition to several sharp peaks, broad bands arise in the disilicate, D3R, and D4R regions. Finally, at a SiO<sub>2</sub> concentration of 5.1 M and a ratio of TEA:Si = 0.25 only broad bands centred at ca. -79, -87, -97, and -108 ppm are present and the only sharp peak in the spectrum is due to monosilicate at ca. -71 ppm. Solid state NMR and X-ray crystallography show that the D3R structure is preserved on crystallization. The solid state <sup>29</sup>Si NMR spectrum of crystals obtained from a TEA silicate solution [29] with a ratio NEt<sub>4</sub><sup>+</sup>:Si = 1.26 is shown in Fig. 5. The strong resonance at -90 ppm indicates that the D3R silicate is dominant beside a small resonance at ca. -67 ppm due to monosilicate.

Similarly, Groenen et al. [34], investigating water-DMSO (1:1) solutions of different tetraalkylammonium/silicate ratios, found that for TEA as the cation the ratio of TEA and silicate had a significant effect (see Fig. 6(a) and Fig. 6(b)). As seen in Fig. 6(a), for an NEt<sub>4</sub><sup>+</sup>:Si ratio of 0.5:1, besides small amounts of monosilicate and D3R-silicate the main peak observed in the <sup>29</sup>Si NMR spectra is that of the silicon atoms of the D4R silicate (type II) (see Section 1). Changing the



Scheme 7.

ratio to 1:1 results in the stabilization of the D3R-silicate, and only traces of D4R-silicate are now observed (Fig. 6(b)). Subsequently, Hoebbel et al. [35] synthesized and characterized by X-ray crystallography the trimethylsilylester of the D3R silicate,  $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$ , which had only been synthesized previously in dilute solutions by the trimethylsilylation of TEA/silicate or silicate solutions [29,30]. However, difficulties were encountered in preparing the crystalline ester due to the high instability of the quite strained Si–O–Si bonds of the D3R structure towards proton attack [36]. The structure of  $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$  is shown in Fig. 7. As seen from the crystal structure of  $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$ ,  $\text{SiMe}_3$  groups are attached to the *exo* oxygen of the  $(\text{Si}_6\text{O}_{15})$  cage, and it is the steric effect of the  $\text{SiMe}_3$  groups which results in the stabilization of the D3R silicate compound. Similar distortions are found in the structure of  $(\text{C}_6\text{H}_{11})_6\text{Si}_6\text{O}_9$  [37].

### 3. Cubane $(\text{Si}_8\text{O}_{12})$ cages

The most studied type of double-ring-silicate system is the cubane  $(\text{Si}_8\text{O}_{12})$  silicate. The first representative

was  $(\text{CH}_3)_8\text{Si}_8\text{O}_{12}$  [38–41,14] synthesized by Scott [41], but many more D4R silicate compounds with alkyl substituents including  $\text{C}_2\text{H}_5$  [5,10,12,38,40,42,43],  $\text{C}_3\text{H}_7$  [38,40],  $\text{CH}(\text{CH}_3)_2$  [40],  $\text{C}_4\text{H}_9$  [38,40],  $\text{C}_5\text{H}_{11}$  [44],  $\text{C}_6\text{H}_{13}$  [15–17], *i*- $\text{C}_9\text{H}_{19}$  [17],  $\text{C}_6\text{H}_{11}$  [38,45], 1- $\text{C}_{10}\text{H}_7$  [20], 2- $\text{C}_4\text{H}_9\text{S}$  [46] and aryl substituents including  $\text{C}_6\text{H}_5$  [6,40,44,47,48], and 4- $\text{CH}_3\text{C}_6\text{H}_4$  [48], have been synthesized. Some polyhedral oligoorganylsilsesquioxanes have been prepared by thermal depolymerization of organyltrichloro and organyltri-alkoxysilane hydrolysis products. However, this method is not popular and so has not been used widely. The thermolysis of polymeric hydrolysis products of  $\text{XSiY}_3$  compounds is performed by heating at 200–400 °C in the presence of a base catalyst [38,39,47,48,46] (sometimes in vacuum). Alkali metal hydroxides and in some cases triethylamine are the most frequently used catalysts [48,46].

The silicate cages with saturated alkyl groups are chemically quite inert species. Compounds like  $(\text{CH}_2=\text{CH})_8\text{Si}_8\text{O}_{12}$  [10,49,50] (1) or  $\text{H}_8\text{Si}_8\text{O}_{12}$  [51–53] (2), bearing a reactive group on the silicon atom, offer the possibility of obtaining new compounds by reaction of the *exo* cage function. However, these seemingly reactive groups, hydride or vinyl, on the D4R silicate cage unit are extremely unreactive compared to analogous Si-substituted linear, cyclic or polycyclic oligosiloxanes, presumably due to the rigid silicon-oxygen framework and different electron density on the D4R silicate cage unit. Two reactions are known for the octavinylsilsesquioxane compound (1). Electron-beam- or X-ray-induced polymerization yields thin films of the corresponding polymer (Scheme 8) used in a dry vacuum submicrometre lithography process [54]. Bromination of (1) in carbon tetrachloride is complex [55]. The main reaction products in the mixtures obtained were  $(\text{CH}_2=\text{CH})_7(\text{CHBr}-\text{CH}_2)\text{Si}_8\text{O}_{12}$  and  $(\text{CH}_2=\text{CH})_6(\text{CHBr}-\text{CH}_2)_2\text{Si}_8\text{O}_{12}$ . Attempts to achieve a more extensive bromination of  $(\text{CH}_2=\text{CH})_8\text{Si}_8\text{O}_{12}$  under the same conditions failed.

Octahydridosilsesquioxane  $\text{H}_8\text{Si}_8\text{O}_{12}$  (2) was first prepared fortuitously in about 0.1% yield in 1959 by Müller et al. [51] while studying the preparation of poly(hydridosilsesquioxanes),  $\text{Me}_3\text{SiO}[\text{HSi}(\text{OSiMe}_3)\text{O}]_n\text{SiMe}_3$ . In 1970 Frye and Collins [52] increased the yield to 13% by an improved method involving the careful hydrolysis of  $\text{HSiCl}_3$  in a benzene-concentrated  $\text{H}_2\text{SO}_4$  mixture. A further improvement was made in 1991 by Agaskar [53], who developed a new synthetic procedure which gave a mixture of  $\text{H}_8\text{Si}_8\text{O}_{12}$  and  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  in high yield (about 27%) by using partially hydrated  $\text{FeCl}_3$  as the source of water for the hydrolysis of  $\text{HSiCl}_3$ . Isolation of  $\text{H}_8\text{Si}_8\text{O}_{12}$  was very easy to implement by crystallization, giving a yield of ca. 17.5% of pure  $\text{H}_8\text{Si}_8\text{O}_{12}$ .

However, the recognition in 1988 that the  $(\text{Si}_8\text{O}_{12})$

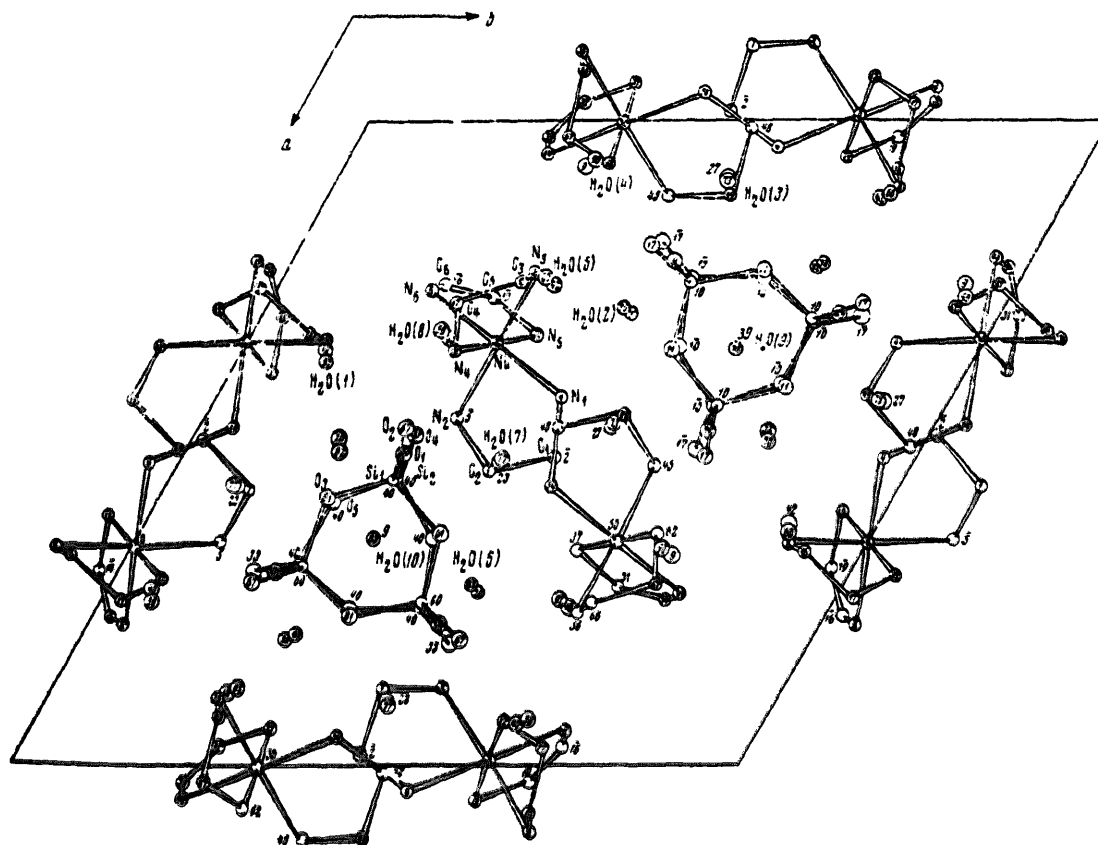


Fig. 3. Crystal structure of  $[\text{Niten}]_3, \text{Si}_6\text{O}_{14} \cdot 26\text{H}_2\text{O}$ .

framework bore a close resemblance to the D4R found in Linde Type A and in Co APO-50 type zeolites [56] (Fig. 8) renewed a particular interest in octahydridosilsesquioxane. In consequence, it was considered that a detailed spectroscopic investigation of  $\text{H}_8\text{Si}_6\text{O}_{12}$

[57–64] would afford a better understanding of zeolites and lead to new chemistry of related structures.

For non-cyclic silanes many reactions of the Si–H function are known, including reaction with organolithium reagents [65,66], alkenes [67], benzene [65–76],

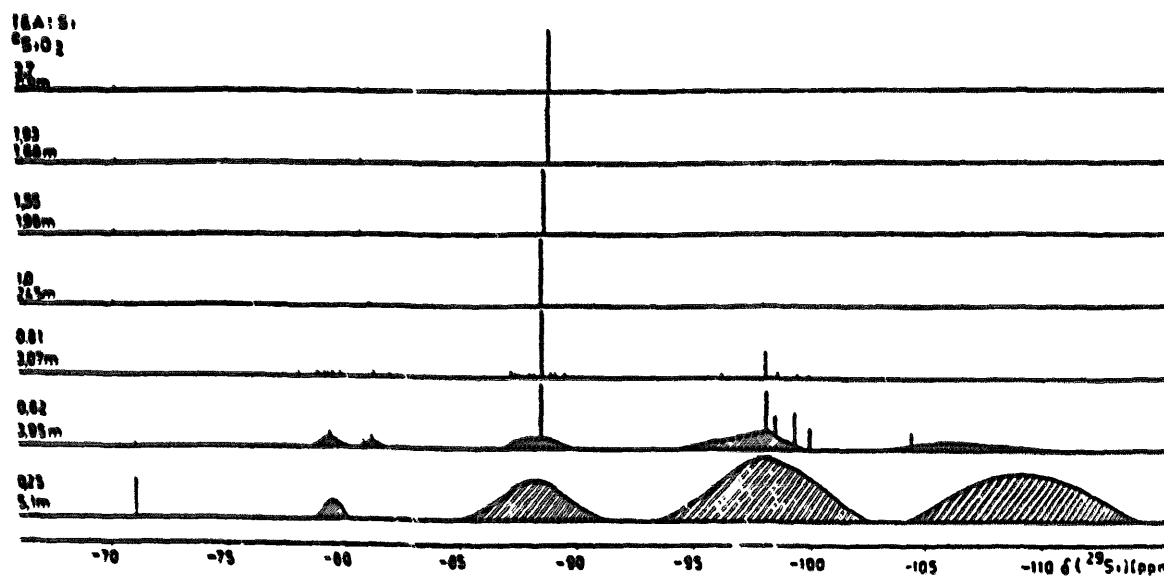


Fig. 4.  $^{29}\text{Si}$  NMR spectra of solutions of various Si concentrations and different  $\text{Si}:\text{NET}_3$  ratios.

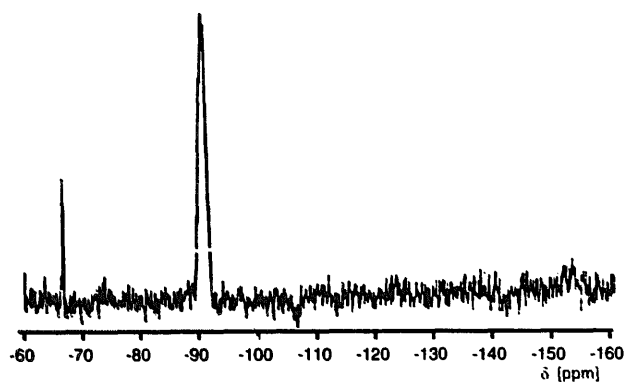


Fig. 5. Solid state  $^{29}\text{Si}$  NMR spectrum of crystals obtained from a TEA silicate solution with a ratio  $\text{NEt}_4^+:\text{Si} = 1.26$ .

diazomethane [77], alkali metals [78–80], alcohols [81–86], alkali-metal alkoxides [87], aldehydes [88], ketones [89–91], carboxylic acids [92,93] and halogens [94–98]. In contrast, however, the hydrido function on octahydridosilsesquioxane (**2**) is relatively unreactive. It is quite remarkable that it took nearly 40 years after the initial synthesis of  $\text{H}_8\text{Si}_8\text{O}_{12}$  before the first Si–H substitution reaction of this cage compound was reported by Day et al. in 1985 [99]. Photochemical chlorination of  $\text{H}_8\text{Si}_8\text{O}_{12}$

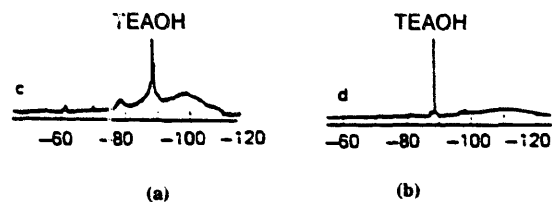


Fig. 6.  $^{29}\text{Si}$  NMR spectra of TEA silicate water–DMSO (1:1) solutions with  $\text{NEt}_4^+:\text{Si}$  ratio of 0.5:1 (a) and  $\text{NEt}_4^+:\text{Si}$  ratio of 1:1 (b).

(**2**) in  $\text{CCl}_4$  (Scheme 9) results in > 95% yield of  $\text{Cl}_8\text{Si}_8\text{O}_{12}$  (**3**), which is less reactive and therefore easier to handle than many other chlorosilanes [99,100]. The corresponding octamethoxy compound  $(\text{MeO})_8\text{Si}_8\text{O}_{12}$  (**4**), is obtained in 45% yield by further reaction of  $\text{Cl}_8\text{Si}_8\text{O}_{12}$  (**3**) with  $\text{MeONO}$  (Scheme 9). The crystal structure of  $(\text{MeO})_8\text{Si}_8\text{O}_{12}$  is shown in Fig. 9 and illustrates the  $\{\text{Si}_8\text{O}_{12}\}$  cubane cage with MeO groups attached to each silicon vertex. The Si–O angles are close to tetrahedral angles due to distortion of the cubane cage. The reactions of octahydridosilsesquioxane (**2**) with  $\text{Me}_3\text{SiOSnMe}_3$ ,  $\text{Ph}_4\text{SbOSbMe}_4$ ,  $\text{Me}_3\text{SiOSbMe}_4$ , and  $\text{Me}_3\text{SnOSnMe}_3$  were successful only in the two latter cases (Scheme 9) giving  $\text{Me}_3\text{SiO}$ - and  $\text{Me}_3\text{SnO}$ -substituted  $\{\text{Si}_8\text{O}_{12}\}$  cages respectively.

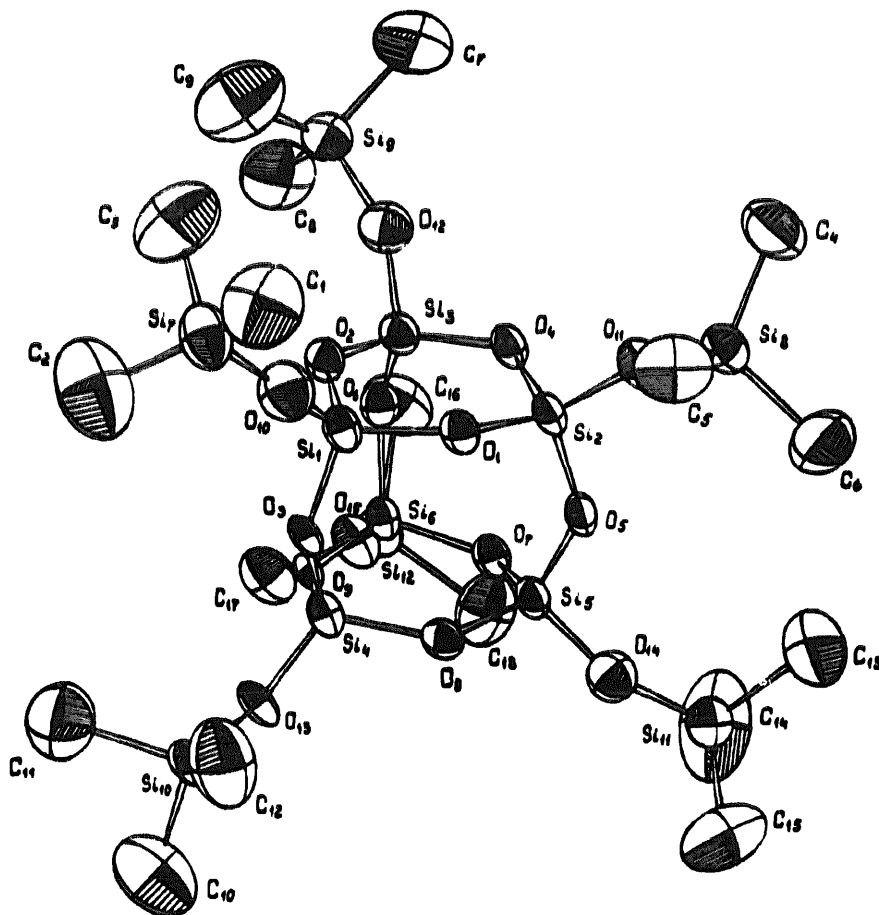
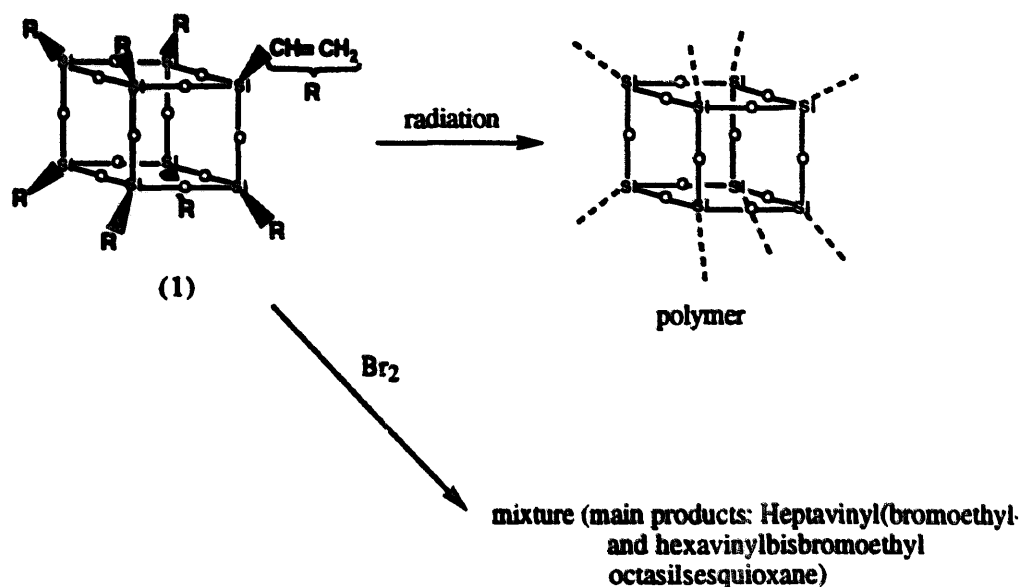


Fig. 7. Crystal structure of  $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{14}$ .



Scheme 8.

With  $\text{Ph}_4\text{SbOSbPh}_4$  the  $\text{Ph}_4\text{SbO}$ -substituted spherosilicate could not be obtained, and only mixtures of  $(\text{C}_6\text{H}_5)_3\text{Sb}$ ,  $\text{C}_6\text{H}_6$ , Si-H-containing products and an intractable solid were found [101].

$\text{H}_8\text{Si}_8\text{O}_{12}$  reacts with the silylation agents  $(\text{CH}_2=\text{CH})\text{Si}(\text{CH}_3)_2\text{Cl}/\text{Me}_3\text{NO}$  or  $(\text{ClCH}_2)\text{Si}(\text{CH}_3)_2\text{Cl}/\text{Me}_3\text{NO}$  to give the silylated spherosilicates  $\text{Si}_8\text{O}_{12}[\text{OSi}(\text{CH}_3)_2(\text{CH}_2=\text{CH})]_8$  (**8a**) and  $\text{Si}_8\text{O}_{12}[\text{OSi}(\text{CH}_3)_2\text{Cl}]_8$  (**8b**) respectively [102]. However,  $\text{Me}_3\text{SnO}$ - and  $\text{Me}_4\text{SbO}$ -substituted  $(\text{Si}_8\text{O}_{12})$  cages could not be obtained by the corresponding reaction of  $\text{H}_8\text{Si}_8\text{O}_{12}$  with  $\text{Me}_3\text{SnCl}/\text{Me}_3\text{NO}$  or  $\text{Me}_4\text{SbCl}/\text{Me}_3\text{NO}$  [101]. However, octahydridosilsesquioxane reacts with  $\text{Me}_3\text{SnOMe}$  to afford a complex mixture of incompletely trimethylstannylated  $(\text{Si}_8\text{O}_{12})$  cages (i.e.  $\text{H}_{8-n}(\text{Me}_3\text{SnO})_n\text{Si}_8\text{O}_{12}$ ) [103]. Feher and Weller [104] showed that reaction of octahydridosilsesquioxane (**2**) with  $\text{Me}_3\text{SnOSnMe}_3$  resulted in the formation of compound (**6**), which could be transformed into compound (**7**) using either  $\text{Me}_3\text{SiOSbMe}_4$  or  $\text{Me}_4\text{COSbMe}_4$  as reagent (Scheme 9).

Bürgy and Calzaferri [105] have reported the palladium-catalysed H/D exchange by bubbling  $\text{D}_2$  into a pentane solution containing octahydridosilsesquioxane (**2**) and Pd/C catalyst at ambient temperature (Scheme 10). Several platinum-catalysed hydrosilylation reactions have been carried out using  $\text{H}_2\text{PtCl}_6$  as catalyst [106]. Octa(1-hexylsilsesquioxane) and octa(cyclohexylmethylsilsesquioxane) have been obtained by reacting octahydridosilsesquioxane (**2**) with hex-1-ene and methylenecyclohexene respectively [107]. This offers a new synthetic route to polyhedral organylsilsesquioxanes, and the general reaction shown in Scheme 10 can lead to a large number of new oligosilsesquioxanes [108–110]. Bassindale and Gentle [111] have employed

the hydrosilation method using octahydridosilsesquioxane to obtain siloxane and hydrocarbon octopus molecules with silsesquioxane cores.

An alternative pathway to  $(\text{c-C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{12}$  is by the catalytic hydrogenation of  $\text{Ph}_8\text{Si}_8\text{O}_{12}$  [112] at 34 atm and 200 °C. The compound obtained is reported to be identical in all respects to that prepared by the hydrolytic condensation of  $(\text{c-C}_6\text{H}_{11})\text{SiCl}_3$  [6].

