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New Metallasiloxane Complexes of Aluminium and Lanthanides

By

Roisín Reilly

A thesis submitted to the University of Dublin for the degree of Doctor of Philosophy.

Department of Chemistry

University of Dublin

Trinity College

October 2003
Declaration

This thesis has not been submitted as an exercise for a degree at any other University. Except as otherwise indicated, the author carried out the work described herein alone.

Roísín Reilly

Roísín Reilly
## List of abbreviations

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<tr>
<td>Ph</td>
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<tr>
<td>Cy</td>
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<td>Ethyl</td>
</tr>
<tr>
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</tr>
<tr>
<td>Tms</td>
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<td>t-Bu</td>
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<tr>
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<tr>
<td>PyHCl</td>
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<td>POSS</td>
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<tr>
<td>TBHP</td>
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<td>TMEDA</td>
<td>Tetramethylethlenediamine, Me₂N(CH₂)₂N-Me₂</td>
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<td>PMDTA</td>
<td>Pentamethyldiethlenetrimine (Me₂NCH₂CH₂)₂N-Me</td>
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<tr>
<td>TfOH</td>
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<td>DME</td>
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<tr>
<td>CAN</td>
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<td>CDCl₃</td>
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<tr>
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<td>PE</td>
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<td>MAO</td>
<td>Methylaluminoxane</td>
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<tr>
<td>MAS</td>
<td>Magic Angle Spinning (NMR)</td>
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<tr>
<td>M41S</td>
<td>Family of mesoporous materials</td>
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ES MS  electro-spray mass spectroscopy  
MCM41  Most prominent member of M41S family (molecular sieve)  
TS-1  Titanium silicate -1  
IR  Infrared  
SBU  Secondary building blocks  
T₈  Octameric silsesquioxane  
D₃  Hexamethylcyclotrisiloxane, D = (CH₃)₂SiO)  
D₄  Octamethylcycloctrasiloxane  
C₇*  An unsubstituted or substituted cyclopentadienyl  
C₇  Cyclopentadiene, C₅H₆  
C₇⁻  Cyclopentadienyl, C₅H₅⁻  
C₅Me₅  Cyclopentamethylenpentaeny  
C₇''  Bis(trimethylsilyl) cyclopentadienyl ligand, C₅H₃(SiMe₃)₂  
C₇'R  Bis(trimethylsilyl)methyl cyclopentadienyl, η-C₅H₄CH(SiMe₃)₂  
N Mandarin alanide, N(SiMe₃)₂⁻
Summary

The main objective of this project was to develop novel metallasiloxane complexes through a variety of synthetic strategies. The work focused mainly on aluminium and lanthanide metallasiloxanes. The catalytic properties of selected metallasiloxanes have been investigated in the terms of they use as molecular models for heterogeneous catalysts and to help illustrate some principles of catalysis. Firstly, investigations of the interaction of disilanols and trisilanols with amines and Lewis acids were performed (Chapter 2) and resulted in the formation of ionic (pyridinium cation – siloxane anion) salts (HO)Ph₂SiOSiPh₂O(PyH) (2) and [PyH][{(C₆H₅)₇Si₇O₉(OH)₂}₂O₂H] (3) which serve as intermediates in the amine-assisted synthesis of metallasiloxanes. The condensation of Ph₂Si(OH)₂ in the presence of FeCl₃ and pyridine yielded the bispyridinium μ-oxo bis[trichloroferrate(III)]-pyridine, [HPy]₂[Fe₂Cl₆O]Py (4).

A number of aluminosiloxanes have been prepared by amine-assisted metathesis and condensation reactions between appropriate aluminium compounds and diphenylsilanediol (Chapter 3). The reactions proceeded with the condensation of Ph₂Si(OH)₂ to higher siloxane units giving anionic or cyclic aluminosiloxanes with the cyclic complex [AlCl(THF){O(Ph₂SiO)₂}]₂ (6) being the first example of a 12-membered cyclic aluminosiloxane. Interactions of AlEt₃ with Ph₂Si(OH)₂ yielded a new molecular aluminopolysiloxane [Al(OH)]₄[(Ph₂SiO)₂O]₄ (8) in which there is a framework of five annelated eight-membered rings, with an Al₄(OH)₄ eight-membered ring lies in the centre of the structure. The heating of a mixture of AlCl₃ and cyclic (Ph₂SiO)₄ under reflux in THF resulted in the formation of the spirocyclic aluminosiloxane [Al₃{O(Ph₂SiO)₂}₂Cl₃] (9), which is the first example of an unprecedented siloxane ring shrinkage, which has not been reported to date. Cleavage of cyclic siloxane frameworks by AlCl₃ in refluxing THF was then applied to the fully-condensed phenyl silsesquioxane, Ph₈Si₈O₁₂ leading to the production of 19. Various lanthanide (La, Ce and Nd) metallasiloxanes have been prepared from the corresponding metal halides or organolanthanide precursors. The Lanthanum complex 11 was found to be analogous to aluminosiloxane 5. Oxidation of a Ce(III) species by 2 equivalents of the
silanol ligand with the formation of a Ce(IV) metallasiloxane [Ce(Ph2SiO2)(THF)2]2 (16) was observed.

In Chapter 4, the reaction of AlCl3 with the silsesquioxane trisilanol (c-C6H11)7Si7O9(OH)3 (1) yielded a new anionic aluminosilsesquioxane [HNEt3][Al{(c-C6H11)7Si7O11(OH)}2] (18). The synthetic pathways used to prepare new aluminosilsesquioxanes have been adapted to synthesise new lanthanide (La, Ce and Nd) metallasilsesquioxanes. The reaction of CeCl3 or CeN”3 with the silsesquioxane disilanol (c-C6H11)8Si8O11(OH)2, proceeded with an oxidation of Ce(III) into a Ce(IV) species. Novel Ce(IV) complexes Ce{(c-C6H11)7Si7O11(OH)}2 (23) and Ce[{(c-C6H11)8Si8O13}2(py)3] (24) are the first Ce(IV) metallasilsesquioxanes reported to date. The interactions between the aluminosilsesquioxane 18 and the appropriate titanium, zirconium or neodymium reagents resulted in novel bimetallic aluminium - group 4 or neodymium metal complexes 25 - 29.

In Chapter 5 selected metallasiloxane derivatives developed in this work have been investigated as potential catalysts in the polymerisation of ethene, the epoxidation of 1-octene and in the Diels-Alder reaction of buten-3-one. The epoxidation of 1-octene by the bimetallic titanium silsesquioxane 26, was found to exclusively epoxidise the alkene with no side-products detected by NMR spectroscopy. This somewhat ‘difficult’ epoxidation of 1-octene was catalysed more effectively by 25. The titanium-aluminium complexes 25 and 26 also demonstrated some catalytic activity in ethylene polymerisation. The metallasilsesquioxanes were found to be inactive in Diels-Alder reactions presumably due to the high sterical hindrance of the metal centers in the compounds.

Chapter 6 contains the experimental details for the procedures and reactions described in this work. Chapter 7 presents the final conclusions and the future outlook for the research performed in this project. Overall the work in this thesis produced a number of very interesting compounds which could potentially be used in catalysis and in Materials Science. The results presented in this thesis should contribute significantly to the development of metallasiloxane chemistry. The synthetic strategies and principles developed in this work can be adopted for other metals and siloxane systems in the future.
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Dedicated to my parents for so many reasons ......
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1.0 Introduction
1.0 Introduction

The preparation of metal-containing porous materials is one of the most important and difficult tasks of modern chemistry and technology. Controlled pore inorganic and organic solids play a key role in modern chemical technology as heterogeneous catalysts, adsorbents, porous membranes and as host-matrices for pharmacology, electronics and nanotechnology.

Zeolites are one of the most well known examples of metal-containing porous materials. Metallasiloxanes containing Si-O-M fragments (M = metal) have been envisaged as molecular analogues of zeolites due to their astonishing geometrical relationship. They have been found to mimic the role of a number of catalysts, and hence are useful in unravelling the reaction mechanisms for catalytic conversions. Moreover, metallasiloxanes can be considered as precursors for siloxane polymers containing metal centers in the polymer backbone. Transition metal complexes anchored on silica surfaces are known to catalyse a variety of organic transformations. Despite the fact that there has been significant progress in metallasiloxane chemistry over the last 10 years, there is still a great need for the further development of alumino- and rare earth- metallasiloxane materials.

This thesis focuses mainly on the synthesis, characterisation and catalytic investigation of new metallasiloxane complexes derived from certain silanediol and silanetriol precursors. In this chapter the most important literature data and background on silicates, silanols and metallasiloxanes will be considered.

1.1 Silicates: general background

The relative abundance of the elements in the earth's crust determines what minerals will form and what minerals will be most common. Therefore, because oxygen and silicon are the most copious elements, the silicate minerals are the most common. In these silicate minerals the radius ratio of Si^{4+} to O^{2-} requires that Si^{4+} be coordinated by 4 O^{2-} ions in a tetrahedral coordination mode. Since each Si^{4+} is a highly charged
cation, Paulings rules state that it should be separated as far as possible from the other Si\(^{4+}\) ions in a [SiO\(_4\)]\(^{4-}\) tetrahedron. The SiO\(_4\)^{4-} tetrahedrons (see Fig. 1.1) are linked together and only corner oxygens will be shared with other SiO\(_4\)^{4-} groups. Several possibilities exist and give rise to the different silicate groups e.g., island, ring, single / double chain, sheet or tectosilicates.\(^1\)

**Fig. 1.1** SiO\(_4\) tetrahedrons.

If all the corner oxygens are shared with another SiO\(_4\)^{4-} tetrahedron a framework structure develops. The basic structural group then becomes SiO\(_2\). The minerals quartz, cristobalite, and trydimite are all based on this structure. If some of the Si\(^{4+}\) ions are replaced by Al\(^{3+}\), this produces a charge imbalance and allows for other ions to be found coordinating in different arrangements within the framework structure. While the tetrahedron is nearly the same with an aluminium at its centre, the charge is now 5- instead of the normal 4-. Since the charge in a crystal must be balanced, additional cations are needed in the structure. This is the main reason for great variations within this silicate subclass. The feldspar and feldspathoid minerals are also based on the tectosilicate framework (see Fig. 1.2).
So by substituting some of the Si\(^{4+}\) ions with Al\(^{3+}\) ions, different types of aluminosilicates may be formed. The Al-O-Si fragment is the most important unit of many natural and synthetic zeolites. A large number of rocks and minerals comprise alkali metal aluminosilicates. Among these are feldspars, which often have a silicon to aluminium ratio close to one. Examples also include the natural zeolite, cancrinite Na\(_6\)Ca\(_2\)Al\(_6\)Si\(_6\)O\(_{24}\)(CO\(_3\))\(_2\) and sodalite Na\(_8\)Al\(_6\)Si\(_6\)O\(_{24}\)Cl\(_2\) which is used industrially.

1.2 Zeolites

Zeolites are one of the best-known and important examples of metal-containing porous materials. They are framework aluminosilicates, which consist of interlocking tetrahedra of SiO\(_4\)\(^{-}\) and AlO\(_4\)\(^{-}\). In order to be a zeolite the ratio of (Si + Al)/O must equal 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Unlike most other tectosilicates, zeolites have large vacant spaces or cages in their structures that allow space for large cations such as sodium, potassium, barium or calcium and even neutral molecules such as water or ammonia. Both the cations and the other molecules have enough freedom of movement to permit cation exchange and reversible dehydration.

Zeolites, which have a cagelike structure of precise geometry with pores of uniform shape throughout the entire crystal, are molecular sieves that can be used for separating gaseous mixtures by molecular sieving effects or by selective adsorption and for shape-selective catalytic reactions.
Zeolites are formed in nature by hydrothermal reactions and are often combined in their paragenesis with postmagnetic minerals. They were discovered in 1756 by Baron Cronstedt, a Swedish mineralogist. It was in 1932 that Mc Bain used the term "molecular sieves" for zeolite minerals to explain the structural properties of these minerals by which they admit or reject absorbates on the basis of molecular size. By the early 1930's X-ray diffraction studies were revealing zeolites to be crystalline materials having within each crystal a system of precisely arrayed cavities and pores. Following the discovery of natural zeolites, Barrer was the first to synthesise identical synthetic forms. By 1953, more than 30 distinct pure zeolite species had been prepared. The discovery of synthetic zeolites resulted in a wide variety of scientific and industrial developments. An example of a synthetic compound belonging to this class is the zeolite Linde Type A (LTA) with the ideal composition (Na$_{12}$Al$_{12}$Si$_{12}$O$_{48}$.27H$_2$O). A characteristic structural feature of LTA is the cubic Al$_4$Si$_4$O$_{12}$ unit. Synthetic zeolites can be prepared by a number of methods e.g., sol-gel processing, chemical vapour deposition, or hydrothermal synthesis.

When properly modified, zeolites also have catalytic properties, which in commercial applications are producing significant improvements over conventional catalyst systems. Although only a small number of natural and synthetic zeolites have reached the commercialisation stage, the potential is obviously immense. At present some 50 naturally occurring zeolite species have been recorded and their structures determined. In addition, more than 200 synthetic species with no known natural counterparts have been reported in the literature.

Catalysis is one of the most important fields of application of zeolites, but by no means the sole one. Since their development and introduction into industry in 1954 by the Union Carbide Corporation as molecular sieve adsorbents, these unique adsorbents have been used commercially in many systems for drying and purification. Zeolites are used on a large scale as ion exchangers in laundry detergents, for the
clean-up of radioactive waste and as adsorbents for the purification and separation of numerous substances.

The growing drive to prepare new zeolite-like materials reflects the importance of improving the performance of zeolites as molecular sieves or catalysts. The structural architecture is the source of the ability of zeolites to separate mixtures of molecules, in both gas and liquid phases, on the basis of their effective sizes. Moreover, zeolites have very special practical advantages over the traditional catalysts because they will admit only certain reactant molecules and this can be potentially tailored to produce selected products (shape-selective catalysts). A matching of size, shape and orientation of the reactant and product molecules to the geometry of the zeolitic network controls the catalysed reaction. In order to improve the performance of zeolites as molecular sieves or catalysts, several modification techniques were developed to vary in a controlled way the zeolitic pore system.

Generally, pore size engineering in zeolites can be the result of:

(a) a modification by a cation exchange process,
(b) a modification by a pre-adsorption of polar molecules, or,
(c) a modification of the zeolitic framework.

Using these modification techniques, both the molecular sieving and the adsorption selectivity of zeolites can be altered in a controlled way, which is an important tool in both separation and encapsulation technology. The internal and external structural modification in zeolites by the implantation of additional atom groups is the result of a chemical reaction of the modifying agents with structural hydroxyl groups or hydration water. This means that the activity of the zeolite for these modifications is either based upon the creation of zeolitic hydroxyls, or by the presence of water molecules in the zeolitic pore structure.
1.3 Silanols

Silanols are organosilicon compounds containing the Si-OH functionality. Silanediols are compounds of the type RR’Si-(OH)₂, disilanediols are the compounds which contain two Si(OH) groups with one or more Si-O-Si siloxane bridges in between them, silanetriols are of the general formula RSi(OH)₃ and trisilanols are compounds with three Si(OH) pendant groups in its structure.

Organosilanols are analogous to alcohols, the most common being simple silanols, e.g. triorganosilanols R₃SiOH, silanediols R₂Si(OH)₂ and silanetriols RSi(OH)₃ (R = organic group). Between them these three classes of compounds have been widely studied and are precursors to materials having a variety of important uses. Compounds containing the silanol group are well known not only in nature, but also in industrial processes in which polymeric materials such as polydimethylsiloxanes (silicones) and sol-gels are produced by condensation reactions of the reactive silanol species. The range of available compounds in the class R₂Si(OH)₂, is much less extensive than that for the related triorganosilanol species. Of the known silanediols, the compounds Ph₂Si(OH)₂ and t-Bu₂Si(OH)₂ are most frequently used for the preparation of metallasiloxanes. Although the silanol functional groups are found in a wide variety of situations, compounds containing such groups are relatively rarely isolated as discrete molecular species, but will exist as hydrogen-bonded molecules.

Silanols are most often produced by the hydrolysis of a compound containing a bond between silicon and a more electronegative atom such as a halogen, O, S, N, or P. The silicone industry is mostly based on the hydrolysis of chlorosilanes. Chlorosilanes are probably the most widely used starting materials for silanol synthesis because of their ready availability and good reactivity. There are however problems associated with their use. The isolation of pure silanols is difficult because of their tendency to undergo condensation reactions. For example, the hydrolysis of methyl chlorosilanes normally gives a mixture of fully- and partially-condensed siloxanes containing Si-O-Si fragments rather than pure silanols as final products. Precautions may be taken to remove or neutralise the the acid formed - e.g., by
adding pyridine to the reaction mixture (so that the HCl formed is removed as a precipitate of pyridinium hydrochloride) or adding NaOH or KOH to the solution to maintain neutrality – then silanols may often be isolated. If larger groups are present, for example phenyl, then formation of siloxanes proceeds less readily, and fewer precautions need to be taken. Thus \( \text{Ph}_2\text{Si(OH)}_2 \) may be obtained by the hydrolysis of \( \text{Ph}_2\text{SiCl}_2 \) in the presence of ammonium carbonate. This hydrolysis can afford diphenylsilanediol in yields of up to 95% (See Scheme 1.1).

Scheme 1.1 Synthesis of \( \text{Ph}_2\text{Si(OH)}_2 \).

Overall the following points must be considered in the synthesis of silanols:

(1) because the condensation reactions are bimolecular in silanol synthesis the use of dilute solutions is beneficial.

(2) the solvolytic system employed generates HCl so the addition of ammonium carbonate gives the hydrochloride salt neutralising the HCl as it is formed.

(3) the reactions should be carried out at the lowest convenient temperature, \( 0^\circ\text{C} \).

(4) the presence of bulky groups e.g. phenyl on the silicon greatly reduces the tendency towards siloxane formation.

The high reactivity and acidity of silanols was commented on in 1946 when it was found that \( \text{Et}_3\text{SiOH} \) reacted readily with sodium in xylene and that the silanolate \( \text{Me}_3\text{SiONa} \) was formed rapidly when the corresponding silanol was treated with a 12N NaOH solution.\(^5\) Many subsequent studies, mainly IR spectroscopic studies monitoring an acid / base titration, have confirmed the relatively high acidity of silanols compared with carbinols. The approximate proportionality between the change \( \Delta \nu \), in the O-H stretching frequency between a free SiOH and one involved in
hydrogen bonding to a suitable base, and \( \Delta H \) for the hydrogen bonding interaction has been used for many years to give an estimative of the strength and relative acidity of the OH groups. Such measurements indicate that silanols have a stronger hydrogen bonding interaction than carbinols. Infrared spectroscopic studies on the O-H band shifts on mixing silanols with the bases diethyl ether and mesitylene reveal the order of relative acidities to be arylsilanols > alkylsilanols > arylcarbinols > alkylcarbinols. An IR spectroscopic study of silanols in the presence of phenol shows that the basicity order is alkylcarbinols > alkylsilanols > arylcarbinols = arylsilanols, i.e., the silanols are nearly as basic as the alcohols despite the fact that they are much more acidic than alcohols. In view of the high acidity and the relatively high basicity of silanols, it is to be expected that they will form strong hydrogen bonds both with themselves and with other suitable species.

A number of silanols have been characterised by X-ray crystallography. The size of the substituents at silicon plays an important role in determining the hydrogen-bonded structure of the silanols. Small substituents allow infinite hydrogen-bonded arrays of molecules to be formed, while larger substituents give simple chains and very bulky groups lead to the formation of simple tetramers or dimers. For example the structure of \( \text{Ph}_2\text{Si(OH)}_2 \) is comprised of columns of hydrogen-bonded molecules.

### 1.4 Silsesquioxanes

Silicates can occur as rings, connected in chains and layers, or in the form of cages. The structure of cage silicates is based on Si-O linkages forming a cage with a silicon atom at each vertex. Silsesquioxanes are a class of 3D oligomeric organosilicous compounds (cages) of the general formula \((\text{RSiO}_3/2)_n\), where \( n \) is an even number and \( R \) can be any of a large number of groups both organic or inorganic (typically methyl, halogen, vinyl or phenyl). (See Scheme 1.2).
Scheme 1.2 Fully-condensed silsesquioxane frameworks.

The terms “silasesquioxanes” or “silsesquioxane” are the general IUPAC names and the nomenclature most commonly used is given by a trivial systematic system. The name sil(a)sesquioxane is derived from sil-oxane (compounds of silicon and oxygen), and sesqui (Latin, meaning one and a half) reflects the ratio of silicon and oxygen, therefore sil(a)-ses-quioxane denotes that each silicon atom is connected to three oxygen atoms, (SiO₃). The prefix ‘oligo’ is often used to indicate a small number of silsesquioxane links.¹²

It is useful to distinguish between “fully-condensed” silsesquioxane frameworks and “incompletely-condensed” frameworks. Fully-condensed silsesquioxanes have the idealised empirical formula [RSiO₃/2]ₙ, whereas incompletely-condensed silsesquioxanes possess reactive Si-OH groups which are potentially capable of forming additional Si-O-Si linkages via the elimination of water (See Scheme 1.3).

Scheme 1.3 Preparation of incompletely- and fully-condensed silsesquioxanes.
Polyhedral oligosilsesquioxanes (POSS) are a particularly interesting class of three-dimensional silsesquioxanes derived from the hydrolytic condensation of trifunctional organosilicon monomers (i.e., RSiX₃). Since their discovery in 1946, many stoichiometrically well-defined POSS frameworks have been reported, including a wide variety of frameworks with synthetically useful functional groups. Interest in polyhedral silsesquioxanes has greatly intensified over the past 20 years as new methods have been devised for preparing useful compounds, and vast improvements in routine analytical instrumentation have made it possible to quickly separate and characterise complex Si/O frameworks. The pool of known frameworks is expanding and many new and potentially valuable applications are emerging.

In general, hydrolytic condensation reactions of trifunctional organosilicon monomers (e.g., RSiCl₃ or RSi(OMe)₃) can produce a wide variety of interesting products, ranging from small oligomers and discrete clusters to complex resins and “T-gels”. It is difficult to make generalisations about these reactions because each reaction appears to be uniquely sensitive to a highly interdependent combination of experimental factors, including product solubilities, initial monomer concentration, nature and stability of the solvent, temperature, pH, the amount of free water available, and the type of catalyst (acid or base) used to facilitate the condensation. Nevertheless, many hydrolytic condensation reactions produce synthetically useful quantities of fully-condensed POSS frameworks containing 6, 8, 10 and/or 12 Si atoms (see Scheme 1.2).

In the synthesis of silsesquioxanes, three important characteristics of POSS frameworks have to be considered:

(1) Silsesquioxane frameworks are strongly electron-withdrawing.

In fact, the electron-withdrawing properties of Si₅O₁₂ are comparable to those of a CF₃ group. Strong electron-withdrawing groups can make it very difficult to oxidise nearby functional groups or preform reactions that require cationic (or partially
cationic) intermediates or transition states. In light of the importance of choosing a synthetic methodology that proceeds cleanly and with very high conversion, the electron-withdrawing effects of a \([\text{SiO}_3/2]_n\) framework must be considered carefully when designing the syntheses of new POSS frameworks.

(2) Silsesquioxane frameworks are susceptible to base-catalysed redistribution and polymerisation reactions.

The reaction of a base or nucleophile with the Si atoms of a fully-condensed POSS framework is inefficient compared to reactions with pendant groups, but many reagents will initiate base-catalysed redistribution or polymerisation of POSS frameworks upon prolonged reaction times and/or elevated reaction temperatures. Strong bases (e.g., NaOH) react rapidly with POSS frameworks, especially in polar aprotic solvents (e.g., THF, DMF, DMSO). The product in many cases is an imprecisely defined resin or “T-gel” rather than discrete molecular clusters, which sometimes (but not always) precipitates from solution. It is generally best to avoid the use of strong bases, and to monitor the progress of the reactions involving any reagent capable of generating a strong base via reaction with water (e.g., dialkylamides, alkoxides, alkyllithium, NaH and Grignard reagents). Weaker nucleophiles and bases including tertiary amines, azide, cyanide, acetate, cyanate and conjugate bases of other weaker acids have also been observed to initiate base-catalysed redistribution or polymerisation of POSS frameworks. Direct attack of these reagents on Si seems unlikely, so most of these probably destroy POSS frameworks by producing hydroxide from traces of water.

(3) Highly symmetric, highly functionalised POSS frameworks can exhibit unexpected solubility properties, and it is sometimes difficult to find an appropriate solvent for a chemical reaction.

This can be a particularly difficult problem to solve when a reaction produces functional groups capable of forming strong intermolecular interactions. Oxidation reactions, which can produce strongly hydrogen-bonded functional groups (e.g., COOH), and hydride reduction reactions, which often produce insoluble
intermediates prior to aqueous work-up, are especially problematic because precipitation can occur at relatively low conversion. The poor solubility of many POSS in non-polar solvents can also present problems.

Synthetic reactions performed in acidic media are kinetically controlled in the sense that they often lead to non-equilibrium mixtures of products containing high yields of only a few compounds. Under basic conditions, the formation of POSS frameworks typically occurs with thermodynamic control because both the formation and hydrolytic cleavage of Si-O-Si linkages are facile. In most cases, product mixtures resulting from the base-catalysed condensation of RSiX₃ or redistribution reactions of [RSiO₃/₂]ₙ are complex and time consuming to separate out on a multigram scale. However, several base-catalysed reactions are known to produce nearly quantitative yields of a single polyhedral framework. The driving force for these reactions is normally precipitation of a very poorly soluble product. The ubiquitous R₈Si₈O₁₂ framework is clearly thermodynamically less stable than many frameworks containing 10 and 12 Si atoms.

A related family of polyhedral Si/O clusters can be prepared via base-catalysed equilibration of tetrafunctional silicon monomers, such as Si(OEt)₄. These clusters (spherasilicates) are functionalised silicates (i.e. [ROSiO₃/₂]ₙ) rather than silsesquioxanes (i.e., [RSiO₃/₂]ₙ), but they exhibit many similarities to fully-condensed POSS frameworks. For example, base-catalysed equilibration of Si(OEt)₄, Si(OEt)₄, Si(OH)₄, or SiO₂ can be performed under conditions where the major Si-containing species in solution is [Si₈O₂₀]₈⁻. It is generally difficult to separate these spherasilicates without producing insoluble silicates or silica gels, but many stable derivatives can be prepared by reacting solutions of [Si₈O₂₀]₈⁻ with chlorosilanes.
The incompletely-condensed and not the fully-condensed silsesquioxanes described above are of major interest in this thesis. This is because there are silanol groups in their frameworks, which can be used for further reactions (for examples see Fig. 1.3).

**Fig. 1.3** Examples of silsesquioxanes containing free Si-OH groups.

The hydrolytic condensation of RSiX₃ monomers to fully-condensed POSS frameworks (e.g., R₈Si₈O₁₂) requires the formation of many intermediates. In many cases, these intermediates occur in small amounts, are unstable under the reaction conditions, and are extremely difficult to isolate from the typical crude product mixture.

Occasionally however high yields of compounds that are logical intermediates can be produced and easily separated. These compounds have a wide range of applications and their chemistry has been extensively further developed over the past 15-20 years. The most extensively studied incompletely-condensed POSS framework is the trisilanol (c-C₆H₁₁)₈Si₇O₉(OH)₃ (1), which is obtained along with (c-C₆H₁₁)₆Si₆O₉, via the hydrolytic condensation of (c-C₆H₁₁)SiCl₃ (see **Scheme 1.4**).¹⁷,¹⁹
Scheme 1.4 Hydrolytic condensation of \((c-C_6H_{11})\text{SiCl}_3\).

The synthesis of trisilanol 1 is therefore straightforward but usually requires an inconvenient gestation period (from 6 weeks to 3 years) before synthetically useful quantities can be obtained. This is because the main products that are formed at the beginning of the reaction are incompletely-condensed dimers (RSi(OH)\(_2\)ORSi(OH)\(_2\), \(R = \text{cyclohexyl}\)) and higher oligomers, that still contain silanol groups. The corresponding cyclopentyl-substituted trisilanol can be prepared similarly, where the reaction times can be greatly reduced by performing the reaction at higher temperatures.\(^{20}\)

With the most common route to incompletely-condensed silsesquioxanes involving the hydrolytic condensation reactions of RSiCl\(_3\), only a few trichlorosilanes are known to produce useful quantities of products. Recently however an alternative route to incompletely-condensed frameworks has emerged: partial strong acid cleavage of fully-condensed \([\text{RSiO}_3\text{C}]_n\), and hydrolysis of metallasilsesquioxanes.
Controlled partial hydrolysis of \([RSiO_{3/2}]_n\) provides a general new route to incompletely-condensed frameworks. Hydrolysis of metallasilsesquioxanes is of much less general utility, but it provides access to several unique and otherwise unavailable incompletely-condensed silsesquioxane frameworks.

### 1.4.1 Cleavage of the Si-O-Si bond

Recent work from the Feher group indicates that fully-condensed POSS frameworks are more susceptible to cleavage by strong acids than products resulting from the cleavage of a single Si-O-Si linkage.\(^{21,22}\) In other words, it is possible to effect cleavage of a single Si-O-Si linkage in high yield and at high conversion without wholesale destruction of the POSS framework. The resulting cleavage products provide access to many new families of useful Si/O and Si/O/M (where M = metal) frameworks.

The reaction of \((c-C_{6}H_{11})_8Si_8O_{12}\) with HBF\(_4/\)BF\(_3\) in non-coordinating solvents produces good yields of the difluoride I via cleavage of a single Si-O-Si linkage (See Scheme 1.5). Similar cleavage reactions are observed with triflic acid (CF\(_3\)SO\(_3\)H) and many other strong acids. Complete stereochemical inversion at Si has been established for the reaction of \((c-C_{6}H_{11})_8Si_8O_{12}\) with HBF\(_4/\)BF\(_3\), and it appears to be generally true for reactions of \([RSiO_{3/2}]_n\) frameworks with strong acids (See Scheme 1.5).
Scheme 1.5 Hydrolysis of difluoride I and ditriflate II.
The Si-F groups in I are surprisingly difficult to hydrolyse, but hydrolysis can be accomplished with complete retention of stereochemistry at Si via sequential refluxing reactions with Me₃SnOH and aqueous HCl. In contrast, the Si-OTf groups in II are very reactive towards water and other nucleophiles, and substitution generally occurs quickly with complete inversion of stereochemistry at Si.

Cleavage of more than one Si-O-Si linkage by strong acids is also possible. For example the reaction of \((c-C_6H_{11})_8Si_8O_9\) with HBF₄/BF₃ produces two tetrafluorides derived from the cleavage of both Si₃O₃ rings in the molecule. Another interesting reaction that probably involves cleavage of multiple Si-O-Si groups is the reaction of \((c-C_6H_{11})_8Si_8O_{12}\) with a large excess of TfOH. The major product from this reaction is III, which appears to form via cleavage of two Si-O-Si linkages (See Fig. 1.4).

![Fig. 1.4 Silsesquioxane III.](image)

### 1.4.2 Modifications of trisilanol 1

Trisilanol 1 is a versatile precursor to a wide range of Si-O and Si/O/M frameworks. Most of the frameworks have been prepared via reactions that transform SiOH groups into new siloxane (i.e., Si-O-Si) or heterosiloxane (i.e., Si-O-M) linkages, but 1 also undergoes a variety of reactions that modifies its Si/O framework in useful ways, e.g., silylation. Silylation reactions of 1 have been
extensively studied, and efficient protocols exist for effecting clean monosilylation with practically any monochlorosilane. The preparation of di- and tri-silylated derivatives are also possible (See Scheme 1.6).

Scheme 1.6 Silylation products of Trisilanol 1.

As with the stereochemistry of trisilanol 1, all of its trimethlysilylated derivatives can also be cleanly inverted via sequential treatment with HBF₄/BF₃, Me₃SnOH and aqueous HCl. The reaction with HBF₄/BF₃ cleanly produces the trifluoride derivative.

1.4.3 Applications of POSS

Silsesquioxanes are very promising models for understanding the surface chemistry on heterogeneous silica particles. Recently these novel compounds have been used as well defined molecular models for silica surfaces and as ligands for main group or transition metal catalysts on silicon surfaces. Their potential to mimic silica surfaces
stems from the close similarity of silsesquioxanes to highly siliceous clusters that possess the structural and electronic features of hydroxylated silica surfaces. They have found widespread use in sol-gel polymerisation, as models for zeolite activity, as alternatives for SiO₂ thin films, as liquid crystal polymers, in hair fixatives and in studies of silica-supported catalysts. Greater exploitation of these unique compounds has in the past been severely restricted by limitations in the synthetic routes followed. Unfortunately, most of the routes employ multistep procedures using a large excess of silane, long reaction times and even then such routes only result in very low yields of the desired products. Recently however, silsesquioxanes have attracted renewed interest, largely because new synthetic strategies have drastically reduced the reaction times, the number of steps involved, and have improved their yields.

The exact nature of the SiO₂ surfaces themselves is often a subject of much debate. Thus, much current research is concerned with the synthesis and characterisation of compounds which may model the specific surface morphologies of SiO₂ supports and their interactions with metal oxides on the molecular level. The use of highly silicous compounds to approximate silica seems quite reasonable, but the mere presence of a large siloxane network does not necessarily provide a model any better than one based on simple silanols, such as Me₂SiOH or Ph₃SiOH. Useful models for both spectroscopic comparisons and chemical reactivity studies must structurally resemble specific surface morphologies that are believed to occur on silica. Trisilanol 1 is ideally suited for such purposes. Its close-range geometric similarity to known SiO₂ morphologies makes it the best model for silica that has been developed to date.

Crystobalite and tridymite are two of the three substantially different known crystalline modifications of silica that crystallise from aqueous solutions under normal hydrothermal conditions. The similarity between cristobalite and 1 is particularly striking, whereas that of tridymite is less remarkable, as tridymite does
not have geometrically comparable sites on the surface. Common to both trisilanol 1 and cristobalite structural units, is a concave silicon-oxygen cavity, whose outer rim is formed by six silicon and six oxygen atoms. The arrangement of potential O-donor centers is also quite similar. The surface topography of tridymite is virtually identical with cristobalite, and would be expected to adopt similar geometries to the extent that immediate coordination environments dictate the properties of the surface, therefore trisilanol 1 should also model tridymite-like surface morphologies. Although bulk cristobalite has a zinc-blend structure and tridymite has a wurtzite structure, the dimensions of their hydroxylated surface layers, which determine the chemical reactivity and many of the physical properties, are virtually identical.

The other silica modification is quartz, which seems to bear surprisingly little similarity to amorphous silica. Although the exact nature of the silica surface (if there is one!) is still the subject of immense controversy, the occurrence of cristobalite-like and tridymite-like surface structures has been frequently suggested and is supported by both theoretical and experimental data. Of particular relevance is the observation that fully-hydroxylated, heat-stabilised amorphous silica (a standard silica gel support) contains a “commonly observed” value of 4.6 SiOH groups per 100 Å². This is in remarkable close agreement with the calculated hydroxyl group concentration on the octahedral face of β-cristobalite (4.55) and the rhombohedral face of β-tridymite (4.56). The corresponding hydroxyl group concentration modeled by trisilanol 1 is 4.81.

Therefore, the close similarity between the bulk physical properties of amorphous silica, cristobalite and tridymite, as well as the observation that crystalline cristobalite and tridymite have been detected in samples of amorphous silica, do suggest that some regions of bulk amorphous silica can be reasonably represented by cristobalite-like and tridymite-like structures. The extrapolation of such structures to the silica surface is therefore reasonable.
1.5 Metallasiloxanes

Metallasiloxanes contain the Si-O-M functional group where M = main group metal, transition metal or f-element. The synthesis of organosilicon compounds containing a Si-O-M group dates back to the end of the last century.\(^{29}\) Metallasiloxanes, formally derived from \([R_3SiO]^−\), \([R_2SiO_2]^2−\), \([R_2SiO_4]^2−\), \([RSiO_3]^3−\), \([R_2Si_2O_{12}]^3−\), or \([(RSiO_2)_n]^n−\) silanolate functionalities, have attracted considerable interest among chemists, material scientists and physicists. The presence of a metal in the siloxane framework often results in high thermal stability and improved catalytic and conducting properties. Metallasiloxanes are structurally similar to modified silica surfaces. They have been found to mimic zeolite catalysts and hence are useful in understanding the reaction mechanisms for such catalytic conversions. Towards this end, there have been many attempts to develop suitable and useful homogeneous model compounds for heterogeneous catalysts. This would in turn offer insight into the molecular level understanding of the complex and insoluble systems, providing clues for controlling parameters such as catalytic selectivity, activity and catalyst lifetime.

In view of the importance of these metallasiloxanes in the last few decades as building blocks, there has been intense activity in the chemistry of silanols, with the use of silanols containing more than one hydroxy group becoming important.\(^{30}\) This is due to the fact that these compounds would be ideal starting materials for the generation of two- and three-dimensional metallasiloxanes with novel structural features. A balance of the steric and electronic factors is a key element in the stabilisation of these compounds, as evidenced by the reactivity studies of such silanols containing many hydroxy groups (due to the fact that these compounds tend to self-condense, by the elimination of water molecules, resulting in the formation of more stable Si-O-Si siloxane frameworks).

Several reports on aluminosiloxanes containing four-\(^{31}\), six- and eight-membered\(^{32,33}\) rings, and also on some soluble aluminosilsesquioxanes\(^{19b}\) have been published. However, investigations in the area of metallasilsesquioxanes of rare earth metals are
often hampered due to difficulties in the crystallisation and characterisation of these compounds.

1.5.1 Disiloxanediolates

Metallasiloxanes may be prepared by using silanols. In this thesis the diphenylsilanediol will be used in the synthesis of metallasiloxanes. This diphenylsilanediol when reacted with metal precursors, shows a tendency to self-condense and form derivatives of the siloxy $\alpha,\omega$-disiloxanate dianion, e.g., $\text{Ti(OSiPh}_2\text{OSiPh}_2\text{OSiPh}_2\text{OSiPh}_2\text{O)}_2^{2-}$ or $[\text{Ph}_2\text{SiO(GePh}_2\text{)}_2\text{OSiPh}_2\text{O}]$.\textsuperscript{35} This observation has been attributed to the strain energy that results in smaller metallasiloxane rings. The X-ray crystal structures carried out on these compounds indicate that cyclic structures are preferred over other forms of the metallasiloxane core. In a few cases where steric conditions play a major role, acyclic products are also obtained. The Si-O bond distances generally fall in the range of 1.60-1.66 Å, while the Si-O-M angles vary over a very wide range (136°-173°). These observed variations in the metric parameters are largely due to:

1. the type of metallasiloxane core (cyclic or acyclic),
2. the ring size,
3. the nature of the hetero / metal atom.

By comparison, organosilanolates of the general formula $R_x\text{Si(OM)}_4-x$ (M = group 1 or 2 metal cation, x = 1, 2 or 3) are less well known. A relatively large number of metallasiloxanes have been produced from the alkali metal $\alpha,\omega$-siloxane diolates, $[\text{MO(R}_2\text{SiO})_n\text{M}]$ (M = Li, Na). The reagents themselves are readily formed on treatment of the parent diol compounds with BuLi or sodium metal. Of all the compounds within this class, the phenyl-substituted analogue has received the most widespread attention. It has been observed that the reaction pathways are highly selective for specific reagent pairs. Studies involving these reagents with various
Precursor target metal compounds have led to a variety of interesting observations concerning ligand behaviour:

1. There may be intact transfer of the diolate ligand with chelate-bridging coordination modes, e.g. \([\text{Cr}\{\text{O(Ph}_2\text{SiO)}_2\}_2\}-\mu-(\text{NaTHF}_2)_2]\).  

2. The transfer may occur with a chain expansion to the trisiloxanediolate moiety, e.g. \([\text{Py}_2\text{Ti}\{\text{O(Ph}_2\text{SiO)}_3\}_2]\).  

