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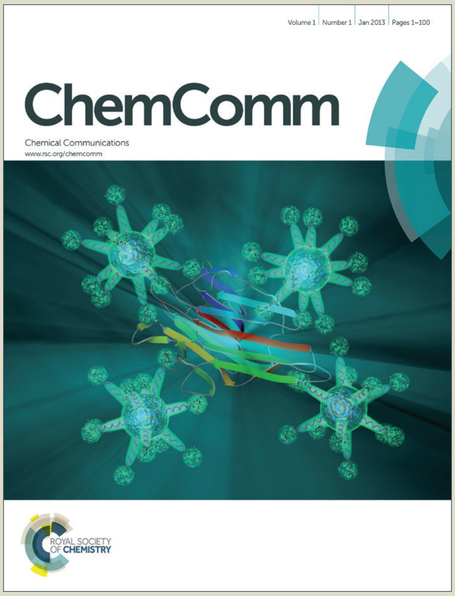

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Organosilicon Platform: Bridging Homogeneous, Heterogeneous, and Bioinspired Catalysis

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Organosilicon compounds, in the forms of cubic metallasiloxane, cage-like silsesquioxane, macromolecular nanocages, and flexible structures such as dendrimers and linear metallsiloxanes, have found useful applications as catalysts, ligands for metal complexes, and catalyst supports. Illustrative examples of these are presented. The well-defined structures of these compounds make them particularly suitable as molecular analogues for zeolites or silica-supported catalysts. An unique feature of many of these compounds is the presence of flexible siloxane bonds, which accommodates large fluctuations in the framework geometry, reminiscent of the adaptability of enzyme in undergoing conformational changes, and distinguishes siloxane containing material from carbon based synthetic materials. New preparative pathways and the use of the versatile silyl ester as a protection group have greatly expanded synthetic possibilities, pointing to the possibility of assembling these structures to form multifunctional catalytic structures. Some nanocage structures, with functionalities organized in close proximity, exhibit nanoconfinement effects.

1 Introduction

The last decade of nanotechnology has ushered in unprecedented growth in the synthesis and characterization of advanced organosilicon material. Since many of these materials are derived from compounds that possess complementary structural and functional properties, their assembly into a single structure could result in interesting intramolecular interactions and introduce new opportunities to design novel catalytic materials for targeted applications. The emergence of mesoscale science as an important area of exploration[1-3] further gives impetus to explore these structurally and functionally diverse nano building blocks as material platforms for catalyst synthesis. Thus, a review of the synthetic possibilities of some representative organosilicon compounds and structures, and an examination of the potential to integrate them into multi-functional, multidentate catalysts appears timely.

Organosilicon compounds have found applications in diverse areas such as medical devices,[4,5] protective coatings,[6,7] adhesives,[8, 9] sorbents,[10] lubricants,[11, 12] and catalysts. As a result of their broad range of applications, there exists a rich source of commercially available precursors and a plethora of detailed literature on their properties. For catalytic applications, researchers have leveraged this large selection of easily available compounds and tethered them onto silica-based materials such as MCM-41 and SBA-15 by either co-condensing with other precursor compounds or post-synthesis grafting. The literature on such modified silica material is extensive, and the subject has been reviewed.[13, 14] Therefore, it is beyond the scope of this review. Here, we focus on structurally well-defined siloxane and carbosilane materials as well as their hybrids, and examine their *synthesis and catalytic applications where the catalysis depends on the precise control of their composition and/or architecture.* The interest in this particular area stems from the fact that a vast array of these materials have complementary attributes that, when integrated appropriately, could be exploited to tune catalytic properties.

Catalytic reactions are multi-step processes that start with adsorption of reactants and end with desorption of products. Often the various steps of the reaction sequence are best satisfied by an active site ensemble with multiple functionalities. Natural enzymes achieve this by having an array of functional groups in close proximity, which not only perform separate designated tasks but also interact collaboratively in a confined space to result in reactivity that far exceeds those of the individual components. Another essential fundamental feature in enzymes is their ability to undergo conformational changes such that the topology of the array of key functional groups changes throughout the reaction cycle. Successful emulation of natural enzymes would require incorporation of both critical features into the catalytic structure. Organosilicon compounds appear to be promising candidates for this.

This review is organized as follows. The next section is a brief overview of the structural properties of Si–O and Si–C bonds that are relevant to the understanding of the materials to be discussed. This is followed by the bulk of the review where illustrative examples of siloxanes and carbosilanes that have been investigated as catalytic materials are discussed. The materials are organized loosely around their relative structural rigidity. Only illustrative examples will be discussed. This is followed by a brief review of the commonly used chemistry to create functional silicone and carbosilane building blocks. The paper will conclude with a few suggestions of how to integrate the various aspects of rigid and flexible organosilicon structures to yield novel catalytic materials.

2 Structural properties of Si–O and Si–C bonds

Both carbon and silicon are Group IV elements in the periodic table and share many common properties. A Si–C bond is strong and only slightly weaker than a C–C bond. The mean bond-dissociation enthalpies for $Si(CH_3)_4$ is 316.4±2.2 $kJmol^{-1}$ vs. 366.9±0.3 for $C(CH_3)_4$.[15] Since a Si–C bond is longer than a C–C bond (1.89 Å vs.1.54 Å), the Si atom is less sterically hindered than its carbon counterpart.[16] Carbon is more electronegative than silicon,[17] which is manifested in a reversal of the polarity of a $Si(\delta+)H(\delta-)$ bond as compared with a $C(\delta-)H(\delta+)$ bond.[18] This also translates to the fact that a Si–C bond is polar. Substituents on both Si and C strongly affect the polarity and stability of a Si–C bond, with the bond being more stable when the substituents on C are positively charged and/or when those on Si are negatively charged.[19] The Si–C–H or Si–C–Si angle does not deviate substantially from the tetrahedral angle: the Si–C–H angle is 111.0 ± 0.2° for tetramethyl silane[20] and the skeletal angle for polysilapropylene is ~110°.[21]

Compared to Si–C and C–C bonds, the structural differences between a Si–O and a C–O bond are much larger. Whereas C–O bond lengths in most aliphatic ethers are close to the sum of the covalent radii of the constituent atoms,[22] the Si–O bond length is significantly shorter. Instead of 1.83Å, many Si–O bonds of organosiloxane fall between 1.63 and 1.67Å.[23] The Si–O–Si bond angle in siloxanes range from 130-150°, which is significantly larger than the 105-115° range for C–O–C angles in aliphatic ethers.[24] The O–Si–O angles vary within a narrow range between 110-120°.[23] It is this asymmetry and the large, open, and variable angle of the Si–O–Si bond that give rise to the unusual conformational flexibility of siloxane polymers. Another interesting property of the O atom in the siloxane bond is its unusually low basicity[25] even though it is highly anionic. This reduced basicity has been attributed to $d\pi$-$p\pi$ conjugation,[26] the ionicity of the Si–O bond,[27] and enhanced hyperconjugative delocalization from the oxygen lone pairs into adjacent antibonding SiH or SiC orbitals.[28, 29] That siloxane bonds are unusual is also reflected in its physical properties. Grabowsky et al. noted that "[there are] only 6 out of 1553 siloxane compounds in the Cambridge Structural Database in which the siloxane oxygen electron lone pair serves as a H-acceptor for a classical hydrogen bond of the type O–H…O or N–H…O".[30]

The difference between Si and C is also reflected in the properties of the silanol vs. alcohol functionality. One difference is that silanol is not as strong a hydrogen-bonding group as alcohol. Whereas the conformation of 1,3-propanediol is strongly affected by intramolecular H-bonding,[31-33] the interaction is weak between silanol groups of tetraphenyl-(or tetramethyl)disiloxanediol, as indicated by the fact that the stretching frequencies of these silanol groups are similar to that of triphenyl (or trimethyl) silanol.[16] The weak hydrogen bonding between vicinal silanols is also observed on a dehydroxylated silica surface: one sharp IR band was observed, even though vicinal silanols accounted for half of the reaction of $Ga(CH_3)_3$ with the surface to form a disilanolate-bridged digallium species $[(CH_3)_2Ga(\mu\text{-}OSi)]_2$.[34]

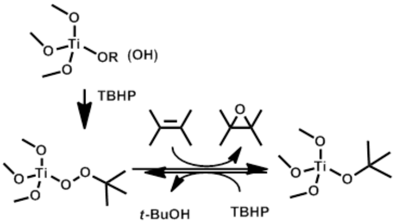
3 Catalytic Structures

Although many interesting organosilicon compounds have been synthesized, extensive studies have been mainly on their structural and not catalytic properties,[35-38] suggesting that there are ample opportunities for further fruitful investigation in the latter area. The catalytic examples in this article are chosen for two purposes. One is to illustrate how a monodisperse, structurally-defined material can be exploited as a platform to construct catalysts to yield insightful mechanistic and/or active site information unattainable with more conventional but complex heterogeneous systems. The other is to demonstrate how controlled placement of functional groups can result in unusual catalytic performance and/or active site properties and how this can be accomplished in a convenient manner using platforms derived from siloxane chemistry.

