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Review

Synthetic methodologies in siloxanes

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This review describes the various types and synthetic strategies for the production of siloxanes. A description is given of the various synthetic methods for the production of organic compounds with silicon–oxygen bonds. The different types of siloxane are described, with the emphasis being on their structural aspects. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: siloxane; synthesis; sol–gel; classifications; silsequioxane

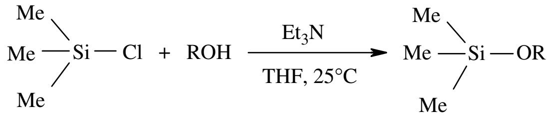
INTRODUCTION

Siloxanes are compounds containing silicon–oxygen (Si–O) bonds. Generally, the term siloxane is concerned with their day-to-day uses as plastic materials. However, the Si–O bond, also being a constituent of the Earth's crust, has major scope for studies. In organic chemistry, the Si–O bond is frequently used as a protective group for alcohols and phenols.[1–5] The importance for synthetic chemistry thus stems from both easy formation and cleavage of the Si–O bond. The role of the Si–O bond in sol–gel synthesis[6–8] and heterogeneous catalysis[9–11] is indispensable. Weak interactions of Si-O-bonded compounds are used to construct supramolecular architectures.[12] The lithographic properties of Si-O-bonded compounds are well documented.[13] Siloxanes also play key roles in photoimaging[14] and nanotechnology.[15–20] Over and above these, aluminosilicate chemistry and the closely allied field have gained interest with regard to the production of novel advanced materials.[15] Thus, the synthetic methodologies at the junction of inorganic and organic chemistry are valuable and are a focus of present research. The chemistry of Si–O bond formation is interesting, as there is the possibility of involvement of silicon d-orbitals and the low-lying σ^* orbitals for hydrolytic cleavage. The Si–O bond can also be formed from a weakly bonded Si–H or Si–Si bond. The possibility of expanding coordination to five or six results in easy nucleophilic substitution reactions at the silicon centre. Thus, synthetic methodology and the types of silicon-bonded compounds go hand in hand.

SYNTHETIC METHODS FOR SI–O BOND FORMATION

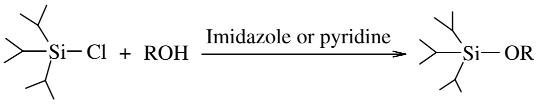
There are several methods for Si–O bond formation. The six types of reaction that are commonly encountered in the synthesis of target molecules and polymeric materials are as follows.

(1) The reaction of silicon halides with alcohols (Eqn (1)) to give the corresponding silylether is the most common Si–O bond-forming reaction. These reactions are generally carried out in the presence of bases like pyridine, imidazole, tertiary amine, etc.[21,22]



$$\mathrm{Me_3Si{-}Cl} + \mathrm{ROH} \xrightarrow[\text{THF, 25°C}]{\mathrm{Et_3N}} \mathrm{Me_3Si{-}OR} \qquad (1)$$

The disadvantage of this reaction is that an acid scavenger is required for removal of the liberated acid, which otherwise can cleave an Si–O bond. Water can hydrolyse a siloxy group, so aqueous work-up is generally not used for silyl chloride alcoholysis. This results in the need to remove the ammonium salts formed in the reaction. However, owing to limited synthetic methodology, this reaction is generally used, but with a nonaqueous work-up procedure. The reaction of triisopropylsilylchloride with alcohols in dimethylformamide in the presence of imidazole or pyridine is a commonly used reaction for alcohol protection:[23]



(2)

The presence of bulky isopropyl substituents on the silicon lowers the rate of reaction compared with other

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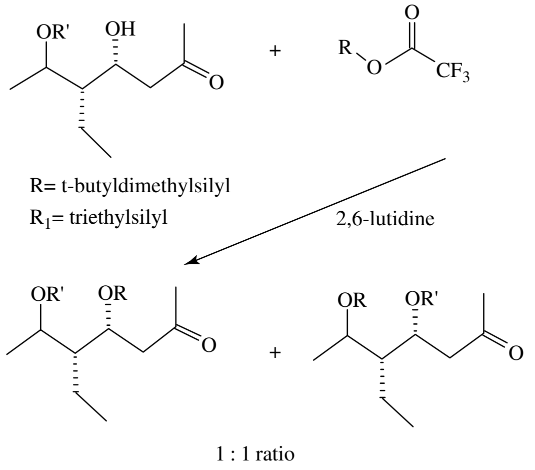
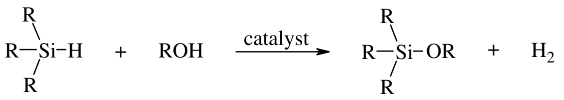
conventionally used silylating agents, such as trimethylsilylchloride or t-butyldimethylsilylchloride. Another advantage of using tri-isopropylsilylchloride as a silylating agent is that it selectively silylates primary alcohols even in the presence of a secondary alcohol. The reaction of silyltriflates with alcohols also leads to silylether.[24] Equation (3) is an example of such a reaction involving the retention of an optical active centre:



(3)

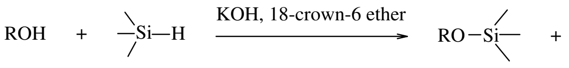
(2) Another widely studied method of Si–O bond formation is the dehydrogenative coupling reactions of silanes with alcohols in the presence/absence of a catalyst:[25–29]



$$\mathrm{R}-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{H} + \mathrm{ROH} \xrightarrow{\text{catalyst}} \mathrm{R}-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{OR} + \mathrm{H_2} \quad (4)$$

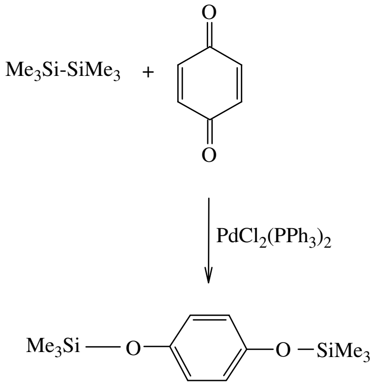
The dehydrogenative coupling reaction is advantageous over other reactions owing to the ease of product isolation and the possibility of continuous processing. A large number of metal complexes can act as catalyst for this reaction. The activation of Si–H bond be achieved by metal powders.[25]

These reactions are also catalysed by alkoxide and amines. The use of catalytic amounts of potassium hydroxide with 18-crown-6 ether in dichloromethane[30] in mild conditions demonstrates an example of supramolecular catalysis in the synthesis of a silylether (Eqn (5)). A wide variety of silylethers are prepared by this method.