3. The diolate has been found to function as an oxo transfer reagent, i.e. the formation of a metal oxide, a process accompanied by the elimination of the cyclic trisiloxane (Ph₂SiO).  

The dilithium reagent, \([\text{O(Ph}_2\text{SiOLi)}_2]\) whose structural identity is still unknown, gives products which result from intact transfer of ligands in reactions with MCl₄ where M = Zr, Hf, Sn and with siloxane chain expanded products for M = Ti. This situation is reversed when the disodium reagent is used. Furthermore, the product of the reaction with MgCl₂ and the dilithium reagent exhibits both the intact transfer and the chain expanded ligand in the same complex, which indicates that the pathways are not mutually exclusive. Attempts to transfer the disiloxanediolate, \([\text{O(Ph}_2\text{SiO)}_2]^2-\), to the target metal center(s) using the parent diol \([\text{O(Ph}_2\text{SiOH)}_2]\) have also been met with varying degrees of success. The ligand can be in bridging, chelate, or chelate-bridging modes. In general, the products obtained from these types of reactions, are largely dependent on the nature of the metal center used. Another interesting discovery was that the \(\alpha,\omega\)-siloxanediolate units may also be abstracted by metal compounds from cyclic or polysiloxanes to give various metallasiloxanes, for example, the formation of \([\text{Al}_3\{\text{O(Me}_2\text{SiO)}_2\}_2\text{X}_5]\) from the precursors (Me₂SiO)₄ and Al₂X₆, where X = Cl, Br. These results suggest that ligand oligomerisation, which occurs en route to metallasiloxane compounds, depends on the combination of reagent and the target metal center employed. The stability of these diols towards oligomerisation varies, but is surprisingly greatly improved by the presence of bulky organic substituents on the silicon atoms. More details on both the properties and the
structures of relevant metallasiloxanes will be considered and discussed in the following chapters.

1.5.2 Metallasilsesquioxanes

Metallasilsesquioxanes containing Si-O-M fragments (M = metal) have been envisaged as molecular analogues of zeolites due to their astonishing geometrical relationship.44 These compounds are formally derived by the substitution of one or more Si atoms in a silsesquioxane cage for a heteroatom. When the heteroatoms are metal atoms, the term “metallasilsesquioxane” is used.

The trisilanol 1 is an excellent precursor for the preparation of metallasilsesquioxanes. The unique coordinating ability of this sterically demanding tridentate ligand, which prevents linear Si-O-M bonding angles and severely limits the extent of aggregation, provides an excellent opportunity to study the chemistry of electrophilic metal alkoxide complexes. Overall there are five general methods for attaching heteroatoms to an incompletely-condensed silsesquioxane framework:

1. reaction of SiOH groups with metal alkyl complexes;
   \[ \text{Si-OH} + \text{M-R} \rightarrow \text{Si-O-M} + \text{R-H} \]

2. metathesis of SiOH groups for less acidic alkoxide or amide ligands;
   \[ \text{Si-OH} + \text{M-Y} \rightarrow \text{Si-O-M} + \text{Y-H} \]
   \( Y = \text{OR} \) or \( \text{NR}_2 \)

3. base-assisted (e.g., Et₃N) reaction of SiOH groups with active metal halides;
   \[ \text{Si-OH} + \text{M-X} \rightarrow \text{Si-O-M} + [\text{R}_3\text{NH}]\text{X} \]

4. reaction of Me₄Sb-stabilised silsesquioxanes with metal halides;
   \[ \text{Si-OSbMe}_4 + \text{M-X} \rightarrow \text{Si-O-M} + [\text{Me}_4\text{Sb}]\text{X} \]

5. reaction of Tl-stabilised silsesquioxanes with metal halides or triflates;
   \[ \text{Si-OTl} + \text{M-X} \rightarrow \text{Si-O-M} + \text{TlX} \]
In rare instances the self-assembly of a metallasilsesquioxane can occur via both Si-O-Si and Si-O-M bond forming reactions and can produce good yields of a single compound, for example, the reaction of polyphenylsilsesquioxane with NiCl₂ can afford good yields of a cluster compound containing four Ni atoms and two Si₆O₆ rings. Structural details on relevant metallasilsesquioxane complexes will be considered in Chapter 4.

1.5.3 Applications of Metallasiloxanes

The chemistry of metallasiloxanes derived from silanediols, disiloxanediols and related Si-OH species is an area of vigorous research activity, because such compounds are valuable precursors for metal oxides and silicates as well as models for silica-supported heterogeneous catalysts. Because of their high Si/O content and short-range structural similarities to known SiO₂ polymorphs, both silsesquioxanes and metallasilsesquioxanes have been used extensively as models for silica surfaces and silica-supported catalysts. Many of these compounds exhibit reactivity patterns reminiscent of heterogeneous catalysts, and several are catalytically active under conditions where traditional model compounds based on simple alcohols and silanols were unreactive.

Metallasilsesquioxanes, which can serve as molecular models for zeolites are well known. Feher et al. have reported on an aluminosilsesquioxane prepared by the "corner-capping" reaction of trisilanol 1 with AlMe₃, however this compound was not very suitable for the construction of zeolites by the sol-gel process, because the Si-C bonds were almost inert towards hydrolysis. Roesky et al. have synthesised various heterosiloxanes, which are soluble organic derivatives of aluminosilicates, by using kinetically stable silanetriols. These aluminosiloxane structures were promising starting materials for the synthesis of new zeolites under mild conditions by sol-gel processes, because both the Si-N and the Al-C bonds could be readily cleaved hydrolytically. A major failing however, of most conventional models is their
inability to mimic the coordination geometry of purported silica-supported species because most often the metal dictates the arrangements of ligands within its co-ordination sphere. Subtle changes in this arrangement, however, can have a profound influence on the chemical reactivity, so it is important to develop models, which mimic the ability of silica to dictate co-ordination geometry.\textsuperscript{24}

Important characteristics that can be replicated in silsesquioxane chemistry include electron-withdrawing bonding sites,\textsuperscript{47} interactions with adjacent oxygen donors\textsuperscript{48} which contribute to the stability of clusters grafted onto surfaces,\textsuperscript{49} and a defined orientation of surface hydroxy groups which can dictate the selectivity by which reagents react with the surface. For example, the enhanced alkene metathesis activity of surface carbon complexes over those of their homogenous analogues has been similarly exhibited in silicone chemistry.\textsuperscript{30} Silsesquioxane based homo- models for hetero- catalysts not only offer a unique opportunity to reach a molecular level understanding of heterogeneous catalysts, they are well underway to becoming applicable catalysts themselves. The steric and electronic properties of the silsesquioxane ligands render metal centres more Lewis acidic than using conventional alkoxide or siloxide ligands. This concept has been exploited in newly developed catalyst models for alkene metathesis, polymerisation and epoxidation and in the Diels-Alder reactions of enones.\textsuperscript{50}

Other applications can be envisioned in the near future. Several metallasilsesquioxanes have been reported to be active in the polymerisation of ethene. The chromium compound $[(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{O}_2\text{CrO}_2)]$\textsuperscript{51} and monomeric and dimeric $[(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9\text{V}=\text{O}]$\textsuperscript{52} are used for ethene polymerisation after activation by trimethylaluminium. Activity for catalysing alkene metathesis reactions is well documented for molybdenum and tungsten complexes. The first report on metallasilsesquioxanes being catalytically active in alkene epoxidation involved the Ti complex $[\text{Ti}(\eta_5-\text{C}_5\text{H}_5)(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]$\textsuperscript{53}
Last but not least, structural chemistry greatly benefits from the enormous variety of ring and cage structures found in various siloxane derivatives. A wealth of novel Si-O-M based polyhedral frameworks and suprastructures have been uncovered and exciting supramolecular assembles are emerging.

1.6 References


2.0 Behaviour of silanol ligands in the presence of selected acids and bases
2.1 Introduction

A variety of well-characterised disiloxanols are known, and some of these have been used for the synthesis of metallasiloxanes. The stability of these diols towards oligomerisation varies, but is surprisingly improved by the presence of bulky organic substituents on the silicon atoms. In comparison to the α,ω-siloxane diolate ligands mentioned in Chapter 1, attempts to transfer the disiloxanediolate O(Ph₂SiO)₂⁻ to target metal centres using the parent diol O(Ph₂SiOH)₂ have been met with varying degrees of success also. In general, the products obtained from the reactions with the diol [O(Ph₂SiOH)₂] are largely dependent on the nature of the target metal centre used.

In reactions involving the diol R₂Si(OH)₂ as reagent, intact transfer of the diolate ligand to a target metal centre is not always observed. In contrast the diolate ligand t-Bu₂SiO₂⁻ is transferred intact, without oligomerisation of the diol ligand to the target metal centres in all reported cases.¹ The difference in behaviour between the two ligands is most likely due to the relative difference in steric bulk of the R-group functionalities present. The t-Bu group being more sterically demanding than the phenyl ring will prevent attack at a given silicon atom, in turn, reducing the likelihood of oligomerisation. With oligomerisation occurring for Ph₂Si(OH)₂, it was decided to monitor its relative degree of oligomerisation to give an insight into, or to possibly elucidate the reaction scheme.

The co-ordination chemistry of α,ω-siloxane diolate ligands [O(R₂Si)ₙ]²⁻, (where n = 1, 2, ...) represents a specific area of metallasiloxane chemistry. The subject area as a whole covers metal complexation by a range of other important siloxanolate ligand types, such compounds containing the RSiO₃, R₂SiO₂ and R₃SiO functionalities. A recent review by Sullivan et al.² was concerned solely with main-group and transition-metal compounds incorporating Dₙ siloxy fragments of the type: O(R₂SiO)ₙ. Another review by Roesky³ based upon literature published prior to 1996, described the chemistry associated with many of the metallasiloxane compounds derived from diorganosilanediols R₂Si(OH)₂, α,ω-siloxane diols [HO(R₂SiO)ₙH] and organosilanetriols RSi(OH)₃. Earlier reviews and books⁴ have dealt more specifically
with hetero- and metalla-siloxanes containing siloxy groups of the type \( \text{R}_3\text{SiOH} \). The general synthetic and structural chemistry of organosilanols has been described in a recent review by Lickiss.\(^1\)

One of the most industrially important fields in which silanols play a vital role, is in the preparation of polysiloxanes often known as silicones. An important reaction of silicon compounds containing electronegative substituents is hydrolysis which often occurs very readily even in atmospheric moisture. The primary reaction in silicone production is the hydrolysis of halosilanes, usually the readily available chlorosilanes, to give silanols, which undergo acid-catalysed condensation with the loss of water, as shown below in Scheme 2.1. The condensation reaction of a silanol to a siloxane is catalysed by acids and bases and is also promoted by high temperatures.

\[
\begin{align*}
2 \text{Me}_3\text{SiCl} + 2 \text{H}_2\text{O} & \quad \rightarrow \quad 2 \text{Me}_3\text{SiOH} + 2 \text{HCl} \\
\text{Me}_3\text{SiOSiMe}_3
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{SiCl}_2 + 4 \text{H}_2\text{O} & \quad \rightarrow \quad 2 \text{Ph}_2\text{Si(OH)}_2 + 4 \text{NH}_4\text{HCO}_3 \\
\text{Ph}_2\text{SiOSiPh}_2 \quad \text{HO} \quad \text{OH}
\end{align*}
\]

Scheme 2.1 The hydrolysis of chlorosilanes.

The synthesis of the majority of metallasiloxanes in this thesis involves the amine-assisted metathesis between the ligands, with either triethylamine or pyridine being used. As previously established, both silanediols and disiloxane diols are susceptible to some degrees of oligomerisation under certain reaction conditions. This oligomerisation process will occur particularly in cases where the organic substituent (\( \text{R} \)) has a low steric demand. Oligomerisation may also occur following prolonged storage of the diol compounds in solution (the dry, solid reagents are generally stable).
2.2 Aims of this work

Amine-assisted metathesis is one of the most popular methods for the preparation of metallasiloxanes. Prior to using amine-assisted metathesis in reactions of metalhalides with silanols, it would be advantageous to acquire a better understanding of the mechanism of the interactions. So far very little is known about the specific reaction mechanism involved, as the intermediate structures in these reactions have very high reactivity potentials and are unstable in solution phase. Therefore, it would benefit siloxane chemistry immensely to clarify the reaction pathways involved by structurally characterising these intermediate species. Reactions utilising amine and silanol ligands for the preparation of metallasiloxanes, even when conducted at low temperature, will often lead to products incorporating chain expanded siloxane units. This result will be demonstrated throughout this thesis. The exact role of the target metal in promoting these oligomerisations is not easy to distinguish from oligomerisation that occurs away from the metal centre in the presence of the amine and solvent alone. This metal-free oligomerisation is of primary focus here in this chapter.

As many of the reactions carried out in this thesis utilises, it was decided to investigate further the mechanism of the Lewis acid catalysed condensation of siloxanes with the corresponding amine-assisted metathesis using FeCl₃ as a model Lewis acid. The interaction between diphenylsilanediol and FeCl₃ was monitored to investigate if the same interaction occurs using FeCl₃ instead of AlCl₃.

2.3 Investigation of siloxane – amine systems

2.3.1 Synthesis of (HO)Ph₂SiOSiPh₂O(PyH) (2)

The simple diphenylsilanol Ph₂Si(OH)₂ was chosen for these studies. It can be prepared by the controlled hydrolysis of dichlorodiphenylsilane. Initial studies involved using this synthesised material, however for more reliable conclusive experimentation a purchased sample from Aldrich was used. What was
mechanistically occurring in the course of the interaction between the amine and Ph$_2$Si(OH)$_2$ was virtually unknown, and could only be speculated upon.

Silanols have relative high acidity compared with carbinols and phenyl, methoxy, fluoro and chloro substituents enhance the acidity. Gas phase acidities of longer chain alkyl silanols have been found to be greater, however it is unclear whether polarisability or inductive effects play a more significant role when the alkyl chain is lengthened. $^1$H NMR studies show that there is less shielding of the OH proton in silanols than in related carbinols, thus indicative of increased protonic character in the silanol.

Ph$_2$Si(OH)$_2$ and pyridine were mixed in a 1:1 ratio using diethylether as the solvent and the mixture was stirred for 48 h (See Scheme 2.2). All volatiles were then removed in vacuo, giving a white powder. The white product 2 was re-crystallised from a concentrated THF solution at 0°C.

![Scheme 2.2 Synthesis of (HO)Ph$_2$SiOSiPh$_2$O(PyH) (2).](image)

$\text{Ph}_2\text{Si(OH)}_2 + \text{NC}_5\text{H}_5 \rightarrow \text{Ph}_2\text{Si(OH)}_2 + \text{O}^{\text{H}}\text{SiO}^{\text{H}}\text{SiO}^{\text{H}}\text{Ph}_2$

The pyridine-siloxanol 2 was produced by an interaction of pyridine and the diol. This compound 2 shows characteristic Si-O-Si stretching between 1050-1110 cm$^{-1}$ in the IR spectrum and characteristic pyridinium bands at 3165, 1589, 720 and 700 cm$^{-1}$.

$^1$H NMR of 2 in C$_6$D$_6$ has shown a spectrum with a number of multiplets relating to the pyridinium cation at 8.31, 7.83, 6.90 and 6.58 ppm and for the Ph$_2$Si- fragment at 7.10 - 7.00 ppm. The $^1$HNMR spectrum of 2 is comparable to the spectrum of the
starting ligand, however the $^1$H NMR has additional signals due to the presence of pyridinium. The signal for the OH group is broadened because of hydrogen-bonding and appears at lower field in the $^1$H NMR compared to that of the precursor. This can be associated to the fact that there is the presence of a pyridinium group in the crystal lattice. In the $^{13}$C NMR three carbon resonances for the pyridinium and a number of resonances for the aromatic carbons were observed. $^{29}$Si NMR of 2 revealed two signals in a 1:1 ratio for the non-equivalent SiPh$_2$-fragments in the structure at -44.99 and -47.40 ppm, with the resonance for the Ph$_2$SiOHpy fragment occurring at slightly higher field.

X-ray quality crystals have been isolated in a 30% yield by slow crystallisation from THF at 0°C. The X-ray structure of 2 is shown in Fig. 2.1 and selected bond lengths and angles are presented in Table 2.1.

Fig 2.1 X-ray structure of (HO)Ph$_2$SiOSiPh$_2$O(PyH) (2).
Table 2.1 Selected Bond Distances and Angles for 2.

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<tr>
<th>Bond Distances (Å)</th>
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<tr>
<td>Si1-O1 1.596(6)</td>
<td>O1-Si1 1.596(6)</td>
<td>N1-C22 1.37(2)</td>
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<tr>
<td>Si1-O3 1.641(9)</td>
<td>N1-C23 1.37(3)</td>
<td>C-C (avg.) 1.36(2)</td>
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<tr>
<th>Bond Angles (deg)</th>
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<tbody>
<tr>
<td>O1-Si1-O3 110.3(4)</td>
<td>Si1-O1-Si1 180.0(1)</td>
<td>C23-N1-C22 106.6(19)</td>
</tr>
<tr>
<td>O1-Si1-C2 112.5(7)</td>
<td>C9-C2-Si1 116.2(18)</td>
<td>C23-C22-N1 125(2)</td>
</tr>
<tr>
<td>O1-Si1-C8 106.6(9)</td>
<td>C15-C2-Si1 131.4(17)</td>
<td>C22-C23-N1 128(3)</td>
</tr>
<tr>
<td>O3-Si-C8 110.6(10)</td>
<td>C12-C8-Si1 118(2)</td>
<td></td>
</tr>
<tr>
<td>O3-Si-C2 108.3(6)</td>
<td>C1-C8-Si1 127(3)</td>
<td></td>
</tr>
</tbody>
</table>

The average Si-O bond length in 2 of 1.611Å is comparable to the idealised Si-O (1.603Å) bond distances in natural tetrahedral silicates, however the Si-O bond length for the Si-O attached to the pyridinium is much higher (1.641Å) than this idealised Si-O bond distance, this is due to the steric effect of the pyridinium cation.

The N-C average bond length is 1.370Å, and the average C-C distance for this molecule is 1.360Å. The Si-O-Si bond angle of 180° is indicative of a linear structure, with no bond angle strain from its pyridinium environment. This molecule is completely strain free within its arrangement in the crystal lattice.

Thus, according to the X-ray diffraction studies, the mixture of diphenylsilanediol and pyridine yielded a tetraphenylsiloxanediol with one of the OH groups hydrogen-bonded to a pyridine molecule. The structure of the unit cell of (HO)Ph₂SiOSiPh₂O(PyH) (2) consists of two [(OH)Ph₂SiO-SiPh₂O]⁻ silanolate anions and of two pyridinium cations. In each adjacent unit cell the pyridinium cations are found lying in alternating fashion with either the N-H of the pyridinium facing the silanolate anion or facing the adjacent unit cell.

The formation of the siloxanol in 2 thus gives valuable information on the reaction pathway that these reactants follow. This compound formed is an intermediate in the
amine-assisted metathesis and siloxane condensation reactions. The reaction presumably involves the condensation of Ph$_2$Si(OH)$_2$ to the higher siloxane – OSiPh$_2$OSiPh$_2$- unit ($\alpha,\omega$-siloxane diolate) followed by a further interaction with the amine to form a tetraphenylsiloxanediol coordinated to a pyridinium ion. This intermediate could in turn either condense to form the trisiloxane ring (Ph$_2$SiO)$_3$ or react with an appropriate metal halide via an elimination of pyridinium salt PyHX (X = halogen).

The dry solid diphenylsilanediol itself is generally stable to oligomerisation when stored. For products incorporating further siloxane chains in metallasiloxanes, the metal employed is thought to have a role to play in promoting this ligand expansion to higher oligomers. This formation of 2 from Ph$_2$Si(OH)$_2$ in the presence of pyridine is in direct contradiction to previous findings by other groups working in this area. It was reported earlier that the oligomerisation of Ph$_2$Si(OH)$_2$ to Ph$_4$Si$_2$O(OH)$_2$ was not promoted by NEt$_3$ or by pyridine, as both silanols were recovered unchanged from solutions of NEt$_3$ or Py after 24 h. In this case perhaps the experimental conditions that regular metallasiloxane synthesis are carried out in were not adhered to, for example, possibly the solvent used in the reaction was not dry enough and there was then water interference in the process.

Even when the reaction between Ph$_2$Si(OH)$_2$ and pyridine was conducted at low temperature (10°C and 0°C), the product with a chain expanded siloxane unit was isolated. Variation in the amount of pyridine utilised in this study did not affect the reaction process significantly, and the intermediate (HO)Ph$_2$SiOSiPh$_2$O(PyH) (2) was invariably detected in all cases.

The structure 2 gives a wealth of important information regarding the mechanistic pathway that these ligands follow. The intermediate (HO)Ph$_2$SiOSiPh$_2$O(PyH) (2), proves the suggestion that initially there is the coordination of the base (amine) to the silanol via hydrogen coordination. This coordination is then followed by the migration of the H (of the OH group) to a pyridine molecule and in turn this pyridinium group is hydrogen-bonded to the O of the [HO(Ph$_3$SiO)$_2$]$^{-1}$ ligand. What happens next is the condensation of these siloxane ligands to form for example, the
fully-condensed trisiloxane or tetrasiloxane, (the trisiloxane being less sterically demanding therefore more stable), or in the case when using a metal precursor, a metathetic exchange between the ligand and the Lewis acid metal center to form the desired metallasiloxane.

Previous work on the 1,3-diol, Ph₂Si(OH)-O-Si(OH)Ph₂, also showed the formation of hydrogen-bonded adducts with organic species. For example, addition of pyridazine to Ph₂Si(OH)-O-Si(OH)Ph₂ afforded a 3:2 adduct [(HOPh₂Si)₂O]₃(C₄N₂H₄)₂ in which there were OH·OH and OH·N hydrogen bonds.⁶ A pyridinium adduct, (HOPh₂Si)₂O.C₅H₅N.HCl was also previously obtained which crystallised from a reaction mixture of the the silanol and TiCl₄ in the presence of pyridine.⁷ This structure is however different from 2 obtained here in this investigation in that the Cl⁻ ion interacts both with the pyridinium proton and the two silanol OH groups. The TiCl₄ is therefore taking part in the metathesis, whereas in 2 there is no metallic reagent present.

It was of great interest to explore if similar interactions occur for the silsesquioxane trisilanol, [(c-C₆H₈)₇Si₇O₉(OH)₃] (1).

2.3.2 Synthesis of [PyH][{(c-C₆H₁₁)₇Si₇O₉(OH)₂}₂O₂H] (3)

The two general silanol ligands that were chosen for the synthesis of aluminosiloxane complexes in this research were the diphenylsilanol, Ph₂Si(OH)₂ and the incompletely-condensed trisilanol [(c-C₆H₁₁)₇Si₇O₆(OH)₃] (1). With the isolation of an intermediate from the interaction between Ph₂Si(OH)₂ and pyridine, it was decided to investigate the simultaneous interaction with the partially-condensed silsesquioxane [(c-C₆H₁₁)₇Si₇O₆(OH)₃], (1). This ligand is of huge interest in metallasiloxane synthesis, and understanding the metathetic pathway involved could solve a lot of mechanistic problems and provide a solution to this ambiguity.

The interaction of the trisilanol 1 with pyridine (1:1) in a solution of diethylether was carried out (Scheme 2.3). The solution was concentrated in vacuo. and stored at 0°C.
After 14 days storage colourless X-ray quality crystals were grown from the ethereal solution and their structure determined by X-ray diffraction studies.

Scheme 2.3 Synthesis of [PyH][{(c-C₆H₁₁)₇Si₇O₆(OH)₂}₂O₂H] (3).

The IR spectrum (nujol) of compound 3 exhibited characteristic pyridine bands at 1599 and 751 cm⁻¹. ¹H NMR in C₆D₆ showed a complex spectrum with broad multiplets between 0.95 and 1.87 ppm for the methine and the methylene protons in the c-C₆H₁₁ substituents. The spectrum also showed four characteristic signals attributable to pyridinium at 8.78, 8.52, 6.66 and 5.68 ppm. In the ¹³C NMR the methine resonances are slightly further upfield (23.69 to 24.07 ppm) than the methylene resonances (26.62 to 26.89 ppm). ²⁹Si NMR revealed three signals (−59.45, −67.40, and −69.09 ppm) in a 3:1:3 ratio. The resonances in the NMR spectra of molecule 3 were slightly shifted comparatively with the correspondent signals for the starting ligand.

The reason lying behind the fact that there are only 3 signals for the different silyl fragments in the solution state NMR is because of the fluxional behaviour of the hydrogen-bonded network. Most likely there is a rearrangement (migration) of the H-
atoms between the different silanol groups in 3, which cannot be detected in the NMR resolution timescale. Thus, the silicon atoms that are coordinated to the different OH groups all appear to have the same chemical environment.

The ortep plot from a single crystal X-ray diffraction study of the unit cell in molecule 3 is shown in Fig. 2.2.

Fig. 2.2 Structure of the Unit cell of [PyH][{(c-C₆H₁₁)₇Si₇O₉(OH)₂}₂O₂H] (3). Si- black, O- red, N - green; c-C₆H₁₁ groups are omitted for clarity.

From the ortep plot it can be seen that the molecule crystallises as isolated ion pairs with strong intramolecular hydrogen bonding. The solid state structure has a space
group P-1 with the two pyridine molecules sitting in the center of the cubic structure and with the dimer molecules on each of the four corners of the cube. The pyridine molecules are not bonded to the silsesquioxane dimers, but are positioned in the crystal structure to counteract the overall charge.

According to the X-ray diffraction study (see Fig. 2.3), the molecule 3 consists of a dimeric hydrogen-bonded silsesquioxane anion and a pyridinium cation. The main bond angles and distances are displayed in Table 2.2.

Fig. 2.3. X-ray structure of of [PyH][{(c-C_{6}H_{11})_7Si_7O_9(OH)_2}_2O_2H] (3).

(carbon atoms are are omitted for clarity).
Table 2.2. Selected bond distances and angles for 3.

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Si1-O2</th>
<th>Si3-O12</th>
<th>Si6-O6</th>
<th>Si1-O1</th>
<th>Si4-O3</th>
<th>Si6-O5</th>
<th>Si2-O2</th>
<th>Si4-O4</th>
<th>Si7-O10</th>
<th>Si2-O9</th>
<th>Si5-O5</th>
<th>Si7-O7</th>
<th>Si3-O3</th>
<th>Si5-O4</th>
<th>Si-C (av.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.598(4)</td>
<td>1.622(4)</td>
<td>1.599(4)</td>
<td>1.618(4)</td>
<td>1.613(4)</td>
<td>1.624(4)</td>
<td>1.622(4)</td>
<td>1.617(4)</td>
<td>1.816(4)</td>
<td>1.600(4)</td>
<td>1.624(4)</td>
<td>1.628(4)</td>
<td>1.612(4)</td>
<td>1.622(4)</td>
<td>1.839</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th>O2-Si1-O11</th>
<th>Si1-O1-Si5</th>
<th>148.5(3)</th>
<th>C3-C2-N1</th>
<th>103(3)</th>
<th>O2-Si1-O1</th>
<th>Si3-O3-Si4</th>
<th>160.6(3)</th>
<th>C2-C3-N1</th>
<th>134(4)</th>
<th>O6-Si1-O2</th>
<th>Si4-O4-Si5</th>
<th>146.8(2)</th>
<th>Si7-O8-Si4</th>
<th>148.4(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>108.8(2)</td>
<td>109.2(2)</td>
<td>109.6(2)</td>
<td>107.9(2)</td>
<td>107.5(2)</td>
<td>110.1(2)</td>
<td>123(3)</td>
<td>O-Si-C(avg)</td>
<td>110.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The bond distances in molecule 3 for the Si-O bonds range from 1.598 to 1.628Å (average 1.615Å) which is comparable to 1.603Å for the idealised tetrahedral Si-O distance in the framework of silicates.\(^9\)

The O-Si-O bond angles in molecule 3 have a distorted tetrahedral arrangement and range from 107.5 to 110.1° (average 109°) and are comparable to the corresponding bond angles of the starting ligand (107.1 – 110.2°). The Si-O-Si bond angles in molecule 3 range from 147.5 to 160.8°; these bond angles here are slightly shorter than those of the starting ligand, presumably due to steric reasons, and possibly due to the central pyridine molecules in the cubic core.
The interaction between the diphenylsilanediol and pyridine (compound 2) described earlier involved an oligomerisation, whereas for this interaction, the formation of the silsesquioxane pyridinium 3 is the resulting stable intermediate in this pyridine-assisted metathetic interaction. The pyridine assisted in the deprotonation of an OH group from the trisilanol 1, to form the mono-anionic derivative, and in the presence of Py the corresponding pyridinium salt was produced. This pyridinium ion was used as the counter cation in the lattice structure for the silanolate anion \([\{c-C_{6}H_{11}\}_{7}Si_{7}O_{10}(OH)_{2}\}^{-}\].

Trisilanol 1 is formally derived from the hydrolytic removal of one silicon atom from a stable octameric silsesquioxane (i.e. \(T_{8}\)). It therefore exhibits a strong tendency to undergo reactions to fill the vacant vertex. Reactions of 1 with \(R'SiCl_{3}\) in the presence of an amine, not surprisingly, leads to completely-condensed products and provides a convenient method for synthesising mixed \(T_{8}\)'s with seven chemically inert cyclohexyl rings and one reactive functional group. The product 3 obtained here gives an idea regarding the interaction that occurs initially between pyridine and the trisilanol 1 before the metathetic reaction that would follow if a metal containing complex were present.

Incompletely-condensed silsesquioxanes are excellent solution-state models for hydroxylated silica surfaces, and they have been used extensively to probe the effects of intramolecular hydrogen-bonding on the reactivity of the Si-OH groups. Although the implications of this work for silica surface chemistry are still controversial, it is abundantly clear that intramolecular hydrogen-bonding can have profound effects on the reactivity of mutually hydrogen-bonded Si-OH groups. Reactions of the trisilanol 1 are several orders of magnitude faster than analogous reactions involving simple silanols.

The chemistry of 1 is similar in many respects to the chemistry of other silanols,\(^3\) but there are a number of notable differences. For example, 1 is monosilylated with remarkable selectivity upon reaction with \(Me_{3}SiCl\) in \(NEt_{3}-THF\).\(^{10}\) Similarly the
reaction of 1 with an excess of SbMe₅ quickly produces a monofunctionalised product, which only slowly reacts further with additional SbMe₅. Mechanistic studies relating these to other observations strongly suggest that the unique reactivity of 1 is a consequence of increased acidity caused by hydrogen bonding between the three siloxy groups which stabilises its conjugate base and also its salts containing the anion present in 3. In the case of silylation reactions, the intermediacy of ion pairs (e.g. anionic mono-deprotonated trisilanol 1) is strongly implicated.

Feher et al. have also reported on the synthesis and characterisation of a stable anion [NBu₄][((c-C₆H₁₁)₅Si₇O₁₀(OH)₂] which was prepared by an exchange reaction of a Tl derivative of 1 and [NBu₄]Cl (See Fig. 2.4). In stark contrast to anions derived from simple alcohols and silanols, the monoanion of 1 did not react with phosphonium ions even in hydrocarbon solvents, and it was stable also with respect to cyclocondensation.

![Fig. 2.4 Previously reported anion prepared by exchange reaction of Tl derivative of 1 and [NBu₄]Cl.](image)

The results here demonstrate that extensive hydrogen-bonding can stabilise anions derived from multiple hydrogen-bonded silanols. Because conjugate acids of stable anions are generally more acidic than conjugate acids of less stable anions, the acidity of silica surface sites possessing multiple hydrogen-bonded siloxy groups must be
greater than the acidity of isolated SiOH groups. Although controversial, this conclusion is completely consistent with recent work by Drago\textsuperscript{13} and Morrow,\textsuperscript{14} which implies the existence of a significant subset of hydrogen-bonded siloxy groups, which are both more acidic and more reactive toward SbMe\textsubscript{2} than isolated siloxyl groups. Thus, the structure 3 is in accordance with the suggested anionic monodeprotonated trisilanol.

2.4 Investigation of interaction of silanediol and FeCl\textsubscript{3}

In the literature on metallasiloxane synthesis using diphenylsilanediol the outcome of the reaction has been shown to vary with changes in the metal precursor used. For example, intact transfer occurred in the formation of [Cp\textsubscript{2}MOSiPh\textsubscript{2}O\textsubscript{2}] (M = Zr) from Cp\textsubscript{2}MCl\textsubscript{2},\textsuperscript{15} and oligomerisation occurred in the complex [Ti(O(SiPh\textsubscript{2}O)\textsubscript{4})\textsubscript{2}] from the use of Ti(OPr\textsubscript{t})\textsubscript{4}.\textsuperscript{16} In the presence of strong Lewis catalysts, e.g., AlCl\textsubscript{3}, diphenylsilanediol undergoes oligomerisation also, and will be demonstrated in the following chapters. As has been mentioned in Chapter 1 the target metal appears to promote oligomerisation but to different degrees and therefore the reagent combinations that are employed greatly affect the nature of the resulting metallasiloxane.

The interaction between Lewis acids (e.g. AlCl\textsubscript{3} and lanthanide halides) and silanols are extensively utilised in this work. Therefore, it was of relevance to study the pathway in which the Lewis acid catalyses the condensation of the silanol to produce a siloxane. The investigation into the condensation of Ph\textsubscript{2}Si(OH)\textsubscript{2} was carried out a number of times incorporating the Lewis acid AlCl\textsubscript{3} with amine-assistance, and in each case the completely-condensed trisiloxane (Ph\textsubscript{2}SiO\textsubscript{3}) was detected. It is now known that the reaction initially goes through the formation of the intermediate (HO)Ph\textsubscript{2}SiOSiPh\textsubscript{2}O(PyH) (2), and with the subsequent condensation yields this trisiloxane cycle. Different behaviour in oligomerisations can be due to steric factors
from the R-group functionalities present, for example, the less sterically demanding phenyl group compared to the \( t \)-Bu group increases the likelihood of the silanediol to oligomerise to some degree. In the synthesis of varied metallasiloxanes however, the diphenylsilanediol can undergo further oligomerisation, hence its stability decreases due to the presence of metal promoting agents. With AlCl\(_3\) being used initially as the Lewis acid in these studies difficulties in isolating any intermediate species prompted the use of another Lewis acid e.g. FeCl\(_3\).

Therefore the reaction between FeCl\(_3\) and Ph\(_2\)Si(OH)\(_2\) was carried out in a THF-pyridine mixture. The Ph\(_2\)Si(OH)\(_2\) and pyridine were initially mixed in THF and the FeCl\(_3\) was added under stirring. The mixture was heated under reflux for 24 hours. The solution was then concentrated and stored at 0°C for two days (See Scheme 2.4).

\[
6 \text{FeCl}_3 + 3 \text{Ph}_2\text{Si(OH)}_2 \\
10\text{Py} \\
\text{THF} \\
3 \text{py.} \quad \left[ \begin{array}{c} 
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Fe} \\
\text{O} \\
\text{Fe} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right] \quad \left[ \begin{array}{c} 
\text{HPy} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]_2 + \quad \begin{array}{c} 
\text{Ph} \\
\text{Ph} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Ph} \\
\text{Ph} \\
\end{array}
\]

Scheme 2.4 Synthesis of [HPy]\(_2\)[Fe\(_2\)OCl\(_6\)].Py (4).

The complex [HPy]\(_2\)[Fe\(_2\)OCl\(_6\)].Py (4) was isolated as orange X-ray quality crystals. Another product obtained in this reaction was the cyclic trisloxane, (Ph\(_2\)SiO)\(_3\). Both of these products have been characterised by elemental analysis, NMR and IR spectroscopy. The structure of complex 4 was also studied by X-ray single crystal diffraction.
The most striking feature in the I.R. spectrum of 4 is an intense broad band at 860cm⁻¹. Strong absorption in this region is characteristic of μ-oxo-di-iron(III) complexes, and therefore this band can be assigned to the Fe-O-Fe asymmetric stretch. It occurs at somewhat higher energy than in most other μ-oxo-dimers of Fe(III) and may be due to a stronger than usual Fe-O interaction, a view consistent with the shorter than usual Fe-O distance. Unfortunately, due to the strong paramagnetic nature of the Fe(III) complex 4, NMR spectroscopy was not very informative. The ¹H NMR spectrum of 4 showed only very broad peaks attributed to pyridine.

An ortep plot of the X-ray diffraction study of 4 is shown in Fig. 2.5.

The complex consists of independent [HPy]⁺ cations and [Fe₂OCl₆]²⁻ anions and pyridine solvent molecules, all of which have crystallographically imposed C₃ symmetry. Since the structure of 4 has been previously published, the structural details will not be discussed here. This analogous oxygen bridged diiron complex was previously obtained by Nelson et al. and the synthesis, crystal structure, and
magnetic properties of the bispyridinium (μ-oxo)bis[trichloroferrate(III)]-pyridine 
[HPy]2[Fe2OCl6].Py (4), have been reported. However the route used for the 
preparation of their complex was quite different: their synthesis involved the 
hydrolysis of FeCl3 in an ethanol-pyridine solvent mixture, with the concentration of 
water not exceeding 2%.

Since then a number of other salts containing the (μ-oxo)bis[trichloroferrate(III)] 
dianion have been synthesised and crystallographically characterised.18,19 Synthesis of 
these species has been achieved by a variety of methods yielding the dinuclear oxo-
bridged complex in many instances as a serendipitously obtained side product. In 
1985, Armstrong and Lippert published a convenient, high-yield synthesis of 
[Et4N]2[Fe2Cl6O],20 which is similar to the procedure published by Do, Simhon, and 
Holm.21

The main approaches to the syntheses of the μ-oxo-monobridged complexes have 
been summarised in Murray’s review and include:22

(1) hydrolysis of ferric chelate complexes or of ferric salts in the presence of a 
chelating ligand, and perhaps a general base, in either water or an organic solvent, 
and

(2) oxidation (usually aerial) of ferrous complexes, usually in nonaqueous solvents.

These two approaches remain valid for complexes in this subcategory. However in 
this work the formation of complex 4 occurred as a result of the Lewis acid (FeCl3) 
catalysed condensation of the disilanol Ph2Si(OH)2. This result might be important 
for understanding the mechanism of Lewis acid catalysed condensation of silanols.
2.5 Conclusions

Interactions of pyridine with both disilanol and trisilanol derivatives have been studied using NMR and IR spectroscopy and X-ray single crystal diffraction studies. It has been proven that due to the acidic nature of the Si-OH functionalities, they become involved in hydrogen-bonding to the amine. It is also confirmed that the siloxanediol \([\text{O(Ph}_2\text{SiOH})_2]\) is stable to further oligomerisation in the presence of pyridine or triethylamine. The compound \((\text{HO})\text{Ph}_2\text{SiOePh}_2\text{O(PyH)}\) (2), obtained must be an intermediate in the amine-assisted metathesis reaction of the diphenylsilanol ligand.

Incompletely-condensed silsesquioxanes have been used immensely to examine the effects of intramolecular hydrogen-bonding on the Si-OH reactivities. In the presence of pyridine, the trisilanol 1 is deprotonated and the corresponding pyridinium salt, \([\text{PyH}][(\text{C}_6\text{H}_{11})_2\text{Si}_7\text{O}_9(\text{OH})_2]_2\text{O}_2\text{H}]\) (3) is formed. The deprotonated anionic trisilanol 1, i.e., its conjugate base, is stabilised by multiple hydrogen-bonding. The discovery of this pyridinium salt 3 gives an insight into the possible metathesis that this important silanol undergoes in the presence of an amine before further reaction with for example a metal complex.