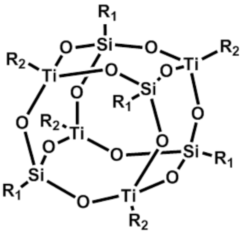
For the purpose of organization, the materials are grouped into cage-shaped "rigid" structures with or without peripheral reactive groups, macromolecular nanocages with internal reactive functionalities whose mobility is restricted due to spatial constraint, and other flexible structures which include carbosilane dendrimers and linear siloxanes. It is understood that the degree of structural rigidity spans a continuum, and the division here is arbitrary. Even those that fall within the group of rigid structures can undergo dynamic structural deformation because of the flexible Si–O–Si bonds. However, because the 3-dimensional construct places limits on the fluxional freedom, these structures are more rigid than 2-dimensional structures.

3.1 Cage-shaped "rigid" structures with or without peripheral reactive groups

There are two types of cage-like siloxane structures: one in which a foreign metal is in the siloxane structure, and another in which the foreign metal is appended to the siloxane structure. The former, also referred to as heterosiloxanes or metallasiloxanes, can be formed with main group elements[39] or transition metals.[40] One structure of particular interest here is a cubic metallasiloxane in which the Si atoms at alternate corners of a Si_8O_{12} polyhedron are replaced by another metal M to form $M_4Si_4O_{12}$. Because this is a well-defined structure with known bond lengths, bond angles, and atomic positions, it has been investigated extensively as models for heterogeneous catalysts such as synthetic zeolites or supported metal catalysts. For example, structure **1**, a Ti_4Si_4 heterocubane, has been investigated as a model for titanosilicate in the catalytic epoxidation of cylcohexene.[41] In the presence of **1**, cyclohexene was epoxidized to cyclohexene oxide by *tert*-butyl hydroperoxide (TBHP) at room temperature in a dichloromethane solution with 61% yield after 21h.[42] The catalytic cycle, as depicted in Scheme 1,[42] in which the titanium (hydroxide) alkoxide species reacted with TBHP to form the titanium *tert*-butylperoxide, had previously been accepted in its general form without direct detection of the proposed intermediates.[43, 44] The validation of the reaction mechanism through isolation and characterization of key intermediates was achieved using structure **1** because of its well-defined structure.



Scheme 1. Catalytic cycle of epoxidation of olefin by titanosilicate catalysts. (Adapted with permission from Ref. [42], Copyright 2002, Elsevier)



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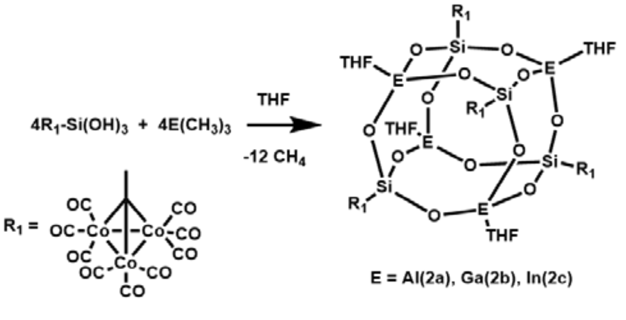
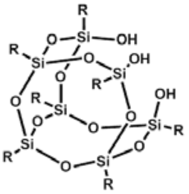
Converting alkene to aldehyde by hydroformylation is a process of commercial interest, and cobalt on zeolites is known to be an active catalyst.[45, 46] Roesky's group synthesized structures analogous to cobalt clusters on a zeolite by reacting equimolar quantities of tricobalt nonacarbonyl methylidyne silanetriol and group 13 metal trimethyl (Al, Ga and In) in THF to form compounds **2a**, **2b** and **2c** as shown in Scheme 2.[47] In these structures, there was one Co_3-$(CO)_9C$ cluster unit at each silicon atom at the alternating corners of the cube. All three complexes (**2a-c**) were active in the hydroformylation of 1-hexene in a biphasic system, with the Al and Ga-containing heterosiloxanes being more active than the In analog. The observed ratio of the linear/branched aldehyde also differed and followed the trend Al>Ga>In, with the latter showing the highest selectivity to the isomerization products. The data suggested that hydroformylation and isomerization proceeded in parallel. Analyses of the reaction mixtures with FTIR before and after reaction indicated that the $Co_3(CO)_9C$ cluster units in **2a** and **2b** decomposed into $Co_2(CO)_8$ in solution during the catalytic process. In contrast, catalyst **2c** underwent structural transformation such that a new absorption band at 1995 cm^{-1} was produced that was different from $Co_2(CO)_8$. This suggested that the active catalytic species was not a $Co_2(CO)_8$ fragment of catalyst **2c**, but some skeletal rearrangements of the $Co_3(CO)_9C$ unit.[47]



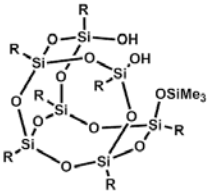
Scheme 2. Synthesis of Group 13 heterosiloxanes $[Co_3(CO)_9CSiO_3E.THF]_4$. Adapted from Ref. [47], copyright American Chemical Society 1996.

Lewis acid catalyzed addition of cyanide group to carbonyl compounds to form cyanohydrins is an important carbon-carbon bond formation reaction.[48] It has been reported that electron-withdrawing silanol ligands, when combined with group 13–15 metals, resulted in increased acidity and hence improved catalytic performance.[49] This information was the basis for the design of a highly active Lewis acid catalyst by the group of Roesky. They synthesized a cage-structured Bi-siloxane that exhibited superior catalytic activity for the addition reaction of trimethylsilyl cyanide (TMSCN) with aldehyde or ketone to form cyanohydrin trimethylsilyl ethers.[35]

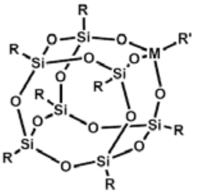
When the cage framework is composed entirely of Si–O–Si bonds, the structures are known as polyhedral oligosilsesquioxanes (POSS) $[RSiO_{1.5}]_n$ or spherosilicates $[ROSiO_{1.5}]_n$, where R is an aliphatic or aryl group. Incompletely condensed POSS is a structure where one or more Si atoms are missing from the cage structure to generate reactive Si–OH groups, such as structure **3a**. Heterofunctional condensation of one of these silanols with chlorosilane generates **3b,** and bonding of all three siloxy ligands to another metal forms a metallasilsesquioxane **3c**. These organosilicate cage compounds are structurally and compositionally very well defined. They differ from the metallasiloxanes in that the Si–O–Si framework is much more flexible than the M–O–Si framework (*vida supra*). This flexibility uniquely accommodates skeletal deformation and accounts for the fluxional behavior of the structures that can be detected readily by variable temperature NMR.[50-53] It also permits equilibration of defined structures of monomers and dimers,[54] as well as formation of stable bulky trimeric structures.[53] The implications of these to the catalytic properties will be discussed when a broad range of these catalytic structures is examined.