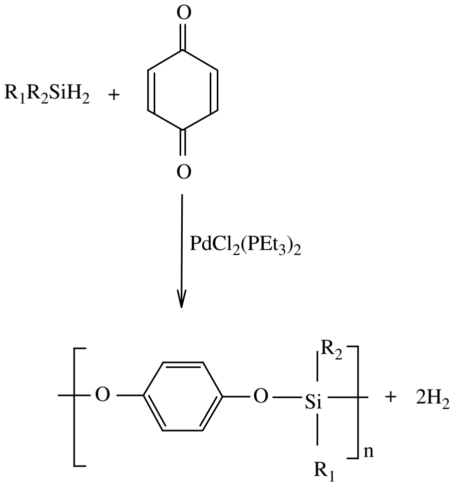
$$\mathrm{ROH} + -\mathrm{Si}-\mathrm{H} \xrightarrow{\text{KOH, 18-crown-6 ether}} \mathrm{RO}-\mathrm{Si}- + \mathrm{H_2} \quad (5)$$

(3) Siloxy ethers of dihydroxy aromatic compounds can be prepared by the reductive disilylation of quinones by disilanes. Such reactions are catalysed by palladium and rhodium catalysts.[31]



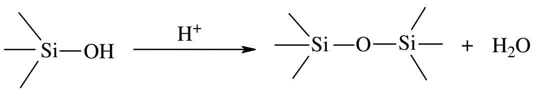
(6)

Equation (6) depicts the palladium-catalysed disilylation of 1,4-benzoquinones with hexamethyldisilane. In a relatively recent study, such a methodology is extended to a co-polymerization reaction of hydrosilanes with 1,4-benzoquinone to give Si–O-bonded oligomers:[32]



(7)

(4) Another method of Si–O bond formation reaction is by the acid-catalysed condensation of silanols:[33]

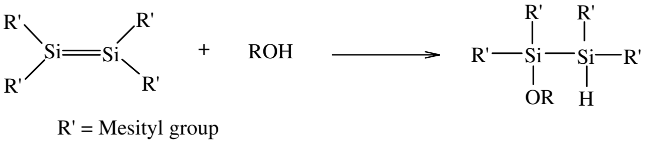


$$-\mathrm{Si}-\mathrm{OH} \xrightarrow{\mathrm{H^+}} -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{H_2O} \quad (8)$$

This reaction is widely used for the synthesis of various macromolecular siloxane architectures, such as linear siloxane, silsesquioxane and silica networks and glasses.[34] However, the use of strong acid in these reactions causes equilibration of the reaction.[35]

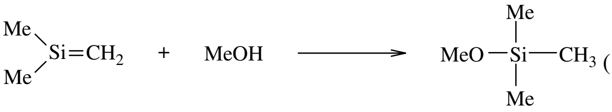
(5) Unsaturated silicon-containing compounds, such as silenes and disilenes, are very reactive and react efficiently with alcohols to give addition products.[36] Nucleophilic addition of alcohols and water to disilene[37,38] (Eqn (9)) requires slightly elevated temperatures in the absence of

a catalyst, but the reactions are much slower than the nucleophilic addition reactions of silenes (Eqn (10)).[39,40]



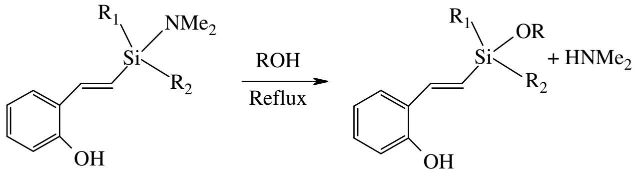
R' = Mesityl group

(9)



$$Me_2Si=CH_2 + MeOH \longrightarrow MeO-Si(Me)_2-CH_3 \quad (10)$$

(6) Si–N bonds are relatively unstable: they can be easily converted to silylethers, and such reactions are used for preparations of silylethers attached to a phenolic group through an intervening carbon atom:[41]



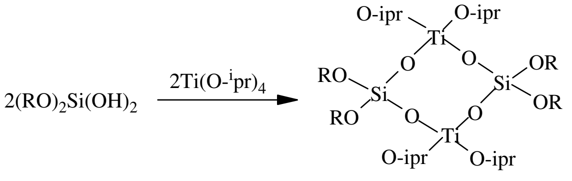
(11)

All the above reactions are useful in the preparation of selective Si–O-bonded compounds having less complicated structures. However, there are many cyclic and acyclic networks of Si–O-bonded compounds that require an understanding of structure to apply these principal reactions. Thus, in the following, the different types of siloxane involving the application of Si–O bond formation are discussed.

TYPES OF SILOXANE

Metallasiloxanes

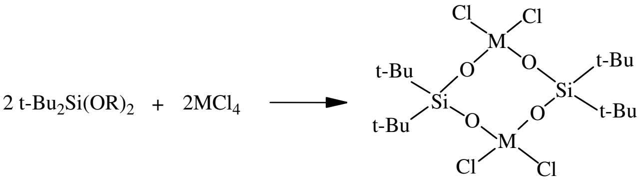
Metallasiloxanes are siloxanes having some of the silicon atoms replaced by an appropriate metal. Incorporation of metal into a siloxane framework can lead to two- and three-dimensional or linear networks. Metallasiloxane can be derived from silanediols, disilanol, silanetriols and trisilanols (Eqn (12)). For example, the transesterification reaction of $Ti(O\text{-}^iPr)_4$ with sterically hindered silanediol $\{(t\text{-}BuO-)_3SiO\}_2Si(OH)_2$ gives cyclic siloxane (**I**). Similarly, cyclic dihalotitanasiloxanes $[t\text{-}Bu_2Si(O)OTiX_2]_2$ (X = Cl, Br, I) can be prepared by the direct reaction of titanium tetrachloride with $t\text{-}Bu_2Si(OH)_2$.[42] Such compounds are made of eight-membered rings having composition $Ti_2Si_2O_4$ (**II**). Both silicon and titanium atoms in the molecule exhibit regular tetrahedral geometry. Analogously, the corresponding zirconium compound $[t\text{-}Bu_2Si(O)OZrCl_2]_2$ was also prepared from the reaction between the dilithium salt of $t\text{-}Bu_2Si(OH)_2$ and $ZrCl_4$ (Eqn (13)).[43]