From the reaction between FeCl\(_3\) and Ph\(_2\)Si(OH)\(_2\) in the presence of pyridine the bispyridinium (µ-oxo)bis[trichloroferrate(III)]-pyridine, \([\text{HPy}_2][\text{Fe}_2\text{Cl}_6\text{O}_2]\)Py (4) was obtained as a side product, along with the major product in this reaction, the cyclic trisiloxane (Ph\(_2\)SiO)\(_3\). This reaction shows the possible mechanism of the Lewis acid catalysed silanol condensation. Analogous complexes with the same and different terminal ligands have been reported on, but the method for the preparation of 4 utilised here is novel. For the first time it can be shown that this compound can be formed as a result of FeCl\(_3\) assisted condensation of the diphenylsilanediol.
2.6 References

Chapter 3 Disiloxanediolates of Aluminium and Lanthanides
3.1 Introduction

3.1.1 Aluminosiloxanes

Aluminosiloxanes are metallasiloxanes containing Si-O-Al fragments. They are the closest molecular analogues to aluminosilicates (zeolites). Although aluminosilicates are widely found in nature and have achieved great practical and commercial significance, the chemistry and applications of aluminosiloxanes is still poorly developed. Meanwhile, molecular aluminosiloxanes are expected to be promising catalysts as well as good starting materials for the synthesis of new zeolites.

In the last few years several research groups, for example H. W. Roesky and co-workers, have shown that aluminopolysiloxanes which are soluble in organic solvents can be relatively easy prepared.\textsuperscript{1} Most of the synthetic approaches to aluminosiloxanes are based on reactions of highly reactive aluminium alkyl derivatives with silanol (SiOH) groups.

Several soluble aluminosiloxanes with Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{4} and Al\textsubscript{4}Si\textsubscript{2}O\textsubscript{6} frameworks have been prepared using these methods.\textsuperscript{1,2,3} These aluminosilicates were obtained from the reaction between a silanetriol and HAl/Bu\textsubscript{2} and depend on the reactant stoichiometry and the temperature used (See Scheme 3.1). The eight-membered aluminosilicate has the same structural unit found in the mineral gismodine (CaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}(H\textsubscript{2}O)\textsubscript{4})\textsubscript{n}. The Al\textsubscript{4}Si\textsubscript{2}O\textsubscript{6} framework can be derived from the Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{4} ring by the additional coordination of two aluminium atoms, which are bound to the hydroxyl group on one silicon atom and to the two oxido bridging ligands on the other silicon atom.
Scheme 3.1 Synthesis of $\text{Al}_2\text{Si}_2\text{O}_4$ and $\text{Al}_4\text{Si}_2\text{O}_6$ aluminosilicate frameworks.

M. Veith et al.\textsuperscript{4} have also reported on aluminopolysiloxanes with the eight-membered $\text{Al}_4(\text{OH})_4$ rings, which have been synthesised by a simple reaction of $[\text{tBuOAlH}_2]_2$ with diphenylsilanediol (See Scheme 3.2). The OSi(Ph\textsubscript{2})O Si(Ph\textsubscript{2})O units present in the molecule can be attributed to the Lewis acid catalysed condensation of the Ph\textsubscript{2}Si(OH)\textsubscript{2} monomers. This aluminium oligosiloxane crystallised with four molecules of diethyl ether. Three of the diethyl ether molecules were coordinated to the hydrogen atoms of the OH groups and the fourth was incorporated within the crystal lattice. They also carried out corresponding host-guest chemistry using different Lewis bases.
Another approach to aluminosiloxanes is via cleavage of the Si-O-Si bond by aluminium halide or aluminium alkyl derivatives. α,ω-siloxanediolate units may be abstracted by metal compounds from cyclic or polysiloxanes to give various metallasiloxanes. Several reports on compounds formed in this way have appeared in the literature.

For example:

$$\text{Al}_2X_6 + (\text{Me}_2\text{SiO})_4 \rightarrow [\text{Al}_3\{O(\text{Me}_2\text{SiO})_2\}_2X_3]^5$$ where $X = \text{Cl, Br}$.

The synthesis and structures of four membered aluminosiloxanes have been described by Schmidbaur et al.$^6$ In their work the tetramethyldisiloxane $\text{Me}_2\text{HSiOSiHMe}_2$ was cleaved by aluminium trihalides to give dimethylhalosilanes and aluminosiloxane dimers $[\text{Me}_2\text{HSiOAlX}_2]_2$ ($X = \text{Cl, Br, I}$). Similar cleavage of cyclodimethylsiloxanes by dialkylaluminium hydrides has been reported and resulted in a series of asymmetrical cyclic aluminosiloxane compounds.$^7$

### 3.1.2 Metallasiloxanes of rare earth metals

There has been an increased interest in the utilisation of siloxide ligands in the chemistry of the f-elements. It is known that alkoxide complexes$^8$ of these metals provide chemically more robust alternatives to the more common cyclopentadienyl complexes in catalytic applications. Literature data on metallasiloxanes of lanthanide and actinide elements is very scant. Most research on disiloxanediolates and
polyhedral metallasilsesquioxanes of the early transition metals and the $f$-elements is covered in a recent review by Edelmann et al.\textsuperscript{9}

There was an early report on the preparation of Me$_3$SiO- complexes of trivalent erbium and gadolinium in the literature,\textsuperscript{10} but the structure of the products were not defined by X-ray crystallography. The synthesis of the tetravalent cerium compounds Ce(OSiR$_3$)$_4$ (R = Ph, Me, Et) has also been accounted for.\textsuperscript{11} Evans et al.\textsuperscript{12} have reported on two synthetic routes for the synthesis of a series of silyloxy complexes of the trivalent lanthanides, namely the triphenylsiloxy complexes [Ln(OSiPh$_3$)$_3$(THF)$_3$](THF) (Ln = Y, Ce, Nd, Pr), and the crystal structure of the Ln = Ce derivative. One route employed anhydrous lanthanide nitrates as starting materials and it demonstrated that these nitrates could be used as a new class of precursors to homoleptic silyloxy complexes. A second route to these silyloxy complexes was based upon an oxo alkoxide starting material derived from a nitrate and demonstrated that alcoholysis of an oxide-containing precursor could generate an oxide-free product. Anhydrous trivalent metal nitrate compounds have been shown to be good alternative precursors to these silyloxides and to oxo alkoxides as well.

There have been some publications on trialkyl and triphenylsilanolates of cerium and some other lanthanides\textsuperscript{15} and most recently several tris(trimethylsilyl)siloxides of lanthanum and gadolinium have been prepared and structurally characterised.\textsuperscript{13} Some research on different phenyl disiloxanediolates of rare earth elements has been reported by Edelmann et al.\textsuperscript{14} The authors prepared and characterised new scandium and $f$-element (Nd, Eu, Sm, Gd and U) complexes. The ‘silylamide route’ and the reaction with dilithiated phenyl disiloxanediols were found to be good methods for making such species. An interesting example is the reaction of U(COT)$_2$ with an excess of tetraphenyldisiloxanediol resulted in the formation of an oxidised U(VI) siloxane derivative containing expanded trisiloxanediolate ligands. This type of siloxane ring expansion had been earlier reported for some main group elements and transition metals by Sullivan et al.\textsuperscript{15}
Heterobimetallic siloxanes are expected to be valuable new precursors for the assembly of unusual metal-containing Si-O frameworks, which might demonstrate interesting catalytic behaviour. Sullivan et al.\textsuperscript{16} have carried out research on the coordination chemistry of disiloxanediolates with various transition metals, and have produced some heterobimetallic structures, for example, \{Ti(Ph\textsubscript{4}Si\textsubscript{2}O\textsubscript{3})\textsubscript{3}Na(py)\textsubscript{2}\} and \{M(Ph\textsubscript{4}Si\textsubscript{2}O\textsubscript{3})\textsubscript{3}Li(py)Li(py)\textsubscript{2}\} where M = Zr, Hf. However there is only report from Edelmann \textit{et al}.\textsuperscript{17} on lanthanide heterobimetallic siloxanes which have been derived from the disiloxanediolate ligands utilising a "silylamide route".\textsuperscript{18} In all cases heterobimetallic complexes with lithium were formed, \textit{e.g.}, Eu[Et\textsubscript{2}O]Li\{Ph\textsubscript{2}Si(O)\textsubscript{2}O\}] (see \textbf{Scheme 3.3}).

\textbf{Scheme 3.3} Heterobimetallic lanthanide-lithium siloxanediolates.

It is important to mention that due to their 4f\textsuperscript{n} ground state electronic configuration, most of lanthanide complexes in the +3 oxidation state are paramagnetic, except those of La\textsuperscript{3+} (4f\textsuperscript{8}) and Lu\textsuperscript{3+} (4f\textsuperscript{14}). Complexes of the middle and late lanthanides(III) have very broadened paramagnetically shifted \textsuperscript{1}H NMR signals, which are very difficult to assign. This sometimes makes their NMR spectroscopic studies difficult.
NMR spectral data on paramagnetic lanthanide(III) complexes are therefore quite scarce.

3.2 Aims of this work

The first main objective of this part of the thesis is to develop new anionic and cyclic aluminosiloxanes using amino-assisted metathesis between silanols and aluminium trichloride, or the reaction of aluminium alkyls and alkyl halides with silanediols. Anionic aluminosiloxanes are particularly attractive as homogeneous models of zeolites, which also have ionic nature. Some research on the potential Lewis acid cleavage of cyclic siloxanes by aluminium trichloride has also been planned. In the preparation of aluminosiloxanes, using \((\text{Me}_2\text{SiO})_4\) and \(\text{AlCl}_3\) as precursors, as described above in equation 2 in Section 3.1.1 an unexpected isolated material was produced \([\text{Al}_3\{\text{O}(&\text{Me}_2\text{SiO})_2\}]_2\text{Cl}_3\). Therefore a synthetic investigation into the phenyl derivative of this cyclic siloxane, \(i.e.\) the \((\text{Ph}_2\text{SiO})_4\), will be carried out and discussed in this chapter.

The second main objective was to prepare and investigate novel lanthanide containing disiloxanediolates. Several different synthetic approaches have been applied here. The work concentrated mostly on representatives of the early lanthanide series such as La, Ce and Nd. These lanthanides have a large atom radius and consequently high coordination numbers, which could lead to some interesting coordination chemistry. Also lanthanide(III) ions with electrophilic siloxane ligands are hard Lewis acids and high coordination numbers might allow one to prepare potentially catalytically active species. Ce has two stable oxidation states (+3 and +4) so it is of great interest to investigate the redox behavior of the cerium atom in the very electrophilic siloxane environment. Ce(IV) siloxane derivatives could also be important as potential oxidation catalysts.

All the reported heterobimetallic siloxanes mentioned in this introduction, formally contain lithium derivatives of silanol ligands acting as monoaonionic ligands. The bimetallic nature of these complexes is due to the presence of this lithium moiety.
Finally, the third main objective in this part of thesis is to prepare heterobimetallic complexes, which contain metals other than alkali metals in the siloxane framework.

3.3 Results and discussion

3.3.1 New aluminosiloxane complexes

3.3.1.1 Synthesis and characterisation of 

\[ \text{[PyH][Al\{OSiPh}_2(OSiPh_2)_2O\}_2] (5) \text{ and } [\text{AlCl(THF)\{O(Ph}_2\text{SiO)_2}\}_2] (6) \]

The reaction of aluminium trichloride with four equivalents of Ph\(_2\)Si(OH)\(_2\) in THF in the presence of an excess of pyridine proceeds with the precipitation of [PyH]Cl identified by NMR and elemental analysis, to produce two new aluminosiloxanes, anionic [PyH][Al\{OSiPh}_2(OSiPh_2)_2O\}_2] (5) and cyclic [AlCl(THF)\{O(Ph}_2\text{SiO)_2}\}_2] (6) with 53 % and 16 % yields respectively (see Scheme 3.4). The products were isolated by fractional crystallisation from THF. Further examination of the remaining mother solution by NMR spectroscopy revealed also the presence of fully condensed trisiloxane (Ph\(_2\)SiO\(_3\)).

The formation of at least three different products indicates a quite sophisticated mechanism for the process. The reaction presumably involves the Lewis acid aluminium chloride catalysed condensation of Ph\(_2\)Si(OH)\(_2\) to higher siloxanes containing -OSiPh\(_2\)OPh\(_2\)SiO- and -OSiPh\(_2\)(OSiPh\(_2\))Ph\(_2\)SiO- units and the following pyridine-assisted metathesis between the ligands and aluminium chloride.

Additional products of the reaction could also be hydroxy- or oxy- chlorides of aluminium, which were not isolated, perhaps due to their small amounts and low solubility in the system.
Scheme 3.4 Synthesis of [PyH][Al{OSiPh$_2$(OSiPh$_2$)$_2$O}]$_2$ (5) and [AlCl(THF){O(Ph$_2$SiO)$_2$}]$_2$ (6).

The complex 5 has shown close elemental analysis. The IR spectrum of 5 in Nujol contains characteristic Si-O-Si stretching between 1012 – 1120 cm$^{-1}$ and pyridinium bands at 3162, 1589, 721 and 700 cm$^{-1}$. $^1$H NMR of 5 in C$_6$D$_6$ gave a complex spectrum with a number of multiplets relating to pyridinium cation and to the Ph$_2$Si-fragments. The $o$-protons of SiPh$_2$ – groups are substantially shifted downfield (7.83 - 7.99 ppm) comparatively to the $m$- and $p$- protons of Ph-groups (7.01 - 7.09 ppm). The pyridinium resonances were found at 7.34, 7.23, 6.42 and 5.92 ppm. In $^{13}$C($^1$H) NMR of 5, three carbon resonances of the pyridinium at 146.94, 124.33 and 114.29 ppm were found and a number of resonances for the aromatic carbons were observed.
\(^{29}\text{Si}\{^1\text{H}\}\text{ NMR of 5 revealed two signals for two different types of SiPh}_2\text{-fragments at -42.36 and -43.56 ppm in a 1:2 ratio. In this case the resonance related to }\alpha\text{-silicones, which are closer to the Al centre, occurs at slightly higher field.} \n\nThe X-ray quality crystals of 5 were crystallised from its concentrated solution in THF at 0 °C.

\[ \text{Fig. 3.1 Crystal structure of the } [\text{Al}\{\text{OSiPh}_2(\text{OSiPh}_2)_2\text{O}\}_2]^+ \text{ anion in 5 (the rest of carbon atoms of aromatic rings are omitted for clarity).} \]

The structure consists of well separated pyridinium cations and aluminosiloxane anions. Selected bond distances and angles are presented in the Table 3.1. The closest N(cation)...C(anion) contact is 4.276 Å. In the anion, the Al atom is coordinated by four oxygen atoms of two cyclic siloxane fragments and has a slightly distorted tetrahedral arrangement with O-Al-O angles varying from 106.45(13) to 111.30(13) °.
Table 3.1. Selected bond distances and angles for 5.

**Bond distances (Å)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)-O(1)</td>
<td>1.733(3)</td>
</tr>
<tr>
<td>Al(1)-O(2)</td>
<td>1.723(3)</td>
</tr>
<tr>
<td>Al(1)-O(3)</td>
<td>1.772(3)</td>
</tr>
<tr>
<td>Al(1)-O(4)</td>
<td>1.724(3)</td>
</tr>
</tbody>
</table>

**Bond angles (deg)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Al(1)-O(3)</td>
<td>106.45(13)</td>
</tr>
<tr>
<td>O(2)-Al(1)-O(4)</td>
<td>111.26(14)</td>
</tr>
<tr>
<td>O(2)-Al(1)-O(1)</td>
<td>111.30(13)</td>
</tr>
</tbody>
</table>

A similar coordination mode of the same ligand was previously reported for Ti in cis-\([Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]\_C_6H_5Me\), but in the latter the Ti is additionally coordinated by two pyridine molecules providing a distorted octahedral geometry.\(^{19}\) This titanasiloxane was synthesised using TiCl\(_4\) and Ph\(_4\)SiO(OLi)\(_2\) in a 1:2 ratio with an excess of pyridine. The apparently facile formation of this cyclic siloxane was probably promoted by ring strain in the cyclic titanadisiloxane system, and the eight-membered rings were found to be almost planar. Previously reported structures of (PhBO)(Ph\(_2\)SiO)\(_3\),\(^{20}\) which has a ring conformation that can be described as a distorted boat shape, and [(py)\(_2\)Li]\(_2\)-\(\mu\)-Mg[\(\{Ph_2SiO\}_2O\]\(\{Ph_2SiO_3\}_3O\)]\(^{21}\) which was formed due to ring expansion of [(Ph\(_2\)SiOH)\(_2\)O] using KOBu\(_1\) and the monometallated derivative [K\(\{O(Ph_2SiO)_2SiPh_2OH\}\]\(_2\)

Two puckered eight-membered aluminosiloxane rings in 5 lie in perpendicular planes similar to those in cis-\([Ti\{OSiPh_2(OSiPh_2)_2O\}_2(py)_2]\_C_6H_5Me\).\(^{22}\) The eight-membered aluminoxane rings may also be considered as four-membered, if only the tetrahedral atoms (Al and Si) are considered such as referred to in zeolites. The diameter of the aluminosilicate rings in 5 is about 4.2 – 4.3 Å, i.e. comparable to those in zeolites such as, for example NaY.\(^{23}\) Al-O bond lengths in 5, ranging from 1.723(3) to 1.772(3) Å with an average of 1.738 Å, are longer than the corresponding...
ones in non-anionic aluminosiloxanes (e.g. from 1.714(4) to 1.718(4) Å in \([c\text{-}C_6H_{11})_7Si_{12}O_{12}Al(OOPPh_3)]^{24}\), but are comparable to those in other anionic aluminosiloxanes structures, e.g.: \([\{Na(\text{thf})_4]\{EtAlO_3SiR\}_4\] (1.753(4) – 1.784(4) Å), \([HNEt_3]_2\{(Ph_2Si)_2O_3\}_4Al_4O_2(OH)_2\] (1.715(3) – 1.829(4)Å),\(^3\) and \([HNEt_3]\{\{(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)O_2\}_2Al\}•C_6H_{14}\) (1.725(7) - 1.788(6) Å).\(^{25}\) Si-O bond lengths in 5, range from 1.588(3) to 1.647(3) Å with an average of 1.619 Å. The average Si-O and Al-O bond lengths in 5 are comparable to the idealised Si-O (1.603 Å) and Al-O (1.761 Å) distances in natural tetrahedral aluminosilicates.\(^{26}\)

The other product from this reaction of AlCl\(_3\) with Ph\(_2\)Si(OH)\(_2\) in the presence of pyridine was the cyclic aluminosiloxane \([AlCl(\text{THF})\{O(Ph_2SiO)\}_2]\] (6) in a 16 % yield. This compound has also been prepared alternatively by the reaction of Et\(_2\)AlCl and Ph\(_2\)Si(OH)\(_2\) in THF with an improved yield of 32 % (See Scheme 3.5). The reaction proceeds with Et\(_2\)AlCl catalysed condensation of Ph\(_2\)Si(OH)\(_2\) to HOSiPh\(_2\)OPh\(_2\)SiOH followed by the replacement of the Et groups on aluminium with the siloxy groups.

Scheme 3.5 Alternative Synthesis of \([AlCl(\text{THF})\{O(Ph_2SiO)\}_2]\] (6).

The IR spectrum of 6 in Nujol contained a very broad band of characteristic Si-O-Si stretching with the maximum at 1091 cm\(^{-1}\).
The $^1$H NMR of 6 has shown multiplets at 7.02 - 7.07 ppm for $m$- and $p$- protons and at 7.89 ppm for the $o$-protons of the Ph$_2$Si- groups and also signals for THF. The $^{13}$C($^1$H) NMR of 6 revealed several carbon resonances, which can be attributed to the aromatic carbons and characteristic THF peaks. The $^{29}$Si($^1$H) NMR spectrum of 6 in benzene contained only one signal for the SiPh$_2$ fragments at $-44.77$ ppm. The solid state $^{29}$Si MAS NMR of 6 has shown one broad peak with a maximum at $-46$ ppm (Fig. 3.2).

![Solid state $^{29}$Si MAS NMR spectrum of 6.](image)

The X-ray quality crystals of complex 6 were crystallised from a concentrated THF solution at $-22$ °C. The structure of 6 is shown in Fig. 3.3, and selected bond lengths and angles for 6 are presented in Table 3.2.
Fig. 3.3 Crystal structure of the [AlCl(THF){O(Ph₂SiO)₂}]₂ (6) (the rest of carbon atoms of THF molecules are omitted for clarity).

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1)-O(1)</td>
<td>1.870(16)</td>
<td>1.662(17)</td>
</tr>
<tr>
<td>Al(1)-O(3)</td>
<td>1.645(17)</td>
<td>2.111(8)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (deg)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Al(1)-O(3)</td>
<td>104.0(8)</td>
<td>111.3(6)</td>
</tr>
<tr>
<td>O(3)-Al(1)-O(4)</td>
<td>118.5(8)</td>
<td>112.2(6)</td>
</tr>
<tr>
<td>O(4)’-Al(1)-O(1)</td>
<td>105.80(10)</td>
<td>103.4(8)</td>
</tr>
</tbody>
</table>

The major difficulty in the investigation of the crystal structure of 6 by the X-ray single crystal method was caused by the rather poor deflection of the X-rays. Even for quite large (about 1 mm) and quite well shaped single crystals, no reflections with
sufficient intensity \( I > 2\sigma(\text{I}) \) could be observed at \( \theta \) greater than 15°. It was decided therefore to apply the 0-15° limits to \( \theta \) for the data used in the structure refinement.

The low reflection capacity at high angles appears to be a more or less general feature for metallasiloxane derivatives, indicating the irregularities in the long-distance ordering.\(^4\) An extra input into long-range disorder in the present compound may in fact be due to incomplete population of the sites occupied by the guest molecules in its crystal structure. However the problems above do not affect too much the central aluminosiloxane core of the molecule and the standard deviation in bond lengths and angles in the \( \text{Al}_2\text{Si}_4\text{O}_6 \) ring fall into the range usually observed and may be discussed here.

The central fragment of 6 is a twelve-membered \( \text{Al}_2\text{Si}_4\text{O}_6 \) ring (see Fig. 3.3), which occurs in natural aluminosilicates.\(^2\) However, to the best of our knowledge, aluminosiloxane analogues have not yet been isolated. Similarly with 5, if you are counting only tetrahedral atoms (Al and Si) like zeolite experts do, the twelve-membered aluminosiloxane rings can be considered as six-membered.

The \( \text{Al}_2\text{Si}_4\text{O}_6 \) ring has a chair conformation with Si(2) and Si(2)' atoms lying at 1.332(3) Å above and below the plane formed by the other ten atoms. A chair conformation was also reported for the eight-membered \( \text{Al}_2\text{Si}_2\text{O}_4 \) ring in \([\text{RN}((\text{SiMe}_3)\text{Si(OH)}(\text{AlBu}^t\text{•THF}))_2\text{ (R =2,6-Pr}^t_2\text{C}_6\text{H}_3)]\) having two oxygen atoms out of the plane.\(^1\)

Al atoms in 6 have a distorted tetrahedral arrangement with angles around Al of 103.4(8) to 118.5(8) °. In the ring Al-O bond lengths of 1.645(17) and 1.662(17) Å (average of 1.654 Å) are shorter than those in 5 and in any other previously reported aluminosiloxanes: e.g. the closest average endocyclic Al-O bond length of 1.71 Å is in \([\text{RN}((\text{SiMe}_3)\text{SiO}_3\text{Al•dioxane})_4\text{ (R =2,6-Pr}^t_2\text{C}_6\text{H}_3)]\).\(^2\) The Al-Cl bond length of
2.111(8) Å is close to those reported in [Me₂HSiOAlCl₂]₂ (2.080(1) and 2.084(1) Å). The silicon atoms also have a distorted tetrahedral geometry with bond angles of 103.9(14) to 113.9(13) °. The Si-O bond lengths vary from 1.579(16) to 1.638(17) Å with an average of 1.607 Å, which is comparable to those in 5 and other aluminosiloxanes and extremely close to the idealised Si-O (1.603 Å) distance in natural tetrahedral aluminosilicates.

3.3.1.2 Linking of aluminosiloxane (6) rings: Synthesis of [Al{O(Ph₂SiO)₂}]₂[OPh₂SiO]₂ (7)

This cyclic aluminosiloxane [AlCl(THF){O(Ph₂SiO)₂}]₂ (6) described above was chosen as a precursor for the preparation of this new polyhedral structure 7 by the use of amine-assisted metathesis with Ph₂Si(OH)₂ in a THF solution. Ph₂Si(OH)₂ was added to a solution of complex 6 and NEt₃ in THF according to Scheme 3.6.

Scheme 3.6 Schematic presentation of the preparation of cyclic aluminosiloxane assembly [Al{O(Ph₂SiO)₂}]₂[OPh₂SiO]₂ (7).
A good reproducible yield of the oligomeric aluminosiloxane was obtained. The product 7 gave satisfactory elemental analysis. From the IR analysis signals for the Si-O-Si stretch were found. There were no signals for the free Si-OH stretch. From the $^1$H NMR spectrum resonances for o-phenyl protons appear between 7.89 and 7.69 ppm. The m- and p- protons are found more upfield between 7.08 and 6.95 ppm. In the $^{13}$C NMR resonances for the phenyl signals were observed between 134.7 and 130.5 ppm and also from 128.8 to 127.2 ppm. $^{29}$Si NMR revealed two signals at $-46.92$ and $-49.09$ ppm with a relative integrated ratio of 1:4 respectively.

The electrospray mass spectrum 7 of contained peaks at $m/z$ 239 ([Ph$_2$SiO$_2$Al]), 100%, 492 ([{AlO(SiPh$_2$O)$_2$}$_2$ - 3 THF]$^{2+}$, 20%), 1095 ([M]$^{2+}$, 12.5%) and 1271 [M + 5 THF]$^{2+}$, 15%), which clearly show the presence of the oligomeric species. The complex 7 is abbreviated as M.

From MS and NMR analysis, it can be deduced that the interaction between the aluminosiloxane ring and the diphenylsilanediol occurred. The synthesis of this polyhedral aluminosiloxane linked by two silanolate ligands through the Al centers in two aluminosiloxane 12-membered rings is a good demonstration of the potential of this aluminosilicate precursor 6. Similar reactions of 6 could be carried out in the future to prepare novel oligomeric or polymeric assemblies using other linkers with different functionalities.

3.3.3 Synthesis of polyaluminosiloxane [Al(OH)]$_4$[(Ph$_2$SiO)$_2$O]$_4$ (8)

With polyaluminosiloxanes in mind, it was of paramount significance to investigate the interaction of AlEt$_3$ and the simple silanediol Ph$_2$Si(OH)$_2$.

The reaction of AlEt$_3$ (in toluene) with two equivalents of Ph$_2$Si(OH)$_2$ in the presence of pyidine in a solution of THF yielded product 8, which was recrystallised from
toluene at 0°C giving colourless crystals. The compound was investigated by NMR and IR spectroscopy and X-ray diffraction studies (See Scheme 3.7).

Scheme 3.7 Synthesis of [Al(OH)]$_4$[(Ph$_2$SiO)$_2$O]$_4$ (8).

Compound 8 gave satisfactory elemental analysis. The $^1$H NMR in C$_6$D$_6$ spectrum of 8 displays a sharp singlet at 6.08 ppm representative of the OH groups. Accordingly the IR spectrum of 8 contained a band at 3590 cm$^{-1}$ and was assignable to the O-H stretches. The $^{29}$Si NMR showed only one signal for the silicons present in 8 at -44.1 ppm.

X-ray quality crystals were grown from toluene, however due to the fact that the R-factor was too high (~0.18) it is not feasible to discuss the bond angles and lengths of molecule 8 here (See Fig. 3.4 for X-ray structure of 8).
As can be seen from the X-ray structure (Fig. 3.4), compound 8 is an isolated polyaluminosiloxane, which crystallises free of any solvent molecules. There is an Al₄O₄ eight-membered ring in the center of the structure of [Al(OH)]₄[(Ph₂SiO)₂O]₄ 8; the Al(OH)Al edges are spanned by four disiloxane bridges and each of the four aluminium atoms are connected through OH bridges to form a ring. This results in a framework of five annelated eight-membered rings, and the molecule has approximately S₄ point symmetry.

Although the reactions of Ph₂Si(OH)₂ with trialkylalanes could lead to [OAlOAlOSi] chains or [Al₂Si₂O₄] rings, no such observation were made here.²⁷

The reaction presumably involves the Lewis acid catalysed condensation of Ph₂Si(OH)₂ to the higher siloxane -OSiPh₂OPh₂SiO- unit and the subsequent metathesis between the ligands and AlEt₃.

Veith et al.⁴ have reported on a similar structure prepared from [BuOAlH₂]₂ and Ph₂Si(OH)₂ in Et₂O solution. This polyaluminosiloxane [(Ph₂Si)₂O₃]₄Al₄(OH)₄• 4Et₂O, also has a similar cross-like structure with an Al₄O₄ eight-membered core, but
where each Al atom was additionally coordinated by one diethyl ether molecule. In contrast the polyaluminosiloxane prepared in this work was solvent free.

Veith et al. have suggested that the hydrogen atoms of the OH groups in this sort of polyaluminosiloxane are available for coordination with Lewis bases. They have investigated the effects that various other Lewis bases with different steric requirements and basic strengths have on their \([(\text{Ph}_2\text{Si})_2\text{O}_3]_4\text{Al}_4(\text{OH})_4\cdot3\text{OEt}_2\) adduct. They have also studied whether the Lowenstein rule (according to which the \(\text{AlO}_4\) tetrahedra in such compounds are always separated by silicon atoms) is also applicable to molecular aluminium- or silicon-oxygen compounds. They found that the Lowenstein rule does not apply for their compounds and that their formation was apparently more "kinetically" rather than "thermodynamically controlled". Attack by bases occurred more readily on their \([(\text{Ph}_2\text{Si})_2\text{O}_3]_4\text{Al}_4(\text{OH})_4\cdot3\text{OEt}_2\) adduct than on their \([(\text{Ph}_2\text{Si})_2\text{O}_3]_4\text{Al}_4(\text{OH})_4\cdot4\text{Py}\) adduct.

It is remarkable that the aluminopolysiloxane 8 is quite stable in air. It was found unchanged after been subjected to the atmosphere for 1 week. In fact the X-ray diffraction studies were repeated on the crystals used for the reported structure and the same structural data was found.

3.3.1.4 Synthesis of spirocyclic Aluminosiloxane

\[\text{[Al}_3\text{O(Ph}_2\text{SiO})_2\text{]}_2\text{Cl}_3\] (9)

It has been previously reported that the reaction \((\text{Me}_2\text{SiO})_4\) and \(\text{AlCl}_3/\text{AlBr}_3\) at high temperature without solvent occurs with a cleavage of the siloxane ring and a formation of the spirocyclic aluminosiloxane (Equation 1).\(^5\)

\[\text{Al}_2\text{X}_6 + (\text{Me}_2\text{SiO})_4 \rightarrow \text{[Al}_3\text{O(Me}_2\text{SiO})_2\text{]}_2\text{X}_5\] where \(X = \text{Cl, Br}\).  

\textbf{Equation 1}
As the aluminium trichloride was active enough to cleave the cyclic methyl substituted siloxane, it was decided to investigate a similar reaction on the phenyl siloxane derivative (Ph₂SiO)₄.

Initially an equimolar mixture of AlCl₃ and (Ph₂SiO)₄ in THF was stirred for 48 hours at room temperature, however the starting materials were retrieved unchanged at the end of the reaction according to NMR analysis. The same mixture was then heated under reflux in THF. This time two main products: the cyclosiloxane (Ph₂SiO)₃ and aluminosiloxane [Al₃{O(Ph₂SiO)₂}₂Cl₅] (9) were isolated from the reaction mixture (See Scheme 3.8). Both of these products have been characterised by elemental analysis and by IR and NMR spectroscopy.

Scheme 3.8 Synthesis of [Al₃{O(Ph₂SiO)₂}₂Cl₅] (9).
A satisfactory yield of 9 was obtained and the elemental analysis obtained was representative of 9. The $^1$H NMR spectrum of 9 contained corresponding phenyl signals at 7.71 - 7.69 ppm for the o-protons and at 7.04 - 7.01 ppm for the m- and p-protons. The $^{29}$Si NMR exhibited a signal at -44.03 ppm for four equivalent silicones present in aluminosiloxane 9.

The aluminosiloxane $[\text{Al}_3\{\text{O(Ph}_2\text{SiO})_2\}_2\text{Cl}_3]$ is formed by condensation of four rings, two four-membered and two six-membered. The former, made up of oxygen and aluminium atoms, are planar. A central five-coordinate aluminium is present in this aluminosiloxane. Five-coordinate aluminium is rare, but has been shown to exist.

The remaining two aluminium atoms each have a distorted tetrahedral coordination with two chlorine atoms and two oxygen atoms.

As mentioned earlier a similar reaction but at very high temperature and without any solvent was carried out by two groups using $(\text{Me}_2\text{SiO})_4$ and $\text{AlCl}_3$ and $\text{AlBr}_3$ with the isolation of the crystalline material $[\text{Al}_3\{\text{O(Me}_2\text{SiO})_2\}_2\text{X}_3]$ (where X = Cl or Br). The chlorine analogue was prepared by Zhdanov et al. and following this, the bromine analogue was prepared similarly. Subsequent to these syntheses Bonamico et al. carried out the X-ray diffraction analysis on the bromine siloxane. The structure of the spirocyclic aluminosiloxane obtained consisted of an AlCl function at the spiro centre, with two 6-membered aluminodisiloxane rings bridged by the AlCl$_2$ groups. In this research here the reaction carried out between $(\text{Ph}_2\text{SiO})_4$ and $\text{AlCl}_3$ produced the comparable phenyl aluminosiloxane derivative (9).

Similar Si-O-Si bond cleavage by aluminium derivatives has been reported for several other siloxane systems. Bissinger et al. found that the linear tetramethyldisiloxane $\text{Me}_2\text{HSiOSiHMe}_2$ was cleaved by aluminium trihalides $\text{AlX}_3$ (X = Cl, Br, I) to give dimethylhalosilanes $\text{Me}_2\text{HSiX}$ and aluminosiloxane dimers $[\text{Me}_2\text{HSiOAlX}_2]_2$. It was noted that the disiloxane $(\text{H}_3\text{SiOSiH}_3)$ on reaction with aluminium halides gave only insoluble and involatile polymeric siloxy-aluminium dihalides. They reported on chlorosilane side products from the cleavage reaction of
(RH$_2$Si)$_2$O by Me$_2$AlCl, which was in contrast to the work done by Barron et al.$^{32}$ and Mulhaupt et al.$^{33}$ in which no silicon containing side products were isolated. Barron et al.$^{32}$ have reported on the reaction between AlCl$_3$ with (Me$_2$SiO)$_3$ and (Me$_2$SiO)$_4$ leading to the elimination of Me$_2$SiCl$_2$ and (Me$_2$ClSi)$_2$O respectively and the formation of the trialuminiun-siloxide compound.

The most remarkable observation made in this experiment was the siloxane ring shrinkage that resulted in the formation of cyclosiloxane (Ph$_2$SiO)$_3$ as a main product. This fact has not been previously reported for similar reactions. The IR spectrum of the cyclosiloxane (Ph$_2$SiO)$_3$ contained characteristic bands for the phenyl substituents present in the structure. The NMR data gave assurance that the trisiloxane ring was present with signals at 8.01 - 7.79 and 7.10 - 7.07 ppm, corresponding to the chemical shifts of the trisiloxane ring. The presence of (Ph$_2$SiO)$_3$ has also been confirmed by X-ray single crystal diffraction. The third product of the reaction has not been isolated Ph$_2$SiCl$_2$, due to its liquid nature, however the $^{29}$Si NMR of the residual mother liquid has clearly shown the presence of this compound in the mixture.

The proposed mechanism for the formation of [Al$_3$(O(Ph$_2$SiO)$_2$)$_2$Cl$_5$] (9) is shown in the Scheme 3.9.
Scheme 3.9 Proposed mechanism of formation of $[\text{Al}_3\{\text{O(Ph}_2\text{SiO})_2\}_2\text{Cl}_5]$ (9).

To develop a rational description of the chlorine transfer reaction from the previously mentioned studies, it is likely that the reaction of AlCl$_3$ with cyclic siloxanes (Ph$_2$SiO)$_n$ occurs via (a) ring opening cleavage, followed by (b) stepwise chain scission. Where long aluminium siloxane chains are formed, e.g., (Ph)$_2$Al(OSiPh$_2$)$_n$OSiPh$_2$Cl, $n \geq 3$, chain scission occurs one silicon at a time, starting
from the terminal silicon unit. The coordination of a siloxane to aluminium center results in the increased electrophilicity of the adjacent silicon atoms and hence increases its receptivity to chloride attack. On cleavage of the Si-O bond, migration of the Cl' ion goes to the Si atom, and the AlCl$_2$ cation coordinates to the O' ion of the linear siloxane. Due to bond angle strain in the linear siloxane, the more stable aluminosiloxane (Ph$_2$SiO)$_2$OAlCl, is formed. In the presence of the Lewis acid AlCl$_3$, two of these aluminosiloxanes side by side, are further cleaved as before resulting in the binary cyclic aluminosiloxane, the spirocycle [Al$_3$(O(Ph$_2$SiO)$_2$)$_2$Cl$_5$] (9).

Aluminium chloride obviously has no activity in ring-opening towards the (Ph$_2$SiO)$_3$ in refluxing THF, as (Ph$_2$SiO)$_3$ was repeatedly isolated from the reaction mixture.

3.4 **New lanthanide siloxanediolates**

In this work, lanthanide(III) metallasiloxanes have been prepared by two methods:

(i) amine assisted metathesis reactions of silanols with anhydrous lanthanide halides, and

(ii) the metathetic exchange of the less acidic amide or cyclopentadienyl ligand in the corresponding lanthanide complex for silanols.

Diphenylsilanediol was used as the siloxane ligand throughout the following syntheses.

3.4.1 **Reaction of Cp"$_2$CeCl and Ph$_2$Si(OH)$_2$.**

The objective of this experiment was to investigate the reaction of lanthanide cyclopentadienyl complexes with the disilanol ligand. The precursor Cp"$_2$CeCl was prepared using CeCl$_3$ and two equivalents of NaCp" in THF, the mixture was stirred for 24 hours. THF was removed in vacuum and the residue was extracted using
hexane. The hexane solution was filtered and then the filtrate was evaporated in \textit{vacuo}, yielding the yellow \( \text{Cp}''\text{CeCl} \).

The reaction between this \( \text{Cp}''\text{CeCl} \) and \( \text{Ph}_2\text{Si(OH)}_2 \) in a 1:1 reagent ratio was carried out in THF (see Scheme 3.10). \( \text{Cp}''\text{CeCl} \) was added to a solution of \( \text{Ph}_2\text{Si(OH)}_2 \) in THF and stirred for 24 hours. The solvent was removed in \textit{vacuo}. The residue was washed with hexane and dried in vacuum.

\[ \text{Cp}''\text{CeCl} \rightarrow \text{Ph}_2\text{Si(OH)}_2 \rightarrow \text{THF} \]

\[ \text{THF} \rightarrow -\text{HCp}'' \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

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\[ \text{Ce} \]

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\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

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\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]

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\[ \text{Ph} \]

\[ \text{Si} \]

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\[ \text{Cl} \]

\[ \text{THF} \]

\[ \text{Ph} \]

\[ \text{Si} \]

\[ \text{Ce} \]

\[ \text{Cl} \]
the structure 10. In solution state product 10 could exist in the monomeric form 10b or dimeric 10a in the solid state.

$^{13}$C NMR of 10 had THF resonances at 68.9 and 25.1 ppm, indicative of coordinated THF molecules in the compound. It also showed resonances for the phenyl carbons at 135.0-134.8 and at 130.4-128.5 ppm.

$^{29}$Si NMR of 10 was recorded in THF and showed only one signal at -77.27 ppm. This resonance found in the $^{29}$Si NMR spectra of 10 was shifted in comparison to the corresponding signal for the starting ligand. As the $^{29}$Si NMR was carried out in THF it is probable that the product exists as the monomer 10b.

Overall the analysis of this data above suggests the formation of either monomeric or dimeric 10 as presented in Scheme 3.10.