3a

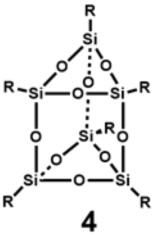


3b



3c

Incompletely condensed POSS is deemed an excellent molecular model for silica surfaces as it possesses an extensive SiO framework, [55] and the isolated and vicinal silanols located at the corners of the incompletely condensed POSS have similar environments [56] and pKa values[57] as their counterparts on a silica gel surface. However, in general, because of the lack of functional groups, completely condensed POSS is not chemically or catalytically active. Nonetheless, silsesquioxane with strained Si_3O_3 six-member siloxane rings **4** catalyzed radical polymerization of methyl acrylate, similar to a SiO_2 sample that had undergone prolonged dehydration at 600^{o}C.[58]



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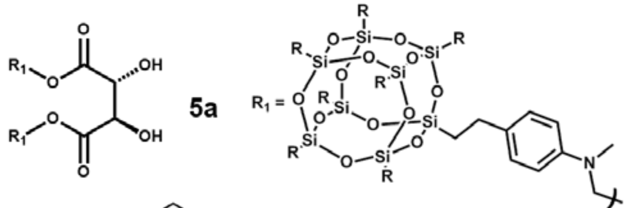
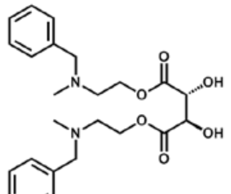
The silanol groups of incompletely condensed silsesquioxane can be coupled to different organic or organometallic compounds to form many catalytically interesting materials. Furthermore, with a judicious choice of solvents, these materials can be used as homogeneous catalysts and yet recoverable by precipitation or phase segregation by simply changing solvents after reaction.[59] An example of POSS derivatization for catalytic application comes from the work of Garcia, et al.,[59] who modified chiral dimethyl tartrate with POSS to form structure **5a** that can be used as a bulky ligand to influence enantioselectivity. The activity and selectivity were compared with another modified dimethyl tartrate **5b** without the pendant POSS side chain. When mixed with an equilmolar quantity of $\mathrm{Ti(O}\mathit{i}\mathrm{Pr)_4}$, both **5a** and **5b** were able to use TBHP as an oxidant and effected the asymmetric epoxidation of cinnamyl alcohol. The enantioselectivity was reversed for **5a** when compared with **5b** and other modified tartrate ligands investigated. This enantioreversion was attributed to the large size of the POSS ligand. Another example of enantioselective catalysis using POSS modified with organic chiral groups is one in which a silsesquioxane functionalized with chiral menthol derivative was used to catalyze diastereoselective [2+2] photoaddition.[60]

In addition to modifying silsesquioxane with organic groups, there is also a substantial effort to construct metallasilsesquioxanes for catalysis. Besides being superior homogeneous catalysts,[61] these metallasilsesquioxanes also serve as excellent molecular analogues of single-site heterogeneous catalysts.[58] One interesting property pointed out by Feher is that, whereas the geometric arrangement of ligands around a metal complex is often directed by the metal, the silanols of incompletely condensed POSS structures direct the bonding to the metal, similar to silanols on a silica surface.[55] Metallasilsesquioxanes have been examined as catalysts for many different reactions including epoxidation, Lewis acid catalyzed addition, and polymerization. The tremendous interest in epoxidation was spurred by the discovery that TS-1, a crystalline titanosilicate where isolated Ti cations are tetrahedrally substituted into the siliceous framework of the MFI structure, is an effective epoxidation catalyst.[43] Since then, other microporous structures that can accommodate Ti in the framework were found to be good epoxidation catalysts also, such as Ti-Beta[62] and Ti-MWW.[63] Later, the list expanded to include Ti embedded in mesoporous molecular sieves such as MCM-41[64] and MCM-48.[65] This general observation, that isolated Ti in a siliceous matrix is active for epoxidation, gave rise to a great impetus to use soluble analogues to better understand the reaction mechanism and active site structure in these heterogeneous catalysts, and Ti-silsesquioxane serves as an ideal model compound for such studies.





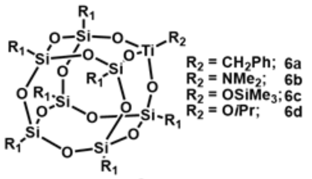
5b

The large volume of studies using Ti-silsesquioxane model compounds has generated significant insights on the solvent, steric, and electronic effects in the Ti epoxidation systems. The study by Crocker et al. illustrated the versatility of POSS derivatives for such investigations. [66] They formed mononuclear Ti complexes of different Ti environments by reacting **3a** (R= *c*-hexyl) with different Ti precursors. Reaction with 1 equivalent of $\mathrm{Ti(R_2)_4}$ generated a tripodal complexes **6**, $\mathrm{[TiR_2[(c\text{-}C_6H_{11})_7Si_7O_{12}]]}$ where $\mathrm{R_2}$= $\mathrm{CH_2Ph}$ (**6a**), $\mathrm{NMe_2}$ (**6b**),$\mathrm{OSiMe_3}$ (**6c**), or O*i*Pr (**6d**). Reaction of 1 equivalent of $\mathrm{Ti(O}\mathit{i}\mathrm{Pr)_4}$ with **3b** yielded complex **7**, and reaction of 2 equivalents of $\mathrm{Ti(CH_2Ph)_4}$ with **3b** yielded the tetrapodal Ti bis(silsesquioxane) complex **8**. These complexes were active as catalysts for the epoxidation of 1-octene with TBHP as shown in Table 1.

Table 1 Epoxidation of oct-1-ene with TBHP catalyzed by titanium silsesquioxane complexes.[66] T= 80°C, Ti=0.2 mmol and oct-1-ene (75 g) as solvent.

Catalysts	$10^2 k_2$/dm^3 mol^{-1}s^{-1}	Selectivity to epoxide[a] (%)
6a	123	95
6b	63	99
6c	97	97
6d	149	93
7	9.3	75
8	4.7	83
Ti-MCM41[b]	2.6	94

a. Selectivity = (mol 1,2 epoxyoctane/mol TBHP). b. Ti content=1.43 mass%.



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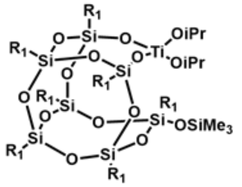

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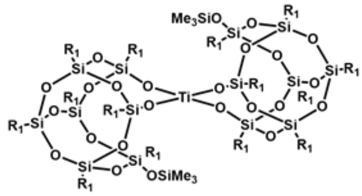

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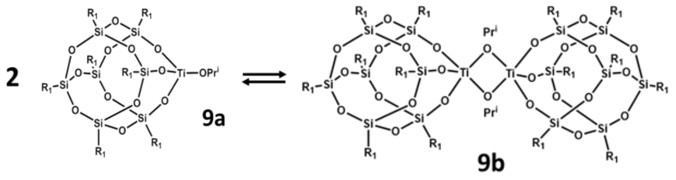
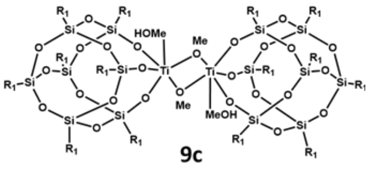
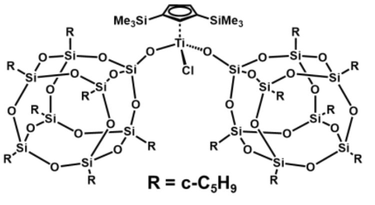
Under these conditions of high alkene/TBHP and constant Ti concentration, the rate was pseudo first order in TBHP. The pseudo first order rate constants varied by a factor of ~25 among the complexes. Importantly they were all higher than Ti-MCM41. The catalysts were highly selective for the epoxide product. The variation in the activities among these Ti complexes can be understood by invoking both electronic and steric effects. With regard to the electronic effect, we speculate that ancillary ligands that donate electrons to Ti decrease the electronegativity of Ti, and thus the overall Lewis acidity and the activity. That is, complexes bearing more electron donating substituents are less active than those bearing less donating groups. With its lone pair electrons, the $\mathrm{NMe_2}$ ligand **6b** exerts the most negative effect on the electronegativity of Ti and the activity. Due to the polarity of the Si–O bond, $\mathrm{OSiMe_3}$ would provide a more anionic electrostatic influence on the Ti, thus negatively affecting the activity. The significant decrease in activity of complex **7** compared with complexes **6a-d** also has an electronic argument due to the loss of one silsesquioxane bond. It has been proposed by Feher that the electron withdrawing tendency of the silsesquioxane core is equivalent to that of a $–CF_3$ group.[67] Thus, replacing one siloxy bond to the silsesquioxane core by –O*i*Pr in complex **7** would reduce the electron withdrawing effect of the silsesquioxane core on the Ti, causing the activity to drop precipitously. The Ti center of complex **8**, with four siloxy bonds, should be highly electronegative and yet it exhibited low activity. In this case, we postulate that the steric effect was likely the controlling factor as Ti was flanked by two bulky silsesquioxane ligands. That Ti-MCM41 was the least active suggested the importance of accessibility to Ti on the activity.