I

ipr = isopropyl

(12)

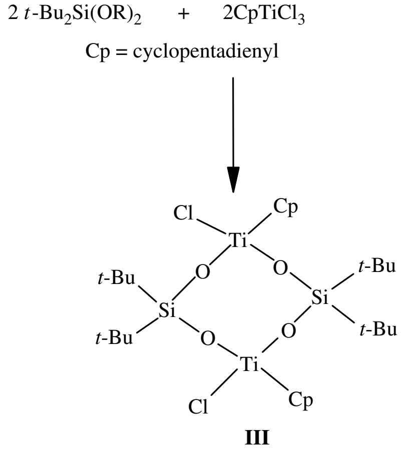


II

M = Ti, R = H
M = Zr, R = Li

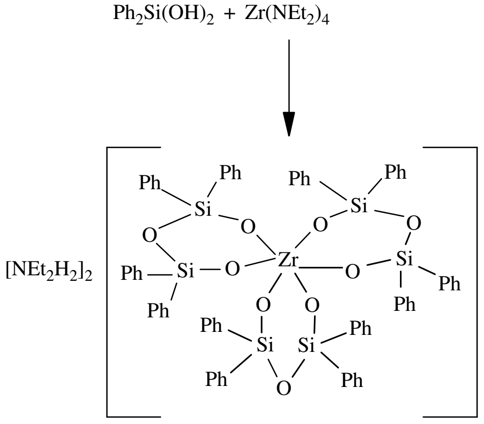
(13)

Cyclopentadienyl-substituted titanasiloxane $[t\text{-}Bu_2Si(O)OTiCpCl]_2$ (**III**) can be prepared directly (Eqn (14)) by the reaction of $CpTiCl_3$ with $t\text{-}Bu_2Si(OLi)_2$. The reaction of the silanediol $Ph_2Si(OH)_2$ with the zirconium amido derivative $Zr(NEt_2)_4$ leads to the formation of the dianonic tris-chelate metallasiloxane $[NEt_2H_2]_2[(Ph_4Si_2O_3)_3Zr]$ (**IV**); (Eqn (15)). In this reaction, the silanediol, prior to coordination to zirconium, is converted into disilanol by condensation of two molecules through elimination of water. In the case of zirconocene, the central zirconium atom is coordinated by six oxygen atoms in a distorted octahedral geometry.[44]



III

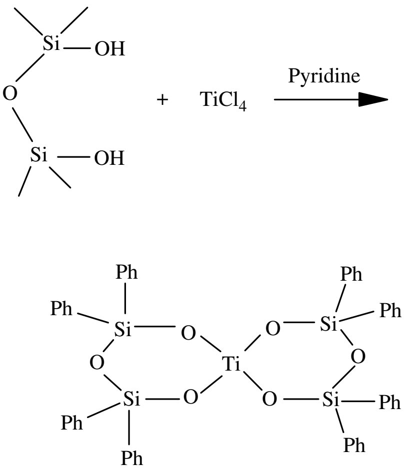
(14)



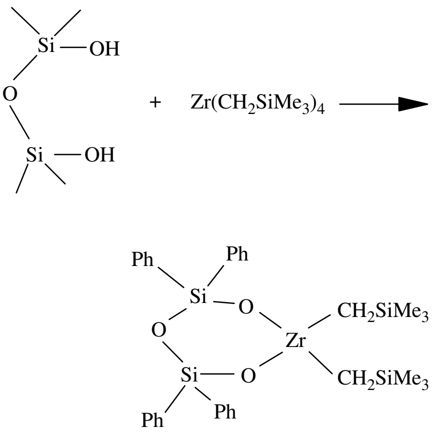
(15)

IV

Disilanols are also used as building blocks for a variety of metallasiloxanes.[45] The disilanols are capable of chelating to form six-membered rings containing the central metal. The reactions leading to Group 4 metallasiloxanes from disilanols are described in Eqns (16) and (17).

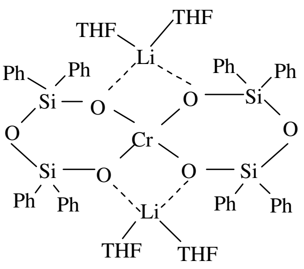


(16)



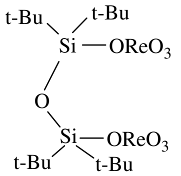
(17)

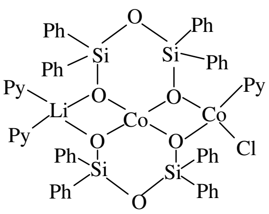
In a similar manner, metallasiloxane derivatives of Group 5, Group 7, Group 9 and Main Group metals can be prepared from disilanols. Some interesting structures of such compounds are shown in **V**, **VI** and **VII**.



THF = Tetrahydrofuran

V

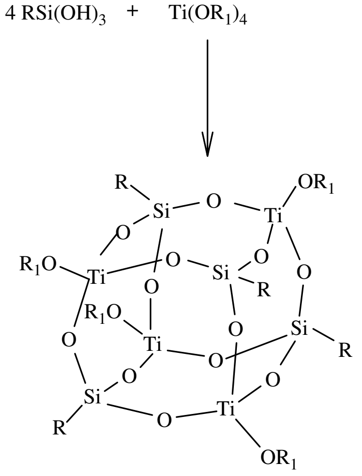




Py = pyridine

VI **VII**

Reactions of simple silanediol and disilanols with titanium halides or titanium amides give cyclic titanasiloxanes. Three-dimensional titanasiloxanes can be prepared by the reaction of the titanium amide with silanol or silanediol. Such reactions serve as a synthetic pathway for preparation of model compounds for titanium-doped zeolites.[46] Cubic titanasiloxanes can be prepared by a single-step synthesis from the reaction of titanium orthoesters and silanetriols.[47] The driving force for formation of zeolite-like structures is the elimination of the corresponding alcohol, which results in the subsequent assembly of the three-dimensional Si–O–Ti frameworks (Eqn (18)).