Tacke et al. [113] have described two synthetic routes to aminoalkyl-substituted cages. The reaction of (**11a**) in refluxing acetonitrile for 18 h yields octa([2-(dimethyl-amino)phenyl]silsesquioxane) (**11**) in 90% yield. A yield of 83% was reported for the hydrolysis of (**11b**); however, for this the reaction time needed to be increased to several weeks (Scheme 11).

Both  $\text{C}_6\text{H}_5$  and  $2\text{-C}_4\text{H}_9\text{S}$  substituents on the silicon atom of octasilsesquioxane can be modified. Treatment of phenyl groups with  $\text{HNO}_3$  [48] results in nitration to give  $\text{NO}_2\text{C}_6\text{H}_4$  substituents, and treatment of  $2\text{-C}_4\text{H}_9\text{S}$  with  $\text{Br}_2$  in  $\text{HBr}$  as solvent [46] gives  $2\text{-C}_4\text{H}_9\text{SBr}$  as the substituent.

A broad range of new highly functionalized organyl-

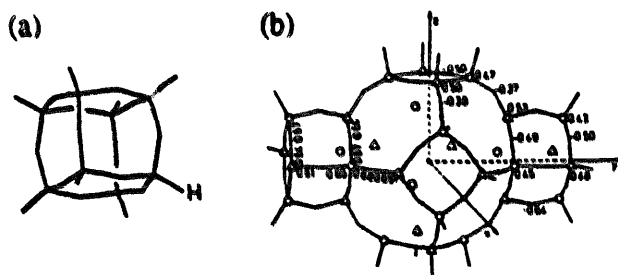
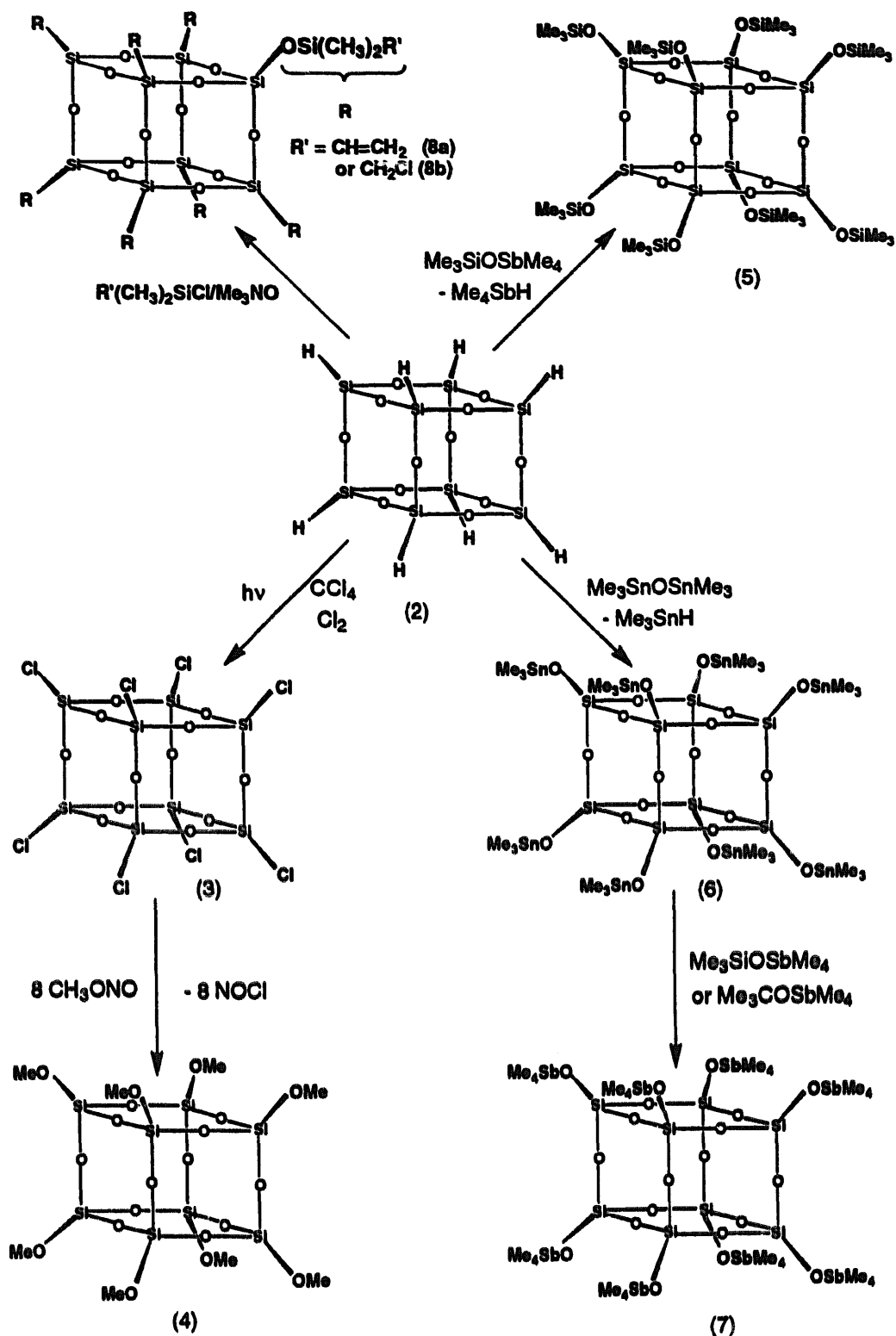


Fig. 8. Structure of  $\text{H}_8\text{Si}_8\text{O}_{12}$  (a) and part of the zeolite A structure (b).





Scheme 9.

silsesquioxanes was reported by Feher and Budzichowski [114] based on  $(p\text{-ClCH}_2\text{C}_6\text{H}_4)_8\text{Si}_8\text{O}_{12}$  (12), formed by the hydrolytic condensation of  $p\text{-ClCH}_2\text{C}_6\text{H}_4\text{SiCl}_3$  in aqueous acetone. (12) is a synthet-

ically useful precursor for the synthesis of several octafunctional polyhedral oligosilsesquioxanes ( $p\text{-XCH}_2\text{C}_6\text{H}_4$ ) $_8\text{Si}_8\text{O}_{12}$ , including  $X = \text{I}$  (13),  $X = \text{OH}$  (14),  $X = \text{ONO}_2$  (15),  $X = \text{OAc}$  (16),  $X = p\text{-}$

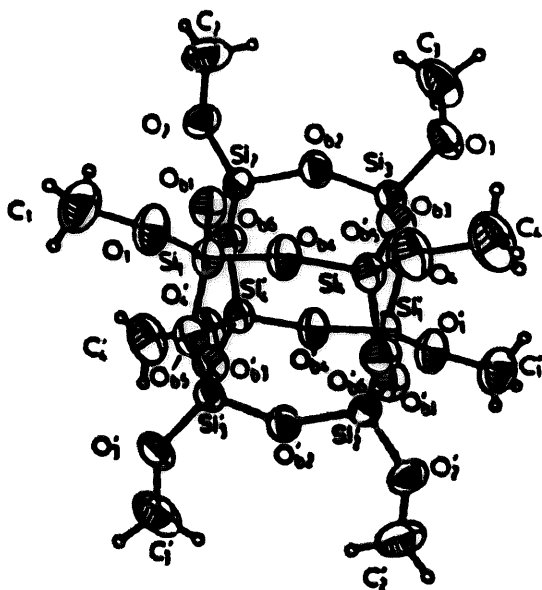


Fig. 9. Crystal structure of  $(\text{MeO})_8\text{Si}_8\text{O}_{12}$ .

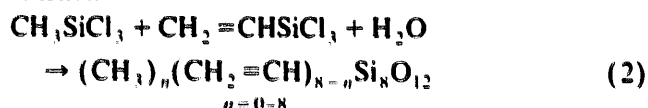
nitrobenzoyl (17) and  $X = \text{methylterephthaloyl}$  (18). A summary of the reaction is given in Scheme 12.

Most of the heterosubstituted oligosilsesquioxanes known, however, have been obtained by co-hydrolysis using different  $\text{XSiR}_3$  ( $R = \text{Cl}, \text{CH}_3, \text{COO}$ ) monomers. A summary of heterosubstituted octasilsesquioxanes  $\text{X}_m\text{X}'_{8-m}\text{Si}_8\text{O}_{12}$  obtained by co-hydrolysis using different  $\text{XSiR}_3$  monomers is given in Table 1.

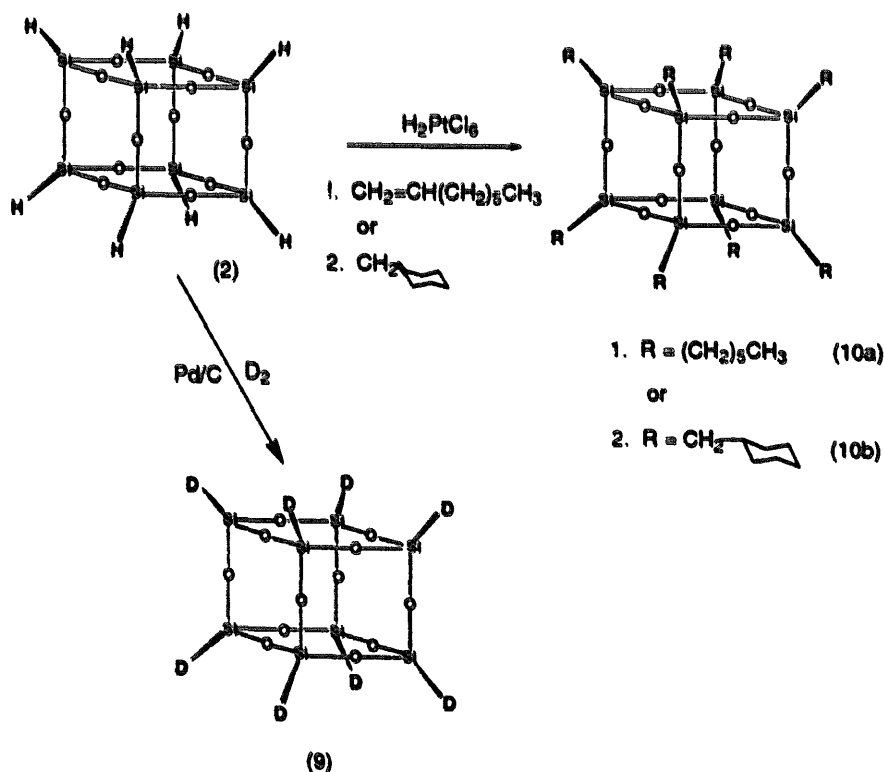
The co-hydrolysis of a mixture of trifunctional  $\text{XSiR}_3$  and  $\text{X}'\text{SiR}_3$  monomers, usually gives a mixture of

heterosubstituted oligosilsesquioxanes with all possible combinations of substituents,  $X$  and  $X'$  [115,116]. When used for the preparation of heterosubstituted octasilsesquioxanes, for example, this reaction leads to a mixture containing nine compounds of the general formula  $\text{X}_m\text{X}'_{8-m}\text{Si}_8\text{O}_{12}$  with  $m = 0-8$ . Compounds of this type with  $m = 2-6$  may, in turn, represent mixtures differing not only in the composition, but also by the substituent position. The relative yield of particular heterosubstituted oligosilsesquioxanes with various  $m$  values depends mainly on the molar ratio and reactivity of the initial monomer. In the case of an equimolar ratio of both monomers and similar rates of hydrolysis, the compound with an equal number of  $X$  and  $X'$ ,  $\text{X}_4\text{X}'_4\text{Si}_8\text{O}_{12}$ , is formed in highest yield. However, variations of the molar ratio of the initial monomers results in different products and yield. Thus co-hydrolysis of  $\text{XSiR}_3/\text{X}'\text{SiR}_3$  mixtures in the molar ratio 1:7 leads to the formation of  $\text{XX}'_7\text{Si}_8\text{O}_{12}$  as the major product. The yields of heterosubstituted oligosilsesquioxanes are significantly affected by differences in reactivity of the initial monomers.

Martynova and Chupakina [120] have shown by GLC-mass spectrometric analysis that the preparation of mixed  $(\text{CH}_3)_n(\text{CH}_2=\text{CH})_{8-n}\text{Si}_8\text{O}_{12}$  compounds via the reaction



in alcoholic medium does not lead to reproducible



Scheme 10.

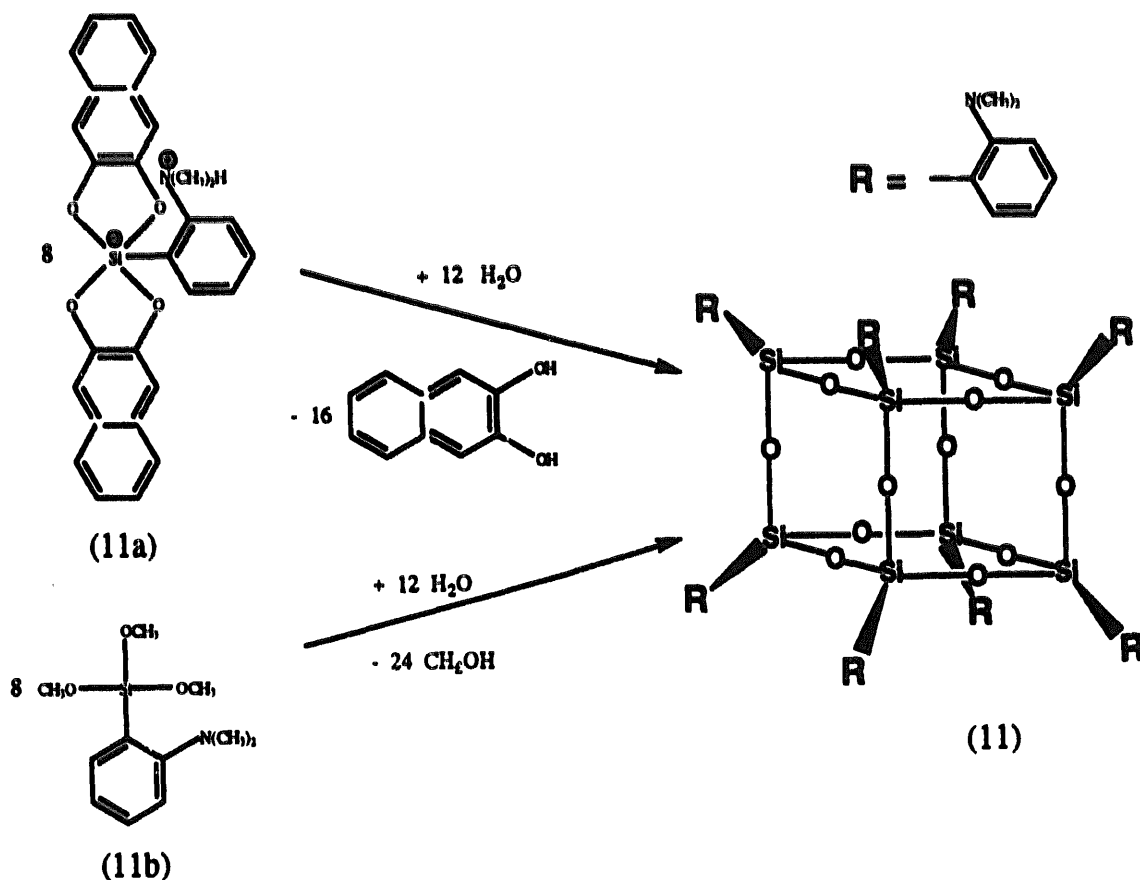
compositions of the oligomers. Reproducible composition however can be achieved in changing using the corresponding acetates,  $\text{CH}_3\text{Si}(\text{OCOCH}_3)_3$  and  $\text{CH}_2=\text{CHSi}(\text{OCOCH}_3)_3$ . The results are shown in Table 2.

The efficient synthesis of compounds with only a single heterosubstituent is rather difficult. The best method appears to be by the reaction of one Si–H function of  $\text{H}_8\text{Si}_8\text{O}_{12}$  (2) with an alkene in a 1:1 molar ratio, whereby compounds (19a, 19b, 19c) have been obtained [109–111,121] (Scheme 13).

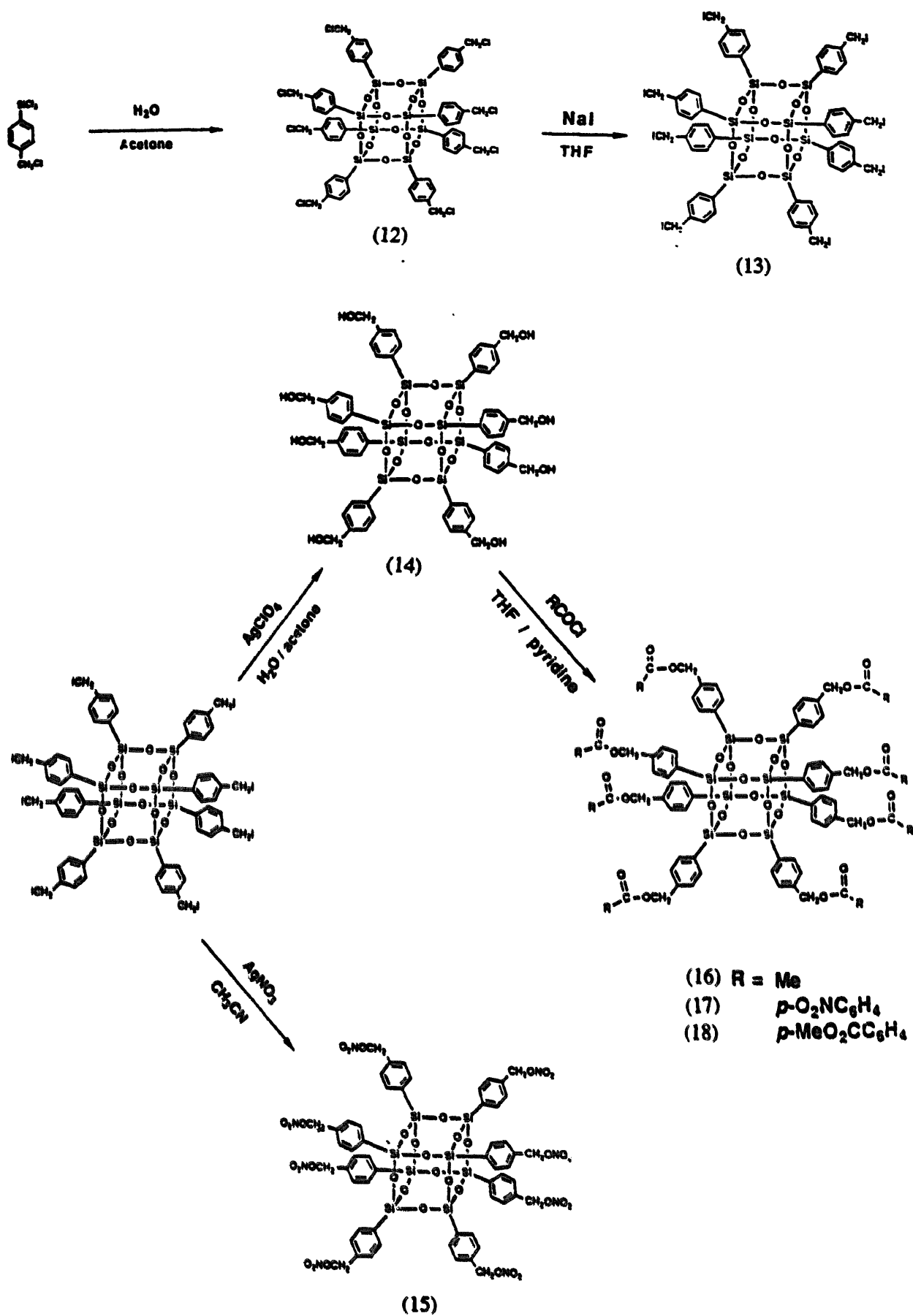
Octacarbonyldicobalt  $\text{Co}_2(\text{CO})_8$  reacts readily with silanes at room temperature (Eq. (12)) [122,123] to give silylcobaltcarbonyl compounds. This type of hydrogen elimination accompanied by cleavage of a metal bond is common in organometallic chemistry and many of the known Si–Co(CO)<sub>4</sub> compounds can be synthesized by applying this reaction [124–126]. The reaction between  $\text{H}_8\text{Si}_8\text{O}_{12}$  and  $\text{Co}_2(\text{CO})_8$  in a 1:1 molar ratio leads to the formation of the first monosubstituted hydridosilsesquioxane  $\text{H}_7\text{Si}_8\text{O}_{12}\text{Co}(\text{CO})_4$  [127] with a silicon–metal bond as shown in Scheme 14. The crystal structure of  $(\text{Co}(\text{CO})_4)_n(\text{H}_7\text{Si}_8\text{O}_{12})_n$  [127] (Fig. 10) illustrates the  $(\text{Si}_8\text{O}_{12})_n$  cage unit with hydrogen atoms

attached to seven of the eight silicon cage atoms. The eighth silicon cage atom is attached to the  $\text{Co}(\text{CO})_4$  substituent via a silicon–cobalt bond. The coordination of the cobalt atom in the structure is trigonal bipyramidal. When a 1:2 molar ratio of reactants is employed, however, the bis-substituted cage (20b) is formed which has been characterized by NMR data [128]. Despite this success, no other reaction between  $\text{H}_8\text{Si}_8\text{O}_{12}$  and a metal carbonyl compound, like the very common reactions of a non-cyclic silane  $\text{R}_3\text{Si-H}$  with  $\text{CpMn}(\text{CO})_3$  [129] or  $\text{Fe}_3(\text{CO})_{12}$  [130], has been reported.

$(\text{c-C}_6\text{H}_{11})_7\text{HSi}_8\text{O}_{12}$  (22) [131,132] and  $(\text{c-C}_6\text{H}_{11})_7\text{ClSi}_8\text{O}_{12}$  (23) [131] have been prepared by the reaction of the incomplete condensed cage  $(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$  [132] (21) with  $\text{SiCl}_4$  and  $\text{HSiCl}_3$  respectively (Scheme 14).  $(\text{c-C}_6\text{H}_{11})_7(\text{Me}_3\text{SnO})\text{Si}_8\text{O}_{12}$  (24a) and  $(\text{c-C}_6\text{H}_{11})_7(\text{Me}_4\text{SbO})\text{Si}_8\text{O}_{12}$  (24b) have been synthesized by reacting  $(\text{c-C}_6\text{H}_{11})_7\text{HSi}_8\text{O}_{12}$  (22) with  $\text{Me}_3\text{SnCl}/\text{Me}_3\text{NO}$  or  $\text{Me}_4\text{SbCl}/\text{Me}_3\text{NO}$  respectively [101] (Scheme 14). Like octahydridosilsesquioxane (2), (22) undergoes palladium-catalysed deuterium exchange which results in the formation of (25) [131] (Scheme 14). All three compounds (22, 23, and 25) undergo Wittig-reactions with  $\text{R}'_3\text{P}=\text{CH}_2$  reagents (Scheme 14),



Scheme 11.



Scheme 12.

Table 1  
Heterosubstituted octasilsesquioxanes  $X_m X'_8 - m \text{Si}_8\text{O}_{12}$

X	X'	m	Reference
$\text{C}_6\text{H}_{11}$	H	7	[45]
$\text{CH}_3$	$\text{C}_2\text{H}_5$	1–7	[115]
$\text{C}_2\text{H}_5$	$\text{CH}=\text{CH}_2$	1–7	[116]
$\text{CH}_3$	$\text{C}_6\text{H}_5$	4, 6, 7	[117,118]
$t\text{-C}_4\text{H}_9$	$\text{C}_6\text{H}_5$	6	[119]
$\text{CH}=\text{CH}_2$	$\text{CH}_2\text{CH}_2\text{Br}$	7	[55]
$\text{CH}_3$	$\text{CH}=\text{CH}_2$	1–7	[120]

and the proposed mechanism is illustrated in Scheme 15. The silsesquioxane-substituted phosphorane (**26a**) can also be used as Wittig reagent and yields many monofunctionalized alkenyl-silsesquioxanes with a wide range of aldehydes [131] (Scheme 16). The product derived from (**26a**) and  $p\text{-(PhCH}_2\text{O)C}_6\text{H}_4\text{CHO}$  affords compound (**29**) in high yield after hydrogenation with Pd/C [131] (Scheme 17).