Another interesting property of titanosilsesquioxanes was reported by Maschmeyer et al.[54] using (*c*-pentyl)$_7Si_7O_9Ti$(O*i*Pr) **9a**, a four-coordinated monomeric Ti complex. As prepared, the fresh sample was monomeric. Upon storage in a $CDCl_3$ solvent, it began to equilibrate with the dimeric 5-coordinated Ti complex **9b**.[58, 68] Apparently, the monomeric form is the kinetic product, but the dimeric form is also thermodynamically possible. The coexistence of the two forms is a consequence of the flexible Si–O–Si bonds that readily accommodate the changes in the bonding of Ti to the silsesquioxane framework. Addition of MeOH to the mixture of complexes **9a** and **9b** in $CDCl_3$ converted the complex into a six co-ordinated Ti complex, **9c,** which had been confirmed by single crystal X-ray diffractive analysis for a silsesquioxane with c-hexyl as the R groups. All three complexes were active for epoxidation of cyclohexene with TBHP and were all more active than Ti-MCM41. Surprisingly, the six co-ordinated complex **9c** was more active than the mixture of complexes **9a** and **b**. The reason for the reactivity differences was proposed to be due to the accessibility of the Ti active site. To confirm this, Maschmeyer et al.[54] tested a series of titanosilsesquioxanes with methoxy, butoxy and isopropoxy groups at the fourth coordination site and observed that their reactivity indeed correlated with the degree of steric hindrance of the ligand. This result is also in line with the observations in the heterogeneous system in which Ti embedded into the MCM-41 framework was a less active catalyst than Ti grafted onto the surface.[69, 70]





POSS has also been used to anchor titanocene complexes for polymerization catalysis. For these systems, essential information of interaction between catalyst and co-catalyst (which impacted on system stability) had been generated from model catalysts. Duchateau et al.[57] tested complexes **10-12** for ethylene polymerization with different cocatalysts. Complex **10**, a monochloride was active for ethylene polymerization in the presence of methylaluminoxane (MAO) as cocatalyst. This indicated that at least one of the siloxy bond had been substituted. Complex **11** also exhibited ethylene polymerization activity in the presence of MAO, suggesting that even the chelating effect of the silsesquioxane ligands was not sufficient to prevent the substitution of Si–O–Ti by a Si–O–Al bond. The observed structural instability was consistent with the work of the group of Soga,[71] who demonstrated significant titanium leaching when silica-supported $(C_5Me_5)TiCl_3$ was treated with MAO. However, the stability issue can be resolved by replacing the MAO cocatalyst. When $B(C_6F_5)_3$ or $BArF_3$ was used as a co-catalyst for complex **12**, stable activity was observed for ethylene and hexene polymerization. In addition, the narrow molecular weight distributions of poly-1-hexene was consistent with the model that complex **12** formed a single site catalyst when activated with $B(C_6F_5)_3$.



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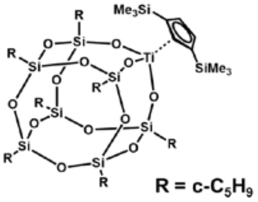

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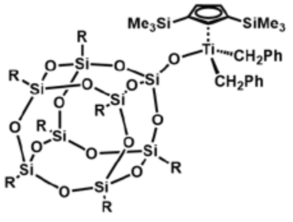

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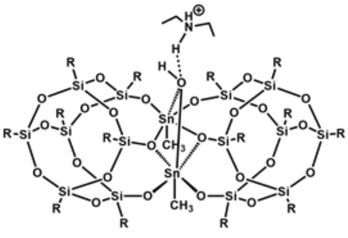

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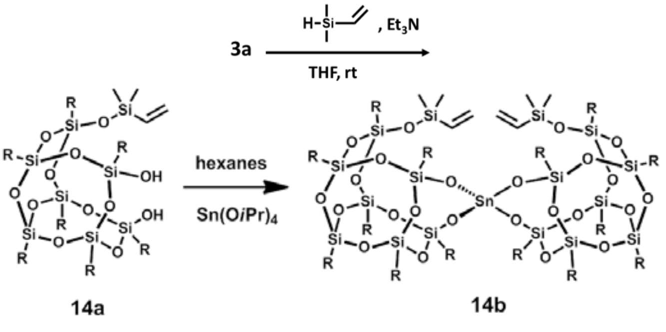
With properties similar to Ti, Sn can also be incorporated into a zeolitic framework to form active and selective catalysts. Sn-beta is a versatile Lewis acid catalyst, capable of effecting reactions such as the Baeyer-Villiger[72] and Meerwein-Ponndorf-Verley-Oppenauer redox equilibrium.[73] Recently, it has been shown to be active in glucose isomerization to fructose,[74,75] where the active site is believed to be a substitutional Sn in the structure, that is, an isolated Sn surrounded by four siloxy bonds or three siloxy and a hydroxyl. Thus, stannasilsesquioxane is a logical structural model to study the active site and the reaction mechanism of this system. However, for reasons yet to be revealed, few successful syntheses of tetrahedral Sn(+4)-silsesquioxane have been reported. Feher et al.[76] synthesized a corner-capped CH_3-stannasilsesquioxane by reaction of CH_3SnCl_3 with $R_7Si_7O_9(OH)_3$, where R= *c*-pentyl, *c*-hexyl, or *c*-heptyl, and triethylamine was added as the chloride scavenger. This structure was also observed in our laboratory when CH_3SnCl_3 was reacted with (*i*-butyl)$_7Si_7O_9(OH)_3$ in the presence of a stoichiometric amount of diethylamine. However, when excess amine was used, a dimeric Sn complex, **13**, was formed.[77] Based on single crystal X-ray crystallography analysis, the structure of **13** was shown to consist of two octahedrally co-ordinated Sn where each Sn atom was ligated to four siloxy ligands and an ancillary methyl ligand, and linked to each other by an $N(C_2H_5)_2H_2^+OH^–$ bridge. ^{119}Sn NMR showed Sn resonance at -534 ppm indicating rapid exchange of the ammonium bridging ligand at the NMR time scale. It dissociated to form the monomeric corner capped CH_3-stannasilsesquioxane species at high temperature in DMSO. The Sn species formed by reaction of silsesquioxane with CH_3SnCl_3 is different from Sn-beta catalyst as the ancillary methyl ligand is stable under reaction conditions. Hence it is not a realistic model for Sn-beta.

Other attempts to form tetrahedral stannasilsesquioxane with $SnCl_4$ were reported to be unsuccessful. Even though (c-$C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ reacted with metal halide precursors such as $TiCl_4$ and $ZrCl_4$ to selectively form the corresponding $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2M$ (M = Ti, Zr), its reaction with $SnCl_4$ produced ill-defined products.[53] Reaction of $(c\text{-}C_5H_9)_7Si_7O_9\text{-}(OH)_3$ with an equimolar amount of $SnCl_4$ in toluene in the presence of NEt_3 did not result in the expected $[(c\text{-}C_5H_9)_7Si_7O_{12}]SnCl$. Instead, an ionic trimer $[[(c\text{-}C_5H_9)_7Si_7O_{12}Sn]_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl]^-[HNEt_3]^+$ was formed in which Sn was octahedrally co-ordinated, and the chloride bridges could be hydrolyzed and replaced with hydroxyl bridges.[53]

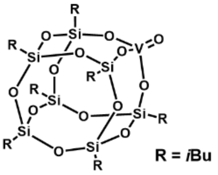
Hypothesizing that the amine added to scavenge chloride may interfere with the formation of defined stannasilsesquioxane structure, we explored using a $Sn(OiPr)_4$ precursor. Vinyldimethylchlorosilane was reacted with **3a** (R=*c*-hexyl) to form the disilanol **14a** as is shown in Scheme 3. Then half an equivalence of $Sn(OiPr)_4$ was added to **14a** to form **14b**. The structure of **14b** was verified using ^{119}Sn NMR, EXAFS and single crystal XRD. The ability of **14b** to catalyze isomerization of glucose to fructose was examined in a mixed solvent system of benzene and DMSO at 100°C. Under reaction condition but in the absence of **14b** catalyst, glucose alone was stable for prolonged period of time, although some dehydration of fructose to 5-(hydroxymethyl)-2-furaldehyde (HMF) was observed for fructose only reaction solution. When **14b** was added to the glucose reaction, fructose and HMF were detected. The HMF yield in the **14b**-catalyzed glucose conversion was higher than that observed in the fructose solution, indicating that catalysis over the Sn catalyst contributed to the HMF yield. This was unexpected since no HMF was formed over a Sn-beta catalyst, and the reaction is a Brønsted acid catalyzed dehydration. By conducting the reaction in a N_2 atmosphere, we eliminated the possibility of DMSO oxidation to methanesulfonic acid as the source of Brønsted acid. Furthermore, no HMF was produced from glucose in the absence of the catalyst. Anchoring complex **14b** via hydrosilylation onto silica that had been surface functionalized with hydrosilane generated a heterogeneous catalyst that could be dispersed in a water-ethanol solution of glucose. This reaction system also yielded significant amounts of HMF, suggesting that Brønsted acidity might be an inherent property of complex **14b**.



Scheme 3 Synthesis of tetrahedral stannasilsesquinoxane.