(18)

IX

R = $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$

R_1= isopropyl, ethyl

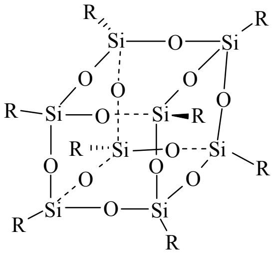
In an analogous manner, the three-dimensional networks of aluminiumosiloxane, indiumsiloxane, galliumsiloxane, etc. can be prepared from the reaction of trisilanols and MMe_3

where M = Al, In, Ga, etc. In all these networks, cubic metallasiloxanes, $M_4Si_4O_{12}$ polyhedrons, are present.[48] The sides of the cubic framework comprise six $M_2Si_2O_4$ eight-membered rings, which adopt an approximate C_4 crown conformation. The O–Si–O angles in all compounds remain close to a tetrahedral geometry.

Silsesquioxanes

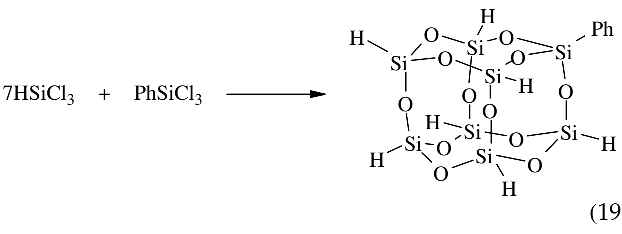
The hydrolysis of silicon trichlorides is a complicated process and usually does not lead to the expected trihydroxy compounds. Instead this gives polycondensations in solution, resulting in the formation of three-dimensional silsesquioxanes having networks of closo cubic geometry. Such compounds have the empirical formula $RSiO_{3/2}$. Incompletely condensed polyhedral silsesquioxanes can be isolated by carefully controlling the steric parameters for the R groups and the reaction conditions.[49,55]

Silsesquioxanes formed from cross-linked Si–O networks, having simple or functional organic residues on every silicon atom are common.[50,51] Silsesquioxanes can have different structures, such as random structures, ladder structures, cage structures and partial cage structures. They are also sometimes termed *ormosils* (organically modified siloxanes). A representative silsequioxane (**IX**) is shown below.



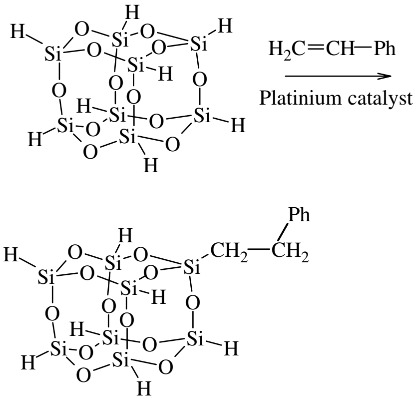
IX

To prepare mono-substituted silsesquioxane, there are three conventional synthetic routes.[51] (1) Co-hydrolysis of trifunctional organo- or hydro-silanes. For example co-hydrolysis of $HSiCl_3$ and $PhSiCl_3$ results in the formation of $PhH_7Si_8O_{12}$ (Eqn (19)):[50]



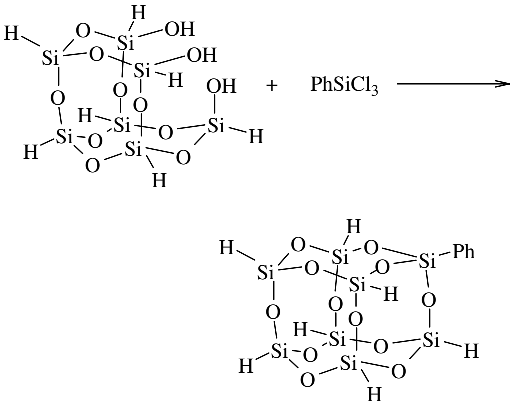
(19)

(2) Substitution reactions at a silicon centre with the retention of the siloxane cage leads to structural modifications of silsesquioxane. For this reaction hydrosilylation is a commonly used reaction (Eqn (20)):



(20)

(3) Silsesquioxanes can also be prepared by corner capping reactions of functional groups present in the incomplete cage (Eqn (21)):

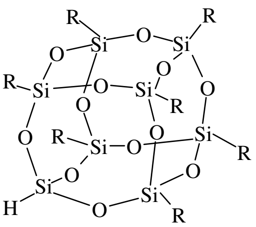


(21)

Silsesquioxane also have three subclasses; they are (1) functional silsesquioxanes, (2) nonfunctional silsesquioxanes and (3) bridged polysilsesquioxanes.

Functional silsesquioxanes

Silsesquioxanes having one or more functional groups (e.g. Si–OH, Si–H) are termed functional silsesquioxanes (**X**).[51]

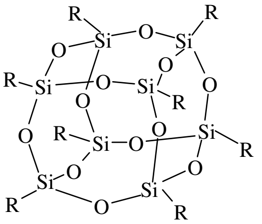


X

Functional silsesquioxanes are prepared from silanes having the formula $RSiX_3$, where R is an organofunctional group and X is an alkoxy or halide, etc. Vinyl, allyl functional, methacryl-functional, amino-functional and epoxy-functional sillsesquioxanes are the most important structural themes from an applications point of view.[49]

Nonfunctional silsesquioxane

As the name implies, a silsesquioxane without any functional group is called a nonfunctional silsesquioxane (**XI**).