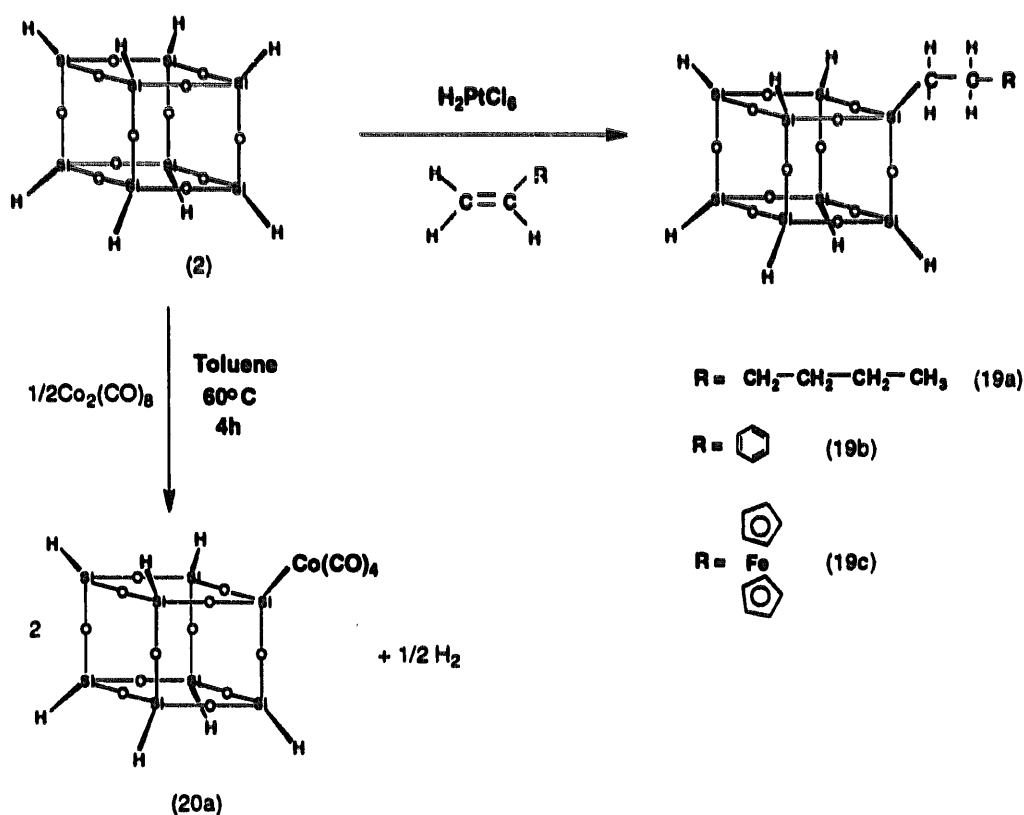
The cubane silicate (**30**) was first synthesized by Hoebbel and Wieker [133] in 1971, after being characterized by X-ray structure in the mineral ekanite ( $\text{K}_2\text{CaThSi}_8\text{O}_{20}$ ) by Mokejewa and Golowastikov [134]. The reaction of a tetramethylammonium hydroxide solution with silica gel in the ratio N:Si = 1:1 results in the formation of crystals of composition  $[(\text{CH}_3)_4\text{N}]_8[\text{Si}_8\text{O}_{20}] \cdot 69\text{H}_2\text{O}$ . Since the development of  $^{29}\text{Si}$  NMR was at its initial stage at this time, the

Table 2  
Co-hydrolysis of  $\text{CH}_3\text{Si}(\text{OCOCH}_3)_3$  and  $\text{CH}_2=\text{CHSi}(\text{OCOCH}_3)_3$

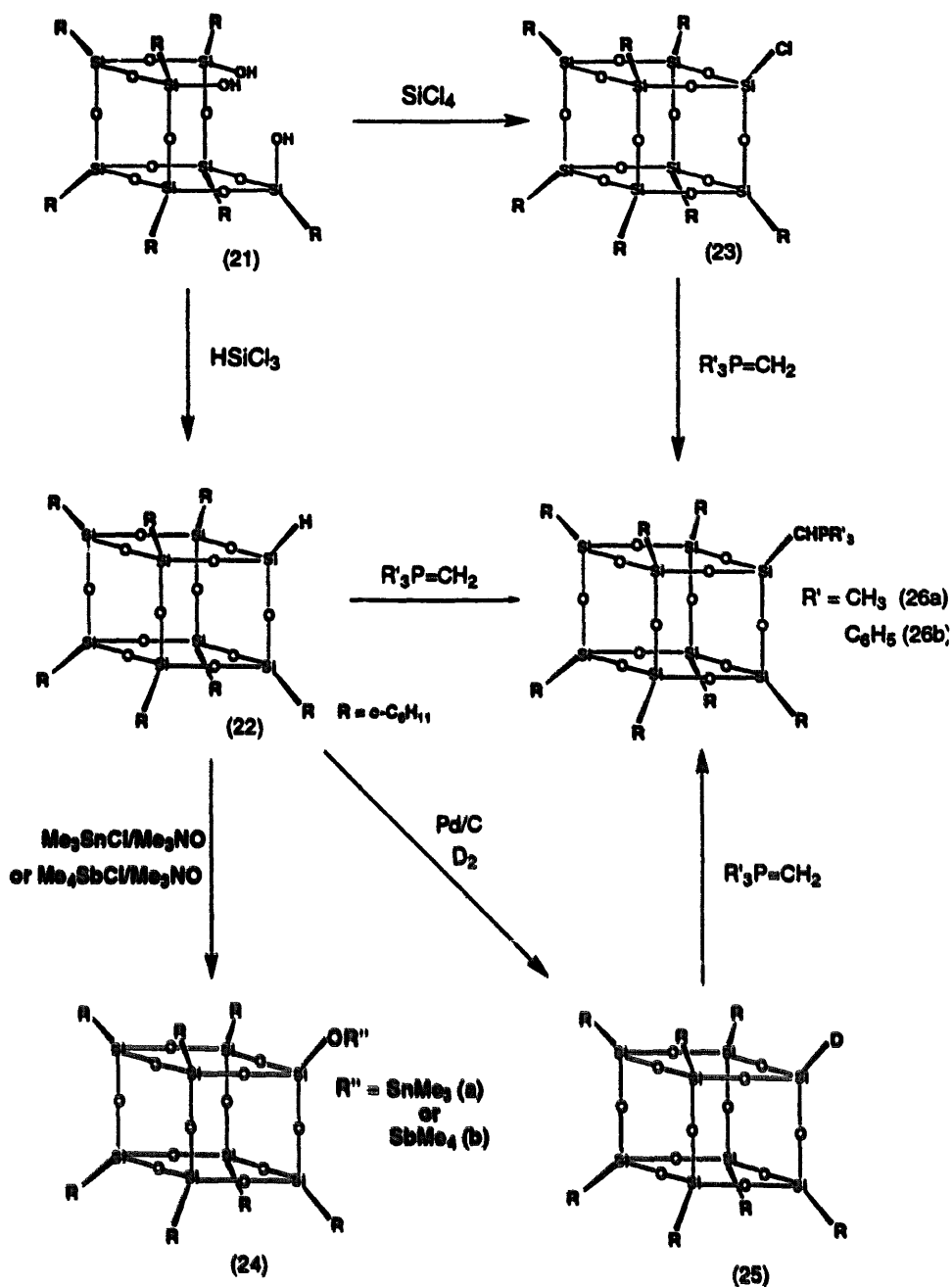
Ratio of the initial reactant $\text{CH}_3\text{-}$ and $\text{CH}_2=\text{CHSi}(\text{OCOCH}_3)_3$	Major component in product
1/7	$(\text{CH}_3)_7(\text{CH}_2=\text{CH})_1\text{Si}_8\text{O}_{12}$
2/6	$(\text{CH}_3)_2(\text{CH}_2=\text{CH})_6\text{Si}_8\text{O}_{12}$
3/5	$(\text{CH}_3)_3(\text{CH}_2=\text{CH})_5\text{Si}_8\text{O}_{12}$
4/4	$(\text{CH}_3)_4(\text{CH}_2=\text{CH})_4\text{Si}_8\text{O}_{12}$
5/3	$(\text{CH}_3)_5(\text{CH}_2=\text{CH})_3\text{Si}_8\text{O}_{12}$
6/2	$(\text{CH}_3)_6(\text{CH}_2=\text{CH})_2\text{Si}_8\text{O}_{12}$
7/1	$(\text{CH}_3)_7(\text{CH}_2=\text{CH})_1\text{Si}_8\text{O}_{12}$

condensation rate of the silicate anions in the tetramethylammoniumsilicate was investigated by the molybdate blue method [135] and paper chromatography [136,137]. However, the use of  $^{29}\text{Si}$  NMR in the following years resulted in a better understanding of this and related systems. Silicate silicon atoms can have different chemical environments and are subdivided in five groups which are described by  $\text{Q}^0$ ,  $\text{Q}^1$ ,  $\text{Q}^2$ ,  $\text{Q}^3$ ,  $\text{Q}^4$  as shown in Fig. 11 with  $^{29}\text{Si}$  chemical shift ranges in Table 3. A typical example of how complex the constitution of a solution may be is illustrated in Fig. 12, which shows the spectrum of a 4.1 M sodium silicate solution with Na:Si ratio of 1:1 in which many different silicon sites may be distinguished.

The copper-complex  $[\text{Cu}(\text{en})_2]_4\text{Si}_8\text{O}_{20} \cdot 38\text{H}_2\text{O}$  has been obtained by reacting an alkaline aqueous

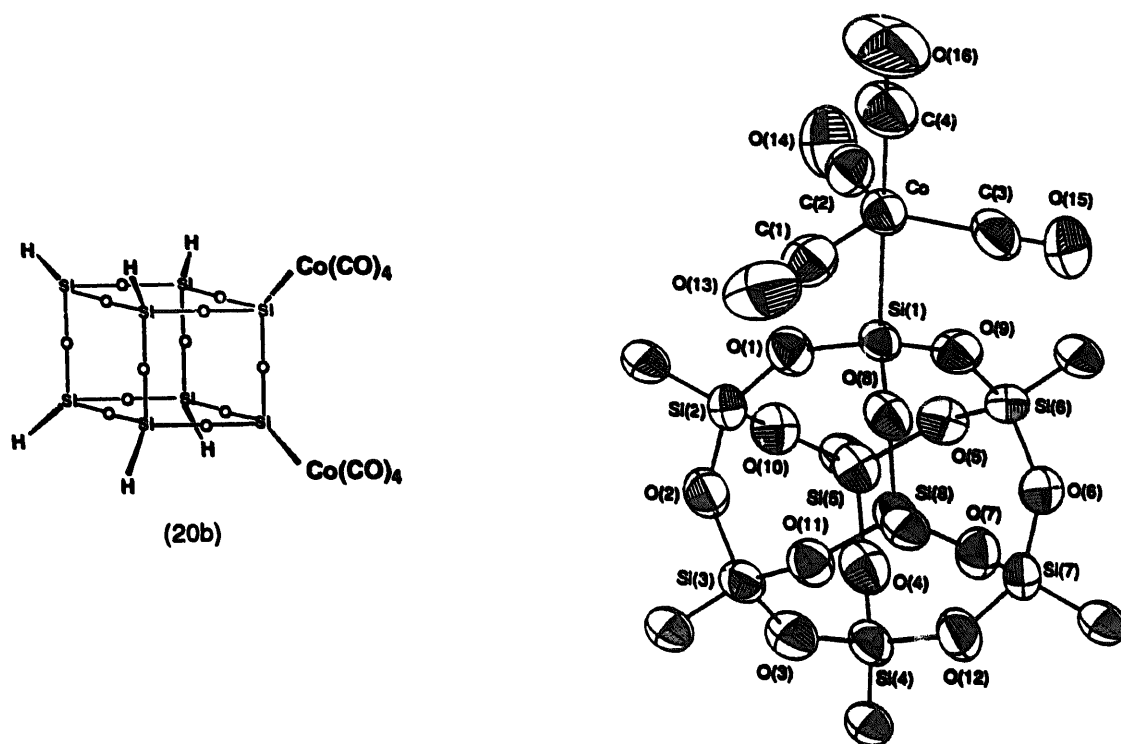


Scheme 13.



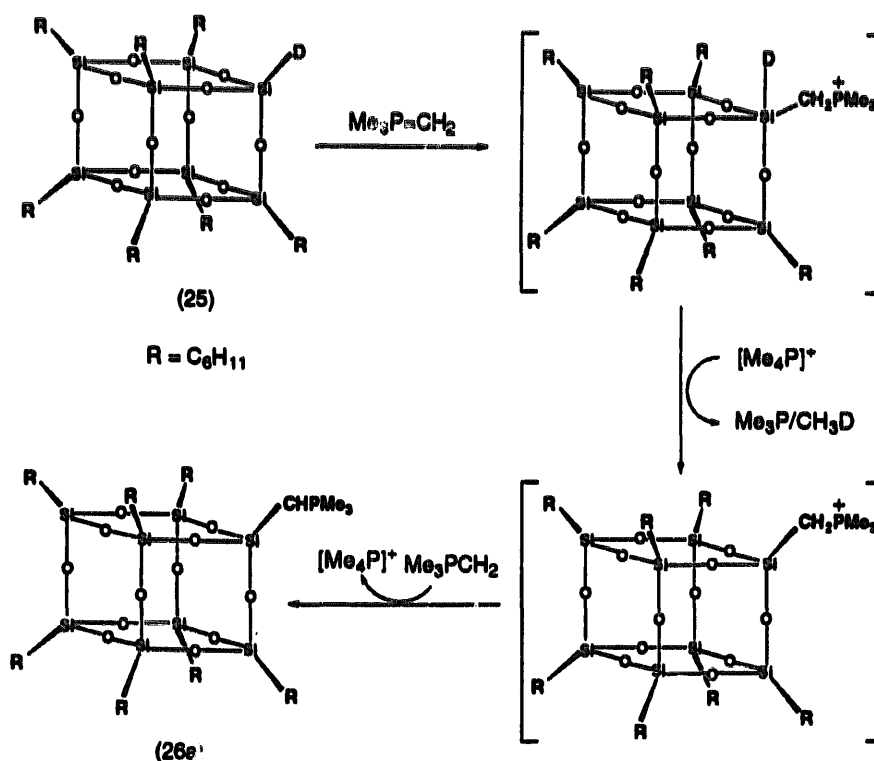
$\{\text{Cu}(\text{en})_2^{2+}\}$  solution with silica gel [138,139]. Fig. 13 shows a projection of the crystal structure onto the (100) plane and illustrates the isolated nature of the  $\{\text{Cu}(\text{en})_2^{2+}\}$  cations and  $(\text{Si}_8\text{O}_{20}^{8-})$  silicate cage anion within the structure. Hydrogen-bonded water molecules are situated between the  $\{\text{Cu}(\text{en})_2^{2+}\}$  cations and the  $(\text{Si}_8\text{O}_{20}^{8-})$  silicate cage anion. To examine the influence of the cation on the silicate cage structure, Hoebbel et al. [140] reacted an aqueous solution of cobalt(III)diammine hydroxide with silica gel or tetramethoxysilane which yielded a compound of the composition  $[\text{Co}^{\text{III}}(\text{en})_2]_2\text{H}_2\text{Si}_8\text{O}_{20}$ . The X-ray structure [141] (Fig.

14) unexpectedly showed the existence of two cage silanols located in opposite corners of the cubane silicate, illustrating how easily the cage oxides can be protonated in order to compensate for the charge of cation. Similar results were obtained when  $[\text{Co}(\text{pn}-1,2)_3]^{3+}$  and  $[\text{Co}(\text{pn}-1,3)_1]^{3+}$  [pn = propyldiamine] were employed as cations. Wiebke and Hoebbel [142] obtained crystals of the composition  $[(\text{CH}_3)_4\text{N}]_{16}[\text{Si}_8\text{O}_{20}](\text{OH})_8 \cdot 116\text{H}_2\text{O}$  by fractional crystallization at room temperature from an aqueous tetramethylammonium silicate solution with a molar ratio N:Si = 3:1 (concentration of Si =  $0.56 \text{ mol l}^{-1}$ ; concen-

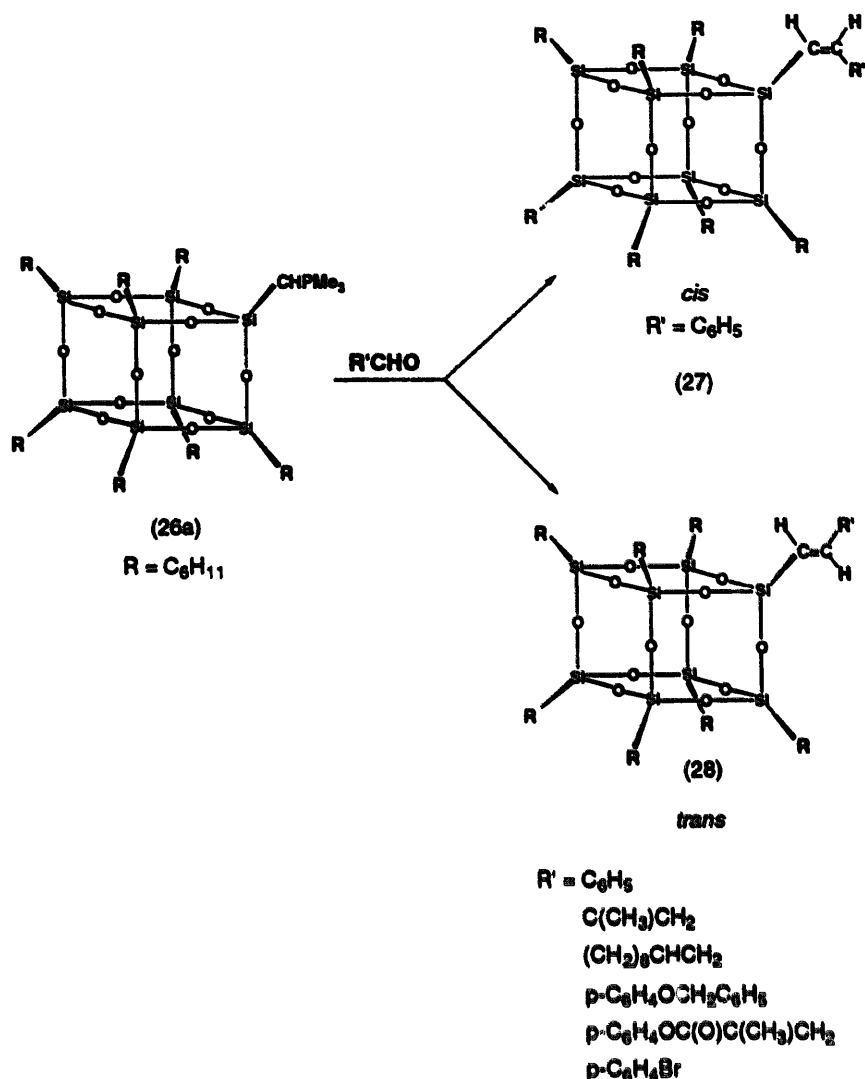
Fig. 10. Structure of  $\text{H}_7\text{Si}_8\text{O}_{12}(\text{Co}(\text{CO})_4)$ .

tration of  $\text{NMe}_4\text{OH}$   $3.47 \text{ mol l}^{-1}$ ). X-ray studies of suitable single crystals showed the compound as a host-guest compound whereby the  $\text{NMe}_4^+$  cation is suited in the cavity of the host structure built up by oligomeric

silicate ( $\text{Si}_8\text{O}_{20}^{8-}$ ) anions,  $\text{OH}^-$  ions and  $\text{H}_2\text{O}$  molecules which are linked via hydrogen bonds. Fig. 15 shows layers within the host structure. Nitrogen atoms of the guest species  $\text{NMe}_4^+$  are shown as filled ellipsoids.



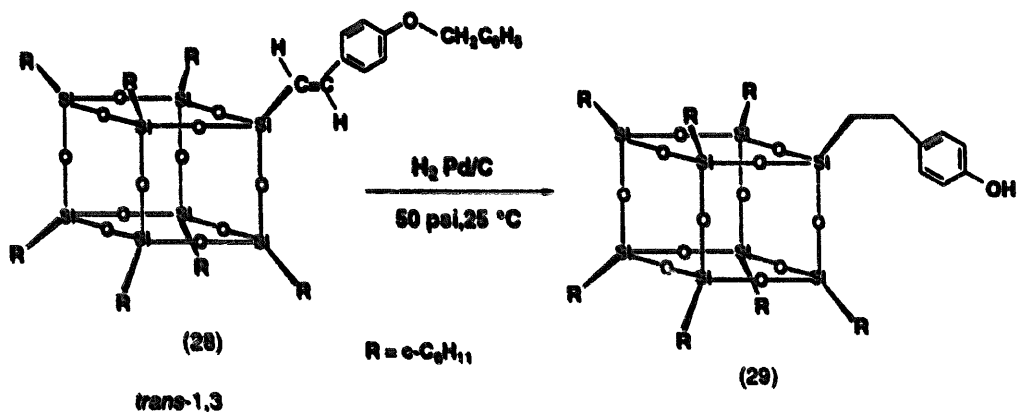
Scheme 15.



Scheme 16.

Using the cations  $\text{NPhMe}_3^+$ ,  $\text{NBnMe}_3^+$  (Bn = benzyl) or  $\text{DMPI}$  ( $\text{DMPI} = 1,1\text{-dimethylpiperidinium}$ ) respectively, instead of the tetramethylammonium cation, yielded three new compounds of the composition

$[\text{NPhMe}_3]_6[\text{Si}_8\text{O}_{18}(\text{OH})_2] \cdot 53.6\text{H}_2\text{O}$  and  $[\text{NBnMe}_3]_8[\text{Si}_8\text{O}_{20}] \cdot 53.6\text{H}_2\text{O}$  and  $[\text{DMPI}]_6[\text{Si}_8\text{O}_{18}(\text{OH})_8] \cdot 48.5\text{H}_2\text{O}$  whose crystal structures also showed host-guest features [143,144].



Scheme 17.



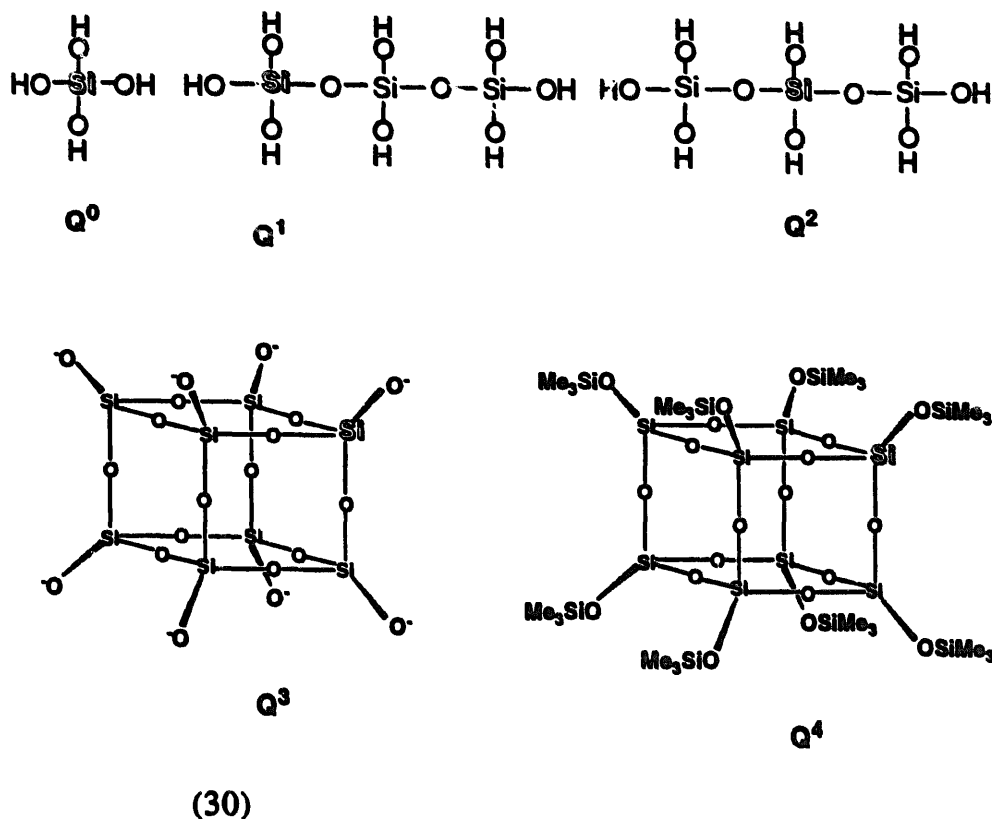
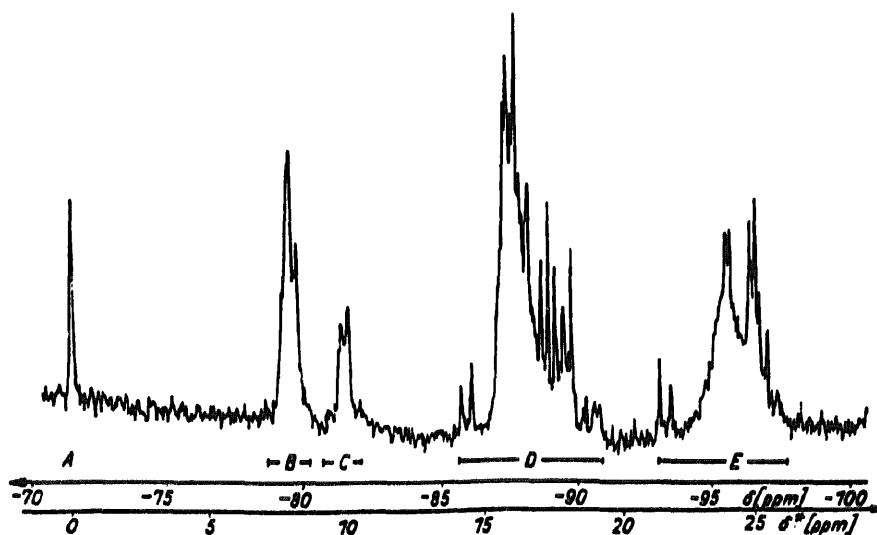


Fig. 11. Different types of Q silicate silicon atom.