### 3.4.2 Amine-Assisted metathesis of LaCl$_3$ and Ph$_2$Si(OH)$_2$

To a mixture of Ph$_2$Si(OH)$_2$ and NEt$_3$ in THF, LaCl$_3$ was added in a 2:10:1 reaction ratio respectively and allowed to stir for 48 hours (See Scheme 3.11).

The resulting white precipitate identified by NMR as [HNEt$_3$]Cl was removed and the THF filtrate used to obtain a $^{29}$Si NMR. The remaining THF product solution (11) was dried in vacuo and analysed by $^1$H and $^{13}$C NMR.

![Scheme 3.11](image)

Scheme 3.11 Amine-assisted metathesis reaction between LaCl$_3$ and Ph$_2$Si(OH)$_2$ giving 11.
The product was obtained in a good yield and gave satisfactory elemental analysis. In the \(^1\)H NMR of 11, a number of signals were observed. The corresponding phenyl resonances were located at 7.11 – 7.08 ppm for the \(o\)-protons, and the \(m\)- and \(p\)-proton signals were found at slightly higher field 7.04 – 7.01 ppm. The signal for the HN- proton of the HNEt\(_3\) counter ion was found 7.34 ppm. Signals for the protons of the NEt\(_3\) were broadened significantly, with their resonances occurring at 2.30 and 0.89 ppm respectively. This broadening and appearance of a shoulder signal indicated that the protons of the counteraction [HNEt\(_3\)] and those of the coordinated NEt\(_3\) are overlapping with the same chemical shift values and therefore could not be resolved for integration purposes. 

\(^{13}\)C NMR revealed a number of resonances for the aromatic carbons of the phenyl groups in 11. Resonances for the HNEt\(_3\) and NEt\(_3\) protons were also observed at 46.33 for the CH\(_2\) carbons and at 8.96 for the CH\(_3\) carbons. 

\(^{29}\)Si NMR revealed two signals in the product spectrum of 11, at −45.73 and −46.93 ppm in a 1:2 integrated intensity ratio, for the different Ph\(_2\)Si- fragments present in compound 11. 

It is believed that the most plausible structure of 11, determined by NMR studies, is analogous to the aluminosiloxane 5, discussed earlier in Chapter 2. It consists of two eight-membered siloxane rings, with the central La(III) atom coordinated to four oxygen atoms, two from each cyclic siloxane. The anionic La(III) siloxane has an overall negative charge which is subsequently balanced by a triethylammonium cation. The only difference between 5 and 11 is that the lanthanum coordination sphere is filled by the ligating NEt\(_3\) molecules. 

3.4.3 Reaction of La\{N(SiMe\(_3\))\(_2\}\(_3\) and Ph\(_2\)Si(OH)\(_2\).

An alternative synthesis of a lanthanum metallasiloxane involving the silylamide approach was performed here. The silylamide La\{N(SiMe\(_3\))\(_2\}\(_3\) was prepared by reacting La(CF\(_3\)SO\(_3\))\(_3\), also written as La(OTf)\(_3\), with 3 equivalents of Li\{N(SiMe\(_3\))\(_2\)\}
in THF. The subsequent reaction between the La\{N(SiMe_3)_2\}_3 with three equivalents of diphenylsilanediol was carried out in a THF solution (See Scheme 3.12). The product was characterised by elemental analysis, IR and NMR spectroscopy.

La\{N(SiMe_3)_2\}_3 + 3 Ph_2Si(OH)_2 \rightarrow \text{THF} \rightarrow \text{Product 12}

Scheme 3.12 Reaction of La\{N(SiMe_3)_2\}_3 and Ph_2Si(OH)_2 giving 12.

The product 12 was obtained in a 50% yield. The elemental analysis found was lower than expected, however the THF loss may have occurred during the analysis or hydrolysis of the product. The reaction between the ligands led to a broadening of the phenyl signals in the ^1H NMR due to the presence of the La atom in the siloxane network. The signals for the phenyl groups occurred at 8.15 - 7.76 ppm for the o-protons, and at 7.11 - 7.05 ppm for the m- and p-protons. A signal for the proton of the Si-OH was found at 6.80 ppm. Proton signals for the THF groups were broadened with resonances at 3.49 and 1.33 ppm, which were shifted upfield slightly in comparison to free THF. The relative intensity integration indicated that there were 3 molecules of THF coordinated to the La^{3+} center.

The ^13C NMR spectrum exhibited signals for the phenyl carbons in 12, at 134.2 – 134.0 and at 129.67 - 127.98 ppm. THF signals coordinated to the La(III) center were observed at 70.1 and at 25.6 ppm.

The ^29Si NMR showed one signal for the equivalent Ph_2Si- fragments present in the siloxane 12 at -43.33 ppm.

It is believed that the the suggested structure of the product as shown in Scheme 3.12 has a La(III) coordination number of nine, with the La(III) center coordinated to nine
oxygen atoms, two from each cyclic siloxane fragment, with one of the O atoms still retaining its hydrogen, and also to three oxygens of THF molecules.

### 3.4.4 Reaction of NdCp"\textsuperscript{3} and Ph\textsubscript{2}Si(OH)\textsubscript{2}.

In this synthesis the reaction between NdCp"\textsuperscript{3} and Ph\textsubscript{2}Si(OH)\textsubscript{2} (1:3) was carried out in THF solution for 48 hours (See Scheme 3.13). The mixture was then dried in vacuo. and washed with hexane to give the product 13, which was investigated using IR and NMR (C\textsubscript{6}D\textsubscript{6}) spectroscopy.

![Scheme 3.13 Reaction of NdCp"\textsuperscript{3} and Ph\textsubscript{2}Si(OH)\textsubscript{2} giving 13.](image)

A satisfactory yield was obtained for the compound and the elemental analysis gave good accurateness. From the \textsuperscript{1}H NMR of product 13, corresponding signals for the protons in the phenyl groups were observed as broadened signals, appearing between 7.61 to 7.57 ppm, and between 7.11 and 7.09 ppm. This broadening was indicative of the presence of the paramagnetic Nd in the complex. Due to signal broadening, it was difficult to resolve the THF signals, however the integration was appropriate for 3 THF molecules. A signal for the proton of the OH groups was found at 6.91 ppm, shifted downfield in comparison to the starting material.

\textsuperscript{29}Si NMR of 13 revealed 2 signals, one for the free SiMe\textsubscript{3} groups at 1.98 ppm (residual free Cp"H), and another for the Si-O-Nd equivalent silicones at -36.32 ppm. Only one very broad signal for the Si-Ph\textsubscript{2} fragments was observed due to the
paramagnetic nature of the compound. In the suggested structure (Structure 13 in Scheme 3.13) the Nd is coordinated to nine oxygen atoms: six from the siloxane fragments and three from the THF molecules.

Attempts to grow X-ray quality crystals of 13, suitable for diffraction studies, was regrettably unsuccessful as the complex recurrently lost its THF solvent molecules.

3.4.5 Reaction of NdCp$^R_3$ and Ph$_2$Si(OH)$_2$.

The subsequent reaction between the NdCp$^R_3$ and Ph$_2$Si(OH)$_2$ (1:1) was carried out in THF solution and stirred for 48 hours (See Scheme 3.14). The mixture was then dried in vacuo. and the product 14 was investigated using IR and NMR spectroscopy.

Scheme 3.14 Reaction of Cp$^R_3$Nd and Ph$_2$Si(OH)$_2$) giving 14a and 14b
Elemental analysis gave satisfactory results. The IR spectrum of the product 14 showed a characteristic band of OH groups at 3545 cm⁻¹.

The ¹H NMR spectrum has shown corresponding signals for the protons in the phenyl groups in 14, which were broadened due to the paramagnetic nature of Nd(III). They were found in the area 7.90 - 7.64 ppm. Corresponding Cp signals were found at 7.11 - 7.01 ppm. The signals for THF were shifted and broadened due to coordination of 2 THF molecules to Nd. The OH proton signal was found at 6.74 ppm. The SiMe₃ protons were found at 0.29 ppm. In solution state product 14 could exist in the monomeric form 14a or dimeric 14b in the solid state.

The ¹³C NMR revealed signals for the phenyl groups in 14, at 138.0 -127.5 ppm and for the Cp signals at 203.1 ppm for the Cp ring, and at 0.71 for the SiMe₃ groups, and at 1.27-1.26 ppm for the CH of the Cp ring. Corresponding coordinated THF signals were observed at 68.18 and 25.52 ppm.

²⁹Si NMR revealed signals for the different silyl fragments present in compound 14. The Si of the SiMe₃ fragments was observed at -21.15 ppm. Two signals for different silyl fragments in the siloxane chain were observed at -41.62 and -44.99 ppm. The integrated intensity of the signals were found to be in a 4:1:1 ratio for the different silicones present in the compound. The Cp⁺ silicones occurring at -21.15 ppm, with the Si-OH silicones at -41.62 ppm and the Si-O-Nd silicones occurring at -44.99 ppm (See Fig. 3.6). As the solution state ²⁹Si NMR was carried out in THF, the product is thought to exist as the monomer 14a.

According to the results there is a metathesis between the NdCp₃ and the diol which occurred with the removal of one Cp group. It can be suggested that there is the subsequent hydrogen bonding of the silanol group to the Nd atom giving bis(cyclopentadienyl)-metallasiloxane 14 as the most plausible structure.
3.4.6 Reaction of \( \{\text{N(SiMe}_3\}_3\}_2\text{La(OTf)}\}_2 \) and \( \text{Ph}_2\text{Si(OH)}_2 \).

The lanthanum precursor \( \{\text{N(SiMe}_3\}_3\}_2\text{La(OTf)}\}_2 \) was synthesised by the reaction between \( \text{La(OTf)}_3 \) and two equivalents of \( \text{Li[N(SiMe}_3\}_2] \) in THF. The resulting \( \{\text{N(SiMe}_3\}_3\}_2\text{La(OTf)}\}_2 \) was reacted with \( \text{Ph}_2\text{Si(OH)}_2 \) in a 1:2 ratio in THF yielding the product 15 which was characterised by elemental analysis, IR and NMR spectroscopy (See Scheme 3.15).
Scheme 3.15 Reaction of \{N(SiMe_3)_3\}_2\text{La(OTf)}_2 and Ph_2Si(OH)_2 (15).

The product was obtained in good yield, however the elemental analysis data revealed low values which may have been due to oxidation or hydrolysis of the complex during analysis.

IR spectroscopy did not reveal any presence of unreacted hydroxyl groups.

From the \(^1\text{H} \text{NMR}\) the signals for the phenyl groups in 15 appeared broadened at 7.83 - 7.65 and at 7.10 - 6.9 ppm. There was no signal for the OH group present in the precursor and there were no signals for the N(SiMe_3)_3 groups. THF signals appeared at 3.56 and 1.39 ppm, with an average relative intensity integration showing in the majority of analyses 3 THF molecules per 2 phenyl groups.

\(^{13}\text{C} \text{NMR}\) of 15 exhibited signals for the phenyl resonances at 134.2 - 134.0 and 129.6 - 127.9 ppm. THF carbon resonances found at 67.11 and 25.09 ppm were thought to be those of coordinated THF. The carbon resonances for the CF_3 groups were shown at 203.10 ppm.
\(^{29}\)Si NMR spectrum of 15 has shown only one resonance at \(-40.5\) ppm for the equivalent silicon atoms present in the compound. According to NMR data, N(SiMe\(_3\))\(_3\) groups have been replaced by silanol ligands. The suggested structure is shown in the Scheme 3.15. From both the \(^1\)H and \(^13\)C NMR it can be deduced that there is THF coordination to the La center as the THF signals are shifted comparatively to those of the free solvent. However it cannot be guaranteed from solution state NMR that there are exactly 3 THF molecules coordinated to the La center, therefore the number of THF molecules is given as \(n\) in the proposed solid state structure in Scheme 3.15.

3.4.7 Reaction of CeCp"\(_3\) and Ph\(_2\)Si(OH)\(_2\).

It has been noticed before that silandiols can interact with U(IV) organometallic compounds with the oxidation of U(IV) to U(VI) and the formation of an U(VI) siloxane derivative containing expanded trisiloxanediolate ligands.\(^{17}\) It was of great interest to investigate the interaction of the silanediol Ph\(_2\)Si(OH)\(_2\) with cerium(III) organometallic compounds and explore the possibility of the formation of cerium(IV) metallasiloxanes. For this reason the interaction of cerium(III) triscyclopentadienyl [Ce\(\{\eta^2-C_5H_3(SiMe_3)\}_2\}\)\(_{-}\)1,3\(_{\}}\)_3], (CeCp"\(_3\)\), with diphenylsilanediol was studied here. The CeCp"\(_3\) was prepared via the previously reported method by Y. K. Gun'ko \textit{et al.}\(^{34}\) The reaction between CeCl\(_3\) and KC\(_5\)H\(_3\)(SiMe\(_3\))\(_2\) in THF with the subsequent extraction with hexane and evaporation of the solvent yielded the deep blue CeCp"\(_3\). From the addition of CeCp"\(_3\) to Ph\(_2\)Si(OH)\(_2\) solvated in THF, a colour change to orange was observed. The THF was removed \textit{in vacuo} to give an orange foam and subsequent analysis was carried out on the product 16 (See Scheme 3.16).
Scheme 3.16 Reaction of CeCp"\textsuperscript{3}" and Ph\textsubscript{2}Si(OH)\textsubscript{2} giving 16.

An adequate yield was obtained for the product 16. The elemental analysis was found to be high which may be due to excessive THF solvent molecules present in the complex. In the \(^1\)H NMR spectrum the \(\alpha\)-proton signals for the phenyl groups were found at 7.80 - 7.63 ppm, and those for the \(m\)- and \(p\)- protons of the phenyl groups were found at 7.11 - 7.01 ppm and were broadened which was indicative of Ce coordination to the siloxane units. Broad signals found at 3.40 ppm and at 1.21 ppm, have been attributed to THF molecules coordinated to the Ce(IV) center. The signals were broadened but not strongly shifted comparatively to the starting material, this indicates the diamagnetic nature of the complex and thus the formation of a Ce(IV) species.

\(^{13}\)C NMR revealed signals for the phenyl carbon resonances at 136.42 - 135.06 ppm and at 131.24 - 130.48 ppm. The signals for the carbon groups in the THF were found at 25.96 ppm and 70.14 ppm.

\(^{29}\)Si NMR revealed one signal for the equivalent SiPh\textsubscript{2}- fragments at \(-46.11\) ppm. This chemical shift of the silicon peak is typical of a diphenylsiloxane ligand coordinated to a diamagnetic metal centre, this again shows the formation of Ce(IV) compound.
According to NMR data the most plausible structure of 16 is the one shown in the Scheme 3.16. The coordination number of the central Ce(IV) is now eight. The cerium has a +4 oxidation state giving a neutral complex. The oxidation of Ce(+3) into Ce(+4) can be explained either by the presence of traces of the oxygen (e.g. from the solvent) in the mixture or by an oxidation from the siloxane ligand. As was mentioned earlier a similar phenomenon was observed with the oxidation of metallasiloxanes of U(IV) into U(VI).17

3.4.8 Amine-assisted metathesis of CeI₃ and Ph₂Si(OH)₂.

In order to better understand the remarkable oxidation of Ce(III) species into Ce(IV) and formation of complex 16, it was decided to investigate the similar reaction using a different cerium(III) precursor. This time cerium(III) iodide CeI₃ was reacted with 2 equivalents of Ph₂Si(OH)₂ in the presence of NEt₃ in a THF solution (See Scheme 3.17). During the course of the reaction white needlelike crystals precipitated. The crystals were identified by NMR spectroscopy as [HNEt₃]I. The solution was dried in vacuo and the product 17 was characterised by elemental analysis, IR and ¹H, ¹³C and ²⁹Si NMR spectroscopy.

Scheme 3.17 Amine-assisted metathesis of CeI₃ and Ph₂Si(OH)₂ giving 17.
Elemental analysis of the product gave close results to the theoretical suggested structure 17 in Scheme 3.17, the difference may be caused by partial hydrolysis of the sample during the analysis. The yield obtained was acceptable. From the $^1$H NMR of 17 there was broadening of the phenyl signals at 7.72 – 7.90 ppm for the $\sigma$- protons, and for the $m$- and $p$- protons at 7.11 – 7.04 ppm. The NEt$_3$ signals were slightly broadened also with their resonances occurring at 2.13 ppm for the methine protons and at 0.70 ppm for the methylene protons.

$^{13}$C NMR showed signals for the phenyl carbons at 136.92 – 130.71 ppm, and at 48.33 and 9.72 ppm for the NEt$_3$ carbons of the compound 17 in the system.

$^{29}$Si NMR showed up two signals in the spectrum -41.1 and -43.0 ppm in a 1:2 ratio respectively for the different SiPh$_2$- fragments in the system. The resonance for the $\alpha$-silicones which are closer to the Ce center occurring at the slightly higher field. Again similarly to the cerium complex 16 above, the NMR peaks of 17 were not so appreciably shifted and indicate on the formation of diamagnetic Ce(IV) species. It can be suggested that the environment around Ce$^{\text{IV}}$ center is the symmetrical, and two molecules of NEt$_3$ are coordinated to the Ce center, filling its coordination sphere.

Again similarly to the previous experiment the cerium has been oxidised from Ce$^{\text{III}}$ to Ce$^{\text{IV}}$. Thus the cerium atom in the complex is coordinated to four oxygen atoms, two from each cyclic siloxane fragment, with each siloxane fragment being 8 membered. The relative integrated intensities, in a 1:2 ratio, of the silicon resonances in the $^{29}$Si NMR supports the suggested structure 17.

This structure should be analogous to the aluminosiloxane structure 5 discussed in earlier and to the La(III) siloxane 11 discussed above, however one structural difference exists, this being that the proposed compound 17 is neutral. Without X-ray diffraction studies it is inappropriate to assume complete analogy. Lanthanide metals behave differently to group 13 metals, for example in this case the cerium has been oxidised to Ce(IV) to accommodate the coordination abilities of the siloxane ligands, and also the higher coordination number of the cerium atom here causes the excess NEt$_3$ donor ligands to fill the coordination sphere of the cerium. From the relative
integrated intensities of the resonances in the $^1$H NMR there are two NEt$_3$ molecules coordinated to cerium centre.

3.5 Conclusions

This work has demonstrated that a variety of aluminosiloxanes can be effectively prepared by the treatment of the correspondent silanols with AlCl$_3$ via the amine-assisted metathesis, or by direct reactions of AlEt$_3$ or AlEt$_2$Cl with the ligand. The reactions can proceed with the condensation of Ph$_2$Si(OH)$_2$ to higher siloxanes containing -OSiPh$_2$OPh$_2$SiO- and -OSiPh$_2$(OSiPh$_2$)Ph$_2$SiO- units giving as result anionic or cyclic aluminosiloxanes. Complex 6 is the first example of a 12-membered cyclic aluminosiloxane. Both aluminosiloxanes 5 and 6 appear to be appropriate molecular models for some fragments of aluminosilicate minerals. It can also be suggested that these complexes could be used as precursors for the preparation of other aluminosiloxanes or polyaluminosiloxanes. It has been demonstrated that the rings of cyclic aluminosiloxane 6 can be linked together giving higher oligomeric structures such as compound 7. Complex 8 prepared is a very good example of an aluminopolysiloxane, which is soluble in a variety of organic solvents. It could possibly be a promising precursor for the synthesis of new zeolitical materials. The presence of OH functionalities greatly amplifies its potential in further reactions.

The interaction between the Lewis acid AlCl$_3$ and the cyclic siloxane (Ph$_2$SiO)$_4$ in refluxing THF led to the cleavage of the tetrasiloxane ring yielding the spirocyclic aluminosiloxane [Al$_3$(O(Ph$_2$SiO)$_2$)$_2$Cl$_3$] (9) and the reduced size cyclic siloxane (Ph$_2$SiO)$_3$ as the main products. This unique ring shrinkage phenomenon has not been reported for these systems to date.

Reactions utilising Ce(III) precursors (e.g. CeI$_3$ and CeCp$^+$)$_3$) with silanediols proceeded with an oxidation of the central cerium atom from Ce(III) to Ce(IV) (Compounds 16 and 17). Cerium(IV) has advantages over cerium(III) for characterisation by NMR as the complexes formed from Ce(IV) are diamagnetic. Other reactions using lanthanide(III) precursors with different functions, for example
NdCp"3, NdCpR, LaN"3, and \{La(N")2(OTf)\}_2, gave the correspondent Ln(III) metallasiloxanes with the lanthanide atoms having high coordination numbers. Different extents in oligomerisation can be observed for the reactions involving the silanediol Ph\_2Si(OH)_2, and lanthanide precursors in the production of the various lanthanide siloxane complexes. This phenomenon has been previously observed by many groups and it has been concluded that silanediols are indeed susceptible to oligomerisation under certain reaction conditions. Chain expansion to the -OSiPh\_2(OSiPh\_2)Ph\_2SiO- units was observed in the presence of amine-assistance when using LaCl\_3 and CeCl\_3. Both Nd(III) and La(III) have been seen to adopt varied coordination numbers depending on their chemical environment. In complexes 11, 16 and 17, the lanthanide metal center is suggested to be coordinated by four oxygen atoms of two cyclic siloxane fragments. A similar coordination mode of the central metal atom in both 11 and 17 has been observed in the anionic aluminosiloxane 5. Complex 11 should be comparable to 5, as both are anionic, but different in that 17 which is neutral due to the oxidation of Ce(III) to Ce(IV) in 17.

Structures for the complexes 10 – 17 have been proposed on the basis of their solution NMR spectral analysis and with reference to previous literature findings. The solution state NMR of the products is not identical to that of the solid state NMR, therefore the structures proposed are for the products in solution state only.

Structural chemistry greatly benefits from the variety of ring and cage structures found in the various metallasiloxane derivatives described above. The reaction pathways described here may provide further access to new types of metallasiloxane complexes.
3.6 References


Chapter 4

Polyhedral Metallasilsesquioxanes of Aluminium and Lanthanides
4.1 Introduction

Acidic (e.g. aluminium) sites in zeolites and clays play an important role in catalysis. However, the study of such catalysts in detail is considerably hampered by the heterogeneity of these systems. Aluminium-containing polyhedral metallasilsesquioxanes possess highly siliceous Si/Al/O frameworks and offer excellent potential as models for the secondary building blocks (SBUs) which formally comprise aluminosilicates and zeolites.\(^1\) Aluminium silsesquioxanes have also been used as precursors for the preparation of microporous aluminosilicates by controlled calcinations. The calcination treatments result in the formation of metal oxide species highly dispersed throughout the amorphous silica.\(^2\)

Feher \textit{et al.}\(^3\) have reported on several aluminosilsesquioxanes that can be considered as homogeneous models of zeolites. Recently an increasing number of metal complexes based on incompletely-condensed silsesquioxanes\(^4\) have been prepared and successfully used as homogeneous models for silica-grafted catalysts.\(^1,5\) The few well defined aluminosilsesquioxane complexes known to date are either based on the cyclohexyl-substituted silsesquioxane trisilanol \((c\text{-}C_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3\) (I) or its monosilylated analogue \((c\text{-}C_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2\).\(^6\)

The first aluminosilsesquioxane reported was prepared by Feher \textit{et al.}\(^1\) by the treatment of \((c\text{-}C_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3\) (I) with AlMe\(_3\), to afford the dimeric aluminosilsesquioxane \({\{(c\text{-}C_6\text{H}_{11})_7\text{Si}_7\text{O}_9\text{Al}\}}_2\). In contrast, the reaction of the cyclopentyl-substituted silsesquioxane \((c\text{-}C_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3\) with AlMe\(_3\) did not yield a dimer, but instead gave a polymeric compound with an empirical formula of \({\{(c\text{-}C_5\text{H}_9)_7\text{Si}_7\text{O}_9\text{Al}\}}_m\) which was completely insoluble in most of the common organic solvents. The disilanol \((c\text{-}C_6\text{H}_{11})_8\text{Si}_8\text{O}_{11}(\text{OH})_2\), a bifunctional building block, is ideal for the construction of organosilicious polymeric material by reaction with organometallics. Interestingly, in contrast to this crystalline polymeric aluminosilsesquioxane, a similar reaction of AlMe\(_3\) with this disilanol \((c\text{-}C_6\text{H}_{11})_7\text{Si}_8\text{O}_{11}(\text{OH})_2\) resulted in the formation of a highly porous polymer with a high hydrocarbon capacity. The aluminosilsesquioxane is polymeric in nature due to the formation of bridging aluminium siloxy units. This
oligoaluminosilsesquioxane was found to accelerate Diels-Alder reactions of enones with several orders of magnitude over the thermal reaction. The apparent small difference in steric bulk between cyclopentyl- and cyclohexyl-substituents is large enough to result in considerably different structures (See Fig. 4.1).

\[
\begin{align*}
\text{Fig. 4.1 Structures of aluminosilsesquioxanes.}
\end{align*}
\]

Novel anionic aluminosilsesquioxanes \([\text{HNEt}_3][\{(c-C_5H_9)\text{Si}_7\text{O}_9(\text{OSiMe}_3)\text{O}_2\}_2\text{Al}\].\text{C}_6\text{H}_{14}\) and the cyclopentyl analogue, \([\text{HNEt}_3][\{(c-C_5H_9)\text{Si}_7\text{O}_9(\text{OSiMe}_3)\text{O}_2\}_2\text{Al}\] have also been reported recently. \([\text{HNEt}_3][\{(c-C_6H_{11})\text{Si}_7\text{O}_9(\text{OSiMe}_3)\text{O}_2\}_2\text{Al}\].\text{C}_6\text{H}_{14}\) was prepared by the triethylamine metathesis reaction of \(\text{Cy}_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2\) with \(\text{AlCl}_3\). Other aluminosilsesquioxanes have been prepared by the treatment of \((c-C_5H_9)\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2\) with \(\text{AlCl}_3\) yielding the corresponding Lewis acidic aluminosilsesquioxane \([\{(c-C_5H_9)\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\}]\text{AlEt}_3\text{NEt}_3\). In addition by allowing \(\text{AlEt}_3\) to react with two equivalents of \((c-C_5H_9)\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2\), the Bronsted acidic aluminosilsesquioxane \([\{(c-C_5H_9)\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\}]\text{Al}[\{(c-C_5H_9)\text{Si}_7\text{O}_{10}(\text{OSiMe}_3)(\text{OH})\}\] is selectively formed. This complex contains a strong hydrogen bond, and although the high strength of this hydrogen bond reduces the Bronsted acidity
substantially, it can be easily deprotonated by amines to yield the corresponding ammonium salts $\{[(c-C_5H_9)_{7}Si_{7}O_{11}(OSiMe_3)]_{2}Al\}X^+$ ($X = \text{Et}_3\text{NH}$, $\text{PhN(H)Me}_2$, $C_3H_5\text{NH}$). The ammonium cation is bonded to the aluminosilsesquioxane via a hydrogen bond.

Other metallasilsesquioxanes such as lanthanide metallasilsesquioxane derivatives are a more recent addition to this area of chemistry. Metallasilsesquioxanes of rare earth metals are potentially very important as homogeneous analogues of rare earth metal silica-supported catalysts and rare earth silicates, which are potential materials for optoelectronics.10 Thus, this area of research is of considerable interest for several fields in chemistry including catalysis and material science. However, investigations in the area of metallasilsesquioxanes of rare earth metals are often hampered due to difficulties in the crystallisation and characterisation of these compounds. As a result, literature data on the synthesis of lanthanide silsesquioxane derivatives is very scant. Structural information is still scarce and many molecular structures of lanthanide silsesquioxanes remain rather speculative.

Silsesquioxane complexes of $M^{3+}$ ions show varied coordination chemistry: due to the facially capping geometry imposed by the silsesquioxane ligand 1, a monomeric complex in the absence of other donors would result in a “bare” metal ion. The “bare” lanthanide coordinated to the highly electron-withdrawing silsesquioxane framework should be strongly Lewis acidic and highly reactive.11 The strong electrophilic nature of such a complex results in formation of a variety of structures (See Fig. 4.2). For most $M^{3+}$ ions (Al,38 Ga,12 V, Cr, Ti13, Ln14) a dimeric structure of the type VII is formed, in which the $M$ ion attains a coordination number of 4. Aspinall et al.11 have prepared and characterised monomeric lanthanide (La, Pr, Eu, Y and Yb) silsesquioxanes with a structural type VI.
Fig. 4.2 Structural variations in metallasilsesquioxanes.

The first rare earth metallasilsesquioxanes derived from the cyclopentyl-substituted trisilanol were reported by Hermann et al. in 1994. In this work yttrium and neodymium complexes were prepared via a 'silylamide route' by reacting the cyclohexyltrisilanol 1 (see structure V in Fig. 4.2) with the corresponding bis(trimethylsilyl)amides Ln[N(SiMe₃)₂]. Due to the high solubility of the yttrium silsesquioxanes they were not able to isolate a 'naked' Y silsesquioxane, but addition of coordinating triphenylphosphineoxide yielded crystals suitable for X-ray diffraction analysis (see structure VI in Fig. 4.2). Organometallic compounds react preferentially with partially dehydroxylated silica surfaces, that is with [Si(OH)₃] centers as opposed to [SiOSi] sites, towards which they usually behave indifferently. However, in the yttrium silsesquioxane coordinated to Ph₃PO, the large size and high electrophilicity of the ion induced a high degree of coordination of siloxide and siloxane groups from the ligand to the metal, showing for the first time, an interaction of a siloxane-bridge with a metal ion.
The synthesis of a bis(silsesquioxane)tungsten complex with structure VIII has been reported.\textsuperscript{17} Recently Edelmann et al.\textsuperscript{18} have demonstrated that interesting new lanthanide frameworks are accessible through reactions involving the alkali metal derivatives of the silsesquioxane precursors, e.g. Cy\textsubscript{7}Si\textsubscript{7}O\textsubscript{9}(OLi)\textsubscript{3}. They found that the resulting bimetallic metallasilsesquioxanes generally exhibit a much better crystallinity. One of the first examples of a reaction product to be structurally characterised by them was [Cy\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}Li\textsubscript{2}]\textsubscript{2}YbN(SiMe\textsubscript{3})\textsubscript{2} (See Fig. 4.3).

![Fig. 4.3 Structure of [Cy\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}Li\textsubscript{2}]\textsubscript{2}YbN(SiMe\textsubscript{3})\textsubscript{2}.](image)

Similar reactions have recently been reported by Aspinall et al.\textsuperscript{14} They obtained the following monosilylated ytterbium complex, with the molecular formula, 

\[ \{\text{Cy}_7\text{Si}_7\text{O}_{12}\}\{\text{Cy}_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\}\text{YbLi}_2(\text{thf})_2(\text{MeCN})\}\cdot 2.5\text{THF}. \]

4.2 Aims of this work

The main objective of this part of the work is to prepare and investigate novel aluminium and lanthanide containing polyhedral metallasilsesquioxanes. Novel anionic aluminosilsesquioxanes would greatly benefit the understanding and modelling in aluminosilicate chemistry. New alternative synthetic strategies are planned to be used in this work for aluminosilsesquioxane preparation.
To date all reports on heterobimetallic siloxanes are limited to lithium derivatives only. One of the objectives of this thesis is to prepare heterobimetallic complexes that contain metals other than alkali metals in the siloxane framework. Aluminosilsesquioxanes containing functional groups would be good starting materials for the production of bimetallic complexes. It would be of interest to prepare titanium, zirconium or lanthanide derivatives of these aluminosilsesquioxanes, incorporating both aluminium and a group 4 or lanthanide metal. To date rare-earth and aluminium bimetallic silsesquioxanes have not been reported in the literature. In view of the industrial importance of lanthanide-doped zeolite catalysts, such rare-earth metallasilsesquioxanes may be of interest as potential molecular models and analogues.

The trisilanol \([(c-C_6H_{11})_7Si_7O_9(OH)_3] (1)\) and the disilanol \((c-C_6H_{11})_8Si_8O_{11}(OH)_2\) were chosen along with the appropriate lanthanide(III) precursors for the preparation of different lanthanide metallasilsesquioxanes. This work concentrates on representatives of the early lanthanide series such as La, Ce and Nd. These lanthanides have a large atomic radius and consequently high coordination numbers, which could lead to some interesting coordination chemistry. Also lanthanide(III) ions with electrophilic siloxane ligands are hard Lewis acids and high coordination numbers might allow the preparation of potentially catalytically active species. Preparation of cerium(IV) metallasilsesquioxanes is very important, not only because structural chemistry greatly benefits from novel metallasilsesquioxane complexes, but also they are expected to be potential oxidation catalysts themselves, for example in the epoxidation of olefins. Cerium for example has two stable oxidation states (+3 and +4). Investigations into the redox behaviour of a cerium ion in the very electrophilic silsesquioxane environment would be interesting.

4.3 Synthesis and characterisation of new aluminosilsesquioxanes

In this work the trisilanol \(C_7H_{17}Si_7O_9(OH)_3\) (1) and the fully condensed \(Ph_8Si_8O_{12}\) have been chosen as ligands to prepare new aluminosilsesquioxanes.
4.3.1 Synthesis of [HNEt₃][Al{(c-C₆H₆)₇Si₇O₁₁(OH)}₂] (18)

A new anionic aluminosilsesquioxane complex [HNEt₃][Al{(c-C₆H₆)₇Si₇O₁₁(OH)}₂] (18) has been synthesised by the triethylamine-assisted metathesis of Cy₇Si₇O₉(OH)₃ (1) with AlCl₃ in a 2:1 ratio in a diethyl ether medium (See Scheme 4.1). The formation of the [HNEt₃]Cl precipitate was confirmed by ¹H NMR spectroscopy. The aluminosilsesquioxane product 18 was crystallised from a THF-hexane mixture at 0°C as colourless crystals.

Scheme 4.1 Synthesis of [HNEt₃][Al{(c-C₆H₆)₇Si₇O₁₁(OH)}₂] (18).

The reaction produces the aluminosilsesquioxane 18 in a very high yield. It is quite remarkable that the reaction proceeds cleanly to 18, without forming detectable amounts of any aluminium containing intermediates.

Complex 18 has been characterised by elemental analysis, IR and NMR spectroscopy and X-ray single crystal diffraction. C,H,N-analysis results were quite close to the
calculated data for the suggested structure 18. The IR spectrum of 18 contained a broad OH stretching vibration at 3165 cm⁻¹. The ¹H NMR spectrum of 18 has shown a number of peaks for cyclohexyl substituents, and the OH resonance at δ = 7.52, which is quite characteristic of hydrogen-bonded acidic hydroxyl groups in silanols. This hydrogen-bonding may be due to the intramolecular interaction of hydrogens in SiOH with the neighbouring oxygens in Al-O-Si bonds. The ¹³C NMR contained the characteristic signals for the cyclohexyl carbons. The HNEt₃ resonances in the ¹H NMR spectrum were observed at 9.60, 2.79 and 0.84 ppm, and in the ¹³C NMR the corresponding resonances were observed at 46.27 and 8.95 ppm. ²⁹Si NMR revealed 5 signals at -56.79, -58.24, -62.82, -65.71 and -67.63 ppm in a 1: 2: 2: 1:1 relative integrated ratio for the different Si atoms present in 18. There exists a slight overlap of the first two upfield signals in the spectrum, with the signal at -56.79 appearing as a shoulder on the adjacent Si peak. The two higher field signals again are overlapping with each other, but the ratio of these signals correspond well to those mentioned above.

X-ray quality crystals of 18 have been crystallised from a concentrated THF-hexane solution. Unfortunately on separation of the crystals from the crystallisation media, the crystals lost their crystalline transparency and became opaque and powdery. Further attempts to grow X-ray quality crystals of 18 always seemed successful, until attempts to remove the crystals from the mother solution became difficult. Attempts using different solvents were just as unprofitable. X-ray diffraction studies on the best crystals obtained gave a poor R factor of 0.15, therefore it is not feasible to discuss the bond angles and lengths of the aluminosilsesquioxane 18 here. However the structure of 18 was clearly identified by X-ray single crystal diffraction analysis. A ball and stick model of the X-ray structure of the anion in 18 is shown in Fig. 4.5. The structure of 18 consists of well separated [HNEt₃]⁺ cations and [Al{(c-C₆H₁₁)₇Si₇O₁₁}(OH)]₂⁻ anions. In the anion the aluminium centre is bonded to four oxygen atoms, two from each silsesquioxane ligand, thus having a distorted tetrahedral geometry and a coordination number four. The closest analogue for 18 to compare it to is the previously reported anionic
aluminosilsesquioxane \([\text{HNEt}_3][\{(c-C_6H_{11})_7Si_7O_9(\text{OSiMe}_3)O_2\}_2\text{Al}]C_6H_{14}\). The major difference between these two structures is the presence of two free non-coordinated hydroxyl groups in \(18\) (O12 and O12') (See Fig. 4.5).

**Fig. 4.5** A ball and stick model of X-Ray structure of the anion in \(18\). Carbon atoms are omitted for clarity.

In the aluminosilsesquioxane \(18\) the tetrahedrally coordinated aluminium in the silsesquioxane matrix could potentially represent a fragment in an aluminosilicate framework. Thus, the anionic complex \(18\) appears to be a suitable molecular model for aluminosilicate minerals and for aluminosilicate-supported heterogeneous catalysts.

It is very interesting to roughly estimate and compare the Brønsted acidity of the free hydroxyl groups in \(18\) to measure their potential in the preparation of different aluminosiloxane derivatives. The IR spectrum of the complex \(18\) has been compared to those of the other aluminosilsesquioxanes containing free silanol groups: \({\{(c-C_5H_9)_7Si_7O_{11}(\text{OSiMe}_3))\text{Al}(c-C_5H_9)_7Si_7O_{10}(\text{OH})(\text{OSiMe}_3)\}}\) and \({\{(c-C_5H_9)_7Si_7O_{11}(\text{OSiMePh}_2))\text{Al}(c-C_5H_9)_7Si_7O_{10}(\text{OH})(\text{OSiMePh}_2)\}}\). The OSiMePh$_2$ derivative has an OH stretching vibration at 3366 cm$^{-1}$ and for the OSiMe$_3$ derivative the OH stretching vibration occurs at 3150 cm$^{-1}$ indicating either stronger hydrogen-
bonding or increased acidity. For complex 18 this frequency was observed at 3165 cm$^{-1}$. The higher frequency is due to decreased hydrogen-bonding, for the OSiMePh$_2$, because of the increased steric bulk of the silyl ether substituent, therefore in comparison, 18 has slightly increased hydrogen-bonding. In the $^1$H NMR in C$_6$D$_6$ of the OSiMe$_3$ derivative, the OH resonance appears at $\delta = 8.50$, whereas the OH resonance in the OSiMePh$_2$ derivative has a resonance at $\delta = 4.90$. The high-field shift from 8.50 to 4.90 is indicative for decreased acidity of the hydroxyl group in the OSiMePh$_2$ derivative. In the aluminosilsesquioxane 18, the OH resonance at $\delta = 7.52$ is indicative of the deshielding of the OH functionality and is characteristic of acidic and/or hydrogen-bonded hydroxy groups. Thus the estimated acidity of the free hydroxyl groups in 18 is somewhere between the acidity of these two reported aluminosiloxane (OSiMe$_3$ and OSiMePh$_2$) derivatives. In contrast to the starting material Cy$_7$Si$_7$O$_9$(OH)$_3$ (1), which has the OH resonance at 6.95 ppm, aluminosilsesquioxane 18 has slightly more acidic hydroxyl groups ($\delta = 7.52$). This fact leads to the suggestion that the SiOH groups in 18 should be quite reactive and might be used for further modifications and for the synthesis of novel aluminosiloxane derivatives (See Section 4.5 Bimetallic silsesquioxanes).

4.3.2 The Interaction of aluminium chloride with Ph$_8$Si$_8$O$_{12}$: Synthesis of Ph$_8$Si$_8$O$_{11}$(Cl)OAlCl$_2$(THF)$_2$ (19).