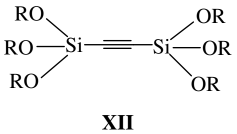


XI

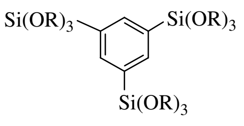
Generally, in this type of silsesquioxane, all silicon atoms are bonded with an alkyl or aryl group.[50,51] Examples of nonfunctional silsesquioxanes are phenylsilsesquioxane, methylsilsesquioxane, substituted phenyl- and benzylsilsesquioxanes. There are different possibilities on the structural features of a nonfunctional silsesquioxane. Based on the cage structure, they can be prismatic cages having 8, 10 or 12 Si–O bonds and are categorized as T_8^R, T_{10}^R and T_{12}^R respectively.

Bridged polysilsesquioxanes

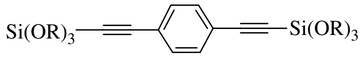
Bridged polysilsesquioxanes have three-dimensional networks. They can be distinguished from other silsesquioxanes as they contain an organic fragment as an integral component of the network. This family of hybrid organic–inorganic materials is prepared by sol–gel processing of monomers having variable organic bridging groups and two or more trifunctional silyl groups.[52–54] Some important monomers (**XII**, **XIII**, **XIV**, **XV**) that are commonly used for the preparation of bridged polysilsesquioxane are shown below.



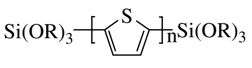
XII



XIII

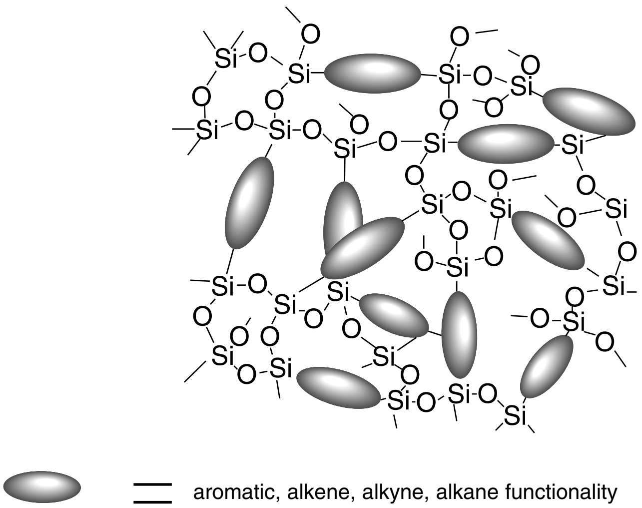


XIV



XV

A representative structure of a bridged polysilsesquioxane (**XVI**) is shown below.

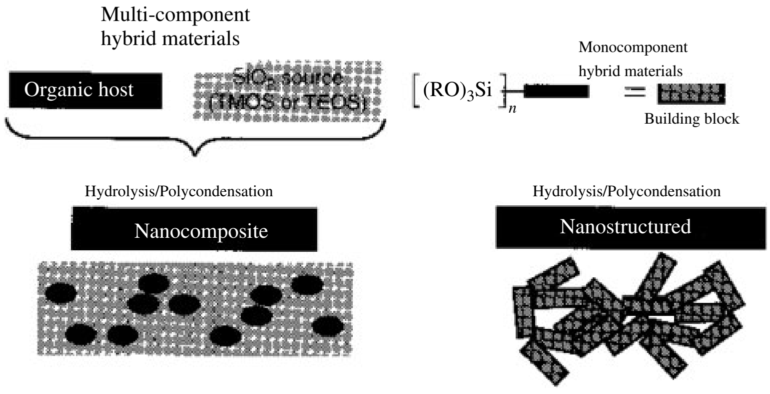


XVI

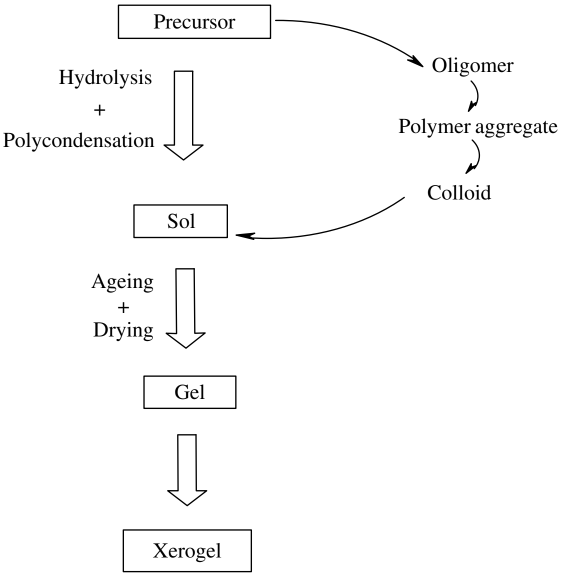
Hybrid organic–inorganic materials can be synthesized through two routes: via the hydrolytic sol–gel route[52–55] or by nonhydrolytic sol–gel routes.[6–8] Each route has its various advantages and disadvantages.

Understanding of bridged polysilsesquioxane requires discussion on hybrid organic–inorganic materials. Hybrid organic–inorganic materials are of two categories: nanocomposites and nanostructured hybrid materials. Nanostructured materials are generally prepared by hydrolysis and polycondensation of mono-component hybrid organic–inorganic precursors, i.e. the organic unit is an integral part of the component (which is generally called the building block unit).[52] On the other hand, nanocomposites are the polycondensed products of an inorganic matrix in the presence of an organic molecule acting as a host.[56] Two routes leading to the formation of nanocomposite and nanostructured hybrid materials are shown in Scheme 1. Bridged polysilsesquioxanes fall into the category of nanostructured hybrid organic–inorganic materials.

Silsesquioxanes can be prepared by the hydrolytic sol–gel route, in which hydrolysis and polymerization leads to the desired product. The polymerization process involved in this kind of reaction is generally catalysed by acid, base or fluoride ions. The main steps involved in such sol–gel process are shown in Scheme 1.[53] The sol–gel process starts from a homogeneous solution of precursor in a solvent. This can lead to the formation of polymers, to colloids or to colloidal gels. Finally, the xerogel is obtained by the elimination of solvent by a drying step. Tetraethoxysilane is generally used as precursor in sol–gel process. Most of the hybrid organic–inorganic materials are prepared through sol–gel routes (Scheme 2) from tetraethoxysilane. Changing any one of these steps shown in Scheme 2 during the formation of hybrid inorganic and organic materials can change the



Scheme 1.