Table 3  
<sup>29</sup>Si chemical shift ranges of different environments

	Number of Si–O–Si bridges	Identification	Signal group (see Fig. 12)
Monosilicates Si(OH) <sub>4</sub>	0	Q <sup>0</sup>	A (ca. = 71 ppm)
End groups Si(OSi(OH) <sub>3</sub> ) <sub>1</sub>	1	Q <sup>1</sup>	B (ca. = 78 to = 81 ppm)
Middle groups Si(OSi) <sub>2</sub> (OH) <sub>2</sub>	2	Q <sup>2</sup>	C,D (ca. = 81 to = 82 and = 86 to = 91 ppm)
Branched groups Si(OSi) <sub>3</sub> (OH)	3	Q <sup>3</sup>	E (ca. = 93 to = 97 ppm)
Net groups Si(OSi) <sub>4</sub>	4	Q <sup>4</sup>	F (ca. = 100 to = 120 ppm)

Fig. 12. <sup>29</sup>Si NMR spectrum of an aqueous sodium silicate solution 4.1 M and ratio Na:Si = 1:1.

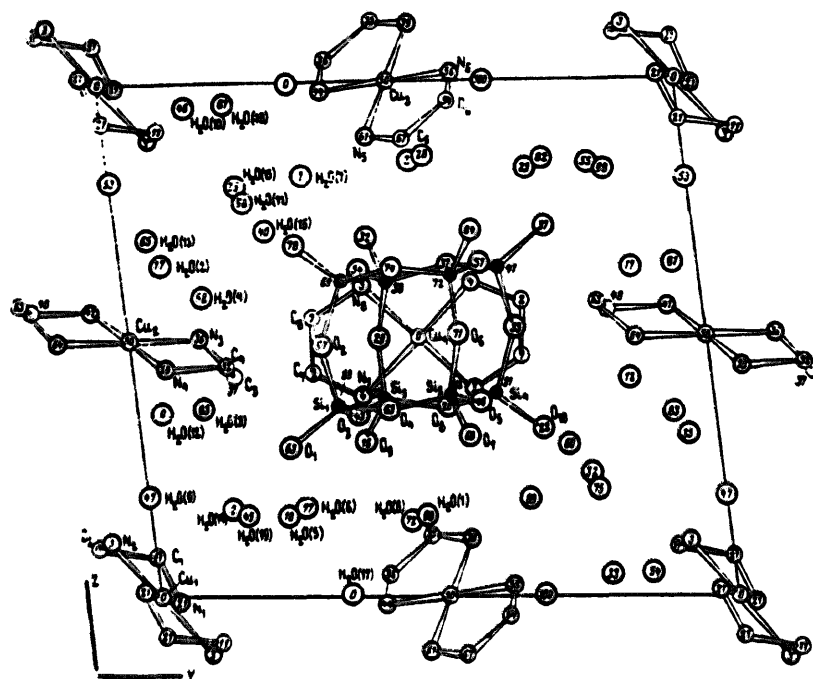


Fig. 13. Crystal structure of  $[\text{Cu}(\text{en})_2]_4\text{Si}_8\text{O}_{20} \cdot 38\text{H}_2\text{O}$ .

$^{29}\text{Si}$  NMR studies have shown that the  $(\text{Si}_8\text{O}_{20}^{8-})$  silicate cage (30) is not stable in alkaline aqueous solution with tetramethylammonium as cation. A significant advance, however, was made in 1986 by Groenen et al. [145] who showed that the  $(\text{Si}_8\text{O}_{20}^{8-})$  silicate cage (30) could be stabilized in solution by using a 1:1 mixture of DMSO– $\text{H}_2\text{O}$ . The 'clean' nature of these solutions is illustrated by the  $^{29}\text{Si}$  NMR spectra (Fig. 16). Spectra for both 0.5:1 and 1:1 ratios of tetramethylammonium/Si exhibit only one sharp peak characteristic of Si in the  $(\text{Si}_8\text{O}_{20}^{8-})$  cage structure, and no resonances due to other species are apparent. The reason for this stabilization was not commented upon, and remains open to speculation.

The cage may also be stabilized against cleavage by silylation of the exo cage oxygens. Hoebbel and Wierker [133] have modified the  $(\text{Si}_8\text{O}_{20}^{8-})$  silicate cage by Lentz trimethylsilylation [146] of  $[(\text{CH}_3)_4\text{N}]_8[\text{Si}_8\text{O}_{20}] \cdot 69\text{H}_2\text{O}$

to yield the stable trimethylsilyl ester  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8]$  (31d). Silylation of  $[(\text{CH}_3)_4\text{N}]_8[\text{Si}_8\text{O}_{20}] \cdot 69\text{H}_2\text{O}$  with vinyltrimethylchlorosilane (or divinyltetramethylsilane), allyldimethylchlorosilane and dimethylchlorosilane leads to the three functionalized spherosilicates (31a–c) [147,148] (Scheme 18). These new compounds (31a–c) have good solubility in organic solvents and are very stable towards hydrolysis and condensation, so that cleavage of the silicate cage does not occur. Further, the capped silicates (31a–c) bear reactive functional groups which should allow the compounds to be precursors for the synthesis of new inorganic–organic polymeric materials. Agaskar [149] has reported a facile one-pot, high

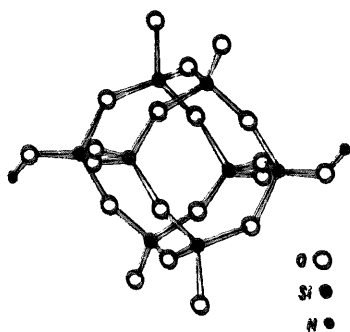


Fig. 14. The  $(\text{H}_2\text{Si}_8\text{O}_{20})^{6-}$  unit in the crystal structure of  $[\text{Co}^{\text{III}}(\text{en})_2]_2\text{H}_2\text{Si}_8\text{O}_{20}$ .

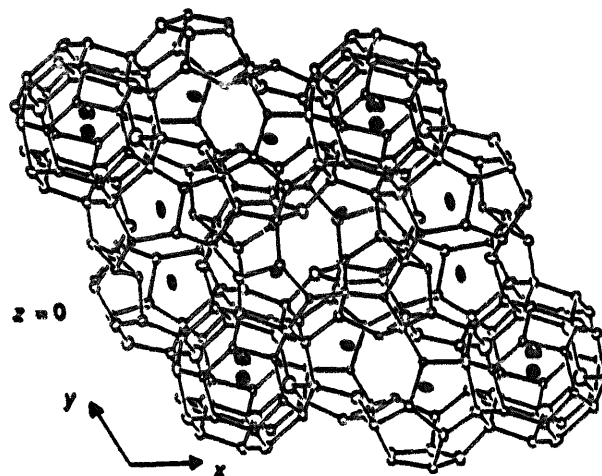


Fig. 15. Crystal structure of  $[(\text{CH}_3)_4\text{N}]_{16}[\text{Si}_8\text{O}_{20}(\text{OH})_8] \cdot 116\text{H}_2\text{O}$ . Nitrogen atoms of  $(\text{CH}_3)_4\text{N}^+$  are shown as filled ellipsoids.

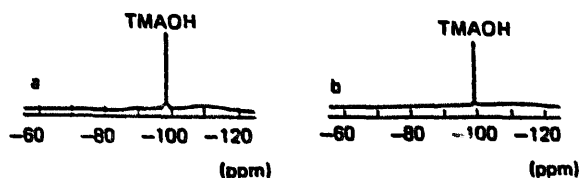


Fig. 16.  $^{29}\text{Si}$  NMR spectra of a tetramethylammonium silicate DMSO– $\text{H}_2\text{O}$  (1:1) solution with tetramethylammonium/Si ratio of 0.5:1 (a) and 1:1 (b).

yield, route for the synthesis of the compounds  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_3]_8$ ,  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_8$  and  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}_2\text{Cl}]_8$  respectively. In the procedure, three solutions are mixed in sequence and the product extracted from the reaction mixture with an immiscible hydrocarbon solvent. The constitutions of the three solutions are as follows:

**S1:**  $\text{H}_2\text{O}$  (20 ml) +  $\text{Me}_4\text{NOH}$  (25% aqueous, 20 ml) +  $(\text{MeO})_4\text{Si}$  (8.1 ml) +  $\text{Me}_2\text{SO}$  (42 ml) +  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}:\text{Me}_2\text{SO} = 1:1$ ;  $[\text{Si}] \sim 0.65 \text{ M}$ )

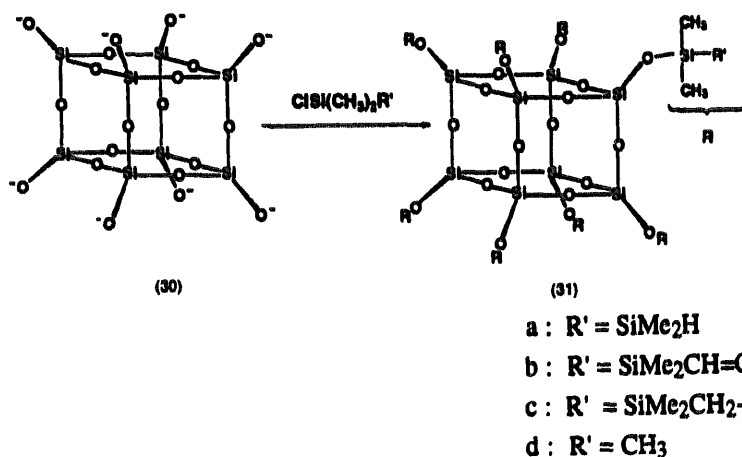
**S2:**  $(\text{H}_3\text{CO})_2\text{C}(\text{CH}_3)_2$  (70 ml) +  $\text{HCl}$  ( $\sim 10 \text{ M}$ , 3.0 ml) +  $\text{YSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Y}$  (10 ml) ( $\text{Y} = -\text{CH}_3, -\text{CHCH}_2, \text{CH}_2\text{Cl}$ )

**S3:**  $(\text{CH}_3)_2\text{NCHO}$  (20 ml) +  $\text{YSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{Y}$  (10 ml) +  $\text{Y}(\text{CH}_3)_2\text{SiCl}_3$  (5 ml) ( $\text{Y} = -\text{CH}_3, -\text{CHCH}_2, \text{CH}_2\text{Cl}$ )

The procedure employed is as follows: solution **S1** which contains the  $[\text{Si}_8\text{O}_{20}]^{8-}$  anion is added dropwise over a period of 20 min to the solution **S2**. This mixture is then stirred for 15 min. During this time the reaction of  $\text{H}_2\text{O}$  in solution **S1** and  $(\text{H}_3\text{CO})_2\text{C}(\text{CH}_3)_2$  in solution **S2** leads to the formation of methanol and acetone, whilst the  $[\text{Si}_8\text{O}_{20}]^{8-}$  anion is partially silylated. Solution **S3** is then added to complete the silylation reaction, and the product is separated by usual methods. More recently, novel highly functionalized D4R cages have been synthesized. Silylation of the  $(\text{Si}_8\text{O}_{20})^{8-}$  cage with  $\text{HMe}_2\text{SiCl}$  followed by catalytic hydrosilylation of the Si–H function with appropriate alkenes yields the

four new compounds (**32a–d**) [150–154] (Fig. 17). The functionalities on the *exo*-cage groups are also available for the reaction; for example, compound (**32c**) can function as chelating ligand towards  $\text{Zr}(\text{O}^n\text{Pr})_4$  giving the complex (**33**) [151,153] (Scheme 19). A similar complex (**34**) has been obtained by the addition reaction of the D4R cage  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{H}]_8$  (**31a**) with (allylacetylacetonato)bis(butoxy)aluminium [153] (Scheme 20). Additional derivatives based on (**31a**) have also been reported. Hydrosilylation with vinylferrocene affords both mono- and octasubstituted products [154], whilst hydrosilylation reactions with 1,1'-divinylferrocene and 1,1'-divinyl(octamethyl)ferrocene result in the formation of poly(ferrocenyloctasilsesquioxane) polymers.

Unsymmetrical cages which have more than one different group attached to the silicon atoms have been obtained by a number of different methods. In 1992 Hasegawa and Motojima [155] investigated the synthesis of  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_8$  by silylating  $(\text{Si}_8\text{O}_{20})^{8-}$  in a methanolic solution using dimethylvinylchlorosilane. The gas chromatogram (Fig. 18) showed that, besides  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_8$  (peak A), incompletely dimethylvinylsilylated derivatives of  $(\text{Si}_8\text{O}_{20})^{8-}$  with one silanol group  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_7\text{H}$  (peak B) and two silanol groups  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_6\text{H}_2$  (peak C) were formed. Furthermore, silylation of the  $(\text{Si}_8\text{O}_{20})^{8-}$  cage with a mixture of vinyltrimethylchlorosilane and trimethylchlorosilane yields, depending on the ratio of the silylating agents, mixed (vinyltrimethylsilyl)(trimethylsilyl)-substituted cages  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_3]_m[\text{SiMe}_2\text{CH}=\text{CH}_2]_{8-m}$  [147]. Capillary gas chromatography of the silylated mixture using the two silylation reagents in a 1:1 ratio showed nine peaks (Fig. 19(A)). The two extremity peaks (peaks a and b) are due to the totally trimethylsilylated  $(\text{Si}_8\text{O}_{20})^{8-}$  cage  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_3]_8$  and totally vinyltrimethylsilylated  $(\text{Si}_8\text{O}_{20})^{8-}$  cage  $[\text{Si}_8\text{O}_{20}][\text{SiMe}_2\text{CH}=\text{CH}_2]_8$ . The inter-



Scheme 18.

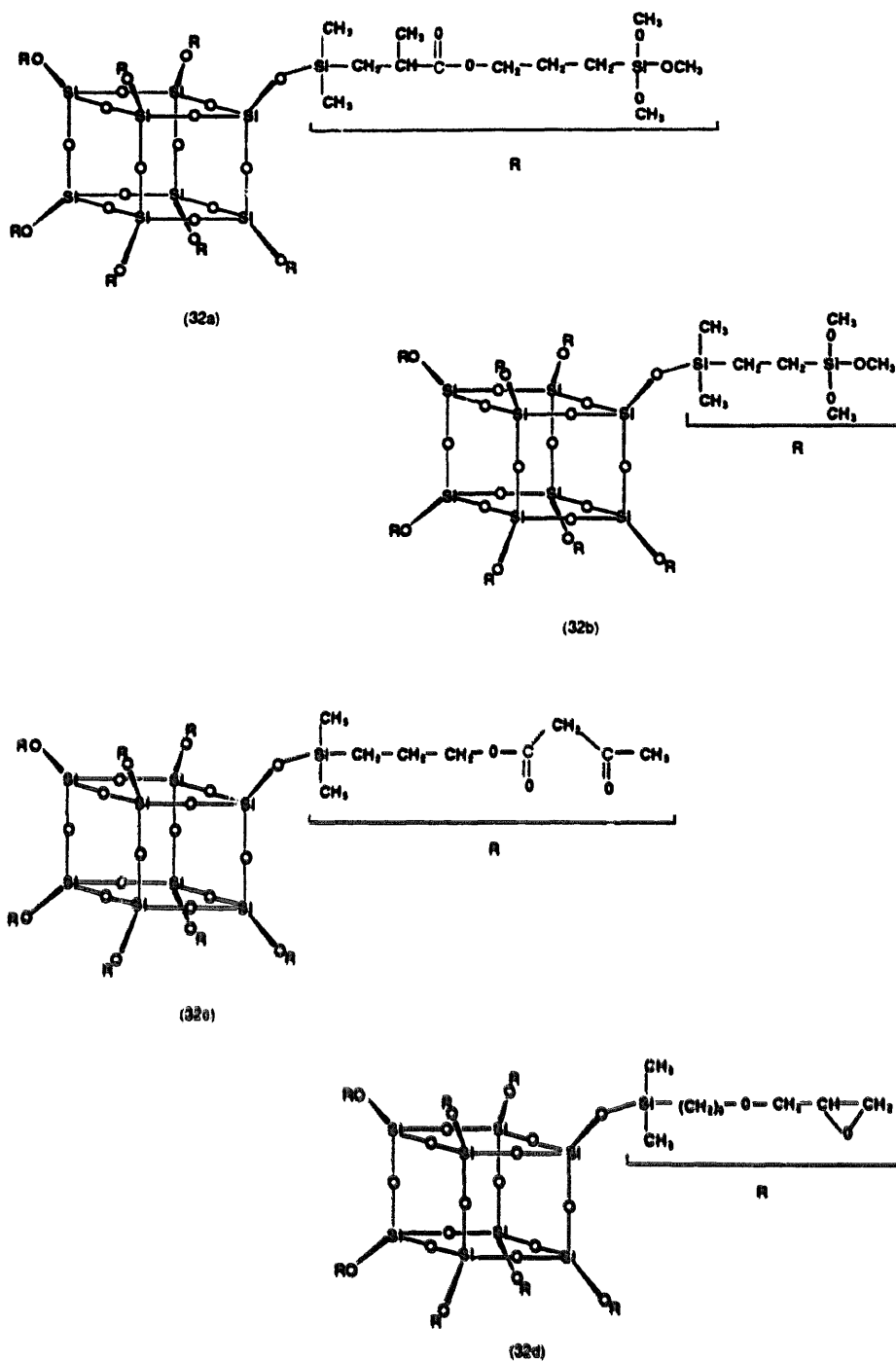
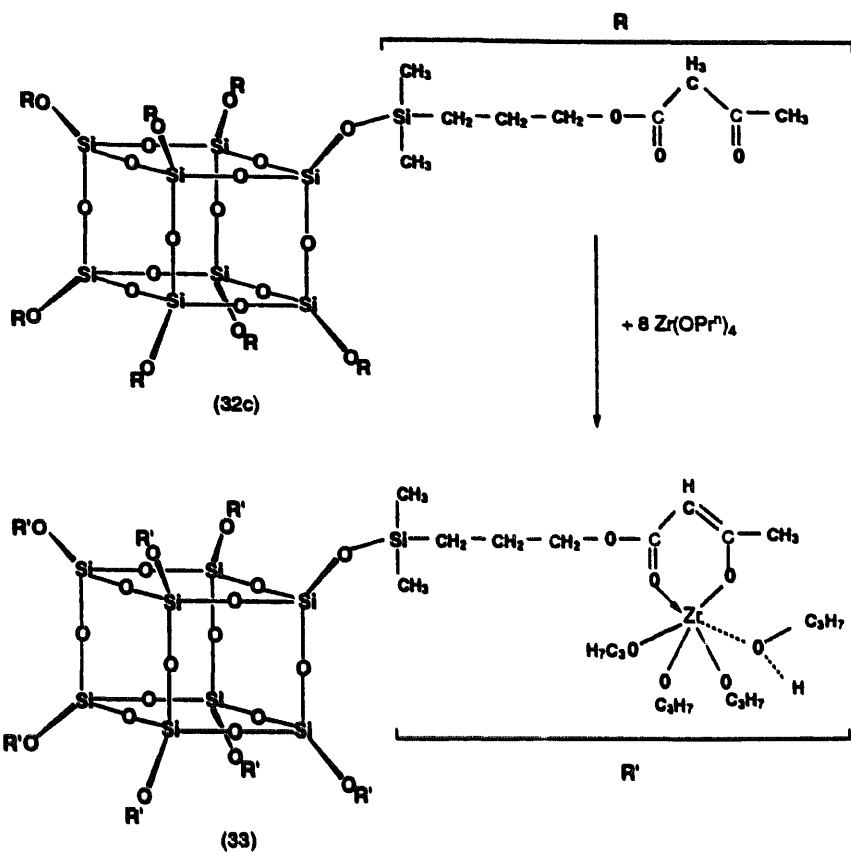


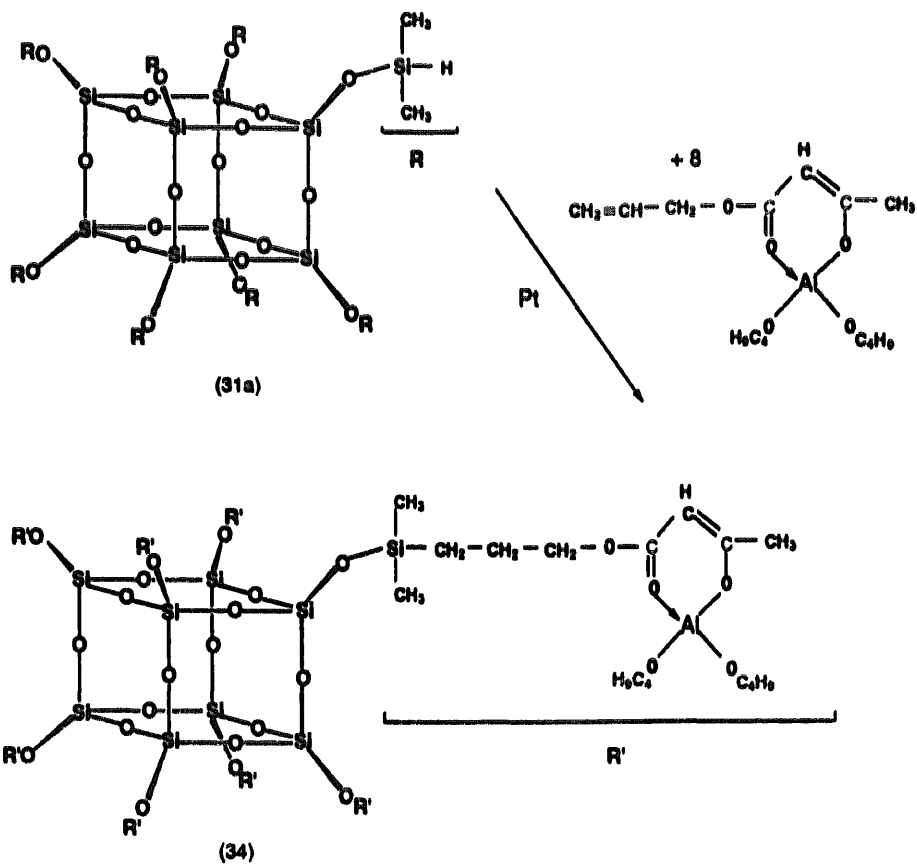
Fig. 17. D4R-cages obtained by catalytic silylation of (31a) with alkenes.

mediate peaks can be assigned to the seven mixed species  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_7(\text{SiMe}_2\text{CH}=\text{CH}_2)$  (peak 1) to  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_8$  (peak 7). The major products are  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_4(\text{SiMe}_2\text{CH}=\text{CH}_2)_4$  (peak 4) and  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_5(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$  (peak 3). Changing of the ratio of silylation agents  $(\text{CH}_3)_3\text{SiCl}$  and  $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiCl}$  to 10:1 results in only three main peaks visible in the capillary gas chromatogram due to  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_8$  (49%), and the mixed silylated compounds  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_7(\text{SiMe}_2\text{CH}=\text{CH}_2)$  (25%)

and  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_3)_6(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$  (7%) (Fig. 19(B)). D4R cages with different functionalities can be obtained by the silylation of  $(\text{Si}_8\text{O}_{20})^{8-}$  cage with a mixture of dimethylchlorosilane and dimethylvinylchlorosilane [153,154,156]. Five peaks are seen in the gas chromatogram, the largest peak being due to  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_2\text{H})_4(\text{SiMe}_2\text{CH}=\text{CH}_2)_4$  (peak 3) (Fig. 20). The others peaks are due to  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_2\text{H})_6(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$  (peak 1),  $[\text{Si}_8\text{O}_{20}]\text{KSiMe}_2\text{H})_5(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$  (peak 2),



Scheme 19.