Incompletely-condensed silsesquioxane frameworks have a wide range of applications and even though their chemistry has been extensively developed over the past two decades, interest is still considerable. For many years, the pool of incompletely-condensed silsesquioxanes available in reasonable quantities was limited to a small number of compounds which were prepared $via$ hydrolytic condensation of trifunctional silanes containing bulky organic groups (e.g. ligand 1). Recently Feher et al.$^{19}$ have outlined a new strategy for preparing functionalised silsesquioxanes by the selective cleavage of fully-condensed [R$_8$Si$_8$O$_{12}$] frameworks.
In the chapter 3 the cleavage of the cyclic siloxane \((\text{Ph}_2\text{SiO})_4\) by aluminium chloride was discussed, which resulted in the formation of the spirocyclic aluminosiloxane 9. This result encouraged the investigation into a potential similar phenomenon for completely-condensed silsesquioxanes. It was anticipated that \(\text{Ph}_8\text{Si}_6\text{O}_{12}\) could also be selectively cleaved by a Lewis acid such as \(\text{AlCl}_3\) providing a completely new route to aluminosilsesquioxanes.

Equimolar amounts of \(\text{AlCl}_3\) and \(\text{Ph}_8\text{Si}_6\text{O}_{12}\) were dissolved in dry THF at room temperature and the mixture was heated under reflux for 12 hours (see Scheme 4.2). During the reaction the mixture changed from colourless to pink. The solvent was removed \textit{in vacuo}, giving a pink foam like product (19). The product was studied by elemental analysis, multinuclear NMR and Mass spectroscopy.

**Scheme 4.2** Synthesis of \(\text{Ph}_8\text{Si}_6\text{O}_{11}(\text{Cl})\text{OAlCl}_2(\text{THF})_2\) (19) and its hydrolysed derivative 19a.

The complex 19 was obtained in a good yield. The \(^1\text{H} \text{NMR}\) spectrum of 19 contained a number of broad resonances at 7.77 and 6.97 – 6.56 ppm attributable to the Ph substituents in the silsesquioxane ligand. There were signals corresponding to two coordinated THF molecules at 3.56 and 1.25 ppm. The \(^{29}\text{Si} \text{NMR}\) spectrum of 19 has shown six signals at -70.28, -73.66, -77.51, -79.20, -80.64 and -81.16 ppm in a 1:2:1:2:1:1 ratio. This is an indication of the presence of six non-equivalent Si atoms in the structure.

For a better understanding of the nature of 19, some of the complex was hydrolysed by a controlled amount of water yielding 19a, which was investigated by ES-MS.
spectrometry. The electrospray mass spectrum of the hydrolysed sample in THF contained peaks at m/z 1063 ([2Ph₈Si₈O₁₂ + Al + 2(OH)]²⁺, 100%), 1115 ([2Ph₈Si₈O₁₂ + 2Al + 6(OH) + 2H]²⁺, 68%) and 1787 ([2Ph₈Si₈O₁₂ + 2Al + 3(OH) - 5Ph + H]⁺, 50%). The most realistic explanation for all these results is the cleavage of the Ph₈Si₈O₁₂ cage with the formation of the new aluminosiloxane complex 19 and its hydrolysed derivative (19a), which are shown in the Scheme 4.2.

Most R₈Si₈O₁₂ frameworks are very stable and surprisingly unreactive toward reagents that can normally cleave cyclic siloxanes.²⁰ Obviously in this case a Lewis acid can cleave the T₈ framework in THF under reflux. This is the first example of a Lewis acid-mediated cleavage of a fully-condensed polyhedral silsesquioxane. To date these frameworks have been reported to be cleaved only by very strong acids (e.g. triflic acid) or by bases (Et₄NOH).²¹ This method is also a novel approach to the one step synthesis of metallasilsesquioxanes starting from a fully-condensed silsesquioxane precursor.

The transformation described here represents an important advance in the chemistry of silsesquioxanes: it is clearly possible to achieve the cleavage of the phenyl-substituted completely-condensed silsesquioxane framework without initiating the formation of undesirable T-gels. This method is a novel alternative route in silsesquioxane cleavage and also in the production of the corresponding aluminosilsesquioxanes 19 and 19a.

### 4.4 Lanthanide Metallasilsesquioxanes

Two main approaches for the preparation of lanthanide metallasilsesquioxanes used in this work were: a silyl-amido route from Ln[N(SiMe₃)₂]₃ and trisilanol 1 and the treatment of trisilanol 1 with the corresponding lanthanide trichlorides in the presence of stoichiometric amounts of triethylamine or pyridine.
4.4.1 Synthesis of [(c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}La(NEt\textsubscript{3})\textsubscript{2}] (20)

The reaction between equimolar amounts of LaCl\textsubscript{3} and trisilanol 1 in the mixture of THF and NEt\textsubscript{3} resulted in the yellow product 20. This product was characterised by elemental analysis and \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{29}Si NMR spectroscopy (See Scheme 4.3).

![Scheme 4.3 Synthesis of [(c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}La(NEt\textsubscript{3})\textsubscript{2}] (20).](image)

Complex 20 was obtained in a high yield with an acceptable elemental analysis. The \textsuperscript{1}H NMR of 20 contained a number of broad resonances for the methine and methylene
protons of the c-C₆H₁₁ substituents between 1.80 and 1.05 ppm. Signals for the free hydroxyl groups were no longer present in 20. The proton resonances for the coordinated NEt₃ ligands were found at 2.30 and 0.86 ppm. ¹³C NMR revealed signals for the methylene carbons between 28.08 - 27.01 ppm, and for the methine resonances between 24.17 - 23.33 ppm in 20. ²⁹Si NMR unveiled 5 signals at -56.55, -58.23, -60.21, -63.78 and -65.95 ppm with the relative integrated intensity ratio of 1:2:1:1:2 respectively.

According to the NMR data it can be suggested that the lanthanum atom fills the vacant vertex site in the silsesquioxane framework by a corner-capping reaction followed by dimerisation and formation of the metallasilsesquioxane 20 (see Scheme 4.3). Each lanthanum atom is coordinated to 4 oxygens of two silsesquioxane ligands giving a siloxy-bridged lanthanum-silsesquioxane dimer.

The coordination sphere of the lanthanum centres in this metallasilsesquioxane are completed by the further coordination of triethylamine ligands.

Crystals of 20 have been prepared and submitted for X-ray crystallography, however diffraction patterns were very poor to solve the structure. Aspinall et al.¹⁴ have reported on a similar structure from the reaction of Y{N(SiMe₃)₂}₃ with trisilanol 1 as mentioned in the introduction. A THF adduct of the monomeric metallasilsesquioxane, [(c-C₆H₁₁)₇Si(THF)₂] was characterised by NMR studies. They also found that subsequent crystal structures were always too disordered to solve.

There was an attempt to react one equivalent of LaCl₃ with two equivalents of trisilanol 1 in the mixture of THF and NEt₃ by analogy with the preparation of aluminosilsesquioxane 18 above. Unfortunately the reaction resulted in a mixture of products, one of which was complex 20 and others were non-identified metallasilsesquioxane species.
4.4.2 Synthesis of \([(c-C_6H_{11})_7Si_7O_{12}Ce(NEt_3)]_2 \) (21)

To further investigate the lanthanide and silsesquioxane trisilanol 1 interactions, a similar synthetic strategy to that in the preparation of 20 was adopted for the preparation of cerium complexes. The cerium complex 21 was prepared by the addition of anhydrous CeCl₃ to a solution of the trisilanol 1 and pyridine in THF, as shown in Scheme 4.4. The reaction occurred with the precipitation of \([HNEt_3]Cl\). After filtration and evaporation of the filtrate, the product was washed with hexane and dried in \textit{vacuo}. The yield obtained was quite good and the complex 21 was characterised by elemental analysis, IR, \(^1\)H, \(^{13}\)C and \(^{29}\)Si NMR spectroscopy.

\[
\text{Scheme 4.4 Synthesis of } [(c-C_6H_{11})_7Si_7O_{12}Ce(NEt_3)]_2 \text{ (21).}
\]
The elemental analysis was consistent with the formula \([(c-C_{6}H_{11})_{7}Si_{7}O_{12}Ce(NEt_{3})]_{2}\) (21). IR analysis revealed the characteristic Si-O-Si stretching between 1050 and 1115 cm\(^{-1}\) and characteristic stretching for NEt\(_{3}\) at 1170 cm\(^{-1}\).

The \(^1\)H NMR spectrum contained very broad signals indicating the presence of the paramagnetic Ce\(^{3+}\) species in the complex. The corresponding methine and methylene protons in the \(c\)-C\(_{6}\)H\(_{11}\) substituents appeared as broad multiplets between 1.71 and 1.05 ppm. The spectrum showed the signals at 2.92 and 0.90 ppm, which were attributable to NEt\(_{3}\) protons. The signal for the OH protons of the trisilanol 1 at 6.95 ppm was not present in this product 21.

In the \(^{13}\)C NMR of 21, the methine carbon resonances were slightly further upfield (24.01 – 22.02 ppm) than the methylene resonances (26.90 – 25.54 ppm).

\(^{29}\)Si NMR revealed 5 signals in a 1:2:1:1:2 ratio at -57.76, -58.96, -65.95, -68.36 and -68.71 ppm. The resonances in the \(^{29}\)Si NMR spectrum of complex 21 are paramagnetically shifted comparatively with the corresponding signals for the starting material and the analogous lanthanum complex 20 previously prepared, this is due to the paramagnetic nature of the compound.

Similarly to the lanthanum complex 20, the cerium fills the vacant vertex site in the silicon framework by a corner-capping reaction of the trisilanol 1 to form the dimeric metallasilsesquioxane 21. The coordination sphere of each cerium in this metallasilsesquioxane is completed by the further coordination of triethylamine ligands giving each Ce(III) a formal coordination number of five.

\subsection{4.4.3 Synthesis of \([(c-C_{6}H_{11})_{7}Si_{7}O_{12}La(THF)]_{2}\) (22)}

This experiment was performed in order to compare if the traditional 'silylamide route' will result in products similar to the previously considered complexes 20 and 21. The reaction between equimolar amounts La[N(SiMe\(_{3}\)]\(_{2}\) and trisilanol 1 was carried out in THF (See Scheme 4.5), yielding the lanthanum metallasilsesquioxane 22 which was characterised by Elemental Analysis, IR and \(^1\)H, \(^{13}\)C and \(^{29}\)Si NMR spectroscopy.
The complex 22 was prepared in good yield and gave reasonable elemental analysis. The IR spectrum of 22 showed Si-O-Si stretching, but there was no presence of OH stretching in the spectrum. The $^1$H NMR contained broad resonances for the methine and methylene protons of c-C$_6$H$_{11}$ at 1.06 - 1.75 ppm. Signals of coordinated THF molecules were found at 3.57 and 1.41 ppm. $^{13}$C NMR revealed signals for the methylene carbons between 26.11 - 25.01, and for the methine carbon resonances between 22.17 - 21.33 ppm in 23. THF signals were observed at 26.52 and 68.58 ppm.

The spectrum of the $^{29}$Si NMR of 22 unveiled 5 signals at in the range -53.42, -56.55, -57.40, -63.78 and -65.95 ppm with relative integrated intensities of 1:2:1:1:2.

With comparison of the spectroscopic data of 22 to the complexes 20 and 21, it was concluded that 22 has a structure similar to that of the lanthanum and cerium.
silsesquioxanes 20 and 21 with the only difference being that 22 has THF molecules coordinated to the lanthanide metal in place of NEt₃ ligands in 21 and 20.

### 4.4.4 Synthesis of Ce\{\((c-C₆H₁₁)₇Si₇O₁₁(OH)\}\}_2 (23)

It was of great relevance to study if the paramagnetic dimeric Ce(III) complex 21 could be further modified or oxidised into a cerium(IV) derivative. With this in mind one equivalent of 21 was heated under reflux with an equimolar amount of trisilanol 1 in toluene (See Scheme 4.6). The product 23 was isolated as a pale yellow powder with a satisfactory yield and has been characterised by Elemental Analysis, IR and NMR spectroscopy.

![Scheme 4.6 Synthesis of Ce\{\((c-C₆H₁₁)₇Si₇O₁₁(OH)\}\}_2 (23).](image)
Elemental analysis showed that there were two silsesquioxane ligands per one cerium atom. The IR spectrum of the compound contained a band at 3179 cm$^{-1}$ characteristic of acidic OH groups. The $^1$H NMR spectral analysis has shown that product 23 is diamagnetic. Peaks for the cyclohexyl protons were located between 1.76 and 1.10 ppm. The signal at 7.01 ppm with the relative integration for two protons was attributed to hydroxyl protons. The $^{13}$C NMR revealed signals for the methylene and methine carbons at 28.15 - 27.20 ppm and at 24.80 - 23.92 ppm respectively. $^{29}$Si NMR analysis revealed 5 signals at -56.07, -57.76, -60.17, -67.39 and -70.04 in a 1:1:2:1:2 ratio.

The diamagnetic nature of 23 indicated that the reaction proceeded with an oxidation of the Ce(III) in 21 into a Ce(IV) species with coordination of a second silsesquioxane ligand to the Ce(IV) centre. From the spectroscopic data above and comparison with aluminosiloxane 18 it can be accessed that the corresponding structure for this complex is a cerium(IV) silsesquioxane of the formula $\text{Ce}\{(\text{c-C}_6\text{H}_{11})\text{Si}_7\text{O}_{11}\text{(OH)}\}_2$ (23), in which the central cerium atom is coordinated by two silsesquioxane ligands. The central cerium atom is coordinated to four oxygen atoms of two silsesquioxane ligands including two hydroxyl groups one from each silsesquioxane ligands as depicted in Scheme 4.6, giving an overall symmetric structure.

In contrast to the ionic aluminia silsesquioxane 18 the cerium complex 23 prepared here is neutral.

This cerium complex 23 could be a very good molecular model for important cerium(IV) silica-supported catalysts. The most exiting feature of this complex is the presence of unreacted hydroxyl groups in close proximity to the cerium centre. The formation of 23 presumably involves the amine-assisted (NEt$_3$ from the initial complex 21) deprotonation of one silanol function from the trisilanol 1 and with an oxidation of Ce$^{3+}$ to Ce$^{4+}$ caused by traces of oxygen in the system. Alternatively, the cerium center might be oxidised by hydroxyl groups from the silsesquioxane ligands themselves. This reaction here results in the production of the very stable Ce(IV) metallasilsesquioxane complex 23 and to the best of our knowledge this is the first
example of this type of a Ce(IV) metallasilsesquioxane. This behaviour is very similar to that discussed earlier in Chapter 3 for cerium metallasiloxanes 16 and 17.

Unfortunately many attempts to prepare X-ray quality crystals of 23 were not very successful.

4.4.5 Synthesis of Ce[{(c-C₆H₉)₈Si₈O₁₃}₂(Py)₃} (24)

In order to better understand the process and confirm the oxidation of Ce(III) into Ce(IV) by silsesquioxane ligands it was decided to use another silsesquioxane silanol ligand instead of the trisilanol 1. It was hoped that good X-ray quality crystals would be obtained to investigate further the structures in these types of compounds.

In the synthesis of this Ce(IV) complex the new interesting silsesquioxane diol ligand (c-C₆H₉)₈Si₈O₁₁(OH)₂, which was recently reported by Feher’s et al.¹⁹ was used. It was produced by a revolutionary new method via the selective cleavage of one Si-O-Si linkage of a completely-condensed Si/O framework by triflic acid (See Scheme 1.5). The ligand (c-C₆H₉)₈Si₈O₁₁(OH)₂ was prepared according to this published procedure. Excess triflic acid was added to a solution of (c-C₆H₉)₈Si₈O₁₂ in toluene. Extraction of the ditriflate derivative by Et₂O and the addition of NEt₃ was followed with hydrolysis via the addition of this Et₂O mixture to water-saturated Et₂O. NMR analysis confirmed the formation of the disilanol (c-C₆H₉)₈Si₈O₁₁(OH)₂.

Subsequent treatment of Ce[N(SiMe₃)₂]₃ with two equivalents of (c-C₆H₉)₈Si₈O₁₁(OH)₂ in diethyl ether in the presence of an excess of pyridine exclusively afforded the diamagnetic complex Ce[{(c-C₆H₉)₈Si₈O₁₃}₂(Py)₃} (24).

The same compound 24, albeit in somewhat lower yield, has also been prepared by the direct reaction of anhydrous CeCl₃ with two equivalents of (c-C₆H₉)₈Si₈O₁₁(OH)₂ in a THF/pyridine mixture (see Scheme 4.7). It is important to note that before this reaction, the CeCl₃ must be solvated by heating in THF under reflux for one day.
Ce[N(SiMe$_3$)$_2$)$_3$ + 2 (c-C$_6$H$_{11}$)$_8$Si$_8$O$_{11}$(OH)$_2$ → py/El$_2$O

or

CeCl$_3$ + 2 (c-C$_6$H$_{11}$)$_8$Si$_8$O$_{11}$(OH)$_2$ → py/THF

R = c-C$_6$H$_{11}$

Scheme 4.7 Synthesis of Ce[$\{(c$-C$_6$H$_{11}$)$_8$Si$_8$O$_{13}\}_2$$(Py)_3$] (24).

In both methods cerium was oxidised to the tetravalent oxidation state similarly to the previously considered synthesis of complex 23. The compound gave satisfactory C, H, N-analysis and was fully characterised by IR and $^1$H, $^{13}$C and $^{29}$Si NMR spectra as well as X-ray single crystal diffraction.

The IR spectrum (KBr) of 24 exhibited characteristic pyridine bands at 1599 and 750 cm$^{-1}$.

$^1$H NMR of 24 in C$_6$D$_6$ showed a complex spectrum of a diamagnetic compound with broad multiplets between 1.04 and 2.12 ppm for methine and methylene protons in the c-C$_6$H$_{11}$ substituents. The spectrum also showed three characteristic signals at 8.86, 7.0 and 6.8 ppm attributable to pyridine. In $^{13}$C NMR the methine resonances are slightly further upfield (22.04 – 25.96 ppm) than the methylene resonances (27.46 – 28.77 ppm).

$^{29}$Si NMR revealed 3 signals at -60.68, -63.81 and -69.59 in a 2:4:2 ratio for the different silicon fragments present in this structure. The resonances in the NMR spectrum of 24 were slightly shifted comparatively with correspondent signals for the
starting ligand, but they were in good accordance with the previously reported structure (from NMR data) of the free ligand.\textsuperscript{19}

X-ray quality crystals of 24 were grown from a concentrated solution in a pyridine/diethyl ether mixture at room temperature. The molecular structure of 24 is shown in \textbf{Fig. 4.6} and selected bond distances and angles are presented in \textbf{Table 4.1}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.6.png}
\caption{Crystal structure of Ce[\{(c-C_{6}H_{11})_{8}Si_{8}O_{13}\}_{2}(Py)_{3}] (24).}
\end{figure}

\begin{table}[h]
\centering
\caption{Selected bond distances and angles for 24.}
\begin{tabular}{ll}
\hline
Bond distances (Å) & \\
\hline
Ce(1)-O(1) & 2.167(3) \\
Ce(1)-O(5) & 2.177(3) \\
Ce(1)-N(2) & 2.610(6) \\
Ce(1)-N(1) & 2.655(4) \\
\hline
Bond angles (deg) & \\
\hline
O(1)-Ce(1)-O(1A) & 142.9(2) \\
O(1)-Ce(1)-N(1A) & 75.12(14) \\
\hline
\end{tabular}
\end{table}
Compound 24 represents the first example of a metallasilsesquioxane derived from the recently reported polyhedral \{(c-C_6H_{11})_8Si_8O_{13}\}^{2-} ligand.\textsuperscript{19,21,22} The central Ce atom is coordinated to four oxygen atoms of two siloxane ligands and to three nitrogens of three pyridine molecules resulting in a distorted pentagonal bipyramidal arrangement (Fig. 4).

O(5) and O(5A) atoms are in axial and O(1), O(1A), N(1), N(1A) and N(2) are in equatorial positions. Some of the angles between two axial [161.5(2)°] and axial and equatorial ligands [89.56(12), 96.32(12), 99.24(9), 86.66(13), 77.98(13)°] differ significantly from the ideal angles of 180 and 90°, respectively, and the pentagonal bipyramid is very distorted. However, the angles between the equatorial ligands [71.43(9), 75.12(14), 68.1(2), 142.9(2), 141.66(14) and 145.93(11)°] are quite close to those for an ideal pentagon (72 or 144°).

There are no structurally characterised cerium(IV) siloxane derivatives for comparison. However, the Ce(III) siloxane derivative \[\text{Ce(OSiPh}_3)_3(\text{THF})_3(\text{THF})\]\textsuperscript{23} and several Ce(IV) alkoxide complexes have been previously reported.\textsuperscript{24} As expected, the Ce-O bond lengths [2.167(3) and 2.177(3) Å] in 24 are substantially shorter than those to the OSiPh\textsubscript{3}ligand [2.188 (4), 2.204 and 2.214 Å] in the Ce\textsuperscript{III} complex, but longer than those to the BuO-ligand [2.024(5) and 2.021(5) Å] in Ce(IV) complex Ce(OBu\textsubscript{i})\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}(HOCBu\textsubscript{i})\textsubscript{2}. The Ce-O distances are also comparable to those in Ce(OBu\textsubscript{t})\textsubscript{2}(\mu-BuO\textsubscript{t})\textsubscript{2}(\mu_3-OBu\textsubscript{t})\textsubscript{2}Na\textsubscript{2}(DME)\textsubscript{2} for the terminal OBu\textsubscript{t} ligands [vary from 2.136(4) to 2.146(4) Å].\textsuperscript{23}

Ce-N distances are equal [2.655(4) Å] for N1 and N(1A), but shorter [2.610(6) Å] for N(2) presumably due to steric reasons. The latter pyridine molecule, which contains
N(2) is sterically hindered by two adjacent c-C₆H₁₁ groups. The Si-O distances range from 1.589(3) to 1.634(3) Å (average 1.615 Å), which is comparable to 1.603 Å for an idealised tetrahedral Si-O distance in the framework of silicates.²⁵

An extensive series of Ce(IV) tert-butoxide complexes have been identified, e.g. Ce(OBu)₂(μ-OBu)₂(μ₃-OBu')₂Na₂(DME)₂ mentioned above, which shows that the OCMe₃ group is a viable ligand to stabilise and solubilise Ce(IV). From this compound, studies show that the co-ordination chemistry of Ce(IV) is similar to that of La(III) and Y(III), yet its difference in charge offers possibilities to vary the metallic components of a polymetallic species without changing the overall charge of the complex.

Surprisingly enough the X-ray structure of 2⁴ is not quite consistent with the NMR data considered above. According to the structure, Si(2) and Si(3) should not be chemically equivalent to Si(5) and Si(8), and consequently four (not three) ²⁹Si NMR signals and two (not one) different sets of resonances for pyridine ligands should be observed. Complex 2⁴ is clearly not rigid in solution, and fast exchange between the fully and partially pyridine solvated forms of the compound presumably occurs. The solvation-desolvation exchange process is too fast to be observed on the NMR timescale.

The most interesting result is that despite starting from Ce(III) precursors selective formation of a Ce(IV) complex occurred in all cases as well as for complex 2³ prepared earlier. A similar phenomenon has been reported before only in the formation of U(VI) siloxane complexes (starting from U(IV) precursors),²⁶ where uranium(VI) species were formed regardless of the oxidation state in the starting material. This behaviour is not totally surprising as the reactions of disiloxanediolates with uranium(IV) precursors always occurred with the clean oxidation to uranium(VI).

Hence, it can be proposed that the reaction pathway here includes initial formation of an anionic Ce(III) complex [PyH][Ce{(c-C₆H₁₁)₈Si₈O₁₃}₂(Py)x], which is similar to the anionic aluminosiloxane 1⁸. The steric and electronic properties of silsesquioxane silanolate ligands render metal centers more Lewis acidic than conventional alkoxide or
silo x id e ligands do. Coordination of the OH group to Ce facilitates in the elimination of 
H⁺ and the formation of the [PyH]⁺ cation. Finally, this Ce(III) intermediate could be 
oxidised by traces of oxygen in the system (e.g. from solvent) or by a hydroxyl group of 
the silsesquioxane ligand to give the final product 24. Oxygen from the atmosphere can 
however be ruled out as the reaction conditions were rigorously maintained, and upon 
repetition of the experiment many times complex 24 was always identified as the 
product. Oxidation by oxygen or a hydroperoxide, which might be present in THF or 
diethyl ether, is less plausible, because the solvents were stored over K/Na -
benzophenone under argon and were freshly distilled shortly before the experiments 
were carried out. It is also important to notice that in all cases above the oxidation of 
Ce(III) into Ce(IV) took place when two equivalents of a silanol ligand were used 
against one equivalent of a cerium(III) precursor. It is quite likely that the second silanol 
molecule plays a crucial role in the oxidation of the metal centre. This is an important 
discovery in metallasiloxane chemistry.

These novel reaction pathways for preparing 23 and 24 described here may provide 
access to other completely new types of metallasilasesquioxane complexes through 
oxidation reactions.

4.5 Bimetallic silsesquioxanes

The anionic aluminosilsesquioxane [HNEt₃][Al{((c-C₆H₁₁)₇)₇Si₇O₁₁(OH)}₂] (18) was 
chosen as the precursor here in this part of the work for the preparation of novel 
bimetallic metallasilsesquioxanes.

As was discussed earlier (see Section 4.3.1) the ionic aluminosilsesquioxane [HNEt₃] 
[Al{((c-C₆H₁₁)₇)₇Si₇O₁₁(OH)}₂] (18) still contains two free acidic hydroxyl functionalities. 
To investigate the reactivity of these free OH groups present in complex 18 it was 
decided to react 18 with other compounds containing less acidic groups, e.g. alkoxides 
and cyclopentadienyl groups.
4.5.1 Synthesis of $[\text{HN} \text{Et}_3] \ [\text{Al}\{(c-\text{C}_6\text{H}_{11})\text{Si}_7\text{O}_{12}\}_2\text{Ti}(\text{OE}t)_2\} \ (25)$

The reactions of the aluminosilsesquioxane $[\text{HN} \text{Et}_3] \ [\text{Al}\{(c-\text{C}_6\text{H}_{11})\text{Si}_7\text{O}_{12}\}_2\text{OH}\}_2 \ (18)$ with the homoleptic titanium (IV) complex $\text{Ti}(\text{OE}t)_4$ occurs with protonolysis, affording a product with the empirical formula $[\text{HN} \text{Et}_3] \ [\text{Al}\{(c-\text{C}_6\text{H}_{11})\text{Si}_7\text{O}_{12}\}_2\text{Ti}(\text{OE}t)_2\} \ (25)$ (see Scheme 4.8) determined on the basis of elemental analysis, IR spectroscopy and solution NMR data.

Scheme 4.8 Synthesis of $[\text{Al}\{(c-\text{C}_6\text{H}_{11})\text{Si}_7\text{O}_{12}\}_2(\text{O})_2\text{Ti}(\text{OE}t)_2][\text{HN} \text{Et}_3]^+ \ (25)$. 
The $^1$H NMR spectrum of 25 contains a number of very signals between 2.14 and 1.00 ppm for the c-C$_6$H$_{11}$ groups and broad signals at 2.42 ppm and 9.6 ppm, which can be assigned to the triethylammonium group. From the $^1$H NMR data it was evident that there were no OH signals present in the product 25. Resonances for the protons from diethylether were found at 3.80 ppm and the other proton signals were masked by the cyclohexyl signals.

The $^{29}$Si NMR spectrum of 25 was particularly informative, with the observation of five resonances for the framework at -63.19, -66.12, -69.15, -70.30 and -72.03 ppm in a 1:1:2:1:2 ratio. Upon substitution, the originally lower field resonance of the silanol group in 18 at -58.9 ppm shifts towards the higher field part of the spectrum.

The $^{13}$C NMR spectrum exhibited singlets at 45.90 and 9.40 ppm characteristic of [HNEt$_3$]$^+$ and a number of singlets for the c-C$_6$H$_{11}$ carbons. Signals for the OEt carbons were observed at 55.5 and at 32.2 ppm.

From the IR spectra of 25, the signal at 1040 cm$^{-1}$ can be assigned to the Ti-O-Si stretching vibration. No OH stretching vibration was observed in 25, which was present in the starting aluminosilsesquioxane material 18.

The molecular structure of 25 maintains an analogous aluminium arrangement to the initial precursor 18, which consists of a tetrahedral aluminium centre coordinated to two bidentate silsesquioxane ligands, but with the two free OH functionalities in the precursor now deprotonated and coordinated to the titanium centre, where the titanium has a pseudo-tetrahedral arrangement. This bimetallic silsesquioxane remains anionic and hence its negative charge is balanced by the presence of the incorporated [HNEt$_3$] cation.

A similar metathetic exchange reaction between Ti(OEt)$_4$ and trisilanol 1 has been previously reported and this ethoxide derivative [(Cy$_7$Si$_7$O$_{13}$)Ti(µ-OEt)(EtOH)]$_2$ was prepared according to Scheme 4.9. The Ti atoms in this dimeric compound were hexacoordinated with the silsesquioxane cages acting as tridentate ligands. The complex contained two bridging ethoxide ligands as well as two terminal ethanol molecules coordinated to titanium.
It is generally accepted that a four-coordinate lattice titanium site is the catalytically active species in titanosilicates. Recent studies point toward the involvement of titanium sites possessing a tripodal geometry, representing the so-called open lattice sites, as the optimum catalytically active species, although the presence of closed lattice sites ('tetrapodal' sites) and bipodal sites have also been inferred (see Fig. 4.7).

**Fig. 4.7** Possible framework titanium sites in titanosilicates: (a) bipodal site, (b) tripodal (open lattice) site, (c) tetrapodal (closed lattice) site.
Bearing this in mind, it was hoped that the soluble analogue 25 prepared here, would be a successful candidate for catalytic reactions (See Chapter 5).

4.5.2 Synthesis of $\text{[HNEt}_3\text{]}\text{[Al}\{\text{c-C}_6\text{H}_{11}\}_7\text{Si}_7\text{O}_{12}\}_2\text{TiCl}_2$ (26)

An alternate reaction of TiCl$_4$ with the aluminosilsesquioxane 18 in the presence of NEt$_3$ was carried out in toluene proceeded with an elimination of [HNEt$_3$]Cl and yielded a new titanium aluminosilsesquioxane 26. The product was similar to 25 above (see Scheme 4.10). Compound 26 has been characterised by Elemental Analysis, IR and NMR spectroscopy.

![Scheme 4.10 Synthesis of $\text{[HNEt}_3\text{]}\text{[Al}\{\text{c-C}_6\text{H}_{11}\}_7\text{Si}_7\text{O}_{12}\}_2\text{TiCl}_2$ (26).]
The IR spectrum revealed an absence of the OH stretching vibration in 26.

The $^1$H NMR spectrum contained characteristic $c$-$C_9H_{11}$ proton signals between 2.24 and 0.91 ppm. Peaks for HNEt$_3$ were found at 9.62, 2.48 and 0.83 ppm. The $^{13}$C NMR spectral analysis has shown a number of signals for the cyclohexyl carbon environments. In the $^{29}$Si NMR spectrum five silicon peaks were found at -62.01, -63.42, -65.40, -68.22 and -69.08 in a 1:1:2:1:2 respective ratio.

All this data confirms the reaction pathway and the products presented in Scheme 4.10. The amine-assisted interaction between the anionic aluminosilsesquioxane 18 and the TiCl$_4$ resulted in the deprotonation of the OH groups in 18, yielding a bimetallic aluminium-titanium metallasilsesquioxane 26. The Ti centre in 26 is coordinated through two oxygen atoms to the aluminosilsesquioxane framework 18, however it still retains two Cl atoms.

An alternative route for the preparation of 26 is a reaction between the titanocene dihalide, Cp$_2$TiCl$_2$, and the aluminosilsesquioxane 18 in toluene. The reaction resulted in exactly the same product 26, which was identified by IR and NMR spectroscopy (See Scheme 4.11). IR and NMR spectra of this product were completely identical to those for the above considered complex 26 prepared from TiCl$_4$. 
Scheme 4.11 Alternative synthesis of [HNEt$_3$][Al{$(c$-$C_6H_{11}$)$_7$Si$_2$O$_{12}$}$_2$TiCl$_2$] (26).

In this case the cyclopentadienyl functionalities of the titanosocene dichloride have been replaced via an interaction with the hydroxyl groups in 18 yielding the bimetallic metallasiloxane 26. A similar Cp-replacement reaction between Cp$_2$TiCl$_2$ and trisilanol ligand 1 has been reported before by Edelmann et al.$^{27}$ (See Scheme 4.12).
Scheme 4.12 Synthesis of μ-oxo dititanium complex (μ-O)[Cy₇Si₇O₁₁(OSiMe₃)Ti]₂.

Other group 4 metals, zirconium and hafnium, have also been successfully incorporated into the silsesquioxane framework of trisilanol 1 by this group. Capping with a Cp*Zr unit has been achieved using Cp*ZrCl₃ and triethylamine to yield Cy₇Si₇O₁₂·ZrCp* This complex was the first polyhedral metallasilsesquioxane reported in the literature.²⁸

4.5.3 Synthesis of [HNET₃][Al{(c-C₆H₁₁)₇Si₇O₁₂}_{2}ZrCl₂] (27)

A similar reaction with the zirconium metalloocene dichloride and the aluminiumosilsesquioxane [HNET₃][Al{(c-C₆H₁₁)₇Si₇O₁₁(OH)}₂] (18) was carried out in toluene to prepare the correspondent zirconium derivative similar the titanium complexes above. The mixture of Cp₂ZrCl₂ and aluminiumosilsesquioxane 18 in a toluene solution was stirred for 48 hours. The product 27 was isolated and characterised by Elemental Analysis, IR and NMR spectroscopy (See Scheme 4.13).
Scheme 4.13 Synthesis of [HNEt₃][Al{(c-C₆H₉)(η-Si₇O₁₂)}₂ZrCl₂] (27).

This reaction led to the formation of a zirconium silsesquioxane derivative, the bimetallic silsesquioxane [HNEt₃][Al{(c-C₆H₁₁)(η-Si₇O₁₂)}₂ZrCl₂] (27).

The IR spectroscopy has shown an absence of OH groups. Characteristic Si-O-Si stretching between 1010 - 1115 cm⁻¹ was observed. The spectrum also contained the characteristic Si-O-Zr band at 956 cm⁻¹.

¹H NMR spectroscopy revealed the presence of HNEt₃ signals at 9.58, 2.63 and 0.87 ppm. Signals for the cyclohexyl groups of the silsesquioxane ligand were found between
2.19 and 1.09 ppm. $^{13}$C NMR spectra exhibited singlets at 45.95 and 9.45 ppm characteristic of $\text{[HNEt}_3]^+$ and a number of signals for the c-C$_6$H$_{11}$ groups.

$^{29}$Si NMR spectrum contained five peaks at -63.54, -65.71, -67.39, -68.38 and -69.56 ppm in a 1:1:2:1:2 ratio for the Si atoms in the silsesquioxane framework. However, it was noticed that the signal for the SiOH groups of the starting ligand 18 was not present. During the course of the reaction the Cp ligands in the starting material were completely replaced upon protonation by the aluminosilsesquioxane 18. This bimetallic silsesquioxane is yet another interesting material for catalytic investigation.

Comparing the use of Cp$_2$ZrCl$_2$ and Cp$_2$TiCl$_2$ as the metal precursors in these reactions analogous products were obtained, the reactivity of the metal precursor goes with removal of the Cp ions and via coordination of the Ti/Zr to the aluminosilsesquioxane framework through its deprotonated silanol groups.

Edelmann et al. have noticed that reactions between the trisilanol 1 or its monosilylated derivative with titanocene dihalides are not always clear-cut and usually lead to the formation of product mixtures. A common feature seems to be the formation of $\mu$-oxo species (see Scheme 4.12 earlier). Different reactivities of group 4 metal complexes with silsesquioxanes can also occur. For example a surprising selectivity was found when the trisilanol 1 was reacted with homooleptic group 4 benzyl complexes M(CH$_2$Ph)$_4$ (where M = Ti, Zr, Hf). In the case of titanium a monomeric corner-capped metallasilsesquioxane complex was formed, while the zirconium and hafnium benzyl complexes were dimeric.

4.5.4 Synthesis of [Al{(c-C$_6$H$_{11}$)$_7$Si$_{17}$O$_{12}$}}$_2$Nd{(Me$_3$Si)$_2$CHC$_5$H$_4$} (THF)$_2$][HNEt$_3$] (28)

Lanthanide and aluminium mixed metallasilsesquioxanes have not been reported to date, despite their potential importance as models for rare-earth doped zeolite materials. Therefore, attempts to produce such complexes were undertaken in this work. The most promising precursor for these syntheses was the aluminosilsesquioxane 18, in which two free hydroxyl functions remained available for further coordination.
The reaction between the aluminosilsesquioxane [HNEt₃][Al{(c-C₆H₄)₇Si₇O₊(OH)}₂] (18) and (NdCp₃) was stirred for 48 hours in a THF medium. The pale green-yellow filtrate was evaporated in vacuo, and subsequent IR and NMR analysis were carried out identifying the product 28 (see Scheme 4.14).

Scheme 4.14 Synthesis of [Al{(c-C₆H₁₁)₇Si₁₀O₁₂}₂Nd{(Me₂Si)₂CHC₅H₄} (THF)₂][HNEt₃] (28).

Complex 28 was obtained in a good yield with an excellent C, H, N-analysis. The IR spectrum of the product 28 in Nujol contained a very broad band characteristic of Si-O-Si stretching with a maximum at 1090 cm⁻¹.

The ¹H NMR of the paramagnetic complex 28 revealed proton signals for the corresponding cyclohexyl groups in the range 1.81-1.09 ppm. The signals were too
broadened by the presence of Nd to resolve them. The cyclopentyl proton signals were located at 6.47, 6.28 and 5.95 ppm. The high field signal for the protons in the SiMe₃ groups was located at -6.70 ppm. The shifted H-N signal was present at 5.69 ppm. The O-CH₂ groups of the the coordinating THF molecules appears at 3.24 ppm, the other CH₂ groups were masked by the cyclohexyl groups in the spectrum.

The superscript ¹³C NMR of 28 revealed signals for the presence of cyclohexyl carbons at 25.96 - 25.41 ppm and at 22.03 - 21.23 ppm and signals for the ethyl carbons at 41.8 and 15.78 ppm for HNEt₃. There were also signals at 149.4, 137.95 and 133.89 ppm for cyclopentadienyl protons. There were also signals for the methyl protons of the bis(trimethylsilyl)methyl-substituted cyclopentadienyl functionality at 125.85 and at 48.16 ppm. Thus indicative of a bis(trimethylsilyl)cyclopentadienyl functionality present in the product, by virtue of the neodymium precursor. The THF signals occurred at 66.10 and 26.19 ppm, shifted due to coordination to the Nd center.

The superscript ²⁹Si NMR revealed a number of signals for 28 and they were assigned accordingly. The signal at -21.15 ppm was assigned to the SiMe₃ group of the cyclopentadiene, and the 5 signals ranging from -65.71 to -71.49 ppm were assigned to the Si atoms of the silsesquioxane framework. The slight high field shift is characteristic of further metallation.

The aluminosilsesquioxane 18 is available for reaction with the extremely reactive NdCp³R₃ precursor, the deprotonation of the aluminosilsesquioxane 18 was followed by the metathetic reaction with the NdCp³R₃, whereby two Cp³ substituents were removed. The resulting deprotonated silsesquioxane was coordinated to the Nd as two bulky monodentate silanolate ligands. The aluminium silsesquioxane is still intact, with each silsesquioxane coordinated to the aluminium as a bidentate ligand, with further Nd coordination through the deprotonated OH groups of 18, resulting in a bimetallic framework. With the Nd atom having high coordination abilities, it coordinates to two THF solvent molecules, thus satisfying its coordination sphere.
4.5.5 Synthesis of \([\text{Al}\{(c-C_6H_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\}_2\text{Nd(THF)}_2][\text{HNEt}_3]\) (29)

It was very interesting to investigate the interaction of aluminosilsesquioxane 18 with tris(cyclopentadienyl)neodymium complexes in more detail by varying the ratio of the reagents. This time the aluminosilsesquioxane \([\text{HNEt}_3][\text{Al}\{(c-C_6H_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\}_2]\) (18) and \(\text{NdCp}_3\) were reacted in THF in a 2:1 ratio respectively (See Scheme 4.15). The product 29 was isolated in good yield and characterised by Elemental Analysis, IR and NMR spectroscopy.