Scheme 2.

morphology of these materials. In the case of silica, the size of the container can have an influence on the final properties of the materials. In materials science, these types of gel are described as unstable solids. On the other hand, because of the high sensitivity towards the experimental conditions, it is possible to achieve very different textures by simple modifications of the kinetic parameters, like temperature, pressure, concentration, solvent, catalyst, nature of leaving group, etc.

In contrast to the hydrolytic route, there are very few reports to date on the use of the nonhydrolytic route to prepare organic–inorganic hybrids.[6] The nonhydrolytic sol–gel method has been developed in recent years as an alternative to the hydrolytic route.[6–8] The synthesis of inorganic oxides via nonhydrolytic sol–gel routes involving Si–O bond is reported.[8] This involves the reaction of a metal halide with an oxygen donor, such as an alkoxide, ether, alcohol, etc., under nonaqueous conditions, as shown in Scheme 3.

A porous solid derived from a siloxane $[\mathrm{Si{-}O}]_n$ network[57] having an imino bis(*N*-2-aminoethylacetamide) polysiloxane ligand system has been found to be very effective for the uptake of metal ions such as Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. An iodo-functionalized modified siloxane network[58] ($[\mathrm{Si{-}O}]_n$) has recently been prepared by polycondensation of $\mathrm{Si(OEt)_4}$ and $\mathrm{(MeO)_3Si(CH_2)_3I}$. This siloxane network exhibits high uptake of various di- and tri-valent cations. Hybrid nanocomposites[59] containing cross-linked octaaminophenyl silsesquioxanes have been synthesized recently and these are proposed as potential advanced material that may have exceptional material properties.

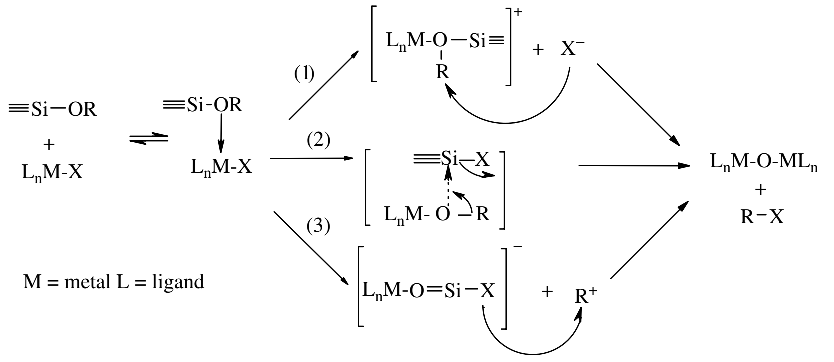
The utility of hydrolysis of trichlorosilanes having long aliphatic chains has been successfully utilized to make self-assemblies having electronic applications.[60] Bilayer within bilayers[61] of silahydroxy compounds can provide nanodimensional confinements. Si–C bond formation reactions are achieved at the porous silicon surfaces by immobilization[62] of $\mathrm{RhCl(PPh_3)_3}$. In a more recent report, gold nanoparticles are used as catalysts for polymerization of alkylsilane to obtain nanowires, filaments and tubes.[63]

Ladder siloxanes

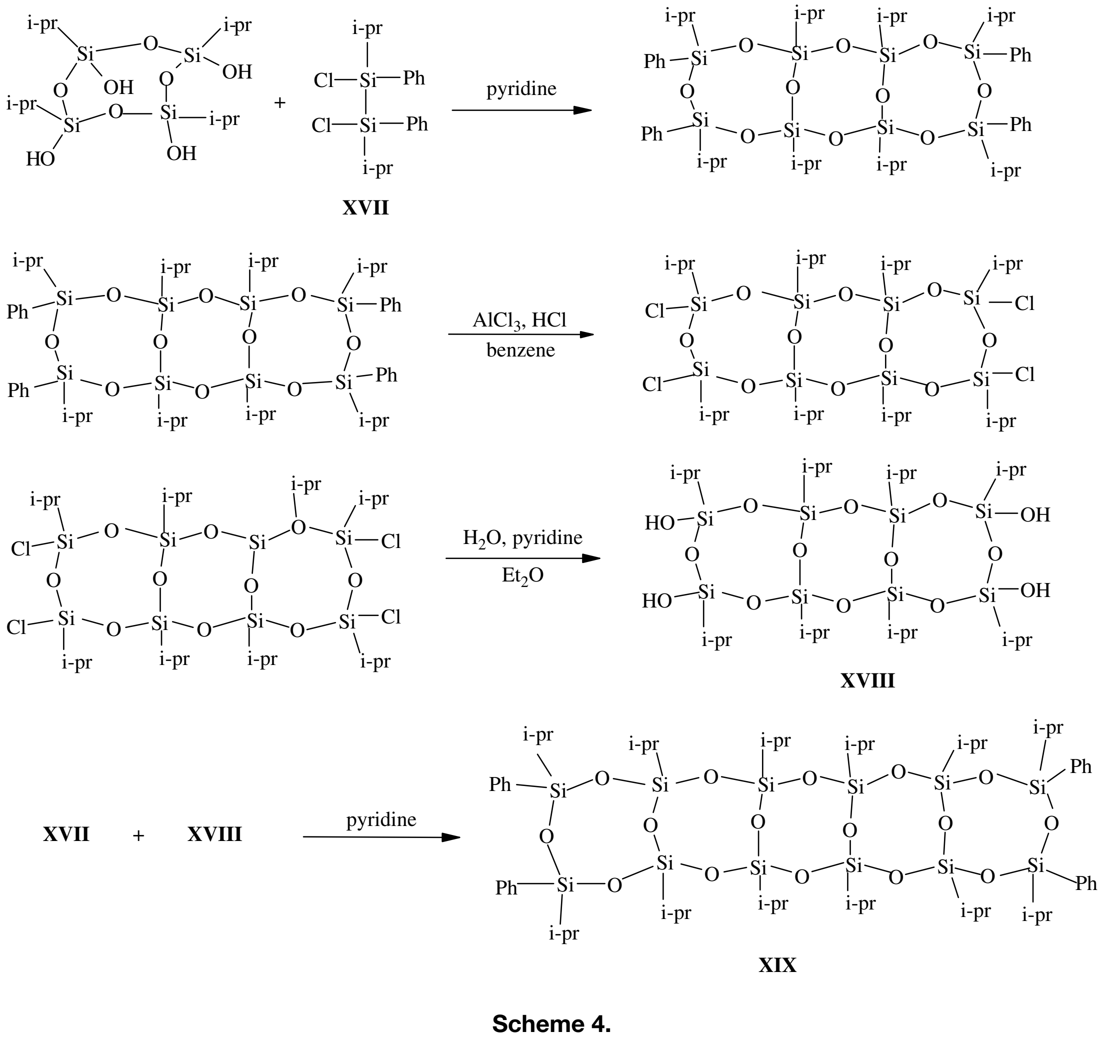
Ladder-type polysiloxane[60,61] have the general formula $(\mathrm{RSiO_{1.5}})_n$. *cis*-1,3,5,7-cyclotetrasiloxanetetraol is used as a versatile precursor for the synthesis of pentacyclic ladder siloxane.[64] Such synthesis of pentacyclic ladder siloxane (**XIX**) proceeds through three key steps: silylation of silanol, followed by chlorodephenylation, hydrolysis and then silylation again (Scheme 4).