The last example of metallasilsesquioxane is vanandium (V) silsesquioxane **15**. Loavat et al.[78] used **15** for room temperature oxidation reactions using cumyl hydroperoxide (CHP). In the oxidation of triethylamine to triethylamine oxide, a sigmoidal conversion versus time profile was observed, suggesting that the reaction was facilitated by the binding of the product to **15**. From the results of a series of coligands of different basicity, the authors proposed that rate enhancement in the oxygen transfer reaction by some of the coligands was due to stabilization of the η^2-peroxometal intermediate responsible for the oxygen transfer process. In other cases, the positive effect of the coligand was in stabilizing complex **15** from degradation by reaction with the byproduct H_2O formed in the oxidation reaction. Their study successfully deconvoluted the effect of the complex interactions between reactants, products and coligands on the activity and stability of the catalytic system.

We conclude this section with a different cage structure than POSS. A linear siloxane of a targeted length can be formed by stepwise condensation of chlorosilane with silanol, followed by oxidation of hydrosilane to generate a new silanol.[79] When coupled with using dichlorosilanes for branching and phenyl ligands that can be converted to bromo ligands for additional branching points, a cage-like bicyclic siloxane **16** has been synthesized.[80] Because the phenyl ligands can be introduced at predetermined siloxane units, the synthetic method permits functionalization at designated positions of the cage structure.



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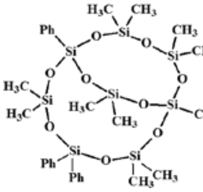
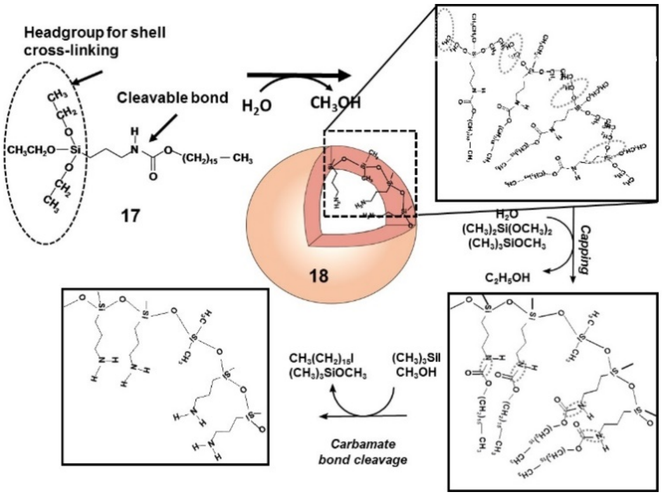


16

3.2 Macormolecular "flexible" nanocages with spatially constrained internal reactive functionalities

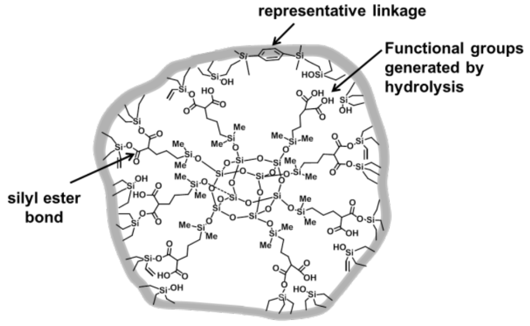
Macromolecular cage-like structures, much larger than cubic silsequioxanes, have been prepared that are more like shells or core-shells, such as structures **18** and **19**. The common method to prepare these structures is by templating. In order to create the interior cavity or detached core from the shell, the template needs to possess a bond that can be cleaved without destroying the rest of the structure. For cavity generation, fragmentation of the template should result in small molecular segments that can exit through the porous shell. Through judicious choices of the template and the cleavable bond, both the size of the cavity and the nature of interior functional groups can be predetermined. Literature reports of shell cross-linked cages usually are much larger and possess thicker shells[81, 82] than **18** and **19**, which are molecular-sized with atom-thick shells. The presence of the flexible Si–O–Si linkages in either the shell in **18** or the core of **19** is probably a vital factor in the efficient formation of the atom thick shell as these flexible bonds help accommodate the continuous changes in the structural configuration during the shell cross-linking process. Detailed synthesis, characterization and application of **18** and **19** are presented below.

The nanocage **18**, synthesized using Scheme 4, used a surfactant micelle as template.[83] The surfactant possessed a headgroup that could be polymerized into a porous, cross-linked shell, and a hydrophobic tail that could be fragmented by bond cleavage and converted into a functional group.[83] Carbamate linkage, which had been employed for the synthesis of a different structure by Katz et al.,[84] was chosen as the cleavable bond for this structure. The cleavage could be accomplished by reaction with trimethylsilyliodide by first forming trimethylsilylcarbamate, which could undergo alcoholysis under mild conditions to produce an amine. In the nanocage synthesis, the surfactant was designed such that after the cleavage reaction, the amine formed would be tethered to the shell, while the tail, liberated from the surfactant in the form of a linear $CH_3(CH_2)_{15}I$, would diffuse from the cage through the porous shell. The diameter of the cage was determined by the size of the surfactant and micelle, and estimated to be ~2 nm by dynamic light scattering (DLS) and transmission electron microscopy (TEM) when a propylcetylcarbamate surfactant was used. This is a dimension that nanoconfinement effect could be present. Indeed, its interior amine groups, numbered around 8 per cage on the average, exhibited a remarkable pK shift. Using binding of amine ligand to Au cation in $Au(NH_3)_{4-x}Cl_x^-$ (n=3-x) as an indicator, the pK for protonation of the interior amine groups was found to shift by 4-5 pH units to an equivalent pH of 3 to 4.[85] Although pK shift of such a magnitude is not uncommon among enzymes and is essential for their catalytic activities, this reported pK shift appears to be among the largest reported for artificial systems.[86-88] This effect arises because only a limited number of similarly charged groups can be accommodated in the restricted space due to charge-charge repulsion and the dearth of charge-shielding solvation molecules. Influence of the molecular-size cavity on sequestered catalytic groups was also manifested in enhanced activity and altered selectivity in the amine-catalyzed decarboxylation of acetoacetone. When compared with amine in free solution,[83] the turnover frequency was higher by about seven times for amines in the nanocage, and the initial selectivity was much higher for the secondary product dimethoxypropane. Presumably, the reactant was concentrated in the cage due to attractive interaction with the siloxane shell, such as hydrogen bonding between carbonyl and amine and van der Waals interaction, resulting in enhanced activity. Likewise, similar interaction led to a longer residence time of the product acetone near the amine, promoting its subsequent reaction that resulted in the higher selectivity for the secondary product dimethoxypropane. In addition to these attributes, the cross-linked, porous siloxane shell limited access into the cavity, effecting molecular size-selectivity.



Scheme 4 Synthesis of nanocage **18** using a micelle template of surfactant **17** that possesses a cleavable carbamate bond. Reproduced with permission from ref. [83]. Copyright American Chemical Society 2006.

The second example is a core-shell structure **19**. It was constructed with a derivatized spherosilicate as the template according to Scheme 5.[89] The hydride at every corner of the commercially available $[SiO_{1.5}R]_8$-$(OSiMe_2H)_8$ was used to couple to malonic acid to form a spherosilicate with 16 carboxylic acid groups at the periphery (**20C**). These acids were further derivatized via silyl ester formation with trivinyl silyl chloride to result in **20d**. Cross-linking to form the shell of a nanosphere was accomplished by hydrosilylating the forty eight peripheral vinyl head groups of **20d** with 1,4-*bis*(dimethylsilyl)benzene. The choice of the linker was based on the rationale that its size and rigidity would reduce the probability of nonproductive cyclization of C=C of the headgroups.[90] The hydrodynamic radius of the nanosphere was between 6.4 and 7.4 nm as determined by dynamic light scattering, and this was in line with the small angle X-ray scattering (SAXS) results which showed that the radius of gyration was 2.1 nm at a low concentration, but increased to 5.0 nm at higher concentrations, possibly due to interparticle adhesion. Partial cleavage of the silyl ester bonds generated a functionalized nanocage **19**, where the dimension of the space between the core and the shell would foster nanoconfinement effects. This was manifested in the reaction of **19** with $Co_2(CO)_8$. Oxidative decarbonylation of $Co_2(CO)_8$ took place within the confined space, and both Co(0) atoms in the carbonyl were oxidized to Co(I), while the dicarboxylic acid groups become carboxylate anions presumably ligated to Co(I).[91] That Co(I) could be stabilized without further oxidation to Co(II) was an indication that the spatially and sterically constrained Co atoms were prevented from reaction with other carboxylic acid groups in the confined space of the cavity. It is unusual to stabilize metal atoms at an uncommon low oxidation state, but the Co(I) formed remained stable in an inert atmosphere.