Scheme 20.

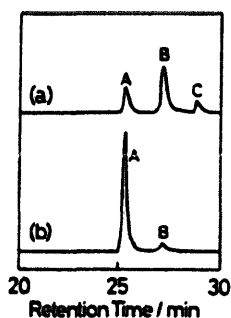


Fig. 18. Gas chromatogram of the products of the silylation of  $(\text{Si}_8\text{O}_{20})^{4-}$  using dimethylvinylchlorosilane after reaction time of 1 h and dimethylvinylchlorosilane/ $(\text{Si}_8\text{O}_{20})^{4-}$  ratio of 32:1 (a) and 48:1 (b).

$(\text{Si}_8\text{O}_{20})(\text{SiMe}_2\text{H})_3(\text{SiMe}_2\text{CH}=\text{CH}_2)_5$  (peak 4) and  $(\text{Si}_8\text{O}_{20})(\text{SiMe}_2\text{H})_2(\text{SiMe}_2\text{CH}=\text{CH}_2)_6$  (peak 5).

#### 4. Double five ring (D5R) $(\text{Si}_{10}\text{O}_{15})$ cages

The D5R cage silicate of general formula  $\text{R}_{10}\text{Si}_{10}\text{O}_{15}$  has five-fold symmetry and comprises two pentasiloxane rings (see Fig. 1). D5R-cages where R = organic group are more common than those D5R-silicates bearing inorganic groups on the cage silicon atom. Relative to D4R-cage silicates, few D5R-silicates have been prepared and characterized, i.e.  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  [52,53],  $(\text{CH}_3)_{10}\text{Si}_{10}\text{O}_{15}$  [38,157],  $(\text{C}_2\text{H}_5)_{10}\text{Si}_{10}\text{O}_{15}$  [12,43,158],

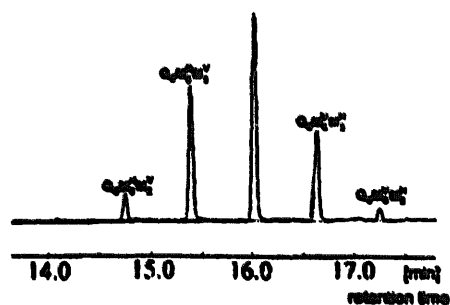
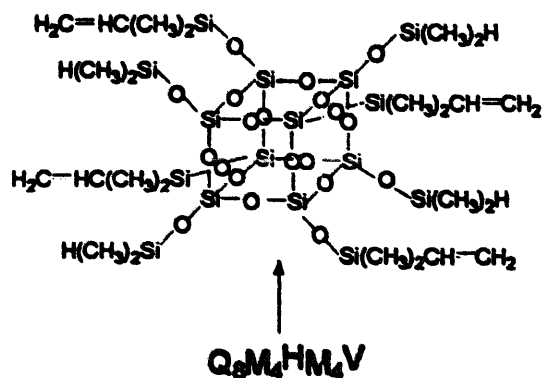


Fig. 20. Gas chromatogram of silylation products of the  $(\text{Si}_8\text{O}_{20})^{4-}$  cage with a mixture of dimethylchlorosilane and dimethylvinylchlorosilane ratio 1:1.

$(i\text{-C}_9\text{H}_{19})_{10}\text{Si}_{10}\text{O}_{15}$  [17],  $(\text{CH}=\text{CH}_2)_{10}\text{Si}_{10}\text{O}_{15}$  [50],  $(\text{C}_6\text{H}_5)_{10}\text{Si}_{10}\text{O}_{15}$  [47,48]. Only two compounds are known which possess a reactive functional group on the

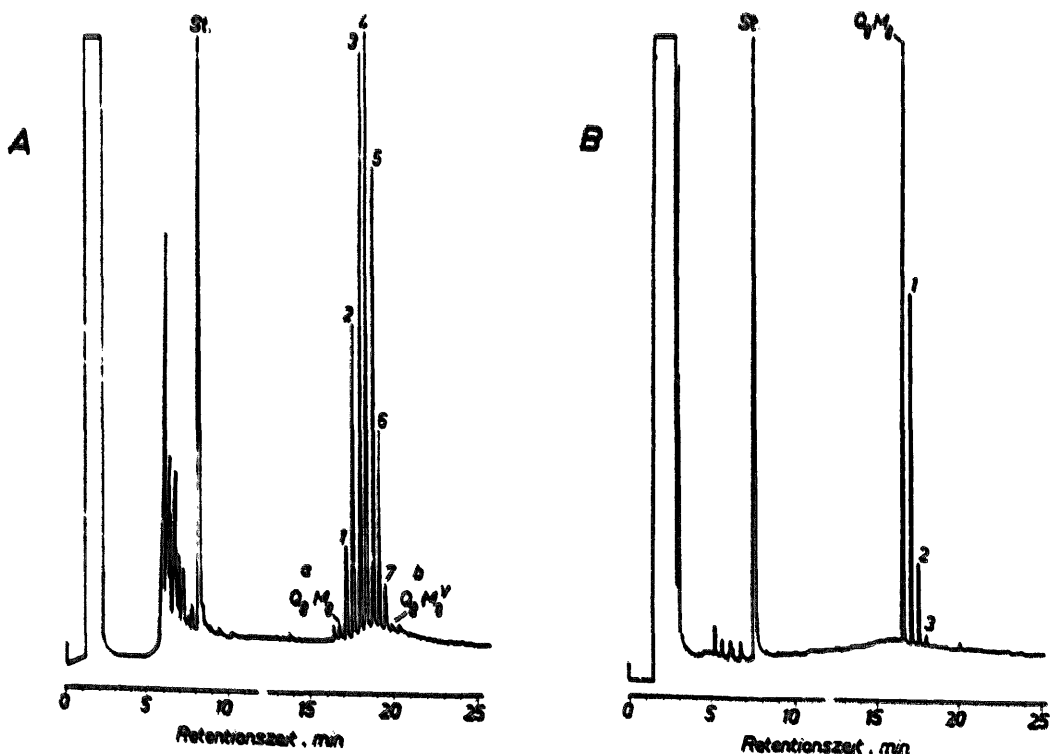
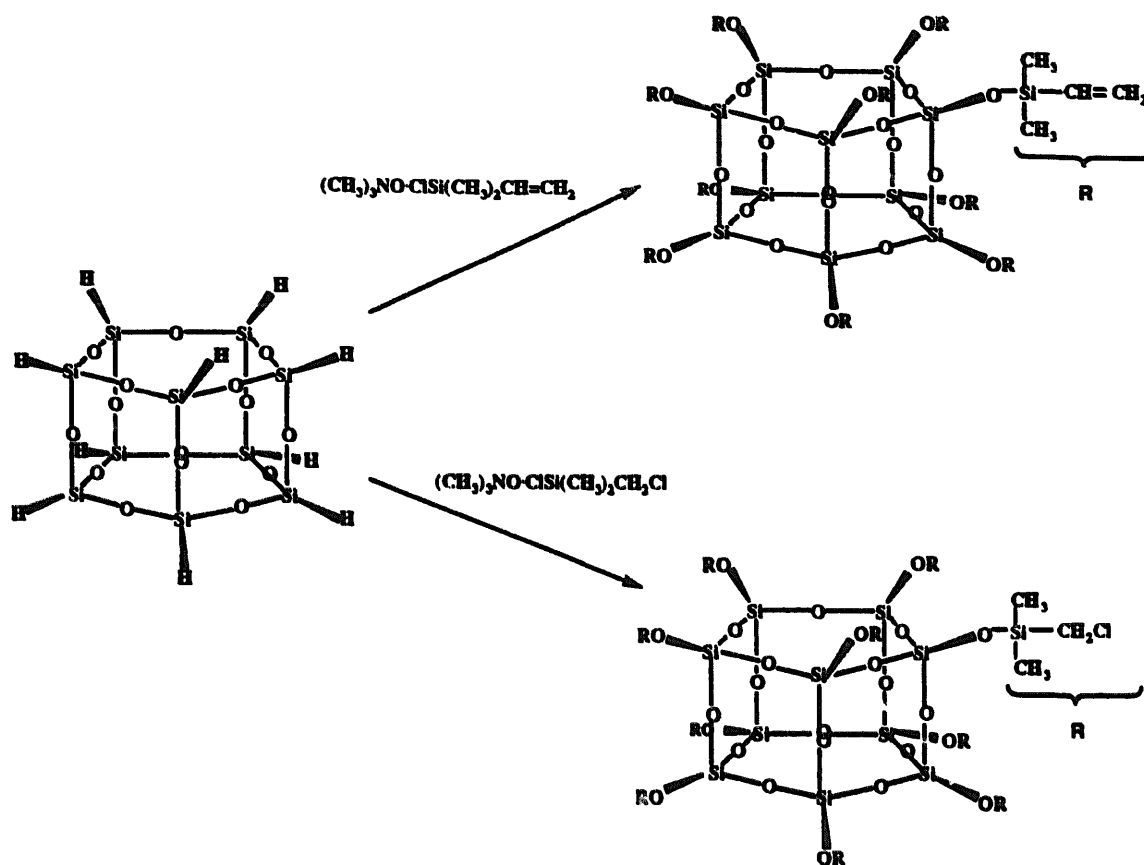


Fig. 19. Gas chromatogram of silylation products of the  $(\text{Si}_8\text{O}_{20})^{4-}$  cage with a mixture of vinyldimethylchlorosilane and trimethylchlorosilane ratio 1:1 (A) and 10:1 (B).



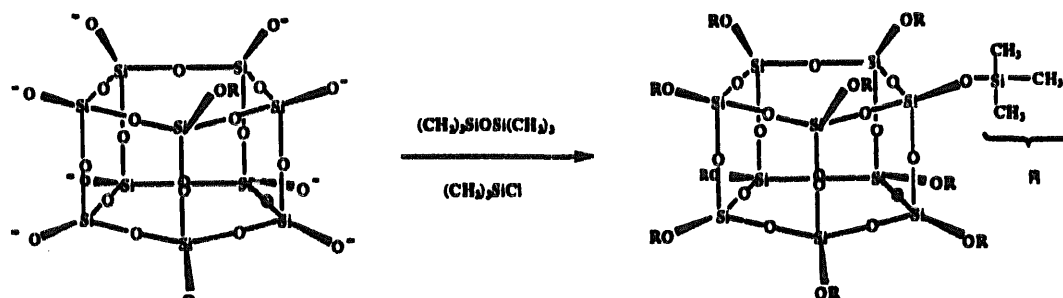
Scheme 21.

D5R-cage silicon atom, H and  $\text{CH}=\text{CH}_2$ , and only reactions involving  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  have been described.

No easy one-pot route is known for the preparation of  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  (35). Its preparation is always accompanied by major quantities of  $\text{H}_8\text{Si}_8\text{O}_{12}$  and higher hydrosilsesquioxanes [52,53], and hence time-consuming purification procedures need to be adopted. It is perhaps remarkable that 29 years elapsed from the initial discovery of  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  to the description of the first reaction of this compound. Using the reagent  $(\text{CH}_3)_3\text{NO} \cdot \text{ClSi}(\text{CH}_3)_2(\text{CH}=\text{CH}_2)$  Agaskar [102] in 1989 converted the Si-H function of  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  thereby obtaining the  $[\text{Si}_{10}\text{O}_{25}][\text{Si}(\text{CH}_3)_2\text{CH}=\text{CH}_2]_{10}$  (36). In the

same way  $[\text{Si}_{10}\text{O}_{25}][\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}]_{10}$  (37) has been synthesized by conversion of the Si-H function of  $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  (35) with  $(\text{CH}_3)_3\text{NO} \cdot \text{ClSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$  (Scheme 21).

Very little work has been carried out so far on compounds containing the anionic  $(\text{Si}_{10}\text{O}_{25}^{10-})$  silicate unit. In 1975 Hoebbel et al. [159] reported a novel silicate consisting of D5R  $(\text{Si}_{10}\text{O}_{25}^{10-})$  anions in  $[n-(\text{C}_4\text{H}_9)_4\text{N}]\text{OH}-\text{SiO}_2-\text{H}_2\text{O}$  and  $[i-(\text{C}_5\text{H}_{11})_4\text{N}]\text{OH}-\text{SiO}_2-\text{H}_2\text{O}$  solutions. The corresponding trimethylsilyl ester  $[\text{Si}_{10}\text{O}_{25}][\text{Si}(\text{CH}_3)_3]_{10}$  [159] (39) has also been synthesized by silylation of  $(\text{Si}_{10}\text{O}_{25}^{10-})$  (38) using the method of Götz and Masson [160] (Scheme 22). Like



Scheme 22.

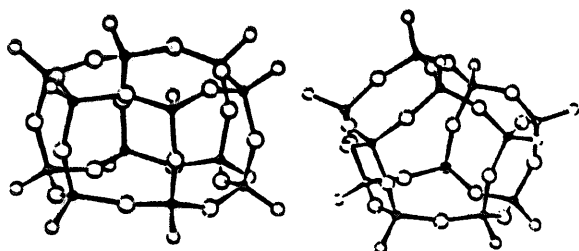


Fig. 21. Geometrical isomers of dodecahydridosilsesquioxane (40).

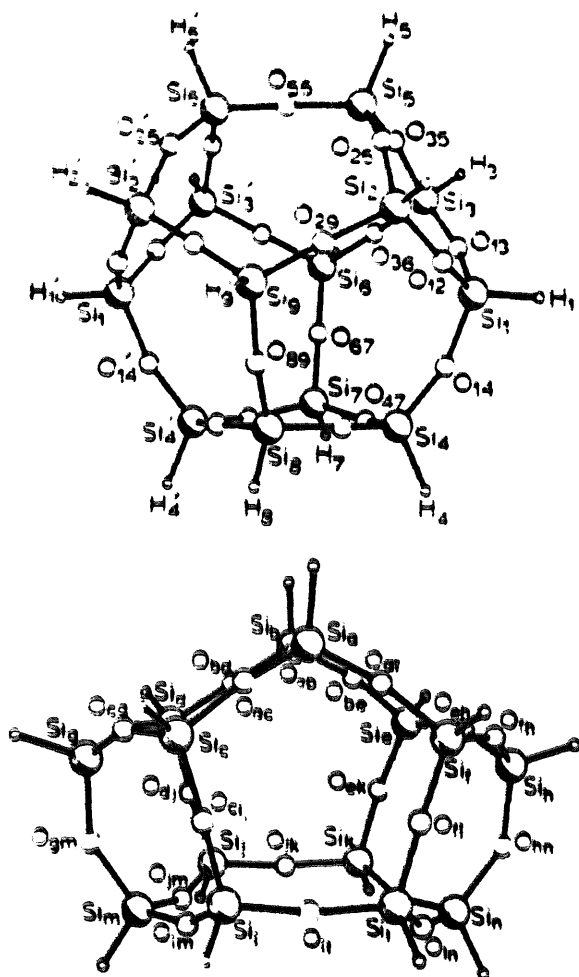
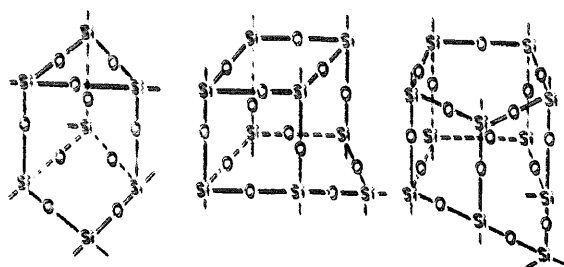
Fig. 22. Crystal structure of  $D_{3h}$ -[Si<sub>14</sub>O<sub>21</sub>](OSiMe<sub>3</sub>)<sub>14</sub> (41a) (a) and  $C_{2v}$ -[Si<sub>14</sub>O<sub>21</sub>](OSiMe<sub>3</sub>)<sub>14</sub> (41b) (b).

Fig. 23. Silsesquioxanes with an extra vertex.

Table 4

Summary of known D6R-silicates and higher silsesquioxanes (RSiO<sub>1.5</sub>)<sub>n</sub>

R	n	Reference
H	12,14,16	[52,161]
CH <sub>3</sub>	12	[5,157]
C <sub>6</sub> H <sub>13</sub>	12,20	[16]
C <sub>8</sub> H <sub>17</sub>	12,24	[17]
<i>i</i> -C <sub>9</sub> H <sub>19</sub>	18,28	[17]
C <sub>6</sub> H <sub>5</sub>	12,22,24	[6,47,162]
C <sub>6</sub> H <sub>11</sub>	12	[112]

the D4R {Si<sub>8</sub>O<sub>20</sub><sup>8-</sup>} anion, the D5R {Si<sub>10</sub>O<sub>25</sub><sup>10-</sup>} anion is labile in aqueous solution. However, like the D4R compound, the presence of DMSO has a stabilizing effect on the D5R {Si<sub>10</sub>O<sub>25</sub><sup>10-</sup>} anion.

### 5. Double-six ring (D6R) {Si<sub>12</sub>O<sub>18</sub>} cages and higher silsesquioxanes

For dodecasilsesquioxane two unstrained geometrical isomers are possible (Fig. 21) and the possibilities for isomeric complexity increase sharply for the higher silsesquioxanes (RSiO<sub>1.5</sub>)<sub>14-16</sub>. Reactions of these compounds are sparse. They are prepared by hydrolysis of their corresponding trifunctional monomers RSiCl<sub>3</sub> (Y = Cl, CH<sub>3</sub>COO). Hydrogenation of Si<sub>12</sub>O<sub>18</sub>Ph<sub>12</sub> in an autoclave at 34 atm and 200 °C yields 100% conversion of Si<sub>12</sub>O<sub>18</sub>Ph<sub>12</sub> to Si<sub>12</sub>O<sub>18</sub>(*c*-C<sub>6</sub>H<sub>11</sub>)<sub>12</sub> (39) [115]. Table 4 summarizes known D6R-silicates and higher silsesquioxanes.

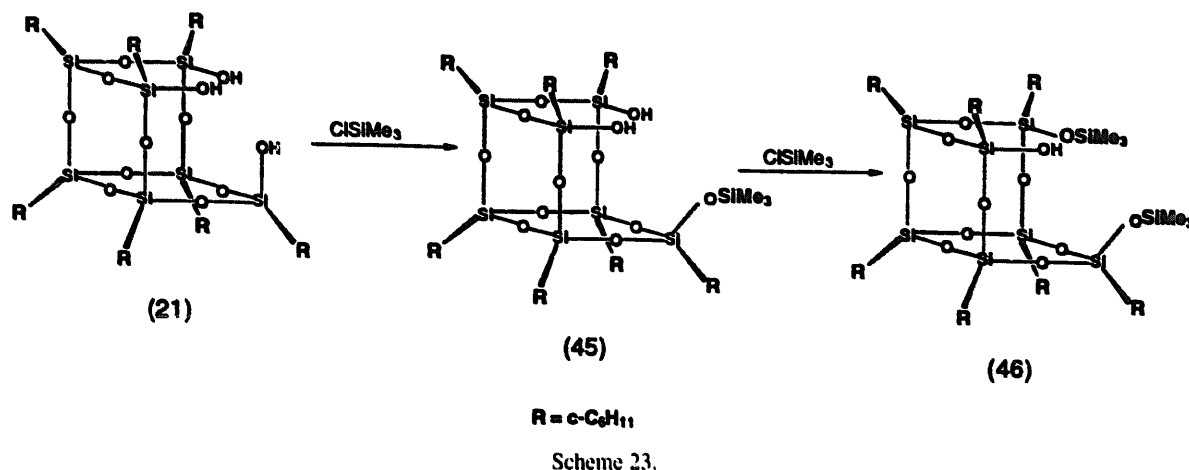
Silylation of H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub> (40) and the two ( $D_{3h}$ - and  $C_{2v}$ -) isomers of H<sub>14</sub>Si<sub>14</sub>O<sub>21</sub> (41) using the (CH<sub>3</sub>)<sub>3</sub>NO/ClSi(CH<sub>3</sub>)<sub>3</sub> reagent yields the new trimethylsilylated cages [Si<sub>12</sub>O<sub>18</sub>](OSiMe<sub>3</sub>)<sub>12</sub> (42),  $D_{3h}$ -[Si<sub>14</sub>O<sub>21</sub>](OSiMe<sub>3</sub>)<sub>14</sub> (43) and  $C_{2v}$ -[Si<sub>14</sub>O<sub>21</sub>](OSiMe<sub>3</sub>)<sub>14</sub> (44). The crystal structures of the two isomers of H<sub>14</sub>Si<sub>14</sub>O<sub>21</sub> (41a) and (41b) are shown in Fig. 22 [161].

### 6. Silsesquioxanes with an extra vertex

The frameworks of silsesquioxanes with an extra vertex as illustrated in Fig. 23 have been obtained as side products in the synthesis of other silsesquioxanes.

Fig. 24. Model of the silylation of a silica surface with RSiX<sub>3</sub>.





However, they appear to be as yet totally uninvestigated [55].

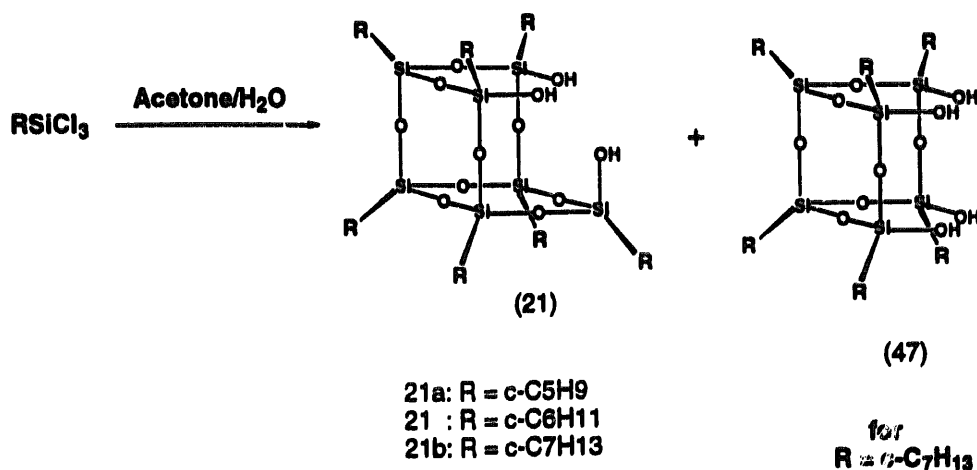
### 7. Incompletely condensed silsesquioxanes

The incompletely condensed silsesquioxane (21) can be prepared in surprisingly good yields by the hydrolytic condensation of  $(n\text{-C}_6\text{H}_{11})\text{SiCl}_3$  [132,163], and has been used as a molecular model for hydroxylated silica surfaces, as ligands in homogeneous analogues of silica-supported catalysts, and as 'building blocks' for the systematic construction of structurally well-defined Si/O/M clusters.