Cyclic siloxanes

Cyclic siloxanes constitute an important class of silicone precursor. The most practical method for preparing high-molecular-weight polysiloxanes is via the ring-opening polymerization of cyclic monomers.[65] Polymerization of hexamethyl cyclotrisiloxane leads to higher molecular weight polymers with low polydispersities. The cyclic dimethylsiloxanes are usually made by the hydrolysis of dichlorodimethylsilane (Scheme 5).[66] The formation of a cyclic siloxane is generally



Scheme 3.

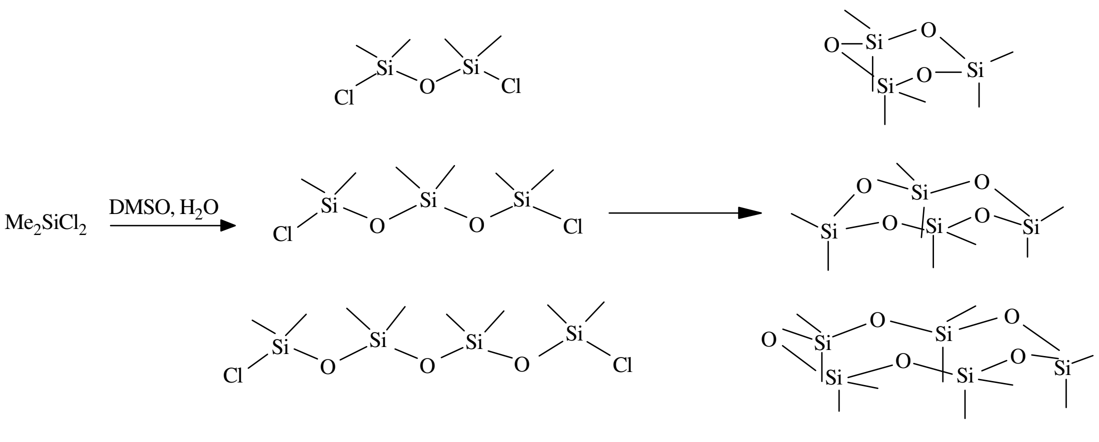


Scheme 4.

accompanied by substantial amounts of linear siloxane. The formation of linear siloxanes can be suppressed by the use of an organic co-solvent for hydrolysis.[65] The reaction between dimethylsulfoxide and dimethyldichlorosilane leads to the formation of cyclic siloxane as the major product and linear siloxanes are not formed.[66]

CONCLUSIONS

This article shows that though conventional methods are in use for the synthesis of Si–O bonds, the emergence of the applications of Si–O-bonded compounds in advanced materials invites an in-depth understanding of the structural



Scheme 5.

aspects of the composites under consideration. The need for reagents able to give specific reactions at a given reaction condition is a central point in Si–O chemistry.