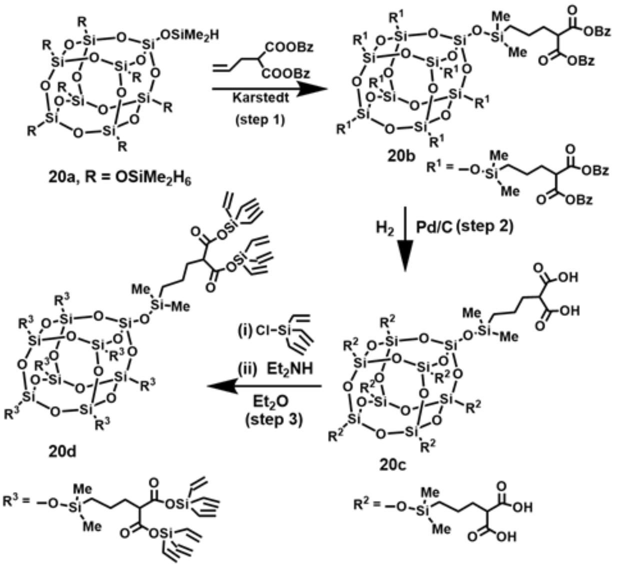


19

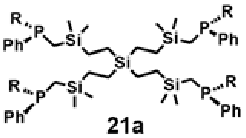
3.3 Other flexible structures: carbosilane dendrimers and linear metallasiloxane

Siloxanes form many other structures in addition to cages. Here we focus on two: dendrimers and short, linear, multifunctional oligomers. Dendrimers are hyperbranched, symmetrical, monodisperse macromolecules. They have well-defined compositions, and their modular construction allows for easy tuning of the density of functional groups. In some flexible dendrimer structures, back-folding may occur resulting in more disordered conformation. This occurs because the peripheral functionalities interact with each other weakly or have strong attraction for the interior functional groups.[92] Among the silicon-based dendrimers, the family of carbosilane dendrimers all have interior that are void of functionalities and differ generally only by the number of $–CH_2$ spacers. Thus, they do not have backfolding problems,[93] and their morphology is relatively well defined. In general, the dendritic wedges are not covalently linked to each other and the intramolecular interaction between them is weak. Therefore, these dendrimers are conformationally quite flexible compared with the cage structures. Nonetheless, they are less flexible than the linear siloxanes. For the latter structure, there is little constrain on its conformation. Thus, when both ends of the chain are functionalized to chelate with metal ions, there could exist a distribution of chains and rings in solution.[94]

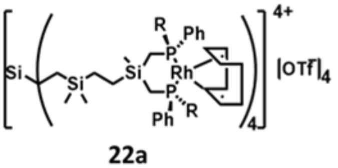
A number of carbosilane dendrimers have been examined as catalysts. In many cases, the dendritic structures exhibited similar catalytic properties or even a negative dendritic effect when compared to the small molecule analogues.[95-99] However, there are examples of positive dendritic effects and/or significant differences in catalytic behaviour. Rodríguez et al. synthesized P-stereogenic monophosphines terminated carbosilane dendrimers (**21a**) as ligands to Pd cations.[100] When used in the asymmetric hydrovinylation of styrene, the Pd-**21a**/NaBARF catalytic system yielded (R)-3-phenyl-1-butene as the predominant isomer, in contrast to its analogous small-molecule model system **21b**/NaBARF which yielded (S)-3-phenyl-1-butene. Surprisingly, **21a**/NaBARF was the only generation of dendrimer investigated that yielded the (R)-3-phenyl-1-butene enantiomer, and the authors indicated that further investigation is needed to understand this.

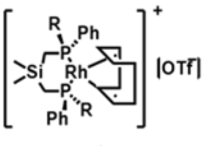


Scheme 5 Synthesis of spherosilicate template for structure **19**. Reproduced from ref. [89]. Copyright 2013 Royal Society of Chemistry.


21a

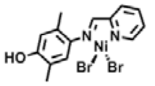

21b

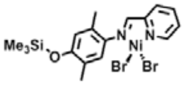

22a

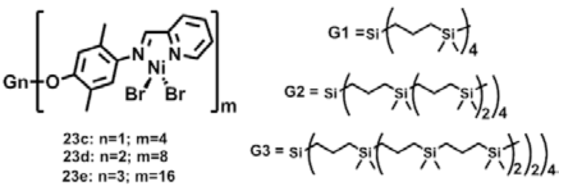

22b

The same group later extended their investigation to carbosilane dendrimers containing P-stereogenic diphosphine at the periphery.[101] These dendrimers were then used to form Rh complexes **22a** by reaction with dinuclear [Rh(μ-Cl)(η^4-cod)]$_2$ in the presence of silver triflate. The resulting complex was a catalyst for the hydrogenation of dimethylitaconate, and the product showed some enantiomeric excess. Structure **22a** was three times more active than the small molecule analogue Rh complex **22b**, but there was no difference in enantiomeric excess. The proposed reason for enhanced activity for the dendritic catalyst was that because of the larger volume of the dendrimer, bulkier species which may limit access to the catalytic center, like [Rh(diphosphine)$_2$]$^+$, would be less likely to be formed. Interestingly, no enantiomeric excess was observed if the carbosilane dendrimer was terminated with monophosphine functional groups.

Since the characteristic of a polymer product is very sensitive to the environment of the metal center in a late transition metal catalyst, Benito et al.[102, 103] investigated the generation effect of a dendrimer on the microstructure of the product polymers in ethylene polymerization. They used different generations of polycarbosilane dendrimers (**23c** to **e**) with peripheral N, N' iminopyridine groups as ligand to a NiBr$_2$, and synthesized small molecule analogues **23a** and **b** for comparison. They observed that the dendrimer generation had a strong effect on the catalytic activity as well as the molecular weight, oligomer/polymer distribution and microstructure of the polyethylene formed. As shown in Figure 1, the oligomer/polymer ratio was much higher for the two larger dendrimers than the other ligands. This was attributed to enhanced chain transfer process, possibly due to steric crowding by the dendrimer.


23a


23b



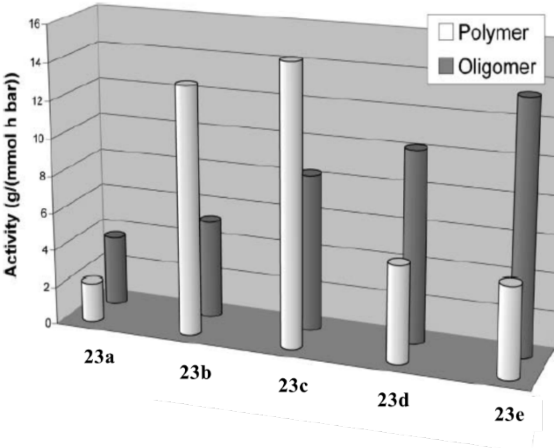
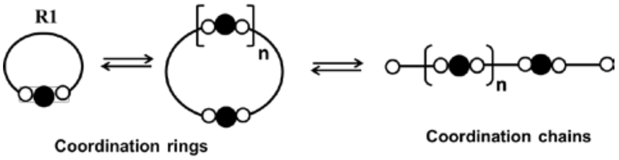


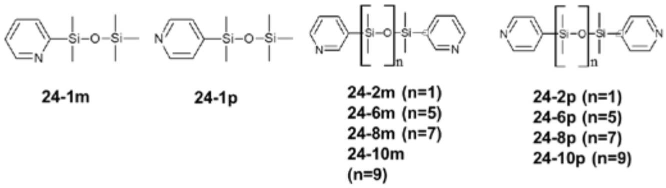
Figure 1 Ethylene polymerization activities and polymer oligomer distribution over Gn–[(ONNMe$_2$)NiBr$_2$]$_m$ catalysts and their small molecule analogue **23a** and **23**b. Adapted from ref. [102]. Copyright Royal Society of Chemistry 2005.

Multifunctional linear siloxane oligomers are interesting molecules because of the high degree of flexibility of the chain. When both ends of the chain are functionalized for chelation with metal ions, multiple rings and chains of different nuclearity and sizes can be formed, as shown in Scheme 6. The speciation depends on the chain length, nature of the functional groups, and concentrations of the siloxane and the metal. This was studied by Missaghi et al.[94, 104, 105] for the system *bis*(pyridyl)siloxane-Pd, which were complexes in which the ligands were linear methylsiloxane oligomers end-capped with pyridyl groups. Their stepwise synthetic methodology permitted varying the number of internal Me_2SiO spacer units in a controlled manner to obtain *bis*(pyridyl)siloxanes of desired lengths, and they prepared a series of ligands with 2-9 spacer units. One challenge in forming square planar complexes of Pd with bidentate ligands is the steric demand on the ligands to adapt a configuration with minimal ring strain for which the structural flexibility of siloxane offers advantages. It is expected that there would be an optimal chain length for the formation of a mononuclear bidentate ring complex in the square planar trans-configuration. When the chain was too short, there would be too much strain for ring formation. When the chain was too long, random motion of the chain would make it difficult for ring closure.