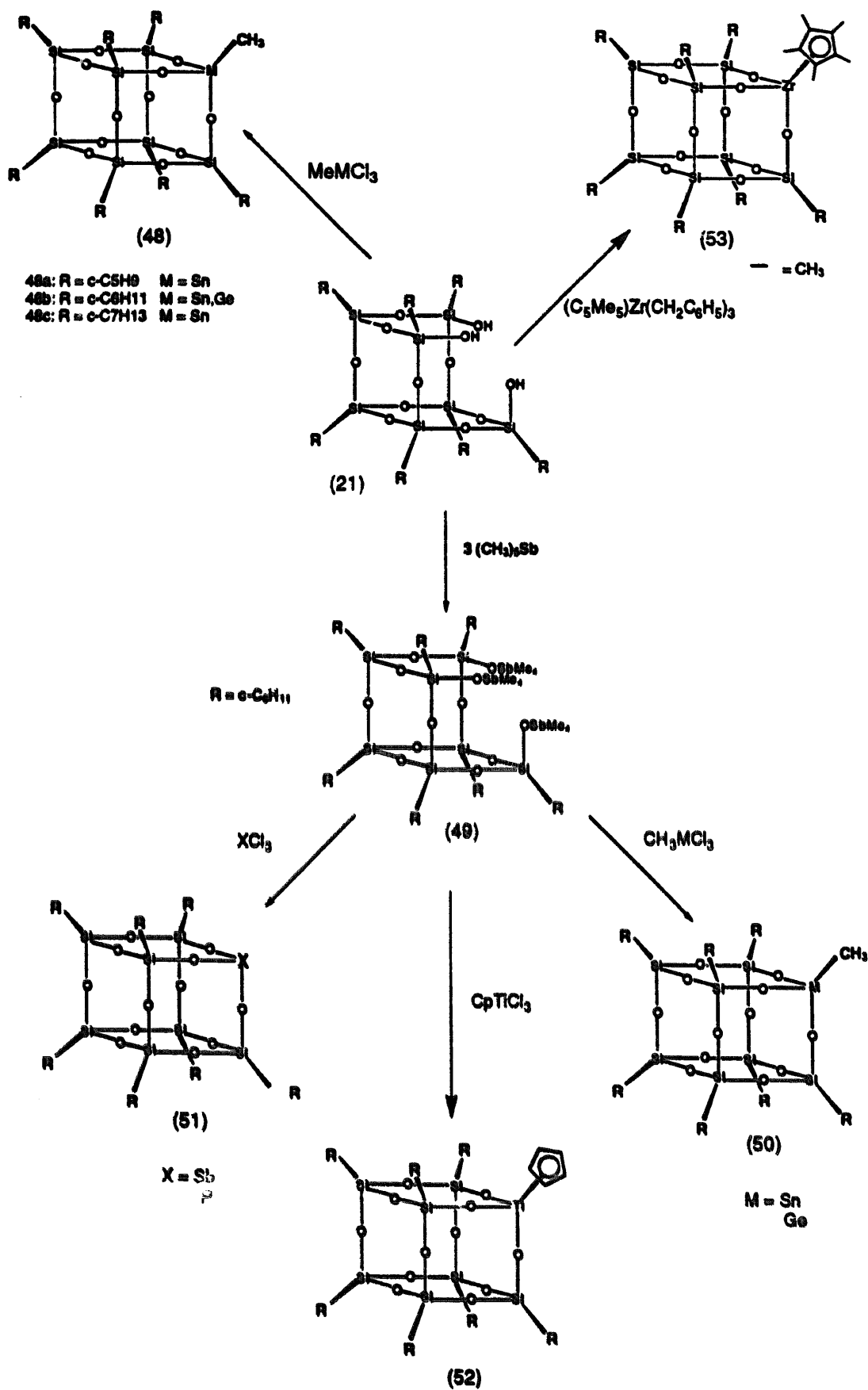
Surface-modified silicas [132] are an important class of materials which have been used extensively as stationary phases in chromatography [164,165] and have found many other useful applications such as ion collection [166], heterogeneous hydrogenation catalysts [167], inorganic polymer fillers [168], and drug delivery agents [169]. For all these applications, the surface properties of the silica can be tailored by modifying the surface by

chemically attaching organic groups to the surface silanol groups, most commonly by silylation using methoxy- or chlorosilanes (Fig. 24). Despite its apparent simplicity, the silylation of silica is an enormously complex process. Silylation of incompletely condensed silsesquioxanes such as (21), however, affords a suitably simplified model system. Examples of compounds (45) and (46) derived from the silylation of (21) [132,170] are illustrated in Scheme 23, where the analogy with the reactivity at silica surfaces may be seen.

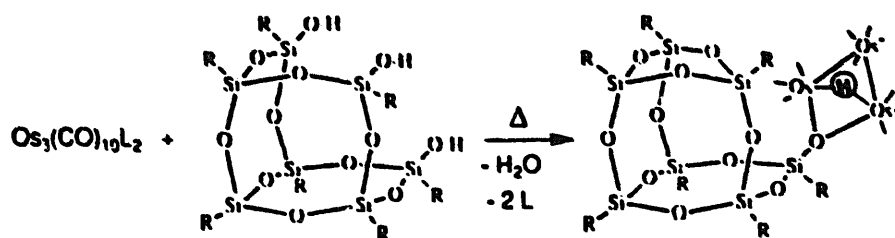
Although the preparation of (21) is straightforward, it requires an inconveniently long gestation period (3–6 weeks) before synthetically useful quantities of the trisilanol compound (21) can be obtained. A facile synthesis of new incompletely condensed polyhedral oligosilsesquioxanes by hydrolysing  $(n\text{-C}_3\text{H}_7)\text{SiCl}_3$  and  $(n\text{-C}_7\text{H}_{13})\text{SiCl}_3$ , respectively, in an  $\text{H}_2\text{O}$ -acetone environment affords compounds (21a and 21b) in a much shorter time (7 days) [171] (Scheme 24). In the case of  $R = n\text{-C}_7\text{H}_{13}$ , the incompletely condensed silsesquioxane with two vacant vertices (47) was also obtained in ca. 40% yield and can be extracted from (21b) with



Scheme 24.



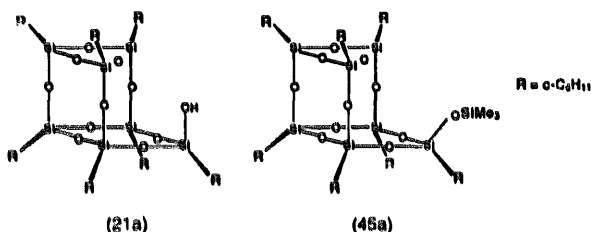
Scheme 25.



Scheme 26.

$\text{CH}_2\text{Cl}_2$ . This silsesquioxane (47) should be capable of accommodating two hetero metal ions forming a completely condensed silsesquioxane framework which would be useful as a model to study bimetallic silica-supported catalysts, e.g. surface dichromates or dimolybdates [171].

Both (21) and (45) under cyclodehydration reactions readily to afford (21a) and (45a) [172]. Such base-assisted reactions are most commonly observed for high valent metal halides and rationalize the failure of (21) and its analogues to react cleanly with reagents such as  $\text{MoO}_2\text{Cl}_2$  and  $\text{CrO}_2\text{Cl}_2$ . Lanthanide complexes of (21) have also been synthesized and structurally characterized [173].



The vacant vertex in compound (21) may be filled with a variety of hetero elements. For example, (21), (21a), (21b) react with  $\text{MeMCl}_3$  ( $\text{M} = \text{Ge}, \text{Sn}$ ) to give the Main Group 14 capped hetero cage compounds (48a, 48b, 48c) [132,171] (Scheme 25). Reaction of (21) with excess of pentamethylantimony ( $\text{CH}_3$ )<sub>5</sub>Sb

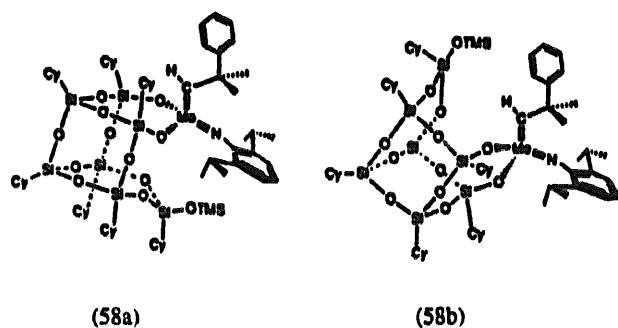
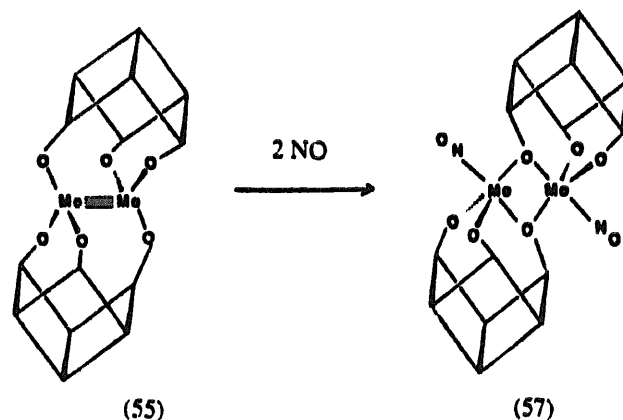
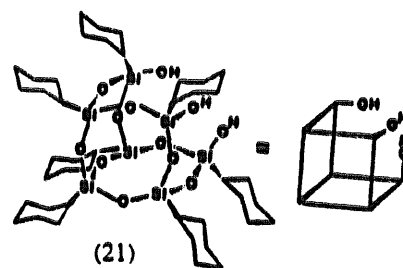
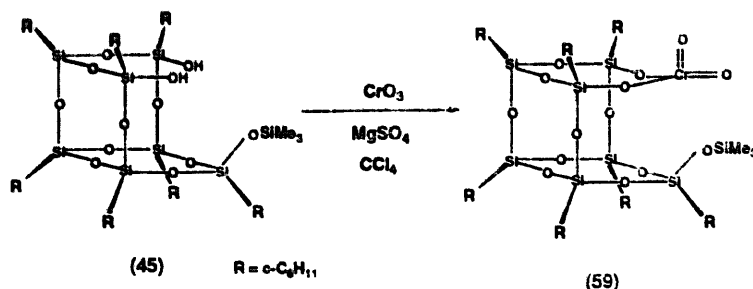


Fig. 25. The two isomers of the molybdenum complexes (58a) and (58b).

results in the synthesis of compound (49), and a large number of reactions of (49) are shown in Scheme 25 leading to the formation of (50), (51), and (52) [174]. In 1986 Feher [175] synthesized compound (53) incorporating Zrcp [cp = cyclopentadiene] into the cube-like silsesquioxane framework as a model of silica-supported catalysts by reaction of (21) with  $(\text{C}_5\text{Me}_5)_2\text{Zr}(\text{CH}_5\text{C}_6\text{H}_5)_3$  (Scheme 25). From the ease with which zirconium, one of the larger transition metals [176], can be incorporated into the cubane siloxane framework, Feher suggested that it would be possible to synthesize more such materials with a wide variety of different metals. Reaction of  $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$  with the trisilanol compound (21) yields compound (54) [177] (Scheme 26), and the reaction between trisilanol (21) and  $\text{Mo}_2[(\text{O}^i\text{Bu})_6]$  or  $\text{W}_2[(\text{O}^i\text{Bu})_6]$  results in the formation of  $[(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]_2\text{Mo}_2$  (55) (Scheme 27) or  $[(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]_2\text{W}_2(\mu\text{-H})(\text{O}^i\text{Bu})$  (56) respectively [178]. Compound (55) reacts with NO with cleavage of the  $\text{Mo}\equiv\text{Mo}$  triple bond to give the NO-



Scheme 27.



Scheme 28.

complex (57) (Scheme 27). Like many other Mo and W complexes [179,180], the two isomers (58a and 58b) (Fig. 25) catalyse rapidly the metathesis of olefins. Compound (45), which can be obtained by monosilylation of (21) (see Scheme 25), yields the chromate compound (59) with  $\text{CrO}_3$  [181] (Scheme 28).

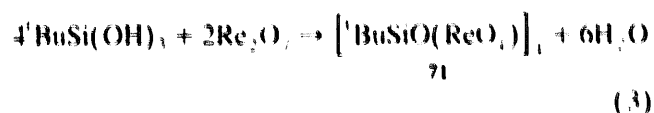
The reaction of (21) with  $\text{VOCl}_3/\text{NH}_3$ ,  $(n\text{PrO})_3\text{VO}$  or  $(\text{Me}_3\text{SiCH}_2)_3\text{VO}$  [182,183] affords compound (60) and a dimer (61). As shown in Scheme 29, a monomer/dimer equilibrium exists. The dimerization of (60) is enthalpy favoured, but at concentrations less than 10 mM and/or temperatures greater than 25 °C, the major (> 95%) V-containing species is the monomer (60). The monomeric vanadium compound (60) and the chromium compound (59) serve as models of silica-supported vanadium or chromium catalysts for alkene polymerization. Compound (60) with  $\text{AlMe}_3$  as co-catalyst shows considerable activity towards ethylene polymerization [183]. In order to examine the role of aluminium during ethylene polymerization the mixed vanadium/aluminium compounds (62a-c) shown in Fig. 26 have been prepared [184]. Indeed, compound (62c) shows similar activity towards ethylene polymerization as observed for the (60)/ $\text{AlMe}_3$  catalyst system. In addition, several silsesquioxane Ti, V, and Cr complexes (63) and (64a-f) have been synthesized in which two cages are linked together by two transition metal atoms as shown in Scheme 30 [185,186].

Many investigations have been carried out on the

synthesis of anionic Al/Si/O frameworks [187-189]. Polyhedral aluminosilsesquioxanes are potentially useful models for such aluminosilicates. Scheme 31 gives a summary of the synthetic routes used to obtain anionic polyhedral aluminosilsesquioxanes (65), (66), (67), (68), and (69). In addition, a boron silsesquioxane dimer (70) is also known [190], and its synthesis is illustrated in Scheme 32.

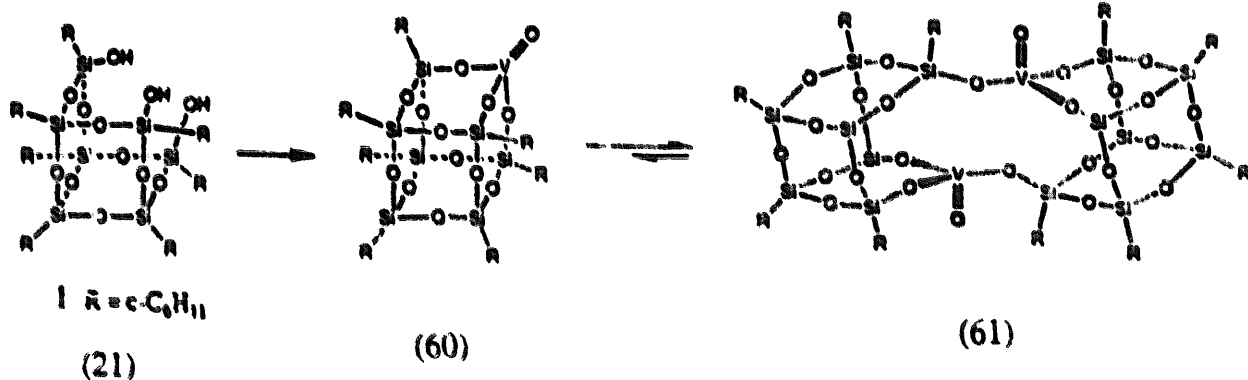
## 8. Metal-rich silsesquioxanes

Several metal-rich cage silicates have been reported, which may also serve as models for similar silica-supported transition metal oxide catalysts. The reaction of  $^t\text{BuSi}(\text{OH})_3$  with  $\text{Re}_2\text{O}_7$  in a 2:1 ratio leads to the Re-oxide four ring silicate (71) [191,192]:



The crystal structure of (71) (Fig. 27) exhibits a silicon-oxygen eight-membered ring. The four silicon atoms of the ring are each bound by an  $(\text{ReO}_4)$  and a  $^t\text{Bu}$  group. All the  $(\text{ReO}_4)$  and  $^t\text{Bu}$  groups are in mutually *cis* configurations.

A simple synthetic route (Scheme 33), using silicon compounds (72a) and (72b) with bulky organic groups



Scheme 29.

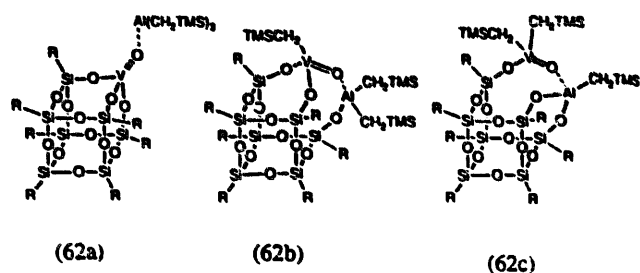
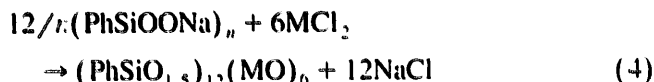


Fig. 26. Examples of mixed vanadium–aluminum compounds (62a–c).

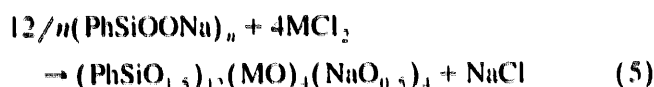
affords several cubane-metallasilsesquioxanes (73) with a high titanium content [193].

Aluminium analogues of (73) are also known [194], and can be obtained by reaction of a silanetriol with an organoaluminium compound (Scheme 34(a)). In addition to these neutral cages, the similar anionic cage has also been prepared by employing Na[Et<sub>2</sub>AlH<sub>2</sub>] (Scheme 34(b)). Both types of cage have been characterized by X-ray crystallography.

The sodium salt, PhSiOONa, reacts readily with transition metal chlorides to afford new spherosilicate materials the compositions of which depend upon the ratio of reactants [195]:



( $n = 3-6$ , M = Cu, Ni, Mn, Co, Cd)

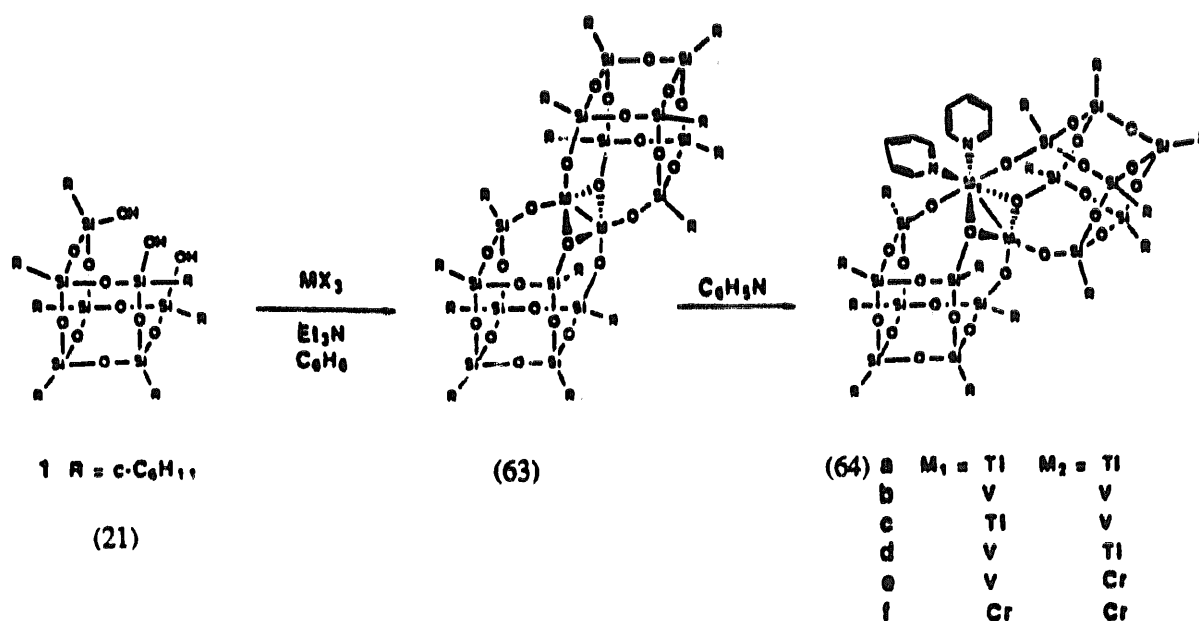


( $n = 3-6$ , M = Cu, Ni, Mn, Cd) For the former reaction

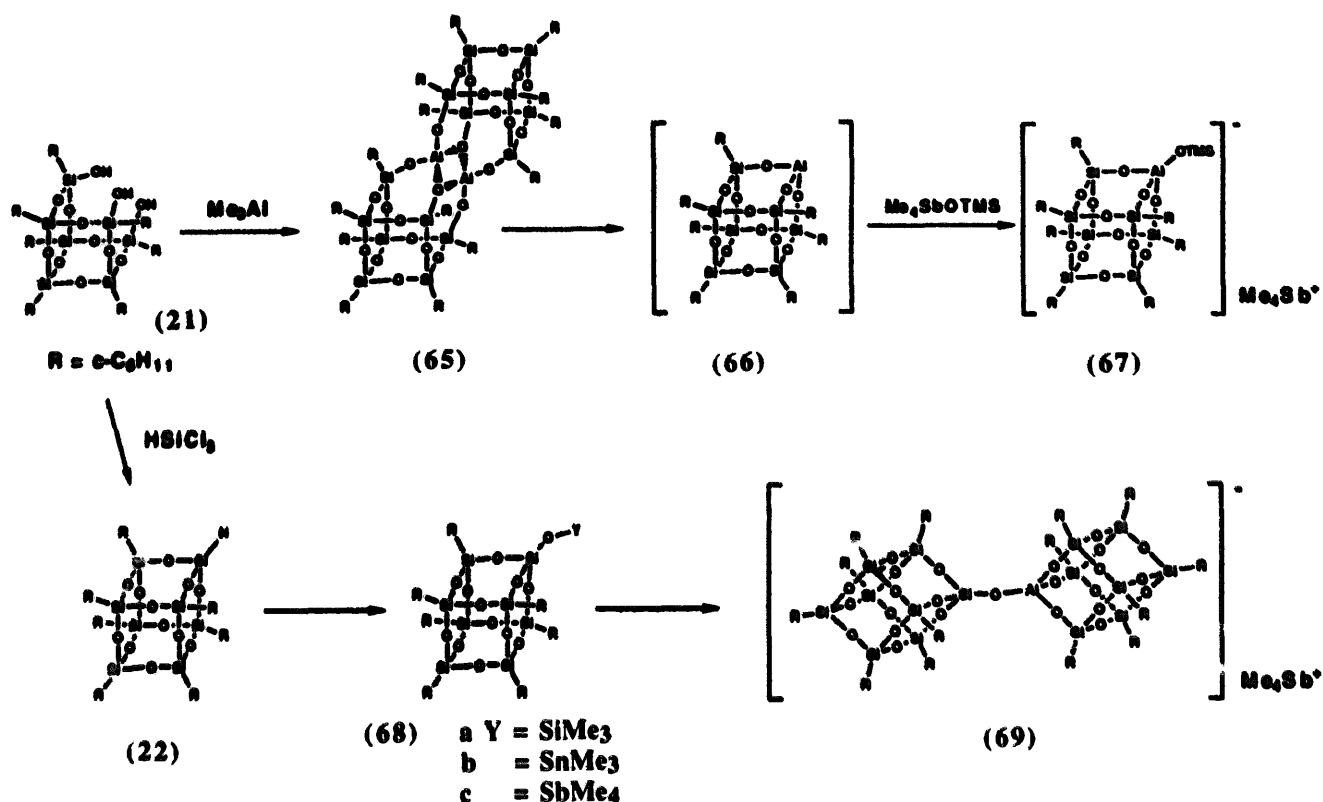
the compounds are obtained in excellent yields (up to 70% after recrystallization) and have an identical three-layered structure shown in Fig. 28(a). The middle layer, formed by six metal atoms, is connected via O-atoms to the Si-atoms of the two outer layering six-membered siloxane rings. One Cl<sup>-</sup> is accommodated within the cage. To compensate for the negative charge, an Na<sup>+</sup> ion is situated in the outer sphere of the cage near the silsesquioxane 'crown'. The best characterized representative is (PhSiO<sub>1.5</sub>)<sub>12</sub>(CuO)<sub>4</sub>(NaO<sub>0.5</sub>)<sub>4</sub> (74) whose crystal structure exhibits two four-membered {Cu<sub>2</sub>O<sub>2</sub>}, four six-membered {Si<sub>2</sub>CuO<sub>3</sub>}, and two 12-membered {Si<sub>5</sub>CuO<sub>6</sub>} rings (Fig. 28(b)).

## 9. Reactions and applications of silicate cages

Polyoligoorganylsilsesquioxanes are highly stable both towards thermolysis and the action of nucleophilic and electrophilic agents compared to analogous linear, cyclic and polycyclic oligosiloxanes. This is due to the rigid Si–O framework and shorter Si–O bond distances in oligo(organylsilsesquioxanes). In polyhedral oligomers with a strained structure, e.g. in tetra- and hexasilsesquioxanes, the Si–O–Si units are cleaved much more readily. The relative stability of silsesquioxanes with  $n = 6, 8, 10, 12$ , and 14 is presumed to be mainly determined by the degree of distortion of the Si–O–Si angle and the nature of the intramolecular interaction of the atoms forming the angles concerned. X-ray diffraction has shown that in oligosilsesquioxanes the O–Si–O angles are all close to the tetrahedral angle (ca. 109.5°). Fairly high angular strains may occur in



Scheme 30.



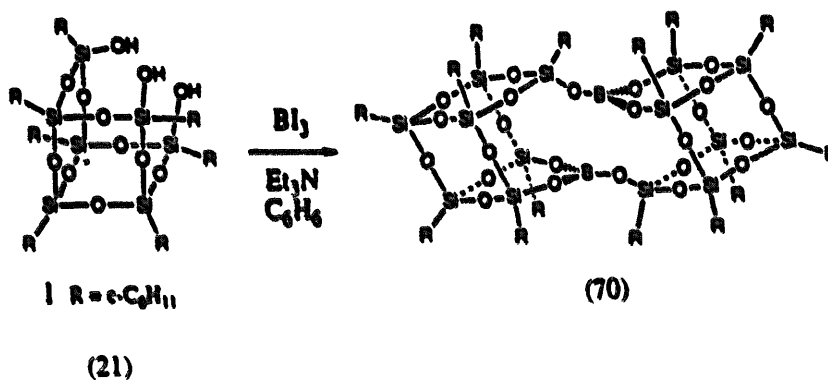
Scheme 31.

hexasilsesquioxanes which accounts for the lower stability of this skeleton [55].