Scheme 4.15 Synthesis of \([\text{Al}\{(c-C_6H_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\}_2\text{Nd(THF)}_2][\text{HNEt}_3]\) (29).
The IR spectrum of the product 29 in Nujol contained a very broad band characteristic of Si-O-Si stretching with a maximum at 1090 cm⁻¹ and also a broad band for the OH group at 3550 cm⁻¹.

The ¹H NMR spectrum revealed the proton signals for the corresponding cyclohexyl groups in 29 in the range 2.05 - 0.90 ppm. The signals were too broadened to resolve them. There was no presence of proton signals for the Cp" ligand. However there was an OH signal observed at 7.69 ppm. There was a corresponding H-N proton signal at 9.88 ppm in the ¹H NMR. The THF proton signals identified were immensely shifted and observed at 2.27 and 0.56 ppm. The signals in the ¹H NMR for the aluminosilsesquioxane 18 were observably different from that of the product 29. The proton signals for the cyclohexyl groups were significantly broadened. The presence of an OH proton signal was an indication that there still remained an OH functional group in the silsesquioxane framework, whereas the absence of cyclopentyl signals in the ¹H NMR indicates that neodymium had lost its bis(trimethylsilyl)cyclopentadienyl functionality. The strong shifts in the ¹H NMR were due to paramagnetic nature of Nd(III) atom present in the compound.

The ¹³C NMR of 29 revealed signals only for the presence of cyclohexyl carbons at 28.27 - 25.70 ppm and at 24.07 - 22.21 ppm and signals for the ethyl carbons at 46.27 and 8.95 ppm for HNEta. THF carbon resonances were observed at 69.51 and at 25.55 ppm.

²⁹Si NMR revealed five signals between -62.80 and -72.69 ppm for the different silyl fragments present in the framework of 29.

Product elucidation was determined therefore from ¹H, ¹³C and ²⁹Si NMR, and IR and Elemental Analysis. The NMR integrated data and that for the IR and Elemental Analysis was consistent with the formation a bimetallic silsesquioxane system.

Hence, deprotonation of the aluminosilsesquioxane Si-OH groups by the triethylamine from the triethylammonium cation in THF solution followed by the metathetic exchange between the ligands seems reasonable, leading to the bimetallic silsesquioxane anion with the HNEt₃ cation present in the structure. During the course of the reaction the Cp" ligand in the starting material was completely replaced upon deprotonation of the
aluminosilsesquioxane 18. As the reaction was carried out in a 2:1 reaction ratio, of aluminium to neodymium, then the proposed structure seems feasible.

Attempts to obtain crystals of the product were met with great difficulty due to the high solubility of the product in hydrocarbon solvents.

4.6 Conclusions

The anionic aluminosilsesquioxane complex 18 appears to be a suitable molecular model for natural aluminosilicates and zeolites. It is also a good precursor for novel heterometallic metallasilsesquioxanes.

The idea of cleavage of cyclic siloxane frameworks was applied to the fully-condensed silsesquioxane, Ph₈Si₈O₁₂. It has been discovered that AlCl₃ can cleave the silsesquioxane framework, giving the new aluminosilsesquioxane 19. This is a novel approach for the synthesis of aluminosilsesquioxane complexes from fully-condensed POSS.

A number of different lanthanide metallasilsesquioxanes have been prepared and characterised. It was anticipated that the Ln(III) metallasilsequioxanes should be monomeric species, however the dimeric metallasilsesquioxanes were the most favourable products. Similar structures were found for both La(III) and Ce(III) silsesquioxanes 20 and 21. NEt₃ was present in both syntheses and was used as an additional coordination ligand for the lanthanide(III) center, completing metal coordination spheres. The alternative synthetic approach using La[N(SiMe₃)₂]₃ yielded a similar product 22, having THF molecules coordinated to two La(III) centres.

The most interesting result here is the discovery of oxidation of Ce(III) into Ce(IV) species when two silanol ligands were used against one equivalent of cerium(III) precursor. This phenomenon might have a fundamental importance for
metallasilsesquioxane chemistry. The novel reaction pathways may provide access to different types of metallasilasesquioxane complexes through oxidation reactions. The new complexes 23 and 24 are the first Ce(IV) metallasilsesquioxanes reported to date.

The remarkable possibilities of further metallation of the aluminosilsesquioxane 18 has been demonstrated here. In the reactions of 18, with metal compounds such as TiL₄ (L= OEt, Cl), Cp₂MCl₂ (M = Ti or Zr), NdCpⁿ⁺ and NdCpᴿⁿ⁺ novel bimetallic metallasilsequioxanes 25, 26, 27, 28 and 29 were obtained in good yields. In these reactions the anionic aluminosiloxane precursor 18 formally served as a bifunctional aluminosiloxane precursor.

These innovative reaction pathways described here may provide access to more completely new types of metallasilsesquioxane compounds that will greatly benefit silsesquioxane chemistry in general.

4.7 References


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5.0 Catalysis by Metallasiloxane Complexes
5.1 General Background

The need for cleaner chemical processes in industry is obvious. Chemical transformations that produce in addition to the desired product, large amounts of by-products and waste are less desirable. Selective transformations using catalytic processes eliminate the requirement of stochiometric auxiliary reagents in many current processes and can eventually help to decrease the amounts of waste. In pharmaceutical and agrochemical industries the need for selective transformations is even larger since delicate bioactive compounds are often not robust enough to withstand the conditions used in bulk chemistry. Moreover, pharmaceuticals and agrochemicals have to be enantiomerically pure if they contain stereogenic centres. The use of enantioselective catalytic processes can improve the efficiency in the production of fine chemicals and pharmaceuticals.

Both commercial importance and scientific significance have stimulated an intense interest into identifying the surface species of heterogeneous catalysts. Although advances in spectroscopic techniques have revealed some information on the reaction chemistry on silica surfaces, the structures of such catalysts and the metal-silica interactions are still difficult to define at the molecular level. The inherent complexity of silica-supported catalysts leaves many unanswered questions and direct study of such catalysts is still a surmountable challenge. An attractive approach to this problem is to design, synthesise and characterise model catalysts based on incorporating M₅-Oₓ-Siₓ interactions and using them as models for silica-supported catalysts.

5.2 Metallasiloxane complexes in catalysis

At present metallasiloxane complexes can be considered as the best chemical models for a variety of silica-supported catalysts. In addition, porous materials have recently been synthesised from silsesquioxane cage precursors, as well as metal-containing polymeric derivatives. As such, this field has matured to the extent where applications to heterogeneous catalysis may become feasible. The presence of a metal in the siloxane
framework not only makes these compounds thermally stable but also improves their catalytic properties.

The transition metal complexes anchored on silica surfaces are known to catalyse a variety of organic transformations. Most of the work in this area has been focused on Group 4 silsesquioxane complexes and the application of these complexes in catalytical processes, such as ethylene polymerisation, alkene epoxidation and Oppenhauer oxidations. With regards to Group 3 silsesquioxanes, Hermann et al., Aspinall et al. and Edelmann et al. have reported on novel Group 3 silsesquioxane complexes, however no catalytic reactions have been performed on all their mentioned complexes, even though most of the papers deal with models for catalysts on silica surfaces. A recent review article by Abbenthuis covers some of the advances in homogeneous and heterogeneous catalysis with most of the metal containing silsesquioxanes synthesised to date.

5.2.1 Epoxidation of Olefins

Epoxidation of alkenes can be achieved by a variety of oxidants. These include perbenzoic acids, dioxiranes, alkylhydroperoxides, hydrogen peroxide, bleach and molecular oxygen. Most of them suffer from the disadvantage that besides oxygenated products, stiochiometric amounts of waste products are formed, which have to be separated from the epoxides. Molecular oxygen is attractive but does not react with alkenes spontaneously and has to be activated with a suitable catalyst. Bleach is a very cheap and easy to use oxidant but suffers from the fact that stiochiometric amounts of salt are formed during reactions and the oxidant is highly diluted. Also the basicity of the reaction medium (pH > 10) can be a problem. The oxidant of choice here is t-Butyl hydroperoxide, which can be handled easily enough and leaves only t-butanol as a by-product. t-Butyl hydroperoxide however, is often partially destroyed during the catalytic act, the competing side-reactions such as the homolytic decomposition of the oxidant and for example the solvolysis of the oxirane ring, usually results in poor yields of the epoxide.
The rate of reaction is much dependent on the nature of the olefin, *i.e.*, the molecular weight, the presence of substituent groups, the number, the position and the electronic properties of the latter, and the steric configuration. Kinetics can be slowed by increasing the chain length or the cross-section of the olefin, and by electron withdrawing groups. Thus, olefins exhibit the following order of reactivity: 1-butene > 1-pentene > 1-hexene > 1-octene >> cyclohexene and 1-butene > allyl chloride > allyl alcohol. For example 1-hexene can be epoxidised two orders of magnitude faster than cyclohexene. Side reactions are increasingly important and selectivities lower as the branching of the alkene increases. The rate of reaction can be enhanced or lowered by substituent groups on the double bond, mostly on the basis of electron-donating or - withdrawing properties. Another aspect to consider in epoxidation reactions is the choice of solvent, as the solvent itself exerts a major effect on kinetics: CH$_3$OH > C$_2$H$_5$OH > t-C$_4$H$_9$OH. The yields decrease and the extent of side reactions grow steadily in the same order.

Metallasilsesquioxanes have now been reported to be active in the epoxidation of alkenes and several groups are currently working on this topic. The first report on catalytic alkene epoxidation involved the known titanium silsesquioxane complex [Ti(η$^5$-C$_5$H$_5$)(C$_6$H$_5$)$_7$Si$_7$O$_{12}$)]$^9$ which was investigated as a catalyst only eight years after its discovery. This compound was found to catalyse alkene epoxidations using tert-butyl hydroperoxide (TBHP). The monomeric tripodal species [TiR{(c-C$_5$H$_n$)$_7$Si$_7$O$_{12}$}] ($R = $ CH$_2$Ph, NMe$_2$, OSiMes, O-Pr)$^{11}$ has been applied to 1-octene epoxidation using TBHP$^{12}$ and their catalytic activities are supposed to be more or less similar to that of the cyclopentadienyl complex [Ti(η$^5$-C$_5$H$_5$)(C$_6$H$_1$)$_7$Si$_7$O$_{12}$)]. Some other interesting metallasilsesquioxanes, for example, dimeric tripodal titanium silsesquioxanes of the formulae [Ti(O-iPr){(c-C$_5$H$_5$)$_7$Si$_7$O$_{12}$}]$_2$.THF and [Ti(OMe){(c-C$_5$H$_5$)$_7$Si$_7$O$_{12}$}]$_2$.MeOH were reported to be active in epoxidation reactions of cyclohexene.$^1$
The reaction of the silsesquioxane disilanol (c-C₆H₁₁)₈Si₈O₁₁(OH)₂ (a bifunctional monodentate ligand) with TiCl₄ or Ti(CH₂Ph)₄ has led to the formation of a titanium containing silsesquioxane gel IX (See Fig. 5.1).

![Image of IX](image_url)

**Fig. 5.1 Titanium Silsesquioxane IX.**

IX effectively catalysed the epoxidation of alkenes by TBHP under mild conditions. Though for the reactions studied, IX is a reasonable to good precatalyst, attempts to filter off the gel during epoxidation, and thus to stop the reaction, were met with complications. NMR studies showed that during epoxidation, rapid hydrolysis of IX by TBHP occurred resulting in the quantitative reformation of the silsesquioxane disilanol and concomitant formation of non-siloxy titanium species that was catalytically active. An essential feature of several of the proposed mechanisms of alkene epoxidation by titanium silicates, involves hydrolysis of a titanium siloxy function in a tetracoordinated active site.¹³ For the titanium gel IX, such a hydrolysis step leads to the rapid degeneration of the material since the titanium siloxy units (Ti-O-Si) here result from the functionalisation of isolated silanol groups.
5.2.2 Polymerisation of olefins

Silica-supported catalysts are used extensively for the coordinative polymerisation of ethylene. The commercial importance of these systems has led to an intense research effort aimed at elucidating the detailed chemistry of these species at the molecular level. Despite this, the mechanism(s) by which heterogeneous catalysts form, function and decay are often unclear and highly controversial.

Several metallasilsesquioxanes have been reported to be active in the polymerisation of ethene. The compound \([ (c-C_6H_{11})_7Si_3O_9(OSiMe_3)(O_2CrO_2) ] \) represents a polymerisation catalyst based on chromium, which contains a CrO4 unit with an almost tetrahedral geometry. This chromium compound is a catalyst precursor for ethene polymerisation that can be activated with trimethylaluminium. The remarkable catalytic activity of chromium silicates has been put to use and chromium supported on silica is being used as a catalyst for the coordinative polymerisation of ethene. Well known examples of industrially used systems are the Phillips catalyst, essentially CrO3 on SiO2 or Al2O3, and the Union Carbide system that is prepared from \([ (\eta^5-C_5H_5)_2Cr]^+ \) and SiO2 (UNIPOL Catalyst). Although the chromate compound \([ (c-C_6H_{11})_7Si_3O_9(OSiMe_3)(O_2CrO_2) ] \) was described as a model for the Phillips catalyst, no further insight was obtained into the nature of the actual catalytic species occurring, nor on its presumed reduction by the alkylating agent. In general, the ‘activation’ of the metal-oxo precatalysts remains elusive. Interestingly, the polyethylene produced by \([ (c-C_6H_{11})_7Si_3O_9(OSiMe_3)(O_2CrO_2) ] \) is quite similar to that obtained from Phillips-type catalysts.

Silsesquioxane based Ziegler-Natta type catalysts were recently reported to result from the reaction of \([ (c-C_6H_{11})_7Si_3O_9(OH)O_2Mg]_n \) (n = 1 or 2) with TiCl4. The resulting bimetallic systems \([ (c-C_6H_{11})_7Si_3O_9(OH)O_2MgTiCl_3]_n \) (n = 1 or 2) could be activated with AIEt3 and were therefore subsequently used for ethene polymerisation. The polymerisation of ethene obtained by this system showed an activity which was higher than that obtained for a commercial Ti/Mg/SiO2 silica-supported catalyst with the same
bimetallic content under similar reaction conditions. On the basis of the analogy in structural synthesis, structural characteristics and polymerisation behaviour, this silsesquioxane system employed could possibly have potential as a bonding model for Ti/Mg-containing bimetallic silica-supported catalysts.

Not only titanium or chromium silicate complexes have been investigated for polymerisation activity, but vanadium complexes too have showed some promise. Some vanadium silsesquioxane complexes have been described that are suitable precatalysts for ethene polymerisation. Monomeric and dimeric \([c-(C_6H_{11})_7Si_2O_3V=O]^{19}\) was used for ethene polymerisation after activation with trimethylaluminium or Al(CH_2SiMe_3)_3. Polymerisation activity was ascribed to the monomeric complex, the dimer being a precursor to the monomer. The reaction sequence was thought to involve successive alkyl transfers and coordination of the vanadium oxo bond to the Lewis acidic aluminium sites was implied as leading to the active catalyst (see Fig. 5.2).

![Fig. 5.2 Structure of the vanadium polymerisation catalyst.](image-url)
The reaction sequence also accounts for the observed dependence of catalyst activity on the \( \text{AIR}_3 \) reagent, which reaches a maximum when about two equivalents of the alkylaluminium agent are added. Larger amounts of \( \text{AIR}_3 \) resulted in reduction and deactivation of the metal centres, while fewer equivalents were not sufficient to result in complete catalyst activation.\(^{20}\) A similar dependence of the activity on the amount of the activating aluminium reagent was found for the silsesquioxane chromate \([\text{c-C}_6\text{H}_{11}]_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{O}_2\text{CrO}_2)]\).\(^{14}\)

### 5.2.3 Diels-Alder Reactions of enones

In the Diels-Alder reaction (in older literature referred to as the "diene synthesis") a six-membered ring is formed through fusion of a four-\(\pi\) component, usually a diene and a two-\(\pi\) component, which is commonly referred to as the dieneophile. The Diels-Alder reactants can consist of hydrocarbon fragments only (homo Diels-Alder reaction) but can also contain one or more heteroatoms on any of the positions \(a-f\) (hetero Diels-Alder reaction) leading to heterocyclic ring systems (See Scheme 5.1). The fact that many different combinations of carbon and hetero-atoms are allowed demonstrates the enormous versatility of this reaction.

![Scheme 5.1 Schematic Representation of the Diels-Alder Reaction.](image-url)
The Diels-Alder reaction has proven to be of great synthetic value, forming a key-step in the construction of compounds containing six-membered rings. The reaction is stereospecific in the sense that conformations of the reacting double bonds are fully retained in the configuration of the product. In this way six new stereocenters can be formed in a single reaction step. The absolute configuration of the two newly formed asymmetric centres can be controlled efficiently.

Heterogeneous systems such as clays, alumina or silica gels and even microporous organic crystals have catalytic potential. Finally, catalysis by Bronsted acids, Bronsted bases and radicals has found application in some special Diels-Alder reactions. By far the most effective method however, is catalysis by Lewis-acids. The beneficial effects of Lewis acids are limited to reagents containing Lewis-basic sites close to the reaction centre. Fortunately, in nearly all Diels-Alder reactions one of the reagents, most frequently the dienophile, meets this requirement.

It has been mentioned in Chapter 4 (page 95) that the silsesquioxane disilanol \((c_{3}H_{11})_{3}Si_{8}O_{11}(OH)_{2}\) can be easily reacted with trimethylaluminium, resulting in concomitant formation of methane and a colourless polymeric aluminosilsesquioxane gel \(X\) which contains a silsesquioxane cage framework similar to that present in its precursor\(^2\) (See Fig. 5.3).

![Fig. 5.3 Aluminosilsesquioxane gel X.](image)
This aluminosilsesquioxane gel was found to accelerate Diels-Alder reactions of enones with several orders of magnitude over the thermal reaction (See Scheme 5.2). The heterogeneity of the catalyst was proven by filtration experiments: upon filtration of the catalyst when reactions had reached about 50% conversion, the reaction rate decreased to the thermal rate.

![Scheme 5.2 Diels-Alder reaction using Isoprene and Buten-3-one.](image)

**Scheme 5.2** Diels-Alder reaction using Isoprene and Buten-3-one.

### 5.3 Aims of this work

The major aim of this part of this research is to investigate the potential catalytic properties of selected metallasiloxane complexes described in the previous chapters 3 and 4. Mainly aluminium, cerium and titanium metallasiloxane complexes have been selected for catalysis, since various siloxane derivatives of these metals are already known to demonstrate some catalytic activity. The focus was placed on liquid-phase Diels-Alder reactions, the epoxidation of 1-octene and on the polymerisation of ethylene.

Another objective of this chapter is to give a brief overview of the developments in metallasiloxane catalysis, and to report new results obtained in this project.
5.4 Catalytic activity of disiloxaneolates of aluminium in Diels-Alder reaction

From the finding that the polymeric Lewis acidic aluminosilsesquioxane gel X, accelerates Diels–Alder reactions\(^\text{21}\) it was decided to test the catalytic activity of some of the prepared aluminosiloxanes. The ionic aluminosiloxane complex \([\text{PyH}][\text{Al}\{\text{OSiPh}_2(\text{OSiPh}_2)_2\text{O}\}\text{,}_2] (5)\), the cyclic aluminosiloxane \([\text{AlCl(THF)}\{\text{O(Ph}_2\text{SiO)}_2\}_2] (6)\) and the oligomeric aluminosiloxane \([\text{Al\{O(Ph}_2\text{SiO)}_2\}_2][\text{OPh}_2\text{SiO)}_2] (7)\) (See Fig. 5.4) were chosen for the investigation of their potential activity in the Diels-Alder reactions of enones.

![Fig. 5.4 Structures of compounds 5, 6 and 7 used for catalytic studies.](image)

Liquid phase catalytic reactions were carried out in a glass reactor (Schlenk) at 20°C. 2.0 mmol of the diene and 2.0 mmol of the dieneophile were reacted over the catalyst (1 mol
% Al with respect to the substrates) in the presence of CDCl₃ as solvent. The conversion was monitored by ¹H NMR studies. However very little of the cyclohexene was formed from the reaction.

The results for the Diels-Alder reactions can be observed in Table 5.1.

Table 5.1 Results for Diels-Alder reactions using aluminosiloxanes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diene</th>
<th>Dienophile</th>
<th>Isomer Ratio</th>
<th>$k_2/1$ mol⁻¹h⁻¹</th>
<th>$k_2/k_2$(thermal)</th>
<th>% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>80:20</td>
<td>0.03</td>
<td>8</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>90:10</td>
<td>0.23</td>
<td>61</td>
<td>9.2</td>
</tr>
<tr>
<td>7</td>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>90:10</td>
<td>0.30</td>
<td>80</td>
<td>12</td>
</tr>
</tbody>
</table>

The value of $k_2$ refers to the average reaction rate measurement. The thermal reaction proceeds with up to 30% of 3,4-dihydropyranes resulting from homo Diels-Alder reactions of the buten-3-one. The isomer ratio of the thermal reaction is 75:25.

The aluminium siloxanes were found not to enhance the Diels-Alder reaction of buten-3-one significantly. Very little of the cyclohexene was formed from the reaction with 5. The activities for 6 and 7 were more significant than that for 5, however the conversions were not above those for the previously reported Diels-Alder catalysts.

The low catalytic activity of the aluminosiloxanes 5, 6 and 7 might be explained by steric hindrance around the metal centres, which are not easily available for substrate coordination. Complexes 6 and 7 have higher activities than 5 presumably due to the anionic nature and the lower Lewis acidity of 5. In overall the activities obtained here are quite reasonable for metallasiloxane complexes, however they could be exploited more perhaps by further modification of complexes 6 and 7, e.g. by the introduction of other metals into the cyclic structures.
5.5 Catalytic activity of metallasilsesquioxane complexes

5.5.1 Catalysis of alkene epoxidation

The complexes chosen for the investigation of epoxidation reactions were 18, 21, 23, 25, 26 and 27. The structures of the aluminium precursor 18 and its bimetallic derivatives 25, 26 and 27 can be seen in Fig. 5.5.

![Fig. 5.5 Structures 18, 25, 26 and 27.](image)

Complexes 21 and 23 were chosen as they contained cerium in different oxidation states, their structures can be seen in Fig. 5.6.
Complex 23 contains a central Ce(IV) ion, which is quite a powerful oxidising agent. Complex 23 also has two free OH functional groups. Complex 21 contains a Ce(III) central ion which could undergo oxidation during the process. It was selected for comparison to the potential activity of 23.

The epoxidation of 1-octene with Bu'OOH (TBHP) was chosen as a convenient test for the epoxidation activity of the complexes. At the alkene/TBHP molar ratio of ca. 1 employed, deviation from 1st order kinetics may be observed, corresponding to a decrease in reaction rate. This can be attributed to the fact that the reaction is auto-retarded by the tert-butanol co-product, a phenomenon observed previously for epoxidation catalysts. However, such an auto-retardation is not observed here for the molar ratio of alkene/TBHP of 1.

In a typical reaction equimolar amounts of alkene and tert-butyl hydroperoxide (TBHP) were reacted over the catalyst (ca. 1 mol % Ti/Zr/Ce with respect to the substrates) in hexane at 50°C.

The results of the catalytic activity for the selected metallasilsesquioxanes are shown in Table 5.2.
Table 5.2 Results for 1-octene epoxidation using metallasilsesquioxanes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Alkene</th>
<th>t/h</th>
<th>Temp. °C</th>
<th>% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>7.5</td>
</tr>
<tr>
<td>21</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>26</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>66</td>
</tr>
<tr>
<td>27</td>
<td>1-octene</td>
<td>24</td>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

The titaniumsilsesquioxanes 25 and 26 efficiently catalyse the epoxidation of the alkene under mild conditions. For the reactions studied, attempts to filter the catalyst off during epoxidation, and thus to stop the reaction, were met with no complications which was indicative of the absence of leaching of the catalytically active species from the titaniumsilsesquioxanes. It is important to note that complexes 25 and 26 were stable under these reaction conditions and this makes them particularly attractive candidates for the epoxidation catalysis.

As has been mentioned earlier, an essential feature of several of the proposed mechanisms for alkene epoxidation by titanium silicates involves hydrolysis of the titanium siloxy function in a four-coordinate titanium active site. For the titanium metallasilsesquioxanes 25 and 26, such a hydrolysis step also involves cleavage Ti-OEt (25) or Ti-Cl (26) bonds and the formation of the correspondent hydroxyl derivatives. In addition the aluminosilsesquioxane fragment is bound to the titanium as a multidentate ligand stabilising the adducts and resulting in more robust catalytic species.

Similar phenomena and activities for titanium metallasilsesquioxanes have been reported earlier. For example, the known complex \[\text{[Ti(}^\eta^5\text{-C}_5\text{H}_3)(c-\text{C}_9\text{H}_{11})_2\text{Si}_7\text{O}_{12}]^{9,10}\] which has a terdentate silsesquioxane ligand, was tested for alkene epoxidation and was found to be effective at low concentration and selectively produced alkene oxides in high yield with good peroxide economy. ‘Easy’ substrates such as cyclooctene and norbornene were virtually quantitatively epoxidised. The somewhat difficult epoxidation
of 1-octene was catalysed efficiently (80 % conversion, 80 % selectively after 24 h). This catalyst resisted hydrolysis and it is likely that due to multidentate silsesquioxane coordination that this complex \([\text{Ti}(\eta^5-\text{C}_5\text{H}_5)(\text{c-C}_6\text{H}_{11})_2\text{Si}_7\text{O}_{12})]\), does not hydrolyse irreversibly during epoxidation reactions; in fact the complex was even stable in 1M HCl!

Similar coordination environments to 25 and 26, for titanium silsesquioxanes have been reported and their catalysis monitored. For example the silsesquioxane titanium complexes XI and XII with bidentate siloxy coordination that are derived from the silsesquioxane disilanol \((\text{c-C}_6\text{H}_{11})_2\text{Si}_7\text{O}_9(\text{OH})_2(\text{OSiMe}_3)\) were found to be catalytically active in the epoxidation of 1-octene with TBHP although the activity was about an order of magnitude less than that of the tripodal species, \([\text{Ti}(\eta^5-\text{C}_5\text{H}_5)(\text{c-C}_6\text{H}_{11})_2\text{Si}_7\text{O}_{12})]\) (See Fig. 5.7).

![Figure 5.7 Silsesquioxanes XI and XII.](image-url)

The silsesquioxanes XI and XII differ from complexes 25 and 26, in that complex XI is monomeric and complex XII has a closed lattice titanium site, whereas complexes 25 and 26 are bis(silsesquioxanes) with an open lattice site. There seems to be a
relationship between the dendacity of silsesquioxane coordination with respect to hydrolysis of the titanium sites: bidentate complexes have been found to undergo hydrolysis by aqueous hydrogen peroxide, while terdentate derivatives do not, or very slowly hydrolyse. Materials with monodentate silsesquioxane siloxy coordination were found not only to hydrolyse quickly, but also readily decompose in organic media containing anhydrous TBHP. Generally closed lattice sites are weaker catalysts due to the difficulty in finding the active titanium centre, therefore steric hindrance in the bimetallic complexes can limit the ease in locating the tetrahedral TiIV centre. Therefore this could have an effect on the rates and selectivity of the complexes in catalysis.

Maschmeyer et al. have reported the preparation of a series of titanosilsesquioxane derivatives encompassing methoxy, butoxy and isopropoxy groups at the fourth coordination site and have found that the reactivity of these catalysts is indeed dependent upon the nature of the alkoxy group (in the order of decreasing activity: MeO > OBu' >> OPr'). For the isopropoxy, a 48 % conversion was achieved after 1 h at 50°C whereas the methoxide complex exhibited much higher catalytic activity (93 % conversion after 1 h). The longer, but linear, butoxy group allows better access to the titanium centre than the shorter but non-linear isopropoxy group. This suggests that the accessibility to the TiIV centre is the main parameter controlling the reactivity of the titanosilsesquioxanes. Access to the titanium centre by the reactant alkene and the sacrificial oxidant (TBHP) must be relatively unhindered so that the coordination shell can expand from four to six during catalysis. This explains the reactivities of 25 and 26, with the accessibility to the titanium centre in both complexes being relatively unhindered, therefore producing a significant catalytic reactivity in these complexes.

The epoxidation of 1-octene by the titanium silsesquioxane 26 was found to exclusively epoxidise the alkene with no side-products detected by NMR analysis. As other alkene oxides were formed in the epoxidation reaction of 25, the effect of the substituent on the titanium starting material may have an effect on the production of these side products. In the titanium silsesquioxane 25 there are ethoxide moieties present and these could form
ethanoic acid or ethanol in the reaction, as only one oxygen atom from the oxidant TBHP is transferred to the alkene to form the epoxide and the other one is left in stoichiometric 'waste products'. With the coordination sites on the titanium in these titanosilsesquioxane foams 25 and 26, having different functionalities their reactivities may be dependent upon the nature of the substituent groups present.

The somewhat, 'difficult' epoxidation of 1-octene was catalysed more effectively by 25 and consistent catalytic performance was found for both 25 and 26, which were repeatedly recrystallised from toluene, which seems to exclude the possibility that undetected trace impurities in 25 or 26 are responsible for the observed catalytic activity. Sheldon and co-workers have concluded that alkyl hydroperoxide catalysed epoxidation of olefins occurs by a heterolytic mechanism in the presence of TiO₂-SiO₂ mixed-oxide catalysts.24 This is also the case for 25 and 26 catalyst systems. With TBHP, negligible side products were observed, indicating the high selectivity of the system with respect to the epoxide. As can be seen from Table 5.2 the epoxide is the major product as the β-scission of the tert-butyloxyl radical has a sufficiently long lifetime for it to abstract a hydrogen atom from 1-octene. This proves that TBHP converts 1-octene into its epoxide by a non-radical mechanism in the presence of both catalysts 25 and 26. If radicals had been involved in these Ti⁺⁴-catalysed oxidations, it would be expected to obtain very little of the epoxide relative to the yields of the side products (See Scheme 5.3).
Pre-treatment of the catalyst 26 with neat TBHP caused the initially white catalyst to turn yellow. This colour was retained after filtration and washing with hexane. Mixing of this yellow catalyst with 1-octene gave little or no epoxide. If all the titanium centres managed to coordinate peroxide and if each of these reacted with 1 molecule of octene, approximately 2% conversion into the epoxide should have been observed. Similar results have been previously obtained for a homogeneous titanium-porphyrin catalyst pretreated with TBHP in a similar fashion. The obvious conclusion is that the yellow titanium-peroxo (presumably containing $\eta^2$-coordinated peroxide, based on a recent crystal structure of a model complex)$^{25}$ is not the oxygen atom transfer agent. This implies a coordination of octene to the titanium centre (as opposed to it merely reacting with coordinated peroxide from outside the coordination sphere).

It is clear that epoxidation proceeds by nonradical chemistry, and the results indicate that the alkene and the peroxide must be coordinated to the titanium centres for reaction to occur. A possible mechanism for the epoxidation reactions can be seen in Scheme 5.4.
Scheme 5.4 Possible mechanism for Oct-1-ene epoxidation using 25 and 26.

The zirconium derivative 27 with an analogous structure to 26 was examined, however not a very high activity in alkene epoxidation was observed. It can be concluded then, that zirconium does not achieve a similar catalytic activity to its titanium derivative, presumably due to the bigger size of the zirconium, which might form very stable and non-active intermediates during the epoxidation process.

Other silsesquioxane complexes synthesised were tested for catalytic alkene epoxidation activity. The precursor 18 was investigated for epoxidation activity, however it was found to be catalytically poor. The complexes [(c-C$_6$H$_{11}$)$_3$Si$_2$O$_3$Ce(NEt$_3$)]$_2$ (21) and Ce{(c-C$_6$H$_{11}$)$_3$Si$_2$O$_{11}$(OH)}$_2$ (23) showed no epoxidation activity under the same reaction conditions. However they did get oxidised and showed decomposition of the reagents with the production of acids and alcohols, as detected by NMR spectroscopy.
5.5.2 Catalysis of olefin polymerisation

It was decided to investigate the aluminosilsesquioxanes and bimetallic aluminosilsesquioxanes derivatives as potential catalysts in alkene polymerisation. This includes complexes 25, 26, 27, 28 and 29. Structures of 28 and 29 are shown in Fig. 5.8.

![Structures of 28 and 29 used for catalytic studies.](image)

Fig. 5.8 Structures of 28 and 29 used for catalytic studies.
It is known that most of the alkene polymerisation catalysts require their activation with aluminium alkyls (co-catalysts) resulting in the formation of the catalytically active species. It was expected that the presence of two metal centres Al and Ti\textsuperscript{IV} (or Zr\textsuperscript{IV} or Nd\textsuperscript{III}) in some metallasilsesquioxanes 25, 26, 27, 28 and 29 might potentially result in an interesting catalytic behaviour in polymerisation reactions. Here preliminary catalytic studies on these complexes in ethene polymerisation will be reported on.

In a typical polymerisation, 200 mg of the chosen catalysts in toluene were charged into a reactor vessel attached to a gas line with an ethylene cylinder. The pre-catalysts were activated by Et\textsubscript{2}AlCl (5 equiv.) before use in the ethylene polymerisation process. Ethylene was pumped through the vessel over a period of 2 h at ambient temperature. At the end of the experiment oily drops were observed adhering to the walls of the vessel indicating that some form of oligomeric or polymeric material had been formed. Further uptake of more ethylene seemed to cease upon gelation of the reaction medium.

Gel permeation chromatography (GPC) was used to determine the molecular weight distributions of the polymers formed.

The polymerisation results are summarised in Table 5.3.

**Table 5.3 GPC Results for ethylene polymerisation using metallasilsesquioxanes.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Activity gPE/g[M]h</th>
<th>M\textsubscript{n} of polymer</th>
<th>M\textsubscript{w} of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>not active</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>32</td>
<td>940</td>
<td>1175</td>
</tr>
<tr>
<td>26</td>
<td>43.8</td>
<td>1270</td>
<td>1525</td>
</tr>
<tr>
<td>27</td>
<td>14.7</td>
<td>107</td>
<td>225</td>
</tr>
<tr>
<td>28</td>
<td>not active</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>not active</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

None of the complexes 18, 28 and 29 were active in ethene polymerisation.
Only Ti or Zr containing complexes 25, 26 and 27 demonstrated a low catalytic activity in ethylene polymerisation giving low molecular weight polymers (oligomers). The formation of the low weight polymers can be explained by the quick deactivation of the metallasilsesquioxane adducts. Presumably there is an interaction between titanium or zirconium centre and Et₂AlCl, which results in an unstable catalytic species (See Scheme 5.5).

\[ L = OH \text{ in } 25, Cl \text{ in } 26 \text{ and } 27 \]
\[ M = Ti \text{ in } 25 \text{ and } 26, Zr \text{ in } 27 \]

Scheme 5.5 Possible interaction of AlEt₂Cl with catalysts before addition of ethylene.

It is also known that many of the good polymerisation catalysts are cationic by nature. The bimetallic complexes 25, 26 and 27 are anionic and this might have an influence on the stability and activity of the catalytically active species. It is also important to take into account that the metal centres in these metallasilsesquioxanes are quite sterically...
hindered by bulky silsesquioxane cages and cyclohexyl substituents. This can also be a cause of the low catalytic activity of these complexes.

However, in overall it is very remarkable that the bimetallic complexes 25, 26 and 27 have demonstrated some catalytic activity. Most likely the Ti/Zr centres were activated by Et₂AlCl in the metallasilsesquioxane framework, which are then involved in the catalytic process. These complexes the titanium and zirconium atoms are in a tetrahedral coordination mode and hence this fulfils one of the criteria for catalytic activity. Whether or not the aluminosilsesquioxane fragment plays a role in promoting or inhibiting catalysis is not quite clear, as it remains intact and non-active in the absence of these neighbouring Ti/Zr atoms. A possible mechanistic pathway in which these catalysts follow is shown in Scheme 5.6.

Scheme 5.6 Possible ethylene polymerisation mechanism.

There is great hope that variation in the amounts (ratios) and types of the trialkylaluminium (AlMe₃, AlEt₃, MAO, etc.) co-catalysts added to the bimetallic metallasilsesquioxanes will result in more catalytically active adducts. It is also very
difficult to describe exactly the nature of the catalytically active sites in the bimetallic complexes without detailed structural studies. These investigations have not been performed here due to small amounts of bimetallic metallasilsesquioxanes being available. This research is however planned for the future.

5.5.3 Catalytic activity in Diels-Alder reactions

As was reported earlier the polymeric Lewis acidic aluminosilsesquioxane gel X, can accelerate Diels–Alder reactions.21 Bearing this in mind it was decided to investigate the aluminosilsesquioxane complexes 18, 21, 25, 26, 27, 28 and 29 for Diels-Alder activity. Liquid phase catalytic reactions were carried out in a glass reactor (Schlenk) at 20°C. In a typical reaction, 2.0 mmol of the diene and 2.0 mmol of the dieneophile were reacted over the catalyst (1 mol % Al/Ti/Ce/Nd with respect to the substrates) in the presence of CDCl₃ as solvent for 4.5 hours. The conversion was monitored by ¹H NMR studies, however very little cyclohexene was formed in the reaction timescale. The results on Diels-Alder catalysis are presented in Table 5.4.

Table 5.4 Results for Diels-Alder reactions using metallasilsesquioxanes.

<table>
<thead>
<tr>
<th>Diene</th>
<th>Dieneophile</th>
<th>Catalyst</th>
<th>Isomer Ratio</th>
<th>(k_2/1\text{mol}^{-1}\text{h}^{-1})</th>
<th>(k_2/k_{2(\text{thermal})})</th>
<th>% Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>18</td>
<td>85:15</td>
<td>0.25</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>21</td>
<td>87:13</td>
<td>0.15</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>25</td>
<td>85:15</td>
<td>0.12</td>
<td>2.4</td>
<td>9.6</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>26</td>
<td>85:15</td>
<td>0.10</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>27</td>
<td>82:18</td>
<td>0.15</td>
<td>3.2</td>
<td>12</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>28</td>
<td>80:20</td>
<td>0.16</td>
<td>2.8</td>
<td>12.8</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Buten-3-one</td>
<td>29</td>
<td>85:15</td>
<td>0.15</td>
<td>3</td>
<td>12</td>
</tr>
</tbody>
</table>
\( K_2 \) refers to the average reaction rate measurement. The thermal reaction proceeds with up to 30% of 3,4-dihydropyranes resulting from homo-Diels-Alder reactions of the buten-3-one. Isomer ratio of the thermal reaction is approximately 75:25.

Unfortunately, all complexes did not seem to hugely accelerate Diels-Alder reactions over or above the related thermal reaction. Non-catalysed reactions however, were found to form 3, 4-dihydropyranes which resulted from the homo Diels-Alder reactions of the eneones. A slight increase in the characteristic substituted cyclohexene signals in the \(^{1}\text{H}\) NMR were integrated and the conversions calculated.

The precursor 18 to the complexes 21, 25, 26, 27, 28 and 29 were found to be very poorly active. The reason behind the inactivity in the Diels-Alder reactions of eneones of the aluminosilsesquioxane 18, compared to that of the aluminosilsesquioxane gel X, is that in 18, the aluminium center present as earlier discussed, is slightly 'tucked away' and has a higher coordination number of 4. It is the reactivity of the OH functions that governs the catalytic potential of this complex. In gel X the aluminium is found coordinated to two O atoms of the siloxy framework in ‘exo’ positions, whereas in the aluminosilsesquioxane 18 the Al is found in a closed lattice type system, with the Al centre bridged to four siloxy units, two from each of silsesquioxane ligands. When the gel X was subjected to hydrolysis followed by organic workup, the silanediol precursor was recovered, the same did occur for the aluminosilsesquioxane 18, but not as smoothly thus indicating a more difficult access to the aluminium centre. Also the aluminosilsesquioxane X was polymeric in nature whereas all the complexes investigated her were not polymeric.