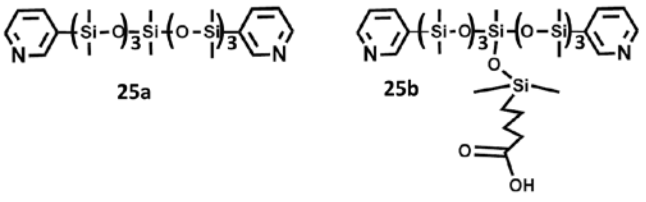


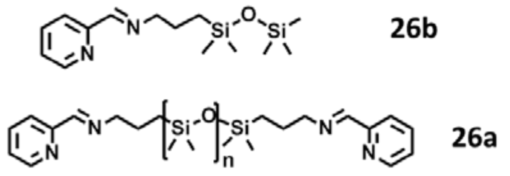
Scheme 6 Schematic representation of some of the various oligomers of $Pd(OAc)_2$ and *bis*(pyridyl)siloxanes

These *bis*(pyridyl)siloxane-Pd complexes were active catalysts for the aerobic oxidation of benzyl alcohol to benzaldehyde. The reaction proceeds via a Pd^{II}/ Pd^0 catalytic cycle and the aggregation of Pd^0 to form Pd black is a major cause of catalyst deactivation.[106] When Pd acetate is used as the catalyst, ligating pyridine is needed to stabilize the Pd^0 from agglomeration. However, effective suppression of the deactivation process requires pyridine in excess of the stoichiometric ratio of 2, which reduces the catalytic activity. Missaghi et al.[104] reasoned that *bis*(pyridyl)siloxanes could stabilize Pd more effectively than pyridine by providing steric protection of Pd^0 as a chelate and by increasing the local concentration of pyridyl groups, hence reducing the need of excess pyridine. The oxidation reaction was investigated as a function of *bis*(pyridyl)siloxane/Pd ratio, separation distance between the pyridyl groups in the ligands, and m- vs. p-pyridyl using a series of *bis*pyridyl ligands **24-2m** to **24-10m** and **24-2p** to **24-10p**. These ligands differed in the number of $–(CH_3)_2Si–O$ spacers between the terminal pyridyl groups. In order to establish that the observed effect was not due to the presence of siloxane, the monopyridyl ligand **24-1m** was also prepared. When compared under identical conditions of pyridyl/Pd ratio and concentrations, temperature, and oxygen bubbling rate into the liquid, the extent of agglomeration of Pd particles and the dependence of reaction rate with pyridyl/Pd ratio differed substantially among the siloxane ligands. In particular, the reaction rate for ligands **6m** and **7m** showed very weak dependence on the pyridyl/Pd ratio. Over the range of 2 to 8 pyridyl/Pd ratios, the reaction rate dropped by less than a factor of 2, whereas the drop was 5 to 10 fold for pyridine or the monopyridylsiloxane **1m**. Ligand **5m** was also the most effective in preventing Pd agglomeration. Siloxane ligands of other chain lengths showed intermediate behavior, including the p-pyridyl analogs. The data correlated well with the ability of the *bis*(pyridyl)siloxane ligands to form monomeric cyclic coordination complex with Pd(OAc)$_2$ (see scheme 6, **R**$_1$).



Variations to the *bis*(pyridyl)siloxane oligomers include addition of reactive functional groups along the chain. An example is *bis*(meta-pyridyl)carboxylsiloxane **25b**, in which a carboxylic acid functionality is added to the central Si atom of **25a**.[105] Complexation of **25b** to Pd was much stronger than **25a** as a significantly higher concentration of pyridine-d_5 was needed to displace an equivalent amount of siloxane ligand from Pd as monitored by NMR. It was also observed that the presence of the carboxylate group suppressed both the first and second oxidation steps of 1,3-benzenedimethanol, with the suppression more severe for the second step.[107] These examples illustrate the versatility of siloxanes as ligands to metal complexes. The relative ease of their preparation and modification creates opportunities to tune the coordination of and influence accessibility to the metal center, affecting their reactivity and stability against metal agglomeration.

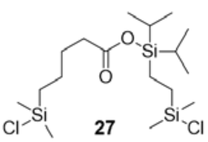




Another example of linear polysiloxane-metal complexes in which the structural conformation plays an important role is the study by Hu et al. on Cu catalyzed benzyl alcohol oxidation.[108] These investigators compared the tetradentate ligand siloxane oligomer **26a**, terminated with bis(pyridyl-imine), with the bidentate complex **26b** that has only one terminal pyridyl-imine ligand. The reaction was conducted in a solvent of CH_3CN and H_2O containing 5 mole % potassium tert-butoxide, and a co-catalyst 2,2,6,6-tetramethylpiperidyl-1-oxy, TEMPO. The benzaldehyde product yield depended strongly on the Cu/**26a** ratio and was 7.6 times higher when the ratio was raised from 1 to 2. The authors proposed that the poor catalytic performance at equimolar of Cu and **26a** may be due to the formation of a tetra-coordinated cyclic complex of Cu with **26a**, thus creating difficulties in generating vacant site on Cu for catalysis. Another observation was that the product yield was significantly higher for **26a** than **26b** at the same Cu/pyridyl-imine ratio. This led the authors to propose that the active catalyst might be a dinuclear Cu system. The results from MALDI-TOF mass spectrometry provided some support for the binuclear proposal.

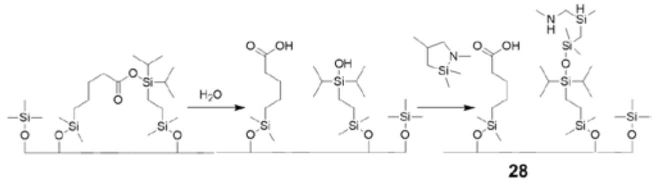
4 Application of siloxane derivatives for catalyst synthesis

The use of silicon chemistry for catalyst synthesis is common, especially for surface modifications and zeolite syntheses. Two of the most used reactions are condensation and hydrosilylation, both of which had been referred to in the synthesis of many of the structure discussed thus far. Here we intend to focus on the application of one functional group - silyl ester. Silyl ester, R–Si–O–(CO)– is a rather reactive bond susceptible to hydrolysis, alcoholysis, and, in general, nucleophilic attack at the Si atom. However, it is quite stable in the absence of moisture. Thus, it can be useful as a protection group for carboxylic acid in reactions such as hydrosilylation and heterofunctional condensation. For this purpose, it has advantage over other protection methods such as by carbamate in that deprotection can be achieved under mild conditions due to the hydrolytic susceptibility.



27

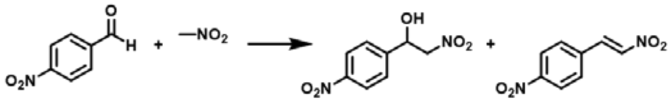
The silyl ester bond can also be used in precursors for the construction of catalytic structures. An example is structure **27** which possesses two terminal silyl chloride for anchoring to a solid via condensation with surface silanols.[109] After anchoring onto a surface and hydrolysis of the silyl ester bond, two functional groups, a carboxylic acid and a silanol, were generated at a distance defined by the precursor, or more precisely, the chain length at each end of the silyl ester bond (Scheme 7, first step). The silanol formed provides a very versatile platform to form other functional groups to pair with the carboxylic acid. This is illustrated in the formation of the structure **28**, in the second step of Scheme 7, where the silanol is reacted with a cyclic silazane to form a secondary amine after ring opening. Other functional group pairs can be formed in a similar fashion, including carboxylic acid/pyridine, and carboxylic acid/phosphine.[109] One potential complication with acid-base pairing is the possibility of the acid and base reacting with each other to form amide or ammonium ion-carboxylate ion pair. Indeed, both have been detected in forming the structure **28**.



28

Scheme 7 Generation of surface-anchored bifunctional carboxylic acid-amine centers with defined separation distance.

The advantage of *prescribed* pairing in the catalytic Henry reaction (Scheme 8) was demonstrated by comparing the activity of **28** to a surface where the amine and the carboxylic acid were placed randomly. A catalyst populated with carboxylic acid only was inactive. When normalized to the free amine present, the initial turnover frequencies (TOF) were 6.8, 14.4 and 26.5 h^{-1} for a sample with amine only, a sample in which the amine and carboxylic acid groups were tethered randomly, and **28**, respectively.[109] The enhanced activity of **28** indicated that, when separated at an appropriate distance**,** the two different functionalities can effect cooperative catalysis.