Infrared spectroscopic data reveals that the thermolysis of octa(methylsilsesquioxane) leads to the formation of a non-volatile solid phase similar to  $SiO_2$ . In a helium atmosphere  $(CH_3)_8Si_8O_{12}$  sublimes almost completely in the temperature range  $150\text{--}300^\circ C$  without marked decomposition. However, in air it decomposes slowly at  $270^\circ C$ , and at  $500^\circ C$  66% is oxidized to  $SiO_2$  [196]. Octa(ethylsilsesquioxane) decomposes slowly at its melting point ( $285^\circ C$ ), and octa(propylsilsesquioxane) decomposes slowly in air at  $150^\circ C$ . In contrast, octaisopropylsilsesquioxane does not change under the same conditions ( $150^\circ C$ ) [40]. Octa(vinylsil-

sesquioxane) begins to react with oxygen at  $170^\circ C$  exothermically, and at  $550^\circ C$  it is completely oxidized to  $SiO_2$ . In vacuo octa(vinylsilsesquioxane) decomposes at  $290\text{--}300^\circ C$  forming a non-volatile solid [197]. Octa(phenylsilsesquioxane) is the most heat resistant oligosilsesquioxane known, and does not change when heated in air to its melting temperature ( $500^\circ C$ ) [47].

The Si–O–Si group in oligoorganylsilsesquioxanes is stable toward sulphuric acid, but oligo(hydro-silsesquioxanes) are susceptible to attack by sulphuric acid [40,52]. However, octa(hydro- and organylsilsesquioxanes) are stable towards both concentrated hydrochloric and acetic acids [6,40,52]. Octa(phenylsilsesquioxane) polymerizes under the action of sul-

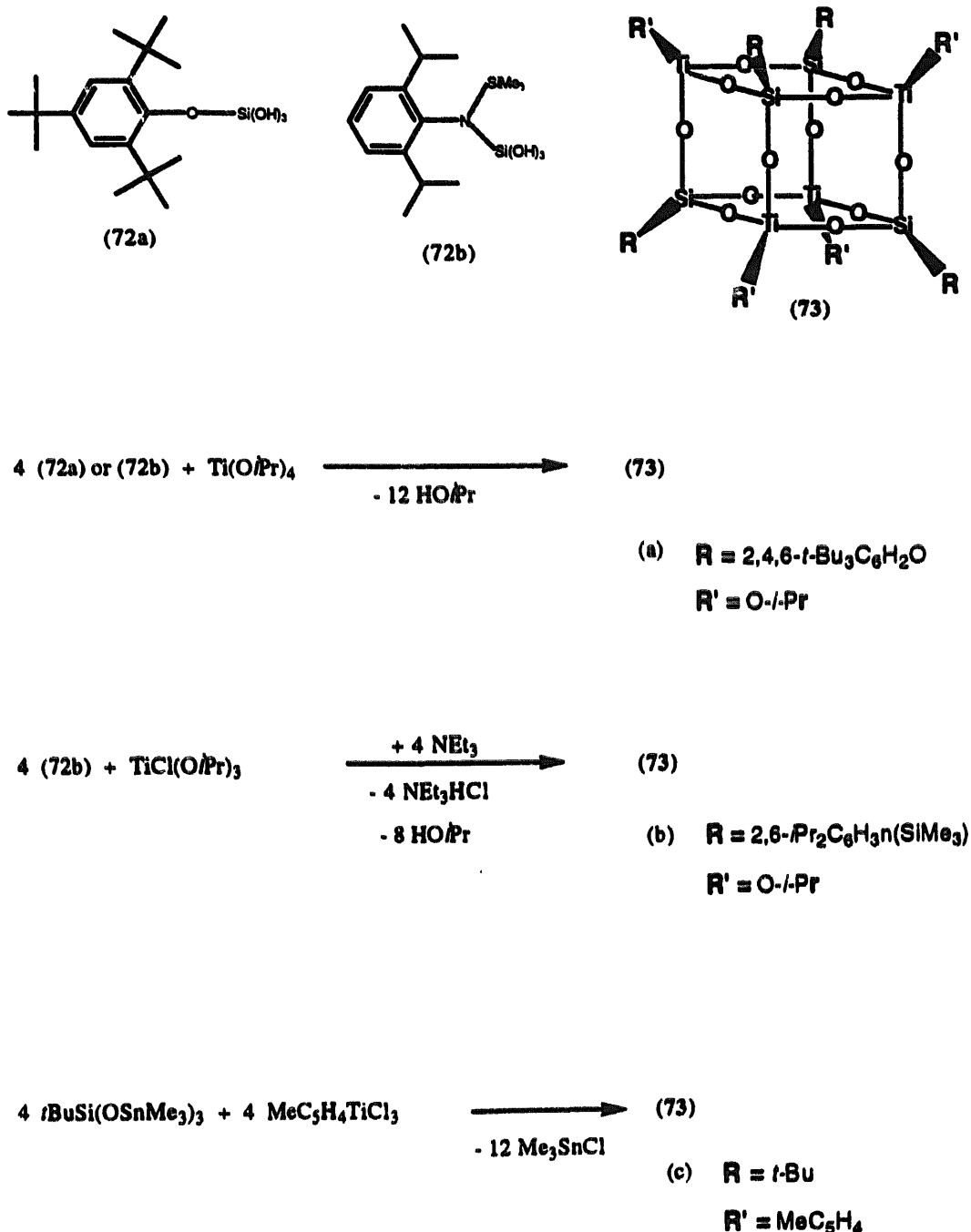


Scheme 32.

phuric acid and reacts with fuming nitric acid [40]. The siloxane bonds in oligo(organylsilsesquioxanes) are cleaved when heated with alkali hydroxides. Heating of oligosilsesquioxanes with a catalytic amount of alkali at 200–250 °C leads to formation of ladder polymers (Scheme 35) [47,162,198–203]. These polymers are very heat resistant, e.g. polyphenylsilsesquioxane starts to decompose above 600 °C. At 900 °C only loss of the phenyl groups occurs, with the Si–O framework of the molecule remaining intact [200]. This behaviour distinguishes sharply the above polymers from linear and

branched polyphenylsilsesquioxanes. In the presence of catalytic amounts of alcoholic alkalis, octavinylsilsesquioxane in chloroform solution undergoes rearrangement to higher silsesquioxanes [204] such as  $(\text{CH}_2=\text{CH})_{10}\text{Si}_{10}\text{O}_{15}$  and  $(\text{CH}_2=\text{CH})_{12}\text{Si}_{12}\text{O}_{18}$ .

Due to their interesting properties,  $\text{SiO}_2$  films have been used for a variety of applications. In semiconductor technology,  $\text{SiO}_2$  films are used for a wide range of applications, for example as masks against impurity diffusion, electrical isolation between contacts and substrates, protection from environmental degradation, as



Scheme 33.

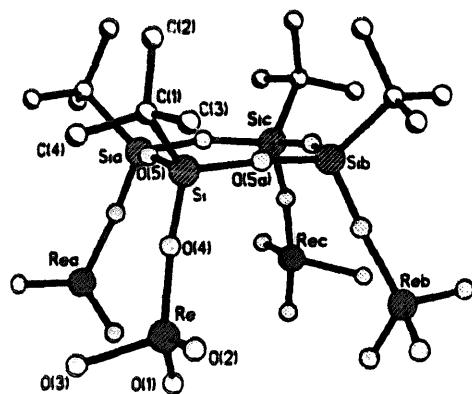
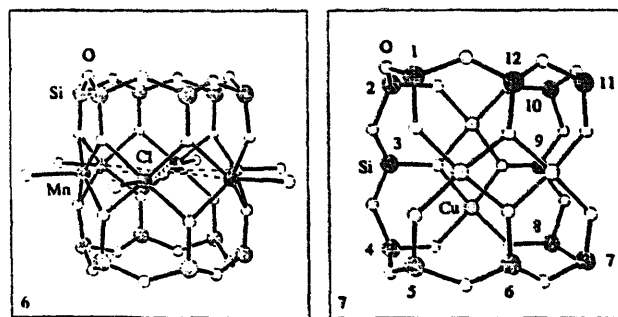


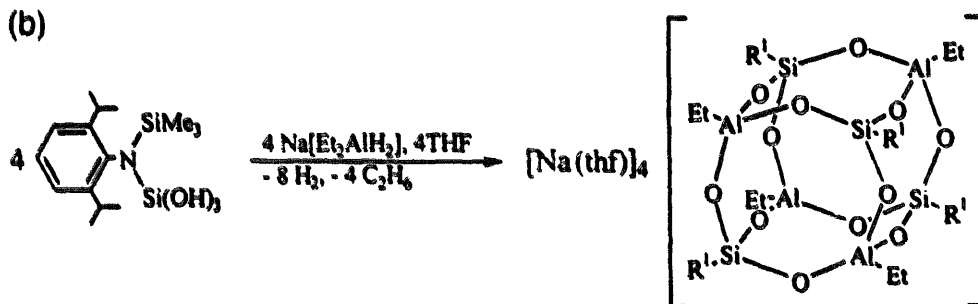
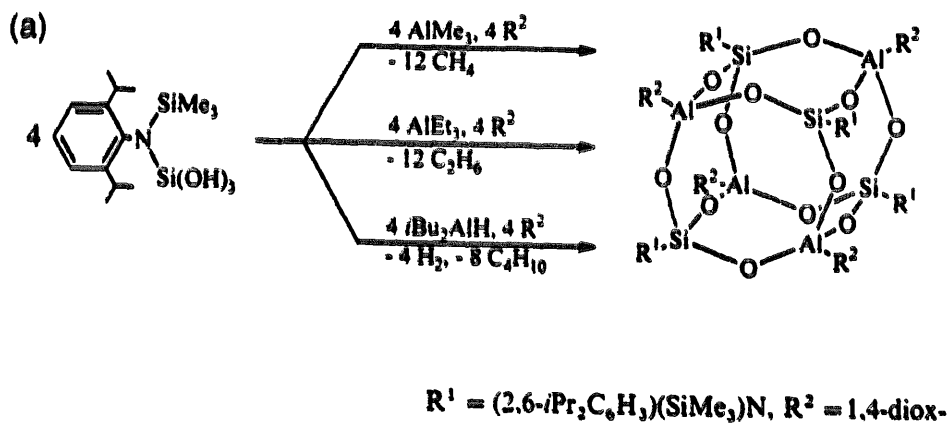
Fig. 27. Crystal structure of (71).

Fig. 28. Crystal structures of  $(\text{PhSiO}_{1.5})_{12}(\text{MnO})_6$  (a) and  $(\text{PhSiO}_{1.5})_{12}(\text{CuO})_4(\text{NaO}_{0.5})_4$  (b).

anti-reflective coatings, high temperature optical filters, and much more [205,206]. In the deposition of dielectric, semi-conducting and metallic layers, volatile element-organic compounds (E.O.C.s) of various types have been utilized [207,208]. The E.O.C.s used to prepare solid films must satisfy two main requirements:

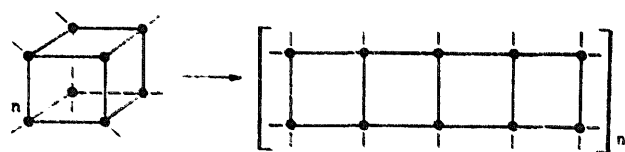
a sufficiently high vapour pressure, and they need to contain a minimal relative content of non-depositing elements (particularly organic constituents).

Most of this work involves the use of tetraethoxysilane or ethyltriethoxysilane to prepare the low temperature dielectric films [207]. The use of cage-like organosiloxanes formula  $(\text{RSiO}_{1.5})_n$  ( $R$  = organic substituent, i.e.  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_2\text{H}_5$  or  $-\text{C}_3\text{H}_7$  and  $n = 6, 8, 10, \text{ or } 12$ ) have also been investigated [54,209]. These compounds have a higher C:Si ratio than tetraethoxysilane, and all the compounds can be synthesized by hydrolysis of organyltrichlorosilane in an alcoholic medium. Octavinylsilsesquioxane is the most sensitive to radiation. The process used for dielectric film



Scheme 34.





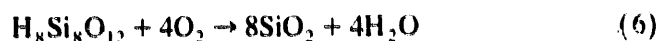
Scheme 35.

fabrication using this compound consists of two consecutive steps:

vacuum condensation of octavinylsilsesquioxane film;  
plasma treatment of the film.

Using a nickel cell, films of polyvinylsilsesquioxanes have been obtained after a polymerization time of 4 min with optimum condensation conditions achieved for 500 nm of film at 1 Pa, current density  $(5-7) \times 10^{-4} \text{ A cm}^{-1}$  and substrate potential of  $-50 \text{ V}$ . Investigations show that, by such treatment, the polymerization of octavinylsilsesquioxanes leads to films exhibiting different physicochemical and electrophysical characteristics than for films derived from tetraethoxysilane. The film deposition temperature of octavinylsilsesquioxane ( $25^\circ\text{C}$ ) is significantly lower than that of tetraethoxysilane at  $300^\circ\text{C}$ . Generally the dielectric properties of the amorphous films prepared by glow discharge treatment of polycrystalline octavinylsilsesquioxane at room temperature have better dielectric properties than  $\text{SiO}_2$  or polymer films obtained from tetraethoxysilane. Studies of  $[\text{CH}_2=\text{CH}-\text{CH}_2]_8[\text{Si}_8\text{O}_{20}]$  have been shown to have also excellent film forming properties [210].

Hydridospherosiloxanes are quite intriguing as precursors because the  $\text{Si}-\text{O}-\text{Si}$  structure of silica exists in the polyhedral cages. Therefore, it is feasible that thermal decomposition of the hydridospherosiloxanes in oxygen to form silica involves simple activation of the  $\text{Si}-\text{H}$  bond and subsequent linkage of the polyhedra by oxygen bridges. Additionally, since the size of the polyhedral silsesquioxanes varies, it is possible that the films deposited will vary in porosity, density, and other related properties as long as the polyhedra are indeed preserved during the CVD process. The mechanism of thermal decomposition of  $\text{H}_8\text{Si}_8\text{O}_{12}$  in an oxygen atmosphere may be described by the overall equation



Characterization of the  $\text{SiO}_2$  films grown by CVD from  $\text{H}_8\text{Si}_8\text{O}_{12}$  precursors showed that the  $\text{SiO}_2$  structure of these films were quite similar to those deposited from an  $\text{H}_8\text{Si}_8\text{O}_{12}/\text{H}_{10}\text{Si}_{10}\text{O}_{15}$  mixture [211]. X-ray diffraction shows that the films are amorphous with good specular reflectance, and appear to have smooth surfaces as seen by SEM. Auger depth profiling shows there is uniform distribution of oxygen and silicon throughout the bulk of the film.

In 1985 Day et al. attempted to obtain ceramic materials by the hydrolysis of  $\text{Si}_8\text{O}_{12}(\text{OCH}_3)_8$ .  $^{29}\text{Si}$

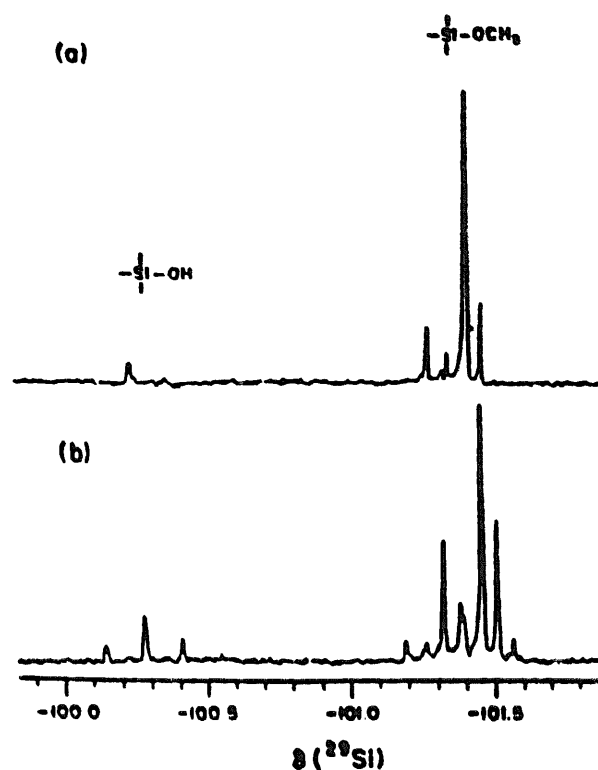


Fig. 29.  $^{29}\text{Si}$  NMR spectra recorded during the hydrolysis of  $\text{Si}_8\text{O}_{12}(\text{OCH}_3)_8$ .

NMR studies (Fig. 29) during hydrolysis, however, showed that significant side reactions also occur, indicating that the cubane cage structure did not remain intact [99]. Later Agaskar tried to obtain microporous macromolecular materials by reacting the decavinyl-D5R cage  $[\text{Si}_{10}\text{O}_{25}](\text{SiMe}_2\text{CH}=\text{CH}_2)_{10}$  with a stoichiometric amount of the bifunctional silane  $[\text{HSi}(\text{CH}_3)_2\text{CrH}_4\text{O}_{0.5}]_2$  in the presence of  $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  as catalyst. The resultant solid is described as a hard, clear resilient, thermally stable (up to  $350^\circ\text{C}$ ) material which absorbs  $> 50\%$  by weight of tetrahydrofuran.  $^{29}\text{Si}$  CP/MAS confirmed that the structural integrity of the spherosilicate cores was retained. XRD traces, however, showed that the polymer (75) is

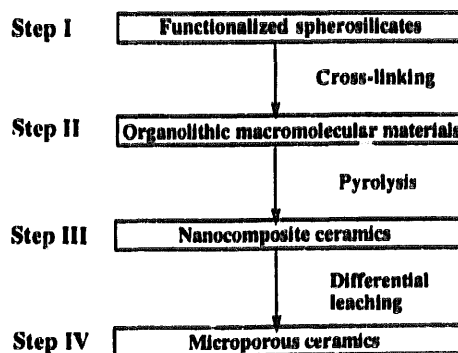


Fig. 30. Illustration of the controlled synthesis route for the preparation of microporous ceramics from functionalized spherosilicates.

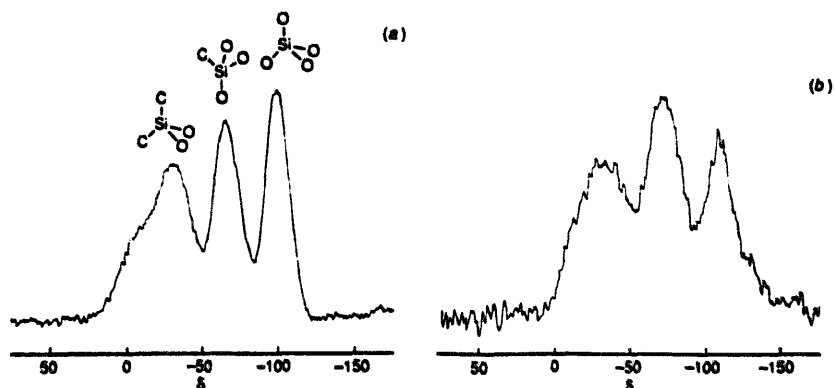


Fig. 31. Solid state  $^{29}\text{Si}$  NMR spectra recorded before (a) and after (b) leaching of the pyrolysed polymer (75) with HF.

amorphous. Unfortunately, low temperature argon adsorption measurements gave no evidence of microporosity [212]. Microporosity with high surface area could, however, be achieved by the controlled synthesis route

illustrated in Fig. 30, using  $[\text{Si}_8\text{O}_{20}(\text{KSiMe}_2\text{CH}=\text{CH}_2)_8]$  as the starting precursor. After leaching out the  $\text{SiO}_2$ -rich phase of the pyrolysed polymer (75) with hydrofluoric acid, the intensity of the resonance in the solid state  $^{29}\text{Si}$

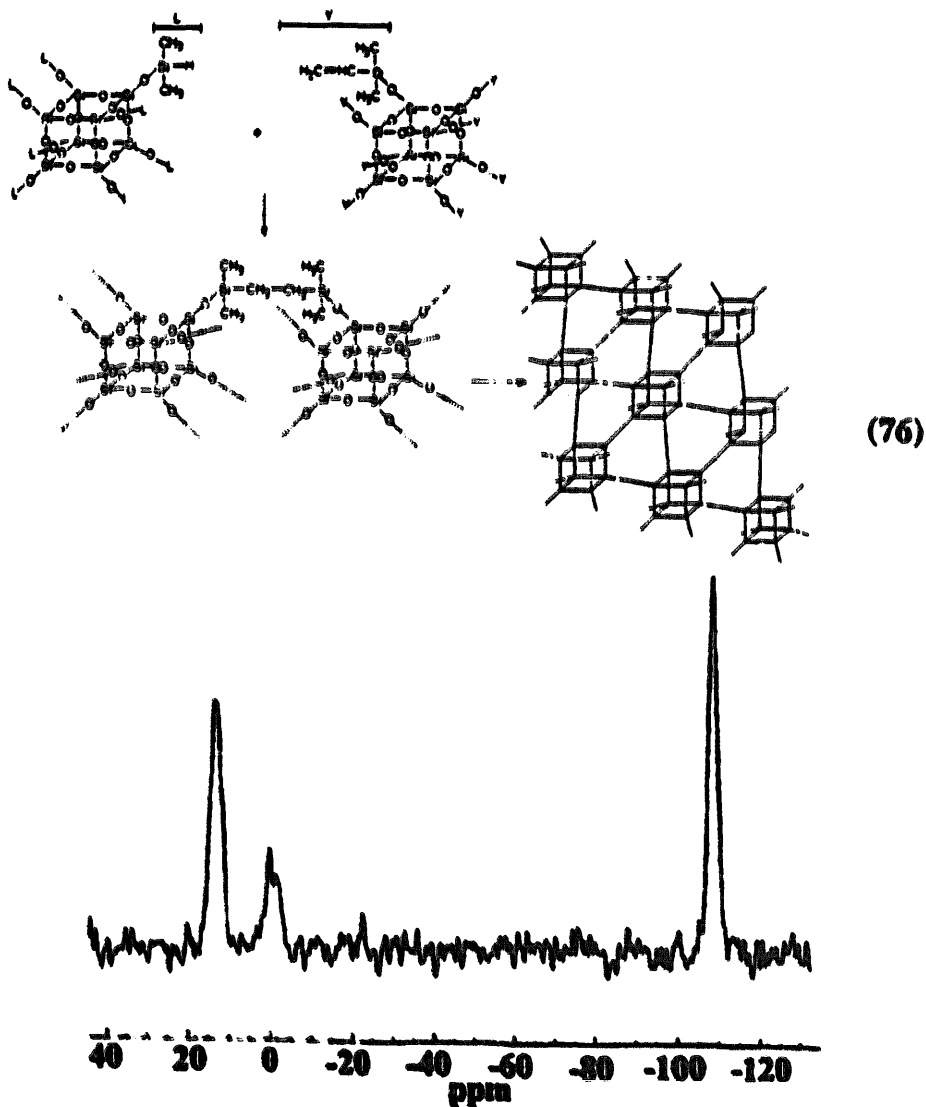


Fig. 32. Solid state  $^{29}\text{Si}$  NMR spectra of polymer (76) obtained by the Pt-catalysed hydrosilylation of  $[\text{Si}_8\text{O}_{20}(\text{KSiMe}_2\text{H})_8]$  with  $[\text{Si}_8\text{O}_{20}(\text{KSiMe}_2\text{CH}=\text{CH}_2)_8]$ .