REFERENCES

1. Denmark SE, Sweis RF. *Acc. Chem. Res.* 2002; **35**: 835.
2. Greene TW, Wurtz PGM. *Protective Groups in Organic Synthesis*, 2nd edn, Wiley: New York, 1991.
3. Christianopoulou M. *Appl. Organometal. Chem.* 2001; **15**: 889.
4. Sinhababu A, Kawase M, Borchardt R. *Tetrahedron Lett.* 1987; **28**: 4139.
5. Lalonde M, Chan TH. *Synthesis* 1985; 817.
6. Hay J, Porter D, Raval H. *Chem. Commun.* 1999; 81.
7. Corriu RJP, Leclercq D. *Angew. Chem. Int. Ed. Engl.* 1996; **35**: 1420.
8. Hay JN, Raval HM. *Chem. Mater.* 2001; **13**: 3396.
9. Abbenhuis HCL, Vorstenbosch MLW, van Santen RA, Smeets WJJ, Spek AL. *Inorg. Chem.* 1997; **36**: 6431.
10. Feher FJ, Budzichowski TA. *Polyhedron* 1995; **14**: 3239.
11. Lindner E, Schreiber R, Schneller T, Wegner P, Mayer HA, Goepel W, Ziegler C. *Inorg. Chem.* 1996; **35**: 514.
12. Sarno DM, Jiang B, Grosfeld D, Afriyie JO, Matienzo LJ, Wayne Jr E. *Langmuir* 2000; **16**: 6191.
13. Karkkainen AHo, Tamkin JM, Roger JD, Neal DR, Homi OE, Ghassan Z, Rantala JE, Descour MR. *Appl. Opt.* 2002; **41**: 3988.
14. Karkkainen AHo, Rantala JE, Maaninen A, Jabbour GE, Descour MR. *Adv. Mater.* 2002; **14**: 535.
15. Corriu RJP, Cerveau G, Framery E. *Chem. Mater.* 2000; **13**: 3373.
16. Biteau J, Chaput F, Lahlil K, Boilot JP. *Chem. Mater.* 1998; **10**: 1945.
17. Celio H, Lozaro J, Cabibi H, Ballast L, White JM. *J. Am. Chem. Soc.* 2003; **125**: 3302.
18. Purkaystha A, Baruah JB. *Appl. Organometal. Chem.* 2001; **15**: 693.
19. Chung M-K, Orlova G, Goddard JD, Schlaf M, Harris R, Beveridge TJ, White G, Hallett FR. *J. Am. Chem. Soc.* 2002; **124**: 10 508.
20. Burkhart T, Mennig M, Schmidt H, Licciulli A. Materials Research Society Symposium Proceedings 779–84, 1994.
21. Hart TW, Metcalfe DA, Scheinmann FJ. *Chem. Commun.* 1979; 156.
22. Bhaumik A, Kumar R. *Chem. Commun.* 1995; 869.
23. Rucker C. *Chem. Rev.* 1995; **95**: 1009.
24. Askin D, Angst D, Danishefsky S. *J. Org. Chem.* 1987; **52**: 622.
25. Mathias J. *J. Organometal. Chem.* 1986; **282**: 175.
26. Purkaystha A, Baruah JB. *J. Mol. Catal. A* 2003; **198**: 47.
27. Lorentz C, Schubert U. *Chem. Ber.* 1995; **128**: 1267.
28. Bedard TC, Corey JY. *J. Organometal. Chem.* 1992; **428**: 315.
29. Brandes D. *Journal of Organometallic Chemistry Library* 1979; **7**: 257.
30. Bideau F, Coradin T, Henique J, Samuel E. *Chem. Commun.* 2001; 1408.
31. Yamashita H, Reddy NP, Tanaka M. *Organometallics* 1997; **16**: 5223.
32. Reddy PN, Chauhan BPS, Hayashi T, Tanaka M. *Chem. Lett.* 2000; 250.
33. Lickiss PD. *Adv. Inorg. Chem.* 1995; **42**: 147.
34. Brinker CJ, Scherer GW. *Sol–Gel Science*. Academic Press: San Diego, 1989.
35. Cypryk M, Apleloig Y. *Organometallics* 2002; **21**: 2165.
36. Raabe G, Michl J. *Chem. Rev.* 1985; **85**: 419.
37. Matsumoto H, Arai T, Watanabe H, Nagai Y. *Chem. Commun.* 1984; 724.
38. Boudjouk P, Han BH, Anderson KR. *J. Am. Chem. Soc.* 1982; **104**: 4992.
39. Davidson IMT, Wood IT. *Chem. Commun.* 1982; 550.
40. Kreil CL, Chapman OL, Burns GT, Barton TJ. *J. Am. Chem. Soc.* 1980; **102**: 841.
41. Pirrung MC, Lee YR. *J. Org. Chem.* 1993; **58**: 6961.
42. Haudi-Mazzah A, Mazzah A, Schmidt H-G, Noltmeyer M, Roesky HW. *Z. Naturforsch. Tecl B* 1992; **47**: 1085.
43. Liu F-Q, Uson I, Roesky HW. *J. Chem. Soc. Dalton Trans.* 1995; 2453.
44. Hossain MA, Hursthouse MB. *Inorg. Chim. Acta* 1980; **44**: 259.
45. Graalmann O, Klingebiel U, Clegg W, Haase M, Sheldrick GM. *Chem. Ber.* 1984; **117**: 2988.
46. Huybrechts DRC, Bruycker DL, Jacobs PA. *Nature* 1990; **345**: 240.
47. Voigt A, Murgavel R, Chandrasekhar V, Winkhofer N, Roesky HW, Schmidt H-G, Uson I. *Organometallics* 1996; **15**: 1610.
48. Brown JF, Vogt LH. *J. Am. Chem. Soc.* 1965; **87**: 4313.
49. Baney RH, Itoh M, Sakakibara A, Suzuki T. *Chem. Rev.* 1995; **95**: 1409.
50. Marcolli C, Calzaferri G. *Appl. Organometal. Chem.* 1999; **13**: 213.
51. Murugavel R, Bhattacharjee M, Roesky HW. *Appl. Organometal. Chem.* 1999; **13**: 227.
52. Loy DA, Shea KJ. *Chem. Mater.* 2001; **13**: 3306.
53. Boury B, Corriu RJP. *Chem. Commun.* 2002; 795.
54. Schottner G. *Chem. Mater.* 2001; **13**: 3422.
55. Duchteau R. *Chem. Rev.* 2002; **102**: 3525.
56. Lee EC, Kimura Y. *Polym. J.* 1998; **30**: 234.
57. El-Nahhal IM, El-Ashgar NM, Chehimi MM, Bargiela P, Maquet J, Babonneau F, Livage J. *Micropor. Mesopor. Mater.* 2003; **65**: 299.

58. El-Nahhal IM, Zaggout FR, Nassar MA, El-Ashgar NM, Maquet J, Babonneau F, Chehimi MM. *J. Sol–Gel Sci. Technol.* 2003; **28**: 255.
59. Choi J, Tamaki R, Laine RM. *Polym. Mater. Sci. Eng.* 2001; **84**: 735.
60. Fendler JS. *Chem. Mater.* 2001; **13**: 3196.
61. Maoz R, Sagiv J. *J. Adv. Mater.* 1998; **10**: 580.
62. Holland JM, Stewart MP, Allen MJ, Buriak JM. *J. Solid State Chem.* 1999; **147**: 251.
63. Prasad BLP, Stoeva SI, Sorensen CM, Zaikovoski V, Klabunde KJ. *J. Am. Chem. Soc.* 2003; **125**: 10 488.
64. Matsumoto H, Suto A, Unno M. *J. Am. Chem. Soc.* 2002; **124**: 1574.
65. Clarson SJ, Semlyen JA (eds). *Siloxane Polymers*. Prentice Hall: Englewood Cliffs, NJ, 1993.
66. Brook MA, Grgoras S, Wenzel S, Yang H, Le Roux C. *Organometallics* 1998; **17**: 556.