The aluminosilsesquioxane gel X actually accelerated the Diels-Alder reaction of a number of different enones by several orders of magnitude over the thermal reaction and its activity is therefore comparable to the best reported catalysts known to date.

The activity of 18 was however slightly greater than those of its bimetallic derivatives. Therefore, the mere presence of extra metal atoms in these frameworks does not enhance the activity of 18 in Diels-Alder reactions of enones.
5.6 Conclusions and the future outlook for metallasiloxane catalysis

Metallasilsesquioxanes have emerged from Chapter 4 as very interesting ligands with varying potential in catalytic reactions. Coordination of (d^0) metals to a silsesquioxane framework tends to generate electrophilic metal centres: the silsesquioxane framework is approximately as electron-withdrawing as a CF$_3$ group, rendering metal centres Lewis acidic.$^{26}$ This property is likely to increase the catalytic activity of silsesquioxane complexes when compared with that of related compounds having conventional alkoxide or siloxide ligands. This concept has been exploited in this chapter with the investigation of the metallasilsesquioxane complexes prepared as potential catalysts in alkene polymerisation and epoxidation, and in the Diels-Alder reactions of enones.

Epoxidation reactions were performed using all aluminium siloxanes, and aluminium, cerium, and group 4 containing silsesquioxanes. Diels-Alder reactions were carried out using all aluminium siloxanes, and aluminium, group 4, cerium(III) and neodymium silsesquioxanes. Investigation of the catalytic activity in ethylene polymerisation was carried out using all anionic aluminium silsesquioxanes and all bimetallic complexes as potential silsesquioxane catalysts.

The aluminosiloxanes 5, 6 and 7 were found not to enhance the Diels-Alder of buten-3-one significantly. Very little cyclohexene was formed from the reaction with 5. The activities for 6 and 7 were more significant than that for 5, however the conversions were not above those for the previously reported Diels-Alder catalysts.

In the epoxidation of 1-octene, the bimetallic silsesquioxanes 25 and 26 were found to be active, with high yields of the epoxide being formed. However in the Diels-Alder reaction of buten-3-one, none of the metallasilsesquioxane complexes synthesised and investigated were significantly active above that of the thermal reaction. In the polymerisation reactions of ethylene, oligomers were obtained for a number of the complexes, however no exciting polymeric material was obtained.

So far all homogeneous epoxidation catalysts reported in the literature have been exclusively active in combination with an organic peroxide. Catalysis involving the use of aqueous hydrogen peroxide proved to be impossible with these systems. This is a
drawback when one considers that a procedure for the epoxidation of alkenes using environmentally friendly oxidants like O₂ and H₂O₂ is an important industrial and synthetic goal. As such, a breakthrough in this field may be the synthesis of the polyoxotitanates, which consist of a cluster type structure. The reaction of the tetrasilanol \((c\text{-}C_7\text{H}_{13})_6\text{Si}_6\text{O}_7\text{(OH)}_4\)\(^{27}\) with titanium tetrachloride followed by reaction with water leads to the clean formation of the polyoxotitanate \([(c\text{-}C_7\text{H}_{13})_6\text{Si}_6\text{O}_{11}]_3[\text{TiOH}]_4\),\(^{28}\) a water-stable complex that only starts to thermally decompose at about 250°C in air. This polyoxotitanate was found to be not only stable in protic oxidising media but also to efficiently catalyse alkene epoxidations including those that use aqueous hydrogen peroxide as the oxidising agent. For example, cyclooctene could be epoxidised with selectivities and conversions higher than 90%. Finally, silsesquioxanes containing a higher titanium content have been reported to result from a one-step procedure by reaction of substituted silanetriols with titanium tetraisopropylate in a 1:1 ratio. To date, the ability of these cluster compounds to catalyse alkene epoxidations or polymerisations has not been reported.\(^{29}\)

In the ethylene polymerisation reactions only Ti or Zr containing metallasilsesquioxanes \(^{25, 26}\) and \(^{27}\) have shown some low catalytic activity yielding low molecular weight polymers (or oligomers). The low activity of the complexes can be caused by several factors such as: the low stability of the catalytically active species, the anionic nature of these compounds and/or the sterical hindrance about the transition metal centres in the complexes. Future work on the improvements of the catalytic properties of the compounds will involve variation in the amounts of (ratios) and types of the trialkylaluminium (AlMe₃, AlEt₃, MAO, etc.) co-catalysts added to the bimetallic metallasilsesquioxanes. The structural characterisation of the catalytically active species will be important in order understand the nature of the catalytically active site in the bimetallic complexes. All this research will be performed in the future.
5.7 References

Chapter 6 Experimental and Procedures
6.1 General Procedures

All manipulations were carried out under a vacuum or argon atmosphere by standard Schlenk techniques. Solvents were dried and distilled over a sodium-potassium alloy under argon prior to use and then condensed into a reaction flask under vacuum shortly before use. The silanols (c-C₆H₁₁)₇Si₇O₉(OH)₃ and (c-C₆H₁₁)₈Si₈O₁₁(OH)₂ were prepared according to the previously reported procedures. Ph₂Si(OH)₂, AlEt₃, Et₂AlCl₃, AlCl₃, FeCl₃, CeCl₃, LaCl₃, CeI₃, La(OTf)₃, (Ph₂SiO)₄, NEt₃, C₅H₅N, Ti(OEt)₄, TiCl₄, Cp₂TiCl₂, Cp₂ZrCl₂, TBHP, 1-octene, Isoprene and buten-3-one were all obtained from Aldrich and stored under argon when appropriate. For NEt₃ and C₅H₅N, these liquids were dried and freshly distilled over sodium metal before use.

Ethylene gas was purchased from BOC Gases, Ireland and was dried using P₂O₅/glass wool column.

CeN₃ were prepared from anhydrous CeI₃, and LaN₃ and [La(OTf)La(N⁺)₂] were prepared from La(OTf)₃. The reactions were carried out by reacting the respective iodide or triflate precursors with LiN(SiMe₃)₂ by the published procedure.³

The following compounds were prepared by known published procedures, KC₆, the bis(trimethylsilyl)cyclopentadienyl derivatives NdCp⁺,⁵ Cp⁺CeCl, CeCp⁺,⁶ and the bis(trimethylsilyl)methylcyclopentadienyl derivative NdCp⁺.⁷ They were all stored under vacuum or under argon atmosphere.

Microanalyses were carried out at the Chemistry Department of Magdeburg University or at the Microanalytical Lab. in University College Dublin.

The NMR spectra were recorded using a Bruker DPX 300 (¹H, 300.1; ²⁹Si, 99MHz) or Varian 400 (¹H, 400 MHz; ¹³C, 125 MHz) instrument in benzene-d₆ at ambient temperature unless otherwise stated, and referenced for ¹H internally to residual solvent resonances. Deuterated benzene, pyridine and THF were dried over a potassium metal mirror and distilled prior to use. IR spectra (500 - 4000 cm⁻¹) were recorded as Nujol mulls using KBr discs on a Perkin-Elmer instrument.
X-Ray crystallography data for structures 2, 3, 5, 6, 8 and 18 were all collected on a Siemens SMART diffractometer by Dr. V. G. Kessler in Uppsala University in Sweden. Crystal data for structure 24 was collected on a Siemens-Stoe AED2 diffractometer by Dr. H.-G. Schmidt in the Chemistry Department of Magdeburg University.

All Mass Spectrometry was carried out using a Waters 2690 Separations Module with a Waters 996 Photodiode Array Detector.

6.2 Experimental for Chapter 2

6.2.1 Synthesis of (HO)Ph₂SiOSiPh₂O(PyH) (2)

Pyridine (0.55 cm³, 6.9 mmol) was added to Ph₂Si(OH)₂ (1.5 g, 6.9 mmol) in diethylether. The mixture was stirred for 48 hours. The solvent was removed in vacuum and the product was crystallised from THF at 0°C as colourless crystals of 2 (0.51 g, 30% in total). The reaction was repeated several times at room temperature, 10°C and at 0°C, for both 24 and 48 hours giving reproducible results. Anal. Calc. for C₂₉H₂₇N₂O₅Si₂: C, 70.53; H, 5.52; N, 2.84. Found C, 69.75; H, 5.32; N 2.77. IR (nujol, cm⁻¹) 3565 (br), 3165 (br), 1730 (s), 1589 (m), 1290 (m), 1110 (m), 1050 (m), 990 (s), 940 (m), 720 (s), 700 (s), 631 (m). ¹H NMR (400 MHz, CeD₆, 22 °C): δ = 8.31 (m, 1H, Py), 7.83 (m, 2H, Py), 7.10-7.00 (m, 20H, C₆H₅), 6.90 (m, 1H, PyH), 6.58 (m, 2H, PyH), 4.37 (s, 1H, OH). ¹³C NMR (125 MHz, CeD₆, 22 °C): δ = 146.8 (Py), 138.8-127.1 (Ph), 124.4 (Py), 114.4 (Py). ²⁹Si NMR (99 MHz, CeD₆, 22 °C): δ = -44.99 (Ph₂Si-OH), -47.40 (Ph₂Si-OHPy).

Crystal data: C₂₉H₂₆N₂O₅Si₂. M = 493.41, triclinic, space group P-1, a = 6.430(6) Å, b = 10.294(9) Å, c = 10.545(9) Å, α = 74.728(19)°, β = 82.191(16)°, γ = 85.115(18)°, T = 295(2)K, Z = 2, μ(Mo-Kα) = 4.127 mm⁻¹, theta range = 2.02 to 15.00°, 1028 reflections collected, 548 independent reflections collected [R(int) = 0.2495], R₁ = 0.0861 for reflections with l>2 sigma(1), wR₂ = 0.1869, R₁ = 0.1104, wR₂ = 0.2031 (all data).
6.2.2 Synthesis of [PyH][{(c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{9}(OH)\textsubscript{2}}\textsubscript{2}O\textsubscript{2}H] (3)

Pyridine (0.24mls, 2.92 mmol) was added to a solution of (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{9}(OH)\textsubscript{3} (0.56g, 0.584 mmol) in Et\textsubscript{2}O (100mls), and the mixture was stirred for 24 hours. The solution was then concentrated in vacuo and cooled to 0°C. Colourless crystals of 3 (0.34g, 59%) precipitated at 0°C within 14 days. Anal. Calc. for C\textsubscript{89}H\textsubscript{160}NO\textsubscript{24}Si\textsubscript{14}: C, 52.9; H, 7.93; N, 0.7. Found C, 53.4; H, 7.87; N, 0.67. IR (nujol, cm\textsuperscript{-1}): 2925 (s), 2855 (s), 1599 (s), 1197 (m), 1120 (s), 1100 (s), 1040 (m), 1030 (m), 892 (m), 751 (m). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): δ = 8.78 (m, 1H, Py), 8.52 (t, 2H, Py), 6.66 (m, 1H, PyH), 5.68 (s, 2H, PyH), 1.61-1.87 (m, 84H, c-C\textsubscript{6}H\textsubscript{11}), 1.21-1.27 (m, 56H, c-C\textsubscript{6}H\textsubscript{11}), 0.95-1.14 (m, 14H, c-C\textsubscript{6}H\textsubscript{11}). \textsuperscript{13}C NMR (125 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): δ = 26.89 (s, CH\textsubscript{2}), 23.69-24.07 (s, CH). \textsuperscript{29}Si NMR (99 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): δ = -59.46, -67.40, and -69.09 (3:1:3).

Crystal data:
C\textsubscript{89}H\textsubscript{160}NO\textsubscript{24}Si\textsubscript{14}, M = 1010.72, triclinic, space group = P-1, a = 14.680(4) Å, b = 14.886(6) Å, c = 15.749(4) Å, α = 67.58(3)°, β = 68.05(2)°, γ = 71.56(2)°, T = 293(2)K, Z = 2, µ (Mo-Kα) = 0.217 mm\textsuperscript{-1}, 11529 reflections collected, 7507 independent reflections collected [R (int) = 0.0396], R\textsubscript{1} = 0.0626 for reflections with I>2 sigma (I), wR\textsubscript{2} = 0.1554, R\textsubscript{1} = 0.1321, wR\textsubscript{2} = 0.1735 (all data).

6.2.3 Synthesis of [HPy]\textsubscript{2}[Fe\textsubscript{2}OCl\textsubscript{6}].Py (4)

FeCl\textsubscript{3} (2.65g, 16.3 mmol) was added to a solution of Ph\textsubscript{2}Si(OH)\textsubscript{2} (1.77g, 8.2 mmol) and pyridine (2.2 cm\textsuperscript{3}, 0.027 mol) in THF (100cm\textsuperscript{3}). The mixture was heated under reflux for 24 hours. After that the solution was concentrated in vacuum and cooled to 0°C. After two days orange crystals of 4 precipitated (0.28g, 12%). Anal. Calc. for C\textsubscript{15}H\textsubscript{17}N\textsubscript{3}OCl\textsubscript{6}Fe\textsubscript{2}: C, 31.08; H, 2.96; N, 7.25. Found C, 42.86; H, 3.52; N, 8.78. IR (Nujol, cm\textsuperscript{-1}): 3235 (s, br), 3170 (w), 860 (s, br), 360 (s, br), 311 (m). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C) δ 10.92 (s, br, 10H, Hpy), 7.67 (s, br, 2H, Hpy), 5.71 (b, 5H, Py).

Crystal data: C\textsubscript{15}H\textsubscript{17}N\textsubscript{3}OCl\textsubscript{6}Fe\textsubscript{2}N\textsubscript{3}O, M = 579.72, monoclinic, space group = P2/m, a = 8.469(8) Å, b = 13.842(13) Å, c = 10.599(10) Å, α = 90°, β = 110.536(18)°, γ = 90°, T = 295(2)K, Z = 2, D\textsubscript{c} = 1.655 Mg/m\textsuperscript{3}, µ(Mo-Kα) = 1.946 mm\textsuperscript{-1}, ε = 0.71073 Å,
4940 reflections collected, 2447 independent reflection collected [R(int) = 0.0735], 
R$_1$ = 0.0522 for reflections with I>2 sigma(I), wR$_2$ = 0.0904, R$_1$ = 0.1529, wR$_2$ = 0.1161 (all data).

6.3 Experimental for Chapter 3

6.3.1 Synthesis of [PyH][Al{OSiPh$_2$(OSiPh$_2$)$_2$O}]$_2$ (5) and [AlCl(THF){O(Ph$_2$SiO)$_2$}]$_2$ (6)

Dry pyridine (2.35 cm$^3$, 29.2 mmol) was added via syringe to a mixture of aluminium 
chloride (0.36 g, 2.92 mmol) and diphenylsilanediol (2.33 g, 10.77 mmol) in THF 
(150 cm$^3$). The mixture was stirred for 24 hours, it was then filtered and the filtrate 
dried in vacuo. The residue was washed with hexane, and dried in vacuo. Fractional 
re-crystallisation from concentrated THF solution at the ambient temperature 
afforded first colourless crystals of 5 (1.26 g, 53 %), and further concentration of the 
mother liquor and cooling to −22 °C gave colourless crystals of 6, (0.49 g, 16 %).

Anal. Calc. for C$_{77}$H$_{66}$AlNO$_8$Si$_6$ (5): C, 69.59; H, 5.01; N, 1.05. Found C, 70.03; H, 5.00; N, 1.03. IR for 5 (Nujol, cm$^{-1}$): 3163 (br), 2725 (s), 2670 (m), 1732 (s), 1589 
(m), 1288 (m), 1120 (s), 1055 (m), 1012 (m), 991 (s), 939 (m), 700 (s), 627 (m), 588 
(m). NMR of 5: $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ 7.99 - 7.83 (m, 24H, C$_6$H$_5$, o), 7.34 (s, 1H, PyH), 7.23 (br, 2H, PyH), 7.09-7.01 (m, 36H, C$_6$H$_5$, m, p), 6.42 (m, 1H, PyH), 5.92 (m, 2H, PyH). $^{13}$C($^1$H) NMR (125 MHz, C$_6$D$_6$, 22 °C): δ 146.94 (Py), 138.85 (Ph), 137.50 (Ph) 135.03 (Ph), 134.83 (Ph), 129.75 (Ph), 129.03 (Ph), 128.03 -127.25 (Ph), 124.33 (Py), 114.29 (Py). $^{29}$Si ($^1$H) NMR (99 MHz, C$_6$D$_6$, 22 °C): δ - 42.36 (s, 1, β-Si), and −43.56 (s, 2, α-Si).

Crystal data for 5: C$_{77}$H$_{66}$AlNO$_8$Si$_6$, M = 1328.83, triclinic, space group P-1, a = 11.8800(9), b = 15.0636(12), c = 20.7172(17) Å, α = 93.716(2), β = 102.95 (3), γ = 107.226(2) °, U = 3519.1(5) Å$^3$, T = 295(2) K, Z = 2, μ(Mo-Kα) = 0.187 mm$^{-1}$, 14160 reflections collected, 9181 independent reflections [R(int) = 0.0325], R$_1$ = 0.0540 for reflections with I > 2σ(I), wR$_2$ = 0.1284 (all data).
Anal. Calc. for C\textsubscript{56}H\textsubscript{56}Al\textsubscript{2}Cl\textsubscript{2}O\textsubscript{8}Si\textsubscript{4} (6): C, 61.5; H, 5.16. Found C, 61.1; H, 5.12. IR of 6 (Nujol, cm\textsuperscript{-1}): 2720 (m), 1963 (s), 1894 (s), 1826 (s), 1778 (s), 1665 (s), 1606 (s), 1591 (s), 1537 (m), 1259 (m), 1091 (br m), 969 (m), 804 (m), 720 (s), 694 (m).

NMR of 6: \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): \( \delta \) 7.89 (m, 16H, C\textsubscript{6}H\textsubscript{12}, o), 7.07 - 7.02 (m, 24H, C\textsubscript{6}H\textsubscript{12}, m, p), 3.49 (m, 8H, THF), 1.35 (m, 8H, THF). \textsuperscript{1}C\textsuperscript{1}H NMR (125 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): \( \delta \) 134.71 (Ph), 134.46 (Ph), 130.68 (Ph), 128.10 - 127.80 (Ph), 68.10 (THF), 26.09 (THF). \textsuperscript{29}Si \textsuperscript{1}H NMR (99 MHz, C\textsubscript{6}D\textsubscript{6}, 22 °C): \( \delta \) 44.77 (Ph\textsubscript{2}Si).

Crystal data for 6: C\textsubscript{56}H\textsubscript{56}Al\textsubscript{2}Cl\textsubscript{2}O\textsubscript{8}Si\textsubscript{4}, M = 1094.228, monoclinic, space group P2(1)/n, \( a = 14.275(4) \), \( b = 16.322(4) \), \( c = 16.560(4) \) Å, \( \beta = 113.911(6) \), \( U = 3527.3(16) \) Å\textsuperscript{3}, \( T = 295(2) \) K, \( Z = 2 \), \( \mu(\text{Mo-K}\alpha) = 0.227 \) mm\textsuperscript{-1}, 5251 reflections collected, 1420 independent reflections [R(int) = 0.1731], \( R = 0.0780 \) for reflections with \( I > 2\sigma(I) \), \( wR_2 = 0.2025 \) (all data).

6.3.2 Alternative synthesis of AlCl(THF){O(Ph\textsubscript{2}SiO)}\textsubscript{2}\textsubscript{2} (6)

Et\textsubscript{2}AlCl (1.66 cm\textsuperscript{3}, 2.98 mmol) was added dropwise to a solution of Ph\textsubscript{2}Si(OH)\textsubscript{2} (1.29 g, 5.96 mmol) in Et\textsubscript{2}O at room temperature. The reaction liberated ethane gas and was exothermic. The mixture was stirred for 24 hours. Then the solvent was removed in vacuo giving a foam like product. The product was washed with hexane and dried in vacuum (0.54 g, 32%). Anal. Calc. for C\textsubscript{56}H\textsubscript{56}Al\textsubscript{2}Cl\textsubscript{2}O\textsubscript{8}Si\textsubscript{4}: C, 61.5; H, 5.16. Found C, 61.3; H, 5.10. IR and NMR spectra were analogous to the above data for 6.

6.3.3 Synthesis of [Al{O(Ph\textsubscript{2}SiO)}\textsubscript{2}\textsubscript{2}][O(Ph\textsubscript{2}SiO)]\textsubscript{2} (7)

Ph\textsubscript{2}Si(OH)\textsubscript{2} (0.22 g, 1 mmol) was added to a solution of aluminosiloxane 6 (1.1 g, 1 mmol) and NEt\textsubscript{3} (1.02 g, 10 mmol) in THF. The mixture was stirred for 48 hours, after which time precipitation of HNEt\textsubscript{3}Cl had occurred. The reaction mixture was filtered and the filtrate was concentrated in vacuo yielding the product 7 (0.88 g, 80%). Anal. Calc. for C\textsubscript{120}H\textsubscript{100}O\textsubscript{16}Al\textsubscript{4}Si\textsubscript{10}: C, 65.90; H, 4.61. Found C, 64.75; H, 4.52. IR (Nujol, cm\textsuperscript{-1}): 2710 (m), 1962 (s), 1899 (s), 1830 (s), 1750 (s), 1665 (s), 171
1606 (s), 1591 (s), 1542 (m), 1266 (m), 1095 (br, m), 970 (m), 795 (m), 720 (s), 696 (m). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 7.89-7.69 (m, 40H, CeHj, o), 7.08 - 6.95 (m, 60H, CsHs, m, p). \(^{13}\)C\{\(^1\)H\} NMR (125 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 134.7- 130.5 (Ph), 128.80 -127.20 (Ph). \(^29\)Si \{\(^1\)H\} NMR (99 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) -46.92 and -49.09 in a 1:4 ratio. MS (ESI, 100% THF): \(m/z\) 239 ([Ph\(_2\)SiO\(_2\)Al], 100%), 492 ([AlO(SiPh\(_2\)O\(_2\))]\(_2\) - 3 THF\(^{2+}\), 20%), 1095 ([M]\(^{2+}\), 12.5%) and 1271 [M + 5 THF\(^{2+}\), 15%].

### 6.3.4 Synthesis of [Al(OH)]\(_4\)[(Ph\(_2\)SiO\(_2\))\(_2\)O]\(_4\) (8)

AlEt\(_3\) in toluene (3.05cm\(^3\), 5.8 mmol) was added dropwise to Ph\(_2\)Si(OH)\(_2\) (2.51g, 11.6 mmol) in THF (100cm\(^3\)) at 0°C. The mixture was stirred for 60 hours resulting in a pale yellow solution. The solvent was removed in vacuo. The product was recrystallised from toluene, giving colourless crystals of 8 (1.78g, 60%). Anal. Calc. for C\(_{96}\)H\(_{44}\)Al\(_4\)O\(_{16}\)Si\(_8\): C, 63.13; H, 4.64. Found C, 60.1; H, 4.21. IR (Nujol, cm\(^{-1}\)): 3590 (s, OH), 3110 (m, ArH), 2950 (s, Ph), 1652 (m, Ph), 1460 (m, Ph), 1040 (m, Ph), 892 (m, Ph), 703 (m, Ph). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) = 6.08 (s, 4H, AlOH), 7.09-6.69 (m, 48H, C\(_6\)Hs, m, p), 7.90-7.88 (m, 32H, C\(_6\)Hs, o). \(^{13}\)C NMR (125 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) = 127.6-139.8 (arom C). \(^{29}\)Si NMR (99 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) = -44.1 (s, SiPh\(_2\)). Crystal data: C\(_{96}\)H\(_{44}\)Al\(_4\)O\(_{16}\)Si\(_8\), M = 1826.27, monoclinic, space group I-4, \(a = 24.95(6), b = 24.951(6), c = 38.811(8)\) Å, \(\alpha = 90.00, \beta = 90.00, \gamma = 90.00, U = 3527.3(16)\) Å\(^3\), \(T = 295(2)\) K, \(Z = 2, \mu(\text{Mo-K}\alpha) = 0.227\) mm\(^{-1}\), 4226 reflections collected, 4887 independent reflections \([R(\text{int}) = 0.2907], R_1 = 0.2676\) for reflections with \(F_o > 4\sigma(F_o), wR_2 = 0.2.228\) (all data).

### 6.3.5 Synthesis of [Al\(_3\){O(Ph\(_2\)SiO\(_2\))\(_2\)}Cl\(_5\)] (9)

AlCl\(_3\) (0.23g, 3.45 mmol) was added to (Ph\(_2\)SiO\(_2\))\(_4\) (1.38g, 1.74 mmol) in THF and heated under reflux for 24 hours. The solution was concentrated in vacuo. The products were separated by fractional crystallisation from THF giving the colourless crystalline (Ph\(_2\)SiO\(_3\)) and the aluminosiloxane [Al\(_3\){O(Ph\(_2\)SiO\(_2\))\(_2\)}Cl\(_5\)] (9) (0.77g, 172
62%). Anal. Calc. for C_{48}H_{40}O_6Cl_5Al_3Si_2: C, 53.21; H, 3.72. Found C, 55.1; H, 4.05. IR (nujol, cm^{-1}): 2918 (s), 2835 (s), 2359 (m), 2330 (m), 1458 (s), 1370 (m), 1298 (m), 1272 (m), 1151 (m), 1066 (s), 1022 (s), 966 (m), 803 (s), 727 (s), 540 (m), 376 (s). $^1$H NMR (400 MHz, C_{6}D_{6}, 22 °C, ppm): δ 7.71 - 7.69 (m, 16H, o-Ph), 7.04 - 7.01 (m, 24H, o-Ph). $^{13}$C NMR (125 MHz, C_{6}D_{6}, 22 °C): δ = 135.07 (C_{6}H_{5}), 130.62 (C_{6}H_{5}). $^{29}$Si NMR (99 MHz, C_{6}D_{6}, 22 °C): δ = -44.03.

### 6.3.6 Synthesis of [Ph$_2$SiO$_2$Ce(μ-Cl)(THF)$_2$]$_2$ (10)

Cp’’CeCl (0.45g, 1.17 mmol) was added to a solution of Ph$_2$Si(OH)$_2$ (0.25g, 1.15 mmol) in THF. The mixture was stirred for 24 hours. The solvent was consequently removed in vacuo. The resulting yellow-brown material was washed with hexane and dried in vacuo giving product 10 (0.5g, 80%). Anal. Calc. for C_{40}H_{32}O_8Si$_2$Ce$_2$Cl$_2$: C, 44.98; H, 4.91. Found C, 42.6; H, 5.16. IR (nujol, cm^{-1}): 3112 (m), 2950 (m), 2840 (m), 1550 (w), 1433 (m), 1389 (m), 1301 (m), 1285 (m), 1210 (m), 1045 (s), 1018 (s), 920 (m), 801 (br), 620 (w), 540 (m), 375 (s). $^1$H NMR (400 MHz, C_{6}D_{6}, 22 °C): δ 7.81 - 7.62 (m, 8H, o-Ph), 7.08 - 6.9 (m, 12H, m-, p-Ph), 3.57 (br, 16H, THF), 1.40 (br, 16H, THF). $^{13}$C{$^1$H} NMR (125 MHz, C_{6}D_{6}, 22 °C): δ 135.0 - 134.8 (s, Ph), 130.4 - 128.5 (s, Ph), 68.9 (s, THF), 25.1 (s, THF). $^{29}$Si{$^1$H} NMR (99 MHz, C_{6}D_{6}, 22 °C): δ -77.27 (s).

### 6.3.7 Synthesis of [HNEt$_3$][La{OSiPh$_2$(OSiPh$_2$)$_2$O$_2$(NEt$_3$)$_2$}] (11)

LaCl$_3$ (0.5g, 2 mmol) was added to a mixture of Ph$_2$Si(OH)$_2$ (0.88g, 4 mmol) and NEt$_3$ (2.8 cm$^3$, 20 mmol) in THF. The mixture was stirred for 48 hours and the precipitate of HNEt$_3$Cl was removed by filtration. The clear pale yellow THF filtrate was concentrated in vacuo giving the powder 11 (2.26g, 68%). Anal. Calc. for C_{90}H_{106}O_{12}N$_3$LaSi$_6$ (11): C, 64.9; H, 6.42. Found C, 63.68; H, 4.97. IR (Nujol, cm$^{-1}$):

- 3154 (m), 2840 (w), 2359 (m), 2333 (m), 1453 (s), 1380 (m), 1301 (m), 1280 (m), 1030 (s), 1018 (s), 965 (m), 795 (s), 725 (s), 540 (m). $^1$H NMR (400 MHz, C_{6}D_{6}, 22 °C): δ 7.34 (s, 1H, H-N), 7.11- 7.08 (m, 24H, o-Ph), 7.34 (s, 1H, H-N), 7.04 – 7.01

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(m, 36H, m-, p-Ph), 2.3 (s, br, 18H, HN-CH$_2$ and N-CH$_2$), 0.89 (s, br, 27H, HN-CH$_3$ and N-CH$_3$). $^{13}$C{$^1$H} NMR (125 MHz, C$_6$D$_6$, 22 °C): δ 135.1 – 134.7 and 130.9 – 128.7 (m, Ph), 46.33 (s, N-CH$_3$CH$_3$), 8.96 (s, N-CH$_2$CH$_3$). $^{29}$Si {$^1$H} NMR (99 MHz, C$_6$D$_6$, 22 °C): δ –45.73 and –46.93 (1:2).

6.3.8 Synthesis of La[{$Ph$_2SiO(OH)}](THF)$_3$ (12)

La(N")$_3$ (0.6g, 0.97 mmol) was added to a solution of Ph$_2$Si(OH)$_2$ (0.63g, 2.9 mmol) in THF/Et$_2$O (50:50 cm$^3$). The mixture was stirred for 24 hours. Then the solvent was removed in vacuo. The residue was washed with hexane and dried in vacuo to give pale orange powder 12 (0.49g, 50%). Anal. Calc. for C$_{48}$H$_{57}$O$_3$Si$_3$La: C, 57.6; H, 5.74. Found C, 43.20; H, 3.53. IR (nujol, cm$^{-1}$): 3545 (m), 3131 (m), 2922 (s), 2840 (s), 2333 (m), 1458 (s), 1420 (m), 1301 (m), 1235 (m), 1150 (m), 1050 (s), 1020 (s), 960 (m), 725 (s), 542 (m). $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ 8.15 – 7.76 (m, 12H, o-Ph), 7.11 – 7.05 (m, 18H, m-, p-Ph), 6.80 (s, 3H, OH), 3.49 (s, 12H, THF), 1.33 (s, 12H, THF). $^{13}$C{$^1$H} NMR (125 MHz, C$_6$D$_6$, 22 °C): δ 134.2 – 134.0 and 129.67 – 127.98 (m, Ph), 70.1 (s, THF), 25.6 (s, THF). $^{29}$Si {$^1$H} NMR (99 MHz, C$_6$D$_6$, 22 °C): δ –43.33 (s).

6.3.9 Synthesis of Nd[{$Ph$_2SiO(OH)}](THF)$_3$ (13)

NdCp$_3$ (0.6g, 0.77 mmol) was added to a solution of Ph$_2$Si(OH)$_2$ (0.5g, 2.3 mmol) in THF (80 cm$^3$). The mixture was stirred for 48 hours. Then the solvent was removed in vacuo. The residue was washed with hexane and dried in vacuo resulting in a red-orange powder 13 (0.31g, 40%). Anal. Calc. for C$_{48}$H$_{57}$O$_3$Si$_3$Nd: C, 57.3; H, 5.7. Found C, 58.85; H, 4.62. IR (nujol, cm$^{-1}$): 3539 (m), 2922 (s), 2840 (s), 2359 (m), 2333 (m), 1453 (s), 1380 (m), 1301 (m), 1280 (m), 1150 (m), 1065 (s), 1018 (s), 960 (m), 801 (s), 725 (s), 540 (m), 375 (s). $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ 7.61 – 7.57 (m, 12H, o-Ph), 7.11 – 7.09 (m, 18H, m-, p-Ph), 6.91 (s, 3H, OH), 3.34 (br, 12H, THF), 1.35 (br m, 12H, THF). $^{13}$C{$^1$H} NMR (125 MHz, C$_6$D$_6$, 22 °C): δ
134.2 - 128.5 (m, Ph), 69.9 (s, THF), 25.8 (s, THF). $^{29}$Si $^1$H NMR (99 MHz, C$_6$D$_6$, 22 °C): δ 1.98 (s, Cp$''$H), -36.32 (s, Ph$_2$Si).

### 6.3.10 Synthesis of [{Cp$^\text{Nd}(\text{THF})_2$(PH$_2$SiO$_2$)(PH$_2$Si(OH)$_2$)}] (14)

NdCp$^\text{R}_3$ (0.5g, 0.87 mmol) was added to a solution of PH$_2$Si(OH)$_2$ (0.19g, 0.87 mmol) in THF (60 cm$^3$). The mixture was stirred for 48 hours. Then the solution was concentrated in vacuo resulting in a blue powder 14 (0.20g, 28%). Anal. Calc. for C$_8$O$_{12}$Si$_2$Nd: C, 58.79; H, 7.9. Found C, 58.85; H, 7.62. IR (Nujol, cm$^{-1}$): 3545 (m), 2920 (s), 2352 (m), 2340(m), 1468 (s), 1388 (m), 1299 (m), 1281 (m), 125 (m), 1056 (s), 1021 (s), 957 (m), 808 (s), 732 (s), 544 (m), 375 (s). $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ 7.90 – 7.64 (br m, 20H, Ph), 7.11 – 7.01 (m, 20H, Cp), 3.40 (br s, 8H, THF), 1.36 (br s, 8H, THF), 6.74 (s, 2H, OH), 0.29 (s, 36H, SiMe$_3$).

$^{13}$C $^1$H NMR (125 MHz, C$_6$D$_6$, 22 °C): δ 203.1 (s, Cp), 138.0 – 127.5 (m, Ph), 68.18 (s, THF), 25.52 (s, THF), 1.27-1.26 (s, CH-Cp), 0.71 (s, SiMe$_3$). $^{29}$Si $^1$H NMR (99 MHz, C$_6$D$_6$, 22 °C): δ -21.15, -41.62 and -44.99 (s, 4:1:1).

### 6.3.11 Synthesis of [La(OTf)(PH$_2$SiO$_2$)(THF)$_3$]$_2$ (15)

{N(SiMe$_3$)$_3$}$_2$La(OTf)$_2$ (1.0g, 0.82 mmol) was added to a solution of PH$_2$Si(OH)$_2$ (0.35g, 1.64 mmol) in THF (100 cm$^3$). The mixture was stirred for 24 hours. The solvent was removed in vacuo. The residue was washed with hexane and then dried in vacuo yielding the powder 15 (0.85g, 72%). Anal. Calc. for C$_{50}$H$_{68}$O$_{16}$F$_6$S$_2$Si$_2$La$_2$: C, 41.78; H, 4.77. Found C, 18.94; H, 1.78. IR (Nujol, cm$^{-1}$): 2722 (m), 2682 (w), 1589 (m), 1304 (m), 1261 (m), 1120 (s), 1085 (s), 1024 (s), 976 (s), 719 (s), 697 (s), 520 (s), 488 (m). $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ 7.83 – 7.65 (m, 8H, o-Ph), 7.10 – 6.90 (m, 12H, m-, p-Ph), 3.56 (s, 24H, THF), 1.39 (s, 24H, THF). $^{13}$C $^1$H NMR (125 MHz, C$_6$D$_6$, 22 °C): δ 203.10 (s, CF$_3$), 134.2 – 134.0 and 129.6 –127.9 (Ph), 67.11 and 25.09 (THF). $^{29}$Si $^1$H NMR (99 MHz, C$_6$D$_6$, 22 °C): δ -40.5. 

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6.3.12 Synthesis of [Ce(Ph₂Si₂O₂)(THF)₂]₂ (16)

CeCp"₃ (1.5g, 2 mmol) was added to Ph₂Si(OH)₂ (0.85g, 4 mmol) in THF (100 cm³). The mixture was stirred for 48 hours; a colour change from deep blue to orange was observed. The THF was removed in vacuo to give an orange foam. The residue was washed with hexane and dried in vacuo giving a product 16 (0.97g, 68%). Anal. Calc. for C₃₂H₃₆O₆Si₂Ce: C, 53.91; H, 5.1. Found C, 61.48; H, 4.86. IR (Nujol, cm⁻¹): 3143 (w), 2715 (m), 2695 (w), 1595 (m), 1320 (m), 1121 (s), 1076 (s), 1014 (s), 975 (s), 716 (s), 652 (s), 520 (s), 468 (m). ¹H NMR (400 MHz, C₆D₆, 22 °C): δ 7.80 – 7.63 (m, 8H, o-Ph), 7.11 – 7.01 (m, 12H, m-, p-Ph), 3.40 (s, 16H, THF), 1.21 (s, 16H, THF). ¹³C {¹H} NMR (125 MHz, C₆D₆, 22 °C): δ 136.42-135.06 and 131.24 –130.48 (m, Ph), 70.14 (s, THF), 25.96 (s, THF). ²⁹Si {¹H} NMR (99 MHz, C₆D₆, 22 °C): δ -46.11.

6.3.13 Synthesis of [Ce{0SiPh₂(OSiPh₂)₂O}₂(NEt₃)₂] (17)

Ce₁₃ (0.52g, 1 mmol) was added to a solution of Ph₂Si(OH)₂ (0.43g, 2 mmol) and NEt₃ (2.8cm³, 10 mmol) in THF (80 cm³). The mixture was stirred for 24 hours. The precipitation of HNEt₃ was crystalline needles occurred. The mixture was filtered and the THF filtrate was evaporated in vacuo. The residue was washed with hexane and dried resulting in a pale yellow powder 17 (0.61g, 39%). Anal. Calc. for C₈₄H₆₀N₈O₈Si₆Ce: C, 64.5; H, 5.8. Found C, 66.48; H, 5.55. IR (nujol, cm⁻¹): 3162 (w), 3112 (w), 2722 (m), 1599 (m), 1314 (m), 1261 (m), 1115 (s), 1075 (s), 1022 (s), 976 (s), 720 (s), 677 (s), 520 (s). ¹H NMR (400 MHz, C₆D₆, 22 °C): δ 7.72 – 7.90 (m, 24H, o-Ph), 7.11 – 7.04 (m, 36H, m-, p-Ph), 2.13 (s, 12H, N-CH₂), 0.70 (s, 18H, N-CH₃). ¹³C {¹H} NMR (125 MHz, C₆D₆, 22 °C): δ 136.92 – 130.71 (s, Ph), 48.33 (s, NEt₃), 9.72 (s, NEt₃). ²⁹Si {¹H} NMR (99 MHz, C₆D₆, 22 °C): δ -41.1 and -43.0 (s, 1:2).
6.4 Experimental for Chapter 4

6.4.1 Synthesis of $[\text{HNEt}_3][\text{Al}\{(c-\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\}_2]$ (18)

$\text{AlCl}_3$ (0.20g, 1.5 mmol) was added to a solution of trisilanol 1 (2.92g, 3 mmol) and triethylamine (2.1cm$^3$, 15 mmol) in $\text{Et}_2\text{O}$ (80 cm$^3$). The solution was stirred for 48 hours. The precipitation of white powder had occurred. The mixture was filtered and the $\text{Et}_2\text{O}$ filtrate was concentrated in vacuo. and cooled to 0°C yielding a pale pink crystalline 18 (2.73g, 88%). Anal. Calc. for C$_{96}$H$_{172}$O$_{24}$NSi$_{14}$Al: C, 52.16; H, 8.37; N, 0.68. Found C, 50.05; H, 8.31; N, 0.59. IR (Nujol, cm$^{-1}$): 3430 (m), 3165(m), 1680 (s), 1308 (s), 1221 (s), 1050 (s), 932 (m), 862 (m), 834 (m), 763 (m), 554 (m). $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C): $\delta = 9.60$ (vbr s, 1H, HNEts), 7.52 (s, 2H, OH), 2.79 (br s, 6H, HNEt$_3$), 2.38-1.00 (v br ms, 154H, c-C$_6$H$_{11}$), 0.84 (m, 9H, HNEt$_3$). $^{13}$C NMR (125 MHz, C$_6$D$_6$, 22 °C): $\delta = 46.27$ (s, NEt$_3$), 30.29-27.70 (s, CH$_2$, c-C$_6$H$_{11}$), 26.07-24.2 (s, CH, c-C$_6$H$_{11}$), 8.95, (s, NEt$_3$). $^{29}$Si NMR (99 MHz, C$_6$D$_6$, 22 °C): $\delta = -56.79$, -58.24, -62.82, -65.71, -67.63 (s, 1:2:2:1:1).