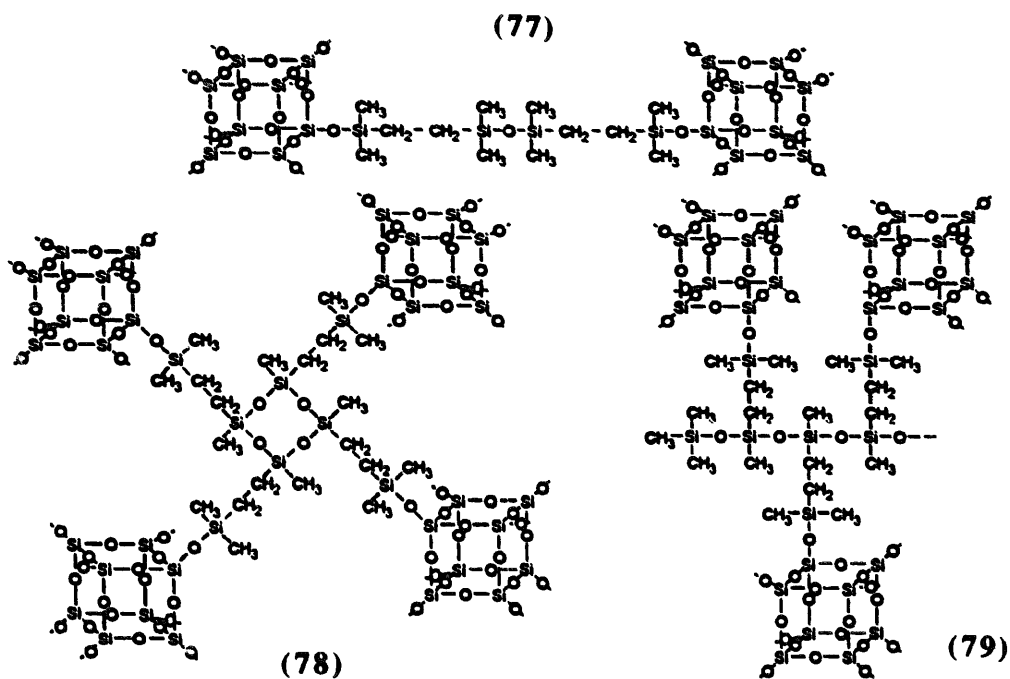
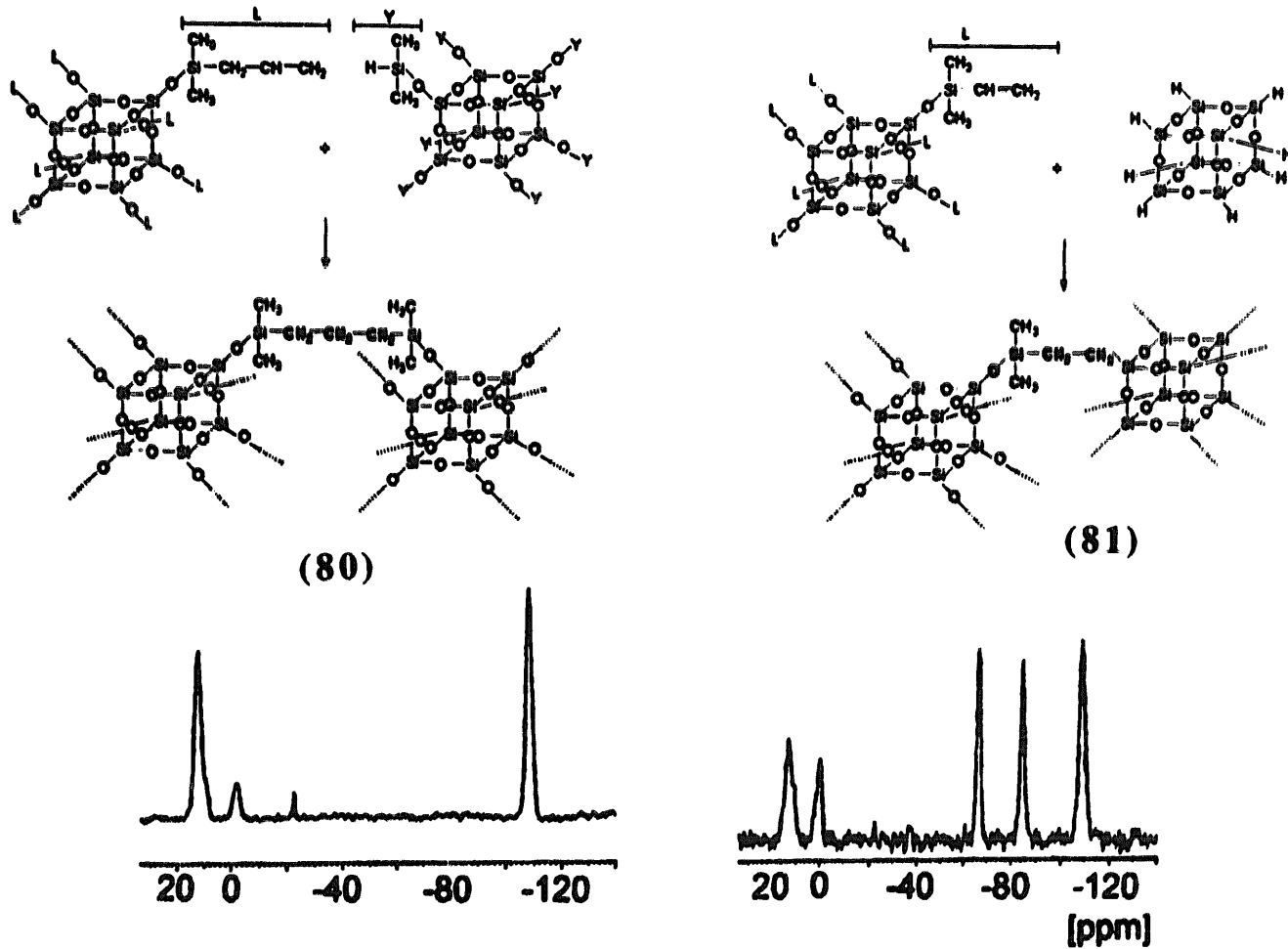
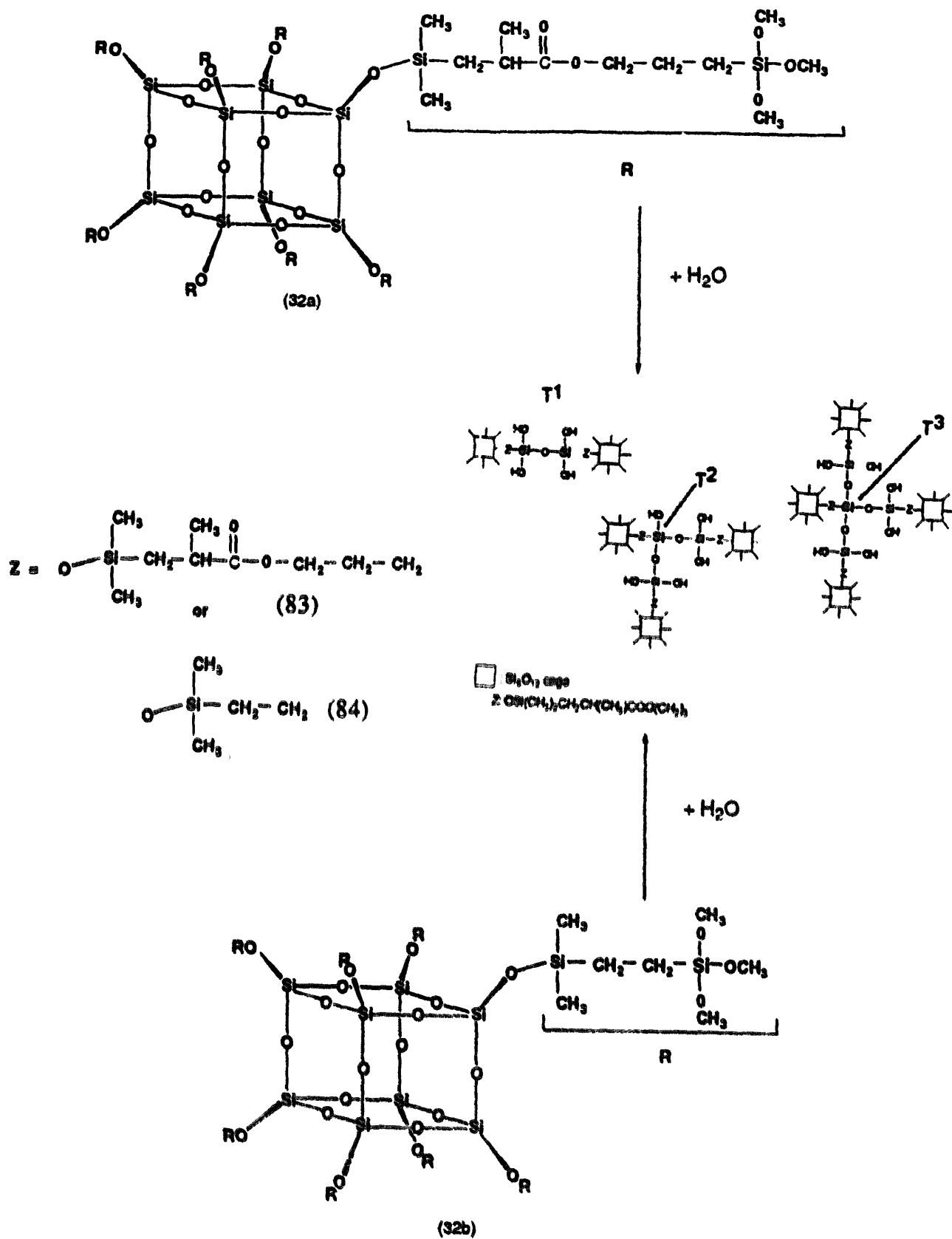


Fig. 33. Polymers with chain-like (77), cyclic (78) or branched (79) bridges between the D4R cages.

Fig. 34. Solid state  $^{29}\text{Si}$  NMR spectra of polymers (80) and (81).



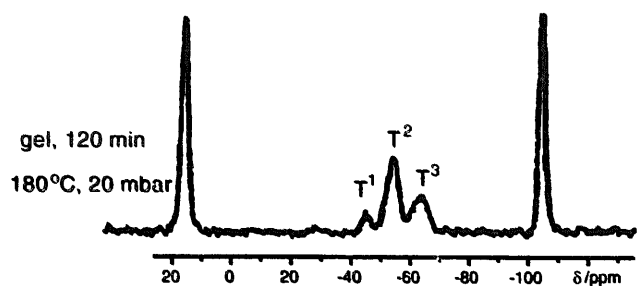


Fig. 35. Solid state  $^{29}\text{Si}$  NMR spectrum of the silanol-rich polymer (83).

NMR assigned to  $[\text{SiO}_3]$  is diminished relative to the other resonances (Fig. 31). The result after leaching is a microporous (pore size in nanometre range) ceramic material with high surface area ( $594\text{ m}^2\text{ g}^{-1}$ ) [213].

A similar microporous material has been obtained by Hoebbel et al. by the Pt-catalysed hydrosilylation of  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8]$  with  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{CH}=\text{CH}_2)_8]$ . The polymer (76) obtained is microporous with a specific surface area of about  $300\text{ m}^2\text{ g}^{-1}$  without post-treatment. Solid state  $^{29}\text{Si}$  NMR of polymer (76) (Fig. 32) shows that on average two functional groups remain unreacted [214]. Heat treatment of polymer (76) shows that it is stable in air up to  $250^\circ\text{C}$ . However, degradation occurs at  $342^\circ\text{C}$ . Thermal oxidation of the methyl groups occurs at about  $450^\circ\text{C}$ , which finally leads to new Q units at the silicon  $(\text{SiO}_{0.5})_4$  with different degrees of polymerization [215].

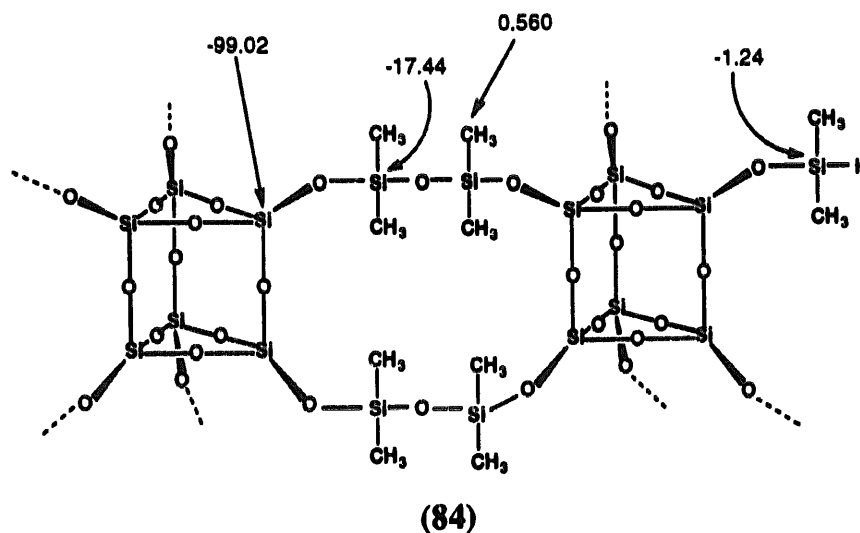
In order to examine the influence of the bridge structure and bridge length on the porosity and structure, hybrid polymers have been synthesized with different types of bridging molecule unit between cubane silicate cages [216]. Fig. 33 shows hybrid polymers with chain-like (77), cyclic (78) or branched (79) bridges between the D4R cages. However, only low specific surface areas of about  $4\text{--}7\text{ m}^2\text{ g}^{-1}$  were found. More

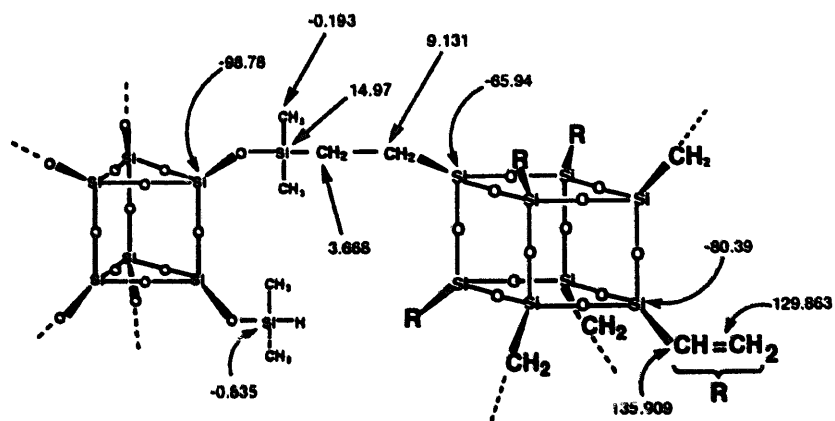
information about the influence of the bridge length on the porosity was obtained using two additional polymers, (80) and (81) [156], whose bridging length is similar to the microporous polymer (76); these were prepared by the reaction of  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8]$  with  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)_8]$  and  $\text{Si}_8\text{O}_{12}\text{H}_8$  with  $[\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{CH}=\text{CH}_2)_8]$  respectively, and contain seven-membered (80) and four-membered (81) bridges. However, unlike polymer (76) polymers (80) and (81) do not exhibit significant specific surface areas. Fig. 34 shows the solid state  $^{29}\text{Si}$  NMR of polymers (80) and (81).

Platinum-catalysed hydrosilylation of a mixed hydro-vinyl-silylated D4R-silicate results in the formation of the polymer (82) in which the cubane silicate cage units are preserved and which has a specific surface area of  $200\text{ m}^2\text{ g}^{-1}$  [156].

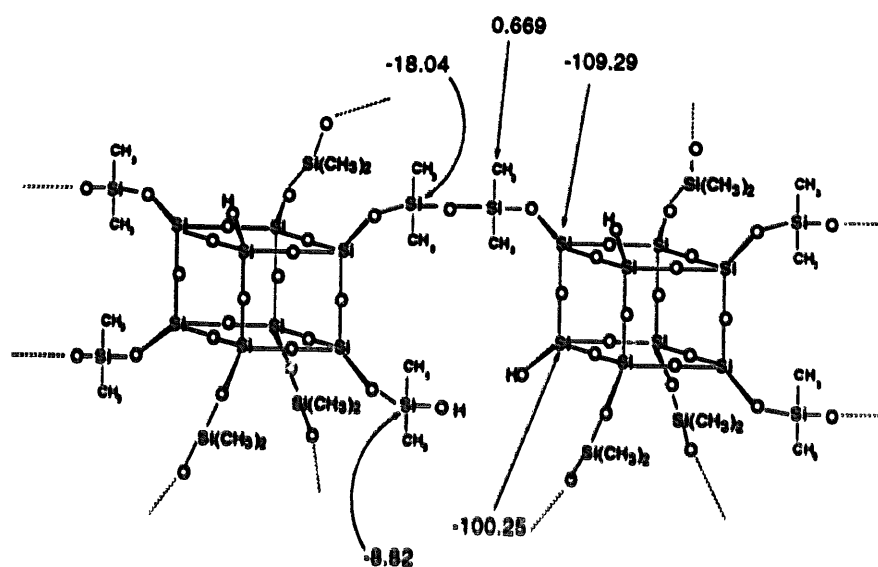
Silanol-rich polymers (83) and (84) have been obtained via hydrolysis/condensation reactions of (32a) and (32b) (Scheme 36). The average number of unreacted silanol groups in both polymers is 8.8. Both polymers, however, showed a low surface area [153,154]. The solid state  $^{29}\text{Si}$  NMR of the obtained silanol-rich polymers (83) and (84) is shown in Fig. 35.

New porous polymers have been synthesized from  $(\text{Si}_6\text{O}_9)$  and  $(\text{Si}_8\text{O}_{12})$  cage precursors and characterized by solid-state- $^{29}\text{Si}$  and  $^{-13}\text{C}$  NMR. Preparative routes to polymers (84)–(88) are shown in Eqs. (7)–(11). Two methods have been employed: (i)  $\text{H}_2\text{PtCl}_6$ -catalysed hydrosilylation of vinyl-substituted cages, and (ii) hydrolysis of bromosilane functions; the general structures of the polymer formed are illustrated schematically in the scheme. The hydrosilylation reactions were carried out in refluxing toluene, gelation occurring after ca. 15 min. Hydrolysis of the bromosilanes was effected by ice-water. After separating off and drying in vacuo, the polymers were isolated as insoluble glassy powders.

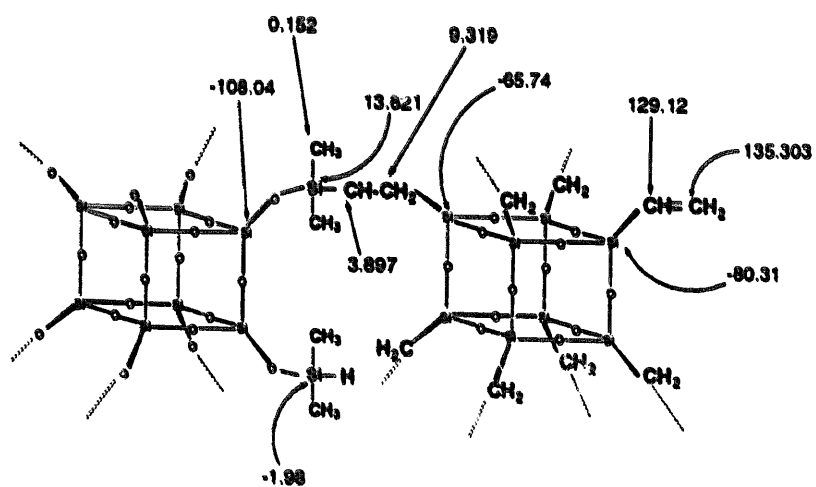




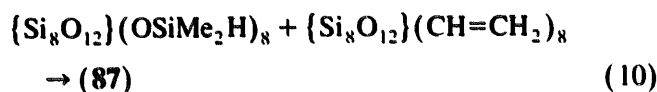
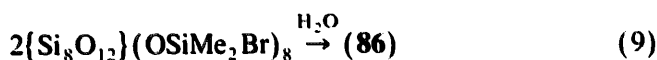
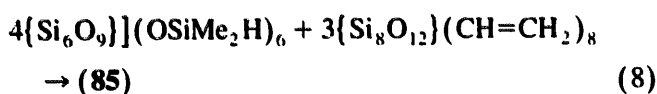
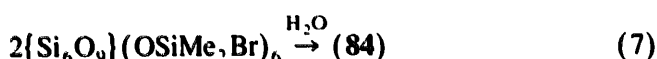
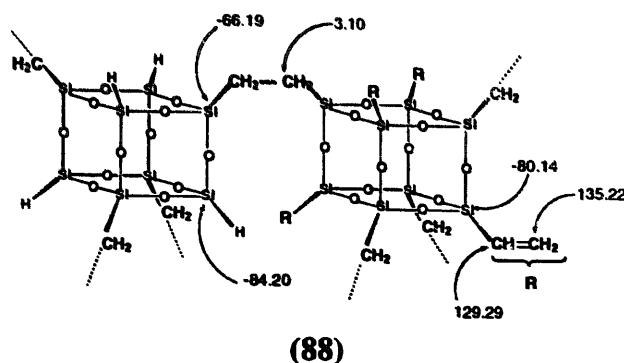
(85)



(86)



(87)

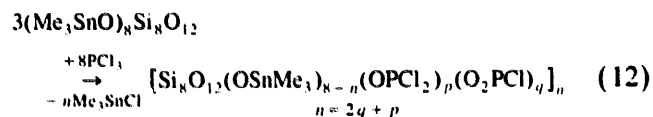


Characterization of the structures of the polymer is most easily accomplished using solid-state- $^{29}\text{Si}$  and  $^{-13}\text{C}$  NMR, and structures (84)–(88) are annotated with appropriate chemical shift data (parts per million). Spectra for polymers (85) and (86) exhibit only very small resonances due to unreacted cage functions, indicating that ca. 89% and 95% respectively of the available exocyclic functions (determined from integrated peak areas) participate in polymer linkage formation. In contrast, spectra for the other polymers show that the degree of polymerization is much less, and only ca. 60–68% of linkage formation occurs under the conditions employed. The two polymers derived from  $\{\text{Si}_6\text{O}_9\}$  cages, (83) and (84), as well as polymer (86) exhibit type II nitrogen adsorption isotherms with hysteresis on the desorption arm, behaviour characteristic of mesoporous materials. Specific surface areas of (84) and (85) are relatively low at  $12.2\text{ m}^2\text{ g}^{-1}$  and  $63.4\text{ m}^2\text{ g}^{-1}$  respectively, but that of (86) is significantly higher ( $218.3\text{ m}^2\text{ g}^{-1}$ ). The adsorption isotherms of (87) and (88) are both type I but also exhibit hysteresis indicative of mixed microporous–mesoporous character. Specific surface area values for these polymers are  $147.0\text{ m}^2\text{ g}^{-1}$  and  $573.7\text{ m}^2\text{ g}^{-1}$  respectively, the latter being comparable to values found in zeolites and much higher than the highest previously reported for polymers derived from molecular  $\{\text{Si}_8\text{O}_{12}\}$  cage precursors [217].

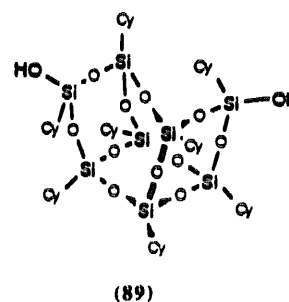
Silylation of  $[(\text{CH}_3)_4\text{N}][\text{Si}_8\text{O}_{20}]$  with dichlorodimethylsilane gives a polymer with low specific surface area. However, heating at  $300^\circ\text{C}$  yields a porous material with a surface area of  $300\text{ m}^2\text{ g}^{-1}$ . It

was presumed that the tetramethylammonium salts encapsulated in the polymer during the synthesis evaporated at higher temperatures leaving cavities which were responsible for the porosity [218].

The reaction of  $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$  with  $\text{PCl}_3$  in a benzene solution produces a gelatinous suspension via Eq. (12) within 15 min.



Additional heating afforded a thick slurry. Approximately 60–75% of the available tin was liberated as  $\text{Me}_3\text{SnCl}$  as indicated by the  $^1\text{H}$  NMR spectrum. The BET surface area of this material measured by nitrogen adsorption is  $500\text{ m}^2\text{ g}^{-1}$  with a pore volume and pore diameter calculated to be  $0.3\text{ cm}^3\text{ g}^{-1}$  and  $24\text{ \AA}$  respectively [219]. Lichtenhan and coworkers [220,221] employed (89) as a bifunctional building block for the construction of linear silsesquioxane–siloxane copolymers via silanol-centred reactions with bifunctional silane and siloxane precursors. Transition-metal-containing silsesquioxane polymers have also been reported using a similar approach.



Further application of current interest for polyhedral silsesquioxanes is in the production of liquid crystalline (LC) copolymers. These materials have been produced by hydrosilylative coupling of oligo(dimethylsiloxanes) with allyloxy-mesogens. The oligo(dimethylsiloxane)

units serve as flexible spacers. The usefulness of LC–inorganic copolymers to combine the superior properties of both components warrants further attention. In addition, polyhedral silsesquioxanes show excellent adhesion to a wide variety of surfaces, including dentin, and are also extremely abrasion resistant. Therefore, hybrid copolymers of LC units and silsesquioxane units offer the opportunity to create single phase copolymers that will have good-to-excellent adhesion, abrasion, resistance, and high processability.

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