Scheme 8 Henry Reaction

5 Common methods of siloxane derivatization

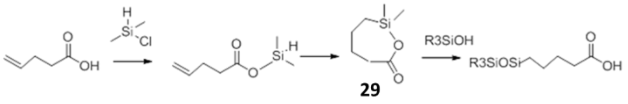
Although there is an abundance of commercially available siloxane and carbosilane precursors that can be used to construct functional structures of catalytic interest, an attractive feature of silicon chemistry is the ease of forming Si–C and Si–O bonds. This enables construction of siloxanes of different sizes, lengths, and shapes, and populated with different densities of various functional groups at specific locations. Some of these are demonstrated with examples described in this review. In applying the common silicon chemistry for synthetic purposes, there are considerations that might affect the feasibility to form the desired product and its purity. Here, we discuss some of these considerations.

A widely used synthetic procedure is hydrosilylation, in which a Si–H bond is added across an unsaturated C=C bond. The classic catalysts for hydrosilylation are Pt based, such as the Speier's catalyst [110] and Karstedt's catalysts.[111] In this reaction, the control of regiospecificity, that is, which of the two carbon atoms of the unsaturated bond is bonded to Si and which to H, is often desirable. This could be tuned with both solvent and temperature of the reaction.[112] Another common concern is deactivation of the catalyst. The active form of the catalyst is the soluble Pt complexes.[113] However, in the reduced state, the catalyst often agglomerates into inactive colloidal Pt and Pt nanoparticles, limiting the achievable yield. We found that an effective way to deter this deactivation was through the addition of diethylsulfide as a stabilizing ligand.[114] When present in the reaction medium, diethylsulfide caused suppression of the initial activity slightly, but was able to maintain the active form of the catalyst, such that eventually higher yields of the product could be obtained with shorter reaction times. It was effective for both the Kardtedt's and Speier's catalysts.

Introduction of functional groups into a catalytic structure is essential but challenging, because many reactive functional groups bind strongly to the metal catalyst for silane transformation. Hydrosilylation in the presence of organic functional groups is demanding, as these groups compete effectively for coordination to Pt. Thus, $(dCp)_2$-$PtCl_2$ and H_2PtCl_6 were totally ineffective in catalyzing the hydrosilylation of N-allylacetamide. However, bis(dialkylsulfido)platinum(II) salts were effective catalysts, with the rate of hydrosilylation faster with ethyl- and benzylsulfido platinum salts than methyl, isopropyl and phenyl sulfides.[115] Hydrosilylation in the presence of alcohol functional groups can result in either C-silylation of O-silylation. It was reported that low concentrations of catalyst or allyl alcohol resulted in significant formation of O-silylation products.[116] When the reaction was conducted using neat allyl alcohol with an appropriate catalyst concentration, selective C-silylation resulted. Kowalewska et al. also noted that under reaction conditions where Pt[0]/[Si–H] silane ratio was high, the selectivity for C-silylation of alkenyl alcohol was excellent.[117]

Another strategy to circumvent the functional group intolerance is to deactivate the functional group with protective groups that can be removed later. Hydrosilylation in the presence of amines is one of the very difficult reactions because of the strong affinity amines have for Pt centers. Binet et al. used N-*tert*-butoxycarbonyl (tBoc) as the protecting group for allyamine to introduce this functionality onto poly(hydrogenmethyl-co-dimethyl)-polysiloxane via hydrosilylation in the presence of $(Et_2S)_2PtCl_2$.[118] Great procedural precision was used for the deprotection of the tBoC group to preserve the integrity of the siloxane backbone, which entailed reaction at −10°C for 6 min, in stringently anhydrous conditions, and with 0.9–1.0 equivalent of fresh trimethylsilyliodide. The reaction was quenched with anhydrous methanol in the presence of an excess of amine functionalized resin.

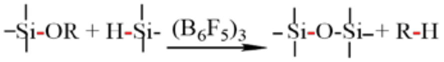
Missaghi[107] used an intramolecular protective strategy for introducing carboxylic acid functionality as is shown in the following equation.



In this strategy, a carboxylic acid is protected with a silyl ester, which does not interfere with the intramolecular hydrosilyation of the double bond to result in **29**. Cleavage of the acyloxy bond with silanol resulted in the formation of a Si–O–Si bond and a pendant carboxylic acid. Thus, reaction of **29** with a surface silanol would result in a tethered carboxylic acid.[105] In this scheme, an unhindered acyloxyl group is prone to exchange with other labile ligands. The cyclic compound **29** could dimerize and even oligomerize in solution, but this would not cause side reactions in the heterofunctional condensation step, as they all yield the same final product.

In the commonly used heterofunctional condensation between Si–Cl and Si–OH, amine is added both as a catalyst to promote activity and selectivity among silanols and a scavenger of the byproduct HCl.[119] Thus, it is impractical to use aminochlorosilane as a precursor for forming siloxane bonds to append amino groups. Instead, Mashayekhi, et al.[120] employed silanol-induced ring opening of a commercially available, highly reactive N-methyl-aza-2,2,4-trimethylsilacyclopentane precursor to introduce secondary amino groups to polysiloxane. Another useful tool in constructing functional siloxanes is the Piers−Rubinsztajn reaction (Table 2). The abundance of readily available Si–OR precursors makes the reaction particularly attractive. Rubinsztajn[121] first reported that tris(pentafluorophenyl)borane, $[B(C_6F_5)_3]$ catalyzed the condensation of alkoxysilane with hydrosilane. Grande et al.[122] examined the functional group tolerance of this reaction and reported that it was completely suppressed by the presence of amine groups. When 3-(glycidoxy)propyltrimethoxysilane was reacted with pentamethyldisiloxane in the presence of catalytic amounts of $B(C_6F_5)_3$ under anhydrous conditions at room temperature, only reductive epoxide ring opening was detected. The Piers−Rubinsztajn reaction could proceed but with difficulty in the presence of thiols, and the condensation of Si–H with Si–OR competed with the formation of Si–S bonds. The Si–H and Si–OR condensation reaction appeared to proceed smoothly in the presence of haloalkanes.

Table 2 Energetics of condensation reaction of alkoxysilanes and organohydrosilanes



$$-\mathrm{Si}\text{-}\mathrm{OR} + \mathrm{H}\text{-}\mathrm{Si}\text{-} \xrightarrow{(B_6F_5)_3} -\mathrm{Si}\text{-}\mathrm{O}\text{-}\mathrm{Si}- + \mathrm{R}\text{-}\mathrm{H}$$

Bond energies (kJ mol^{-1})	-340	-378	-549	-420

6 Conclusions and perspectives

It is apparent that there are many diverse, well-characterized, structurally-defined organosilicon compounds that have been examined as models of active sites in heterogeneous catalysts. The definitive knowledge of the structure and composition of the organosilicon compounds make possible in-depth interrogation from which detailed understanding of reaction mechanisms and active site structures of the corresponding heterogeneous catalysts could be derived. Some of these structures are excellent homogeneous catalysts that exhibit catalytic properties superior to their heterogeneous counterparts. In part, this is due to the absence of diffusional limitation that heterogeneous solid often encounter.

Initial studies on organizing the organosilicon compounds into more complex structures such as nanocages have yielded unexpected and interesting nanoconfinement effects, such as large pKa shifts and stabilization of metals in unusual oxidation states, in addition to cooperative catalysis. These results bode well for further in-depth studies, and steer the investigation of catalysis into the domains of multidentate, multifunctional structures. The flexible siloxane bond is a feature that is uniquely valuable for assembling small molecules into more advanced and complex 3-dimensional structures. The importance of considering the 3-dimensional environment of a catalytic center is demonstrated in the examples shown, suggesting that the addition of small siloxane molecules or fragments could serve to mediate the interactions between different catalytic components and is a fertile ground for exploration. The fluxional behavior and the rapid dynamic inter-conversion from monomer to dimer of metal-containing silisesquioxanes are reminiscent of the enzyme's ability to change conformation as it undergoes the catalytic cycle. Further exploration is warranted.

Finally, the ease of applying silicon chemistry to build larger molecules and to introduce a variety of catalytically interesting functional groups with atomic precision on the structure and location has the potential to be developed into techniques for the fabrication of multi-faceted, multifunctional advanced catalysts. Such structures may have both rigid and flexible regions, where cooperative catalysis or cascade reactions would proceed by design. The chemical and thermal stability of silicon compounds would bring such bio-inspired catalysis to operating in regimes unattainable in biological systems.

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