6.4.2 The Interaction of aluminium chloride with Ph$_8$Si$_8$O$_{12}$: synthesis of Ph$_8$Si$_8$O$_{11}$(Cl)OAlCl$_2$(THF)$_2$ (19)

$\text{AlCl}_3$ (0.134g, 1.0 mmol) was added to a mixture of Ph$_8$Si$_8$O$_{12}$ (1.04g, 1.0 mmol) in THF (50 cm$^3$). The mixture was heated under reflux for 12 hours. The solvent was removed in vacuo. The residue was washed with hexane and dried in vacuum yielding the pink product 19 (0.53g, 48%). Anal. Calc. for C$_{56}$H$_{56}$Si$_8$O$_{14}$AlCl$_3$: C, 51.3; H, 4.3. Found C, 51.86, H, 3.9. $^1$H NMR (400 MHz, C$_6$D$_6$, 22 °C, ppm); $\delta$ 7.77 (m, 16H, o-Ph), 6.97 – 6.56 (m, 24H, m-, p- Ph), 3.56 (s, 8H, THF), 1.25 (s, 8H, THF). $^{13}$C NMR (125 MHz, C$_6$D$_6$, 22 °C): $\delta = 68.16$, (s, THF), 30.30-27.75 (s, CH$_2$, c-C$_6$H$_{11}$), 25.11 (s, THF), 24.12-23.22 (s, CH, c-C$_6$H$_{11}$), $^{29}$Si NMR (99 MHz, C$_6$D$_6$, 22 °C): $\delta = -70.28$, -73.66, -77.51, -79.20, -80.64, -81.16 (1:2:1:2:1:1). MS (ESI, 100% THF) of 19a: m/z 1063 ([2Ph$_8$Si$_8$O$_{12}$ + Al + 2(OH)]$^{2+}$, 100%), 1115 ([2Ph$_8$Si$_8$O$_{12}$ + 2Al + 6(OH) +2H]$^+$, 68%) and 1787 ([2Ph$_8$Si$_8$O$_{12}$ + 2Al + 3(OH) – 5Ph +H]$^+$, 50%).

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6.4.3 Synthesis of \([(c-C_6H_{11})_7Si_7O_{12}La(NEt_3)]_2\) (20)

LaCl\(_3\) (0.39g, 1.6 mmol) was added to a solution of trisilanol 1 (1.57g, 1.6 mmol) and NEt\(_3\) (1.16cm\(^3\), 8 mmol) in THF (80 cm\(^3\)). The mixture was stirred for 24 hours. The mixture was filtered and the filtrate was removed in vacuo. The residue was washed with hexane and dried in vacuo to give a yellow foam 20 (1.36g, 70%). Anal. Calc. for C\(_96\)H\(_{84}\)O\(_{24}\)Si\(_4\)La: C, 47.61; H, 7.66; N, 1.16. Found C, 46.16; H, 7.37; N, 0.42. IR (KBr, cm\(^{-1}\)): 2918 (br), 2732 (s), 1277 (s), 1184 (s), 1101 (s), 891 (s), 725 (s), 513 (s), 471 (s), 419 (s). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 1.80 - 1.05 (m, 154H, c-C\(_6\)H\(_{11}\)), 2.3 (s, 12H, N-CH\(_3\)), 0.86 (s, 18H, N-CH\(_3\)). \(^{13}\)C\(^{\{1\}H}\) NMR (125 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 47.1 (s, N-CH\(_2\)), 28.08 - 27.01 (s for CH\(_2\)), 24.17 - 23.33 (s for CH), 9.23 (s, N-CH\(_3\)). \(^{29}\)Si \(^{\{1\}H}\) NMR (99 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) -56.55, -58.23, -60.21, -63.78, -65.95 (s 1:2:1:1:2).

6.4.4 Synthesis of \([(c-C_6H_{11})_7Si_7O_{12}Ce(NEt_3)]_2\) (21)

CeCl\(_3\) (0.38g, 1.5 mmol) was added to a solution of trisilanol 1 (1.46g, 1.5 mmol) and triethylamine (1.05cm\(^3\), 7.5 mmol) in THF (70 cm\(^3\)). The mixture was stirred at room temperature for 24 hours. The precipitation of [HNEt\(_3\)]Cl occurred. The mixture was filtered. The filtrate was evaporated in vacuum. The residue was washed with hexane and dried in vacuo yielding 21 (1.3g, 72%). Anal.Calc. for C\(_{96}\)H\(_{84}\)Ce\(_2\)N\(_2\)O\(_{24}\)Si\(_4\): C, 47.57; H, 7.65; N, 1.16. Found C, 46.39; H, 7.37; N, 0.46. IR (KBr, cm\(^{-1}\)): 2925 (br), 2727 (s), 1269 (s), 1170 (s), 1115 (s), 1050 (s), 891 (s), 726 (s), 511 (s), 467 (s), 409 (s). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 2.92 (s, 12H, N-CH\(_2\)), 1.71-1.05 (m, 154H, c-C\(_6\)H\(_{11}\)), 0.90 (s, 18H, N-CH\(_3\)). \(^{13}\)C\(^{\{1\}H}\) NMR (125 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) 45.5 (s, N-CH\(_2\)), 26.90 - 25.54 (s, CH\(_2\)), 24.01 - 22.02 (s, CH), 8.85 (s, N-CH\(_3\)). \(^{29}\)Si \(^{\{1\}H}\) NMR (99 MHz, C\(_6\)D\(_6\), 22 °C): \(\delta\) -57.76, -58.96, -65.95, -68.36, -68.71, (s, 1:2:1:1:2).
6.4.5 Synthesis of [(c-C₆H₁₁)₇Si₇O₁₂La(THF)]₂ (22)

La[N(SiMe₃)₂]₃ (1g, 1.6 mmol) was added to a solution of trisilanol 1 (1.58g, 1.6 mmol) in THF (80 cm³). The mixture was stirred for 24 hours. Then the solvent was removed in vacuo. The residue was washed with hexane and dried in vacuo producing a cream coloured foam 22 (1.29g, 68%). Anal. Calc. for C₉₂H₁₇₀O₂₆Si₄₄La₂: C, 48.78; H, 7.25. Found C, 42.28; H, 6.43. IR (KBr, cm⁻¹): 2918 (br), 2732 (s), 1184 (s), 1101 (s), 1020 (m), 1040 (m), 891 (s), 725 (s), 513 (s), 471 (s), 419 (s). 

6.4.6 Synthesis of Ce{(c-C₆H₁₁)₇Si₇O₁₁(OH)}₂ (23)

Trisilanol 1 (1g, 1 mmol) was added to a solution of [(c-C₆H₁₁)₇Si₇O₁₂Ce(NEt₃)]₂ (21) (2.38g, 1 mmol) in THF (100 cm³) and was refluxed for 24 hours. The solution was concentrate in vacuo and cooled to 0 °C yielding 23 (0.58g, 28%). Anal. Calc. for C₈₄H₅₆O₂₄Si₄₄Ce: C, 48.42; H, 7.55. Found C, 48.50; H, 7.62. IR (KBr, cm⁻¹): 3179 (br, OH), 2920 (br), 2852 (br), 1599 (s), 1450 (m), 1111 (s), 894 (s), 848 (s), 820 (s), 752 (s), 516 (s) 400(s). 

6.4.7 Synthesis of Ce[{(c-C₆H₁₁)₈Si₈O₁₃}₂(Py)]₃ (24)

A solution of (c-C₆H₁₁)₈Si₈O₁₃(OH)₂ (2.52g, 2.3 mmol) in diethyl ether (60 cm³) was added to a Ce[N(SiMe₃)₂]₃ (0.713 g, 1.15 mmol) at ca. 20 °C. The mixture was stirred for 3 hours. Pyridine (2.1 g, 23 mmol) was added and the mixture was stirred for 24 h. The mixture was then filtered and the filtrate was concentrated to ca. 20 cm³
in vacuo. Pale yellow crystals of 24 were gradually deposited. Further concentration of the remaining mother liquor (ca. 10 cm³) in vacuo and cooling to -22 °C afforded an additional crop of colourless crystals of 24 (1.00 g, 67% in total).

Anal. Calc. for C_{114}H_{191}Ce_{3}O_{26}Si_{16}: C, 53.4; H, 7.45; N, 1.6. Found: C, 52.9; H, 7.36; N, 1.4. IR (KBr, cm⁻¹): 2923 (br), 2850 (br), 1599 (s), 1448 (m), 1108 (br m), 1067 (m), 949 (br), 847 (s), 823 (s), 750 (m), 700 (s), 622 (br m), 518 (br), 403 (br).

¹H NMR (400 MHz, C₆D₆, 22 °C): δ 8.86 (m, 6H, pyr), 7.0 (m, 3H, pyr), 6.8 (m, 6H, pyr), 2.12-1.27 (br m, 160H, CH₂ in c-C₆H₁₁), 1.04 (16H, CH in c-C₆H₁₁).

¹³C¹H NMR (125 MHz, C₆D₆, 22 °C): δ 150.45, 136.28, 123.76 (s for pyr), 28.77, 28.36, 28.12, 27.92, 27.62, 27.46 (s for CH₂), 25.96, 25.16, 24.04 (s for CH).

²⁹Si¹H NMR (99 MHz, C₆D₆, 22 °C): δ -60.68, -63.81 and -69.59 (s 2:4:2).

Crystal data for C_{111}H_{193}Ce_{3}O_{28}Si_{16}, M_r = 1304.63, monoclinic, space group C2/c, a = 20.474(5), b = 21.244(5), c = 32.843(10) Å, β = 102.95 (3)°, U = 13922(6) Å³, Z = 4, ρ calculated = 1.245 g cm⁻³, F(000) = 5552, T = 153(2) K, μ(MoKα) = 0.529 mm⁻¹, 3.60 < 2θ < 22.54°; of 13986 reflections 9079 were independent (Rint = 0.0356); the final R indices [I > 2σ(I)] are R₁ = 0.0511, wR₂ = 0.1358, with R indices (all data) R₁ = 0.0596, wR₂ = 0.1471; goodness-of-fit on F² 1.094; largest diff peak /hole + 1.211/-0.447 eÅ⁻³.

Alternatively, complex 24 was prepared by heating anhydrous CeCl₃ (0.152 g, 0.615 mmol) for 24 h in THF under reflux and subsequent reaction with (c-C₆H₁₁)₈Si₈O₁₁(OH)₂ (1.35 g, 1.23 mmol) in THF (60 cm³) / pyridine (15 cm³) mixture. Crystallisation from concentrated pyridine solution yielded 0.87 g (55%) of 24.

6.4.8 Synthesis of [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₂}_2Ti(OEt)₂] (25)

Ti(OEt)₄ (0.034 g, 0.15 mmol) was added to aluminosilsesquioxane [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₁(OH)}₂] (18) (0.3 g, 0.15 mmol) in toluene (50 cm³). The mixture was stirred for 48 hours. The solvent was removed in vacuo. Yielding a pale green oil. The product was extracted with dried hexane. The concentrated hexane solution gave
25 (0.19g, 57%) as yellow powder. Anal. Calc. for C_{94}H_{180}O_{26}NSi_{14}AlTi: C, 51.12; H, 8.22; N, 0.63. Found C, 49.37; H, 7.82; N, 0.54.

IR (Nujol, cm⁻¹): 3425 (s), 1686 (m), 1590 (m), 1522 (m), 1270 (m), 1196 (m), 1108 (s), 1040 (s), 957 (m), 895 (s), 847 (s), 824 (m), 755 (m), 722 (m), 513 (m), 454 (s).

¹H NMR (400 MHz, C_{6}D_{6}, 22 °C): δ = 9.69 (d, 1H, HNEt₃), 3.80 (q, 4H, OEt), 2.42 (s, 6H, NCH₂), 2.14-1.00 (m, 160 H, c-C₆H₁₁ and OEt), 0.80 (t, 3H, N-CH₃).

¹³C NMR (125 MHz, C_{6}D_{6}, 22 °C): δ = 55.5 (s, OCH₂), 45.90 (s, NEt₃), 32.2 (s, OCH₃), 27.5-23.1 (s, CH₂, c-C₆H₁₁), 23.8-23.1 (s, CH, c-C₆H₁₁), 9.40 (s, NEt₃).

²⁹Si NMR (99 MHz, C_{6}D₆, 22 °C): δ = -63.19, -66.12, -69.15, -70.30 and -72.03 (s, 1:1:2:1:2).

6.4.9 Synthesis of [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₂}₂TiCl₂] (26)

TiCl₄ (0.038g, 0.2 mmol) was added to a solution of aluminosilsesquioxane [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₁(OH)₂}] (18) (0.41g, 0.2 mmol) and triethylamine (0.2g, 2 mmol) in toluene (50 cm³). The mixture was stirred for 48 hours and then filtered. The filtrate was concentrated in vacuo, giving the product 26 (0.23g, 53%).

Anal. Calc. for C₉₀H₁₇₀N₂₄Si₁₄Cl₂AlTi: C, 49.37; H, 7.83; N, 0.64. Found C, 48.79; H, 7.97; N, 0.50. IR (Nujol, cm⁻¹): 3390 (w), 1682 (m), 1590 (m), 1525 (m), 1274 (m), 1199 (m), 1110 (s), 1040 (s), 956 (m), 899 (s), 846 (s), 820 (m), 755 (m), 715 (m), 511 (m), 454 (s). ¹H NMR (400 MHz, C₆D₆, 22 °C): δ = 9.62 (s, 1H, HNEt₃), 2.48 (s, 6H, NEt₃), 2.24-0.91 (m, 154 H, c-C₆H₁₁), 0.83 (m, 9H, NEt₃). ¹³C NMR (125 MHz, C₆D₆, 22 °C): δ = 46.76 (HNEt₃), 28.18-27.65 (s, CH₂, c-C₆H₁₁), 24.10-25.5 (s, CH, c-C₆H₁₁), 10.48 (HNEt₃). ²⁹Si NMR (99 MHz, C₆D₆, 22 °C): δ = -62.01, -63.42, -65.40, -68.22, -69.08 (s, 1:1:2:1:2).

6.4.10 An alternative synthesis of [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₂}₂TiCl₂] (26)

Cp₂TiCl₂ (0.3g, 1.2 mmol) was added to a solution of aluminosilsesquioxane (18) (2.5g, 1.2 mmol) in toluene (50 cm³). The mixture was stirred for 48 hours. Then it was concentrated in vacuo, giving the product 26 (1.18g, 45%). Anal. Data C₉₀H₁₇₀NO₂₅Si₁₄Cl₂AlTi (26): C, 49.37; H, 7.83; N, 0.64. Found C, 51.95; H, 8.14;
N, 0.70. IR of 26: (Nujol, cm⁻¹): 3020 (w), 2922 (vs), 2850 (vs), 1682 (m), 1595 (m), 1525 (m), 1346 (vw), 1262 (m), 1196 (m), 1110 (s), 1040 (s), 944 (m), 895 (s), 846 (s), 812 (m), 755 (m), 715 (m), 643 (w), 617 (vw), 511 (m), 499 (m), 454 (s).

NMR of 26: ¹H NMR (400 MHz, CeD₆, 22 °C): δ = 7.60 (m, 1H, HNEt₃), 2.67 (6H, NEt₃), 1.72 -1.03 (m, 154H, Cy), 0.96 (m, 9H, NEt₃). ¹³C NMR (125 MHz, CeD₆, 22 °C): δ = 45.5 (HNEt₃), 28.5 -27 (CH₂, Cy), 26.2 -24 (CH, Cy), 10.04 (HNEt₃). ²⁹Si NMR (99 MHz, C₆D₆, 22 °C): δ = -59.41, 60.54, 63.15, 66.03, -69.05 (s, 1:1:2:1:2).

6.4.11 Synthesis of [HNEt₃][Al{(c-C₆H₁₁)₇Si₇O₁₂}₂ZrCl₂] (27)

Cp₂ZrCl₂ (0.3g, 1 mmol) was added to a solution of aluminiosilsesquioxane (18) (2.1g, 1 mmol) in toluene (50 cm³). The mixture was stirred for 48 hours. Then it was concentrated in vacuo giving the product 27 (0.94g, 42%). Anal. Calc. for C₉₀H₁₇₀O₂₄Si₄AlZr: C, 48.41; H, 7.68; N, 0.63. Found C, 47.61; H, 7.77, N, 0.33. IR (Nujol, cm⁻¹): 3452 m, 1682 m, 1590 m, 1525 m, 1274 m, 1199 m, 1110 s, 1040 s, 956 m, 899 s, 846 s, 820 m, 755 m, 715 m, 511 m, 454 s. ¹H NMR (400 MHz, C₆D₆, 22 °C): δ = 9.58 (s, 1H, HNEt₃), 2.63 (s, 6H, N-CH₃), 2.19 - 1.09 (m, 154 H, c-C₆H₁₁), 0.87 (m, 9H, N-CH₃). ¹³C NMR (125 MHz, C₆D₆, 22 °C): δ = 45.95 (HNEt₃), 28.18 - 27.65 (s, CH₂, c-C₆H₁₁), 24.1 - 25.5 (s, CH, c-C₆H₁₁), 9.45 (HNEt₃). ²⁹Si NMR (99 MHz, C₆D₆, 22 °C): δ = -63.54, -65.71, -67.39, -68.38, -69.56, (s, 1:1:2:1:2).

6.4.12 Synthesis of [Al{(c-C₆H₁₁)₇Si₇O₁₂}₂Nd{(Me₃Si)₂CHC₅H₄}] (THF)₂][HNEt₃] (28)

NdCp₃ (0.6g, 1 mmol) was added to a solution of the aluminiosilsesquioxane (18) (2.07g, 1 mmol) in THF (70 cm³). The mixture was stirred for 48 hours. The green solution was concentrated in vacuo producing 28 (1.34g, 55%). Anal.Calc. for C₃₁₀H₂₀₉NO₂₆Si₁₆AlNd: C, 51.16; H, 8.16; N, 0.54. Found C, 51.22; H, 8.2; N, 0.62. IR (Nujol, cm⁻¹): 3435 w, 2990 vs, 2849 vs, 1624 v, 1448 s, 1346, v, 1262 s, 1196 s, 1108 vs, 1090 s, 945 m, 896 s, 845 s, 804 s, 755 m, 965 w, 640 w, 516 s, 499 m, 455 s, 415 m. ¹H NMR (400 MHz, C₆D₆, 22 °C): δ = 6.47 (s, 2H, Cp), 6.28 (s, 2H,
Cp), 5.95 (s, 1H, Cp), 5.69 (s, 1H, H-NEt), 3.24 (br s, 8H, THF), 1.81- 1.09 (m, 162H, c-C₆H₁₁ and THF), -6.70 (s, 18H, SiMe₃). ¹³C NMR (125 MHz, C₆D₆, 22 °C): δ = 149.4 (Cp-CH), 137.95 (Cp-CH), 133.89 (Cp-CH), 125.85 (CHSiMe₃), 66.10 (THF), 48.16 (SiMe₃), 41.8 (HNEt₃-CH₂), 26.19 (THF), 25.96 - 25.41 (Cy-CH₂), 22.03 - 21.23 (Cy-CH), 15.78 (HNEt₃-CH₃). ²⁹Si NMR (99 MHz, C₆D₆, 22 °C): δ = -21.15 (s, 2, SiMe₃), -65.71, -67.39, -68.60, -69.80 and -71.49 (m, 14, c-C₆H₁₁-Si, 2:1:1:1:2).

6.4.13 Synthesis of [(Al{(c-C₆H₁₁)₇Si₇O₁₁(OH)}₂)_2Nd(THF)₂][HNEt₃] (29)
NdCp'₃ (0.3g, 0.5 mmol) was added to a solution of the aluminosilsesquioxane (18) (2.07g, 1 mmol) in THF (60 cm³). The mixture was stirred for 48 hours. The solvent was removed in vacuo. The residue was washed with hexane and subsequently dried in vacuo giving the red-brown product 29 (1.37g, 62%). Anal. Calc. for C₁₈₂H₃₄₄O₅₀NSi₂₈Al₂Nd: C, 50.47; H, 8.0; N, 0.32. Found C, 49.24; H, 7.51; N, 0.1. IR (Nujol, cm⁻¹): 3550 s, 3345 s, 2922m, 1685 m, 1495 s, 1390 s, 1285 m, 1205 m, 1110 s, 1090 s, 1020 m, 905 m, 855 m, 720 m, 550 s, 485 m, 450 m. ¹H NMR (400 MHz, C₆D₆, 22 °C): δ = 9.88 (s, 1H, HNEt₃), 7.69 (s, 2H, OH), 2.62 (4H, N-CH₂), 2.27 (s, 8H, THF), 2.05 - 0.90 (m, 308H, Cy), 0.8 (m, 9H, N-CH₃), 0.56 (s, 8H, THF). ¹³C NMR (125 MHz, C₆D₆, 22 °C): δ = 69.51 (s, THF), 46.27 (s, HNEt₃), 28.27 - 25.70 (s, Cy), 25.55 (s, THF), 24.07 - 22.21 (s, Cy), 8.95 (s, HNEt₃). ²⁹Si NMR (99 MHz, C₆D₆, 22 °C): δ = -62.80, -64.52, -64.78, -68.63, -72.69 (1:2:2:1:1).

6.5 Experimental for Chapter 5

6.5.1 Epoxidation reactions
In a typical reaction equimolar amounts of alkene (1.6mmol) and tert-butyl hydroperoxide (TBHP) (1.6mmol) were syringed into the hexane solution containing the catalyst (ca. 1 mol % of metal with respect to the substrates) at 50°C. The mixture was left to stir for 24 hours. Attempts to filter the catalyst off during epoxidation, and
thus to stop the reaction, was met with no complications. Under the reaction conditions, the complexes were stable and did not leach titanium. At the end of the reaction time 0.5mls of the reaction medium was syringed into an NMR tube and 0.25mls of CDCl₃ was added as standard and the conversion was monitored by ¹H NMR studies.
NMR of epoxide of Oct-1-ene: 0.96 (3H), 1.33 (2H), 1.29 (6H), 1.42 (2H), 2.51 (2H) and 2.53 (1H).

6.5.2 Alkene polymerisation reaction conditions
In a typical polymerisation, 200 mg of the chosen catalyst and Et₂AlCl (5 equiv.) were charged into a reactor vessel (Schlenk attached to vacuum manifold with gas line attached to an ethylene cylinder). All polymerisation reactions were performed in toluene. The reaction vessel with the catalyst in toluene was connected to the ethylene gas line. The mixture was intensively stirred under 1.5 bar of ethylene gas pressure over a period of 2 h. At the end of the experiment, oily drops were observed adhering to the walls of the vessel. Further uptake of more ethylene drops were observed adhering to the walls of the vessel. Further uptake of more ethylene seemed to cease upon gelation of the polymerisation medium. After the reaction the mixture was hydrolysed by HCl in ethanol. The organic layer was separated and the solvent was removed in vacuum. The molecular weight of the oligomers were determined by GPC. The GPC was performed with a Waters 600 E differential spectrometer provided with 7.810 mm styragel columns HT3 (500- 3000 Å), HT5 (50000 – 4106 Å) and HT6E (5000 – 1107 Å). The polymer solution was injected into 60°C trichlorobenzene stream (flow rate 1ml/min).

6.5.3 Diels-Alder reaction conditions
Liquid phase catalytic reactions were carried out in a glass reactor (Schlenk) at 20°C. In a typical reaction, 2.0 mmol of the diene and 2.0 mmol of the dieneophile were reacted over the catalyst (1 mol % metal with respect to the substrates) in the presence of CDCl₃ as a solvent. The conversion was monitored by ¹H NMR studies. Non-catalysed reactions were found to form 3, 4-dihydropyranes.
NMR of 1,3 substituted cyclohexene isomer: 1.70 (3H), 1.89 (2H), 1.94 (2H), 2.09 (3H), 2.25 (2H), 2.60 (1H) and 5.40 (1H).
NMR of 1,4 substituted cyclohexene isomer: 1.71 (3H), 1.89 (2H), 1.96 (2H), 2.09 (3H), 2.20 (2H), 2.50 (1H) and 5.37 (1H).
NMR of hydropyrane: 1.90 (4H), 4.00 (2H), 4.60 (1H), 6.40 (1H).

6.6 References

Chapter 7 Conclusions and Future Outlook
7.1 Conclusions

The primary objective of this project was the development of novel alumino- and rare earth-siloxanes and silsesquioxanes (rings and cages), which could serve as molecular models for natural silicates, zeolites and/or silica-supported catalysts.

Amine-assisted metathesis was chosen and successfully used as the major method for the preparation of these metallasiloxanes. Investigation into the interaction of amines and silanols have shown that the first step in the amine-assisted metathesis (and also in the silanol condensation) involves hydrogen-bonding of the amine to a hydroxyl group, the deprotonation of the silanol and the subsequent formation of the correspondent salt. This salt then can participate in successive reactions, e.g. with metal halides through a simple exchange of the ammonium (e.g. pyridinium) cation and the metal cation. The isolation of the amine-silanol intermediates 2 and 3, provides an enhanced understanding of the mechanistic pathway followed in these interactions. Another interaction between the Lewis acid, FeCl₃, and diphenylsilanediol in the presence of pyridine resulted in the full condensation of Ph₂Si(OH)₂ to a cyclic trisiloxane, and the formation of bispyridinium (μ-oxo)bis[trichloroferrate(III)]-pyridine, [Hpy]₂[Fe₂Cl₆O]py (4). These results obtained here are very important and lead to an enhanced awareness about the interactions in the metal halide–amine–silanol systems. The outputs of this research might be useful for the further development of new synthetic approaches in silanol chemistry.

The synthesis of aluminosiloxanes and aluminosilsesquioxanes by interactions between AlCl₃, Et₂AlCl and AlEt₃ with disilanols (e.g. diphenylsilanediol) and trisilanols (e.g. (c-C₆H₁₁)₇Si₇O₉(OH)₃ (1)) in the presence of amines (e.g., pyridine or triethylamine) were also investigated, leading to some interesting cyclic and anionic aluminosiloxane species e.g., 5, 6, 7, 9 and 18. Structural chemistry greatly benefits from this array of ring and cage structures found in the various metallasiloxane derivatives produced here. Alternative routes for the preparation of aluminosiloxanes
from fully-condensed siloxanes have been developed. A reaction between AlCl₃ and
(Ph₂SiO)₄ in THF led to the cleavage of the tetrasiloxane ring by the Lewis acid and
resulted in the formation of the spirocyclic aluminosiloxane [Al₃{O(Ph₂SiO)₂}₂Cl₅]
(9). It has been demonstrated that in this system the remaining siloxane units combine
to form the stable smaller trisiloxane ring (Ph₂SiO)₃, which was the most favourable
product of this reaction. A similar cleavage of the fully-condensed POSS Ph₈Si₈O₁₂ by
the Lewis acid AlCl₃, has been reported for the first time in this thesis. It has been
shown that the Lewis acid can cleave the T₈ framework in THF under reflux yielding
new aluminosilsesquioxanes. This is the first illustration of a Lewis acid-mediated
cleavage of fully-condensed silsesquioxanes and initiates a novel effective approach to
the synthesis of metallasilsesquioxanes starting from fully-condensed silsesquioxanes.
Overall, anionic aluminosiloxane precursors developed in this work seem to be good
molecular models for natural aluminosilicates (zeolites).

Lanthanide metallasiloxanes have also been prepared here by two different methods:
(i) amine-assisted metathesis of lanthanide(III) halides (for example CeI₃, CeCl₃ and
LaCl₃) with silanediols, and (ii) by direct reactions using different metallorganic
lanthanide precursors, (for example NdCp”₃, NdCp”₃, LaN”₃, Cp”₂CeCl and
{La(N”₂)₂(OTf)}₂) with silanols. It has been shown that these reactions may result in
erather dimeric (two metal centres) or monomeric (one metal centre) complexes. In all
these compounds the lanthanide atoms saturate their coordination sphere either via
dimerisation or by coordination of extra solvent molecules resulting in high
coordination numbers. Some of the lanthanide metallasiloxanes formed have been
found to incorporate chain expanded siloxane units. For example in the use of Nd
siloxanes, the silanediol was promoted to the α-ω-siloxane diloate i.e., -
OSiPh₂OPh₂SiO- unit, whereas for the lanthanum and cerium complexes the
resulting chain expanded siloxanes contained the -OSiPh₂(OSiPh₂)Ph₂SiO- units.

Several reactions involving cerium(III) compounds unexpectedly produced Ce(IV)
metallasiloxanes as major products. The oxidation of Ce(III) into Ce(IV) always
occurred when two equivalents of a silanol ligand were used against one equivalent of the cerium(III) precursor. It is obvious that the second silanol molecule must play a crucial role in the oxidation of the metal centre. The reactions with silsesquioxanes were particularly interesting, for example the auxiliary interaction of the Ce(III) silsesquioxane 21 with another equivalent of the trisilanol 1 resulted in novel Ce(IV) silsesquioxane 23. Similarly the reaction between the diol (c-C₆H₅)₈Si₈O₁₁(OH)₂ and CeN₃ or CeCl₃ yielded exclusively the novel Ce(IV) metallasilsesquioxane 24. In these systems the reaction pathway most likely includes initial formation of an anionic Ce(III) complex similar to the anionic aluminosilsesquioxane 18. The steric and electronic properties of the silsesquioxane silanolate ligands render metal centers more Lewis acidic than conventional alkoxide or siloxide ligands do. It is believed that the Ce(III) intermediate is most likely oxidised by traces of oxygen in the system (e.g. from solvent) or by hydroxyl groups on the silsesquioxane ligand to give a Ce(IV) complex as the final product. These novel reaction pathways described here in the thesis may provide access to completely new types of metallasilsesquioxane complexes through oxidation reactions.

The aluminiumsilsesquioxane 18 containing two hydroxyl functionalities is an excellent precursor for the preparation of different metallasilsesquioxane derivatives including novel heterometallic complexes. The addition of group 4 metals to the silsesquioxane framework to produce bimetallic systems were very promising for both metallasilsesquioxane chemistry and in its potential catalytic applications. Reactions using this metallasilsesquioxane precursor 18, along with Ti(OEt)₄, TiCl₄, Cp₂TiCl₂, Cp₂ZrCl₂, NdCp"₃ and NdCp"₃ to produce bimetallic systems were carried out, leading to some very interesting novel bimetallic metallasilsequioxanes 25, 26, 27, 28 and 29.

Catalytic studies were carried out on the most promising metallasiloxane complexes prepared in this work. The typical catalytic reactions preformed were the epoxidation of 1-octene, the Diels-Alder reaction of buten-3-one and the polymerisation of...
ethylene. It was found that most of the metallasiloxane derivatives prepared in this work do not demonstrate a significant catalytic activity, presumably due to the ionic nature of the compounds and sterical hindrance about the metal centers rendering them unavailable for substrate coordination. However, in the epoxidation of 1-octene, the bimetallic silsesquioxanes 25 and 26 were found to be quite active, with high yields of the epoxide being formed. However in the Diels-Alder reaction of buten-3-one, the metallasilsesquioxane complexes investigated were not significantly active above that of the thermal reaction. In the polymerisation reactions of ethylene, oligomers were obtained for a number of the complexes, however no exciting polymeric material was produced. The main reasons for these low catalytic activities are associated to the sterical hindrance around the metal centers rendering them unavailable for substrate coordination.

7.2 Future Outlook

Recently there has been a proliferation of cube-based cages in which a variety of main group elements occupy corner sites and oxygen atoms bridge the main group atoms. Many cubic sections of the cages have the general formula X₄Y₄O₁₂ and adopt the double four-ring (D₄R)(4-4) structure. The positioning of the X and Y atoms at alternate corners is noteworthy and has been observed with various combinations of group 13, 14 and 15 elements including those with X = Si and Y = Al.¹ Spalding et al.² have published work on molecular borosilicates. The new cube-based compounds with both 3 and 4 co-ordinate corner sites synthesised, were from reagents containing only single silicon and boron, whereas all the silsesquioxane-based compounds synthesised before this were from silsesquioxane fragments and single boron-containing reagents. Therefore synthesis of new silsesquioxane based compounds from reagents containing only single silicon and aluminium rather than from silsesquioxane fragments, using triethylaluminium, cyclohexyltrichlorosilane and water in refluxing toluene using different bases e.g. aniline and triethylamine for the amine-assisted metathesis of the reactants could lead to very interesting and
unusual products. There is hope that this will occur because the ring-opening polymerisations of cyclic siloxanes are known to proceed initially to their linear polymer with subsequent rearrangement to the more thermodynamically stable cyclics.

Host-guest reactions on 6 and similar cyclic metallasiloxanes could lead to some very interesting materials. As the elementary building blocks of zeolites are SiO$_4$ and AlO$_4$ tetraherda, and zeolites contain channels, channel intersections and/or cages, this aluminosiloxane 6 is an ideal model to explore. From the IUPAC classification$^3$, zeolites are microporous materials, with a pore diameter not greater than 2nm. However, the pore diameter of aluminosiloxane 6 (5.204 Å) falls into the range given for mesoporous materials, 2nm – 50nm. Zeolitic mesoporous materials exist for example the M41S family with the most prominent and most extensively investigated member being MCM-41. This family of materials is often referred to as ‘mesoporous zeolites’. MCM-41 resembles a zeolite with respect to its regular system of pores with their uniform width. There is however, one significant difference, namely the non-crystallinity of the silica-alumina pore walls in MCM-41. Zeolites with 6-membered-ring pores, or six TO$_4$ (T = atom other than just Si or Al) tetrahedra are generally too narrow (around 0.2nm) to admit the molecules involved in catalytic reactions, but can be tuned by post-synthesis modification, i.e., ‘pore size engineering’.

Reactions involving the use of the aluminosiloxane 6 with stronger Lewis bases such as, NEt$_3$, Py and TMEDA may be carried out. The anticipated result will be the replacement of the THF molecules with these new amines, as the Al-Al distance is large enough to accommodate these amines. The presence of good leaving Cl-groups on each of the two Al-atoms in 6 can be used for further modifications e.g, linkage of the rings into larger assemblies. The ligands can be easily replaced by other substituents (e.g. Cl $^-$ via Wurtz coupling using an alkali reagent. Thus the aluminosiloxane 6 is a promising starting material for the preparation of novel materials with controlled pore size.
Scheme 7.1 Schematic presentation of the route for the preparation of assemblies of cyclic metallasiloxanes.

Attention should also be turned back to the lanthanides, and attempts to obtain more novel complexes anticipated. Fully characterised lanthanide metallasiloxane complexes would be highly desirable and would help in the elucidation of other complexes. Investigation into the reaction between LnCp₃ with Ph₂Si(OH)₂ by amine-assisted metathesis, to produce lanthanide-containing metallasiloxane rings similar to those in the aluminosiloxane would be attractive.

The synthetic chemistry of 1 and especially the study of related metallasilsesquioxanes as molecular models for silica-supported metal catalysts must be further developed in the near future. Novel lithium, sodium or potassium silanolates derived from the trisilanol 1 would be of paramount interest as they could serve as useful starting materials for the preparation of other polyhedral metallasilsesquioxanes. In fact, it was first demonstrated by Feher et al. that deprotonation of the trisilanols R₃Si₃O₃(OH)₃ (R = cyclopentyl, cyclohexyl,
cycloheptyl) with one equivalent of sodium t-butoxide cleanly affords the corresponding mono-sodium derivatives, but these products were found to be stable only for short periods of time in solution and could not be isolated as crystalline materials.\(^4\)

Silica-based mesostructured and mesoporous materials have sparked much interest among researchers over the last decade by expanding their functionality with the incorporation of functional organic compounds, by the substitution or addition of other inorganic materials or by templating them into carbon based materials.\(^5\) Perhaps some focus could therefore be put on magnetic mesoporous materials. At the moment research on mesoporous iron-containing silicates is scarce and limited to the back filling the pores of the mesoporous materials with iron oxide particles.\(^6\) New approaches to metallasilsesquioxane developed in this project can be used to prepare mesoporous ironsiloxanes which can serve as precursors and as building blocks for novel magnetic mesoporous materials.

The complexes 18 and 23 containing reactive hydroxyl groups offer great potential for the synthesis of novel heterometallic metallasilsesquioxanes. It has been shown that the hydroxyl functionalities in these compounds are quite reactive and can be used to replace alkoxide-, cyclopentadienyl-, amido- or alkyl- ligands providing an easy access to bimetallic metallasilsesquioxanes.

New ionic metallasiloxanes developed in this project will be very promising precursors for other ionic species. It will be very interesting to investigate the ionic exchange reactions of these compounds.

The field of catalysis by silsesquioxane metal complexes would profit further from new synthetic methodologies for both existing and novel incompletely-condensed silsesquioxanes. Ongoing developments in the field of silsesquioxane-based network solids and hybrid inorganic-organic materials will further pave the way for applications in the field of (heterogeneous) catalysis.

In oxidation catalysis, silsesquioxanes have appeared as rigid, chemically inert ligands that display a rich co-ordination chemistry. Efficient catalysts for alkene
epoxidation with organic peroxide have resulted, and a new area is surfacing that uses silsesquioxanes for the construction of polyoxometalates. Silsesquioxane-supported polyoxometalates could be further developed to catalyse oxidation processes that use environmentally friendly oxidising agents such as $O_2$ and $H_2O_2$. The use of Lewis acidic (aluminosilsesquioxanes) silsesquioxane-based derivatives will undoubtedly be further explored; their use in promoting Diels-Alder reactions should be regarded as a first demonstration on their catalytic potential.

Finally one more potential future application of the metallasilsesquioxanes developed in this work is the use of them as single source precursors for the preparation of low-$k$ dielectric materials for integrated circuit fabrication. Integrated circuits designers are currently packing features closer together on tiny semiconductor chips in order to meet the relentless demand for faster more capable internet devices and networking equipment. Within these tight spaces, low-$k$ dielectric insulating materials become essential because they prevent electrical signals travelling into these tightly packed circuits and interfering with each other and limiting the performance of the chip. The perpetually shrinking design has led to increased interconnection delay caused by parasitic capacitance of interconnection wiring. One way to reduce the interconnection delay is to reduce the dielectric constant ($k$) of the dielectric layer between the device layer and the interconnection layer. Atomic-scale porosity of metallasilsesquioxanes with open cage- or ring-like structures makes them very promising precursors for the deposition of porous low-$k$ dielectric layers. This can be achieved by using two methods: pulsed injection metallorganic chemical vapour deposition (PI-MOCVD) techniques or by a spin-on coating of substrates with solutions of the precursors followed by the thermal treatment using new single-source metallasiloxane precursors. New dielectric materials developed from metallasilsequioxanes by their nature should be similar to zeolite materials. It is well known that zeolites in general have $k$ values generally below 2.7, have uniform pore distribution, bear good mechanical strength and adhesion, are relatively little affected by moisture and are thermally stable. All this makes metallasilsequioxanes very promising precursors for the preparation of new low-$k$ dielectrics.
7.3 References


Appendix
Journal Publications


(3) Aluminosiloxanes as Molecular Models for Aluminosilicates, R. Reilly, Organosilicon Chemistry Vol. V. (Accepted, April 2003).


Conference Presentations


(5) Oral Presentation: Metallasiloxanes, at 54th Irish Universities Chemistry Research Colloquium, May 2002, Queens University, Belfast, Ireland.
