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**Group 4 Metallocene and Half-sandwich Derivatives of Spherosilicate:
Preparation from $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and Their Olefin Polymerization Activity**

A Dissertation
Presented for the
Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Suree Saengkerdsub

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Dedication

To my family, especially my mother and my sister,
whose sacrificial love is beyond any description

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Abstract

Three metallocene and half-sandwich Group 4 complexes of cuboctameric spherosilicate ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$) were successfully prepared by the exchange reaction of Group 4 metal chlorides with the spherosilicate starting material, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$. These complexes were found to be catalytically active in olefin polymerization. Their preparative reactions clearly demonstrate a synthetically useful route towards many other derivatives of spherosilicate through the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ starting material. A new synthesis of the key precursor, octa(trimethyltin) cuboctameric spherosilicate $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, was developed. It was found that most of the waters of hydration of the initial hydrate ($[\text{NMe}_4][\text{Si}_8\text{O}_{20}] \cdot n \text{H}_2\text{O}$, $n = 60 - 70$) could be removed by heating to $90 - 100^\circ\text{C}$. This “dehydrated” material proved to be synthetically useful and could be exhaustively silylated and stannylated in good to fair yields. The structures of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ are reported.

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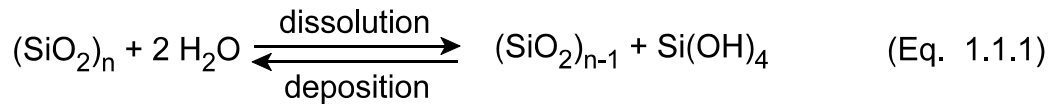
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Chapter 1

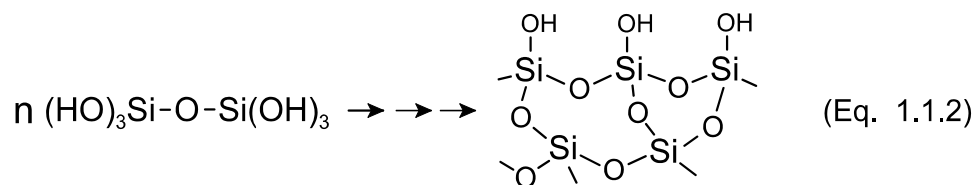
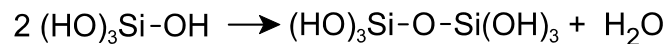
Introduction and Background

1.1 Silicate Chemistry

Silica, $(\text{SiO}_2)_n$, is not only the major component of the earth's crust, it also is a solid with unique solubility behavior in water. The dissolution of silica involves a chemical reaction, forming monosilicic acid, $\text{Si}(\text{OH})_4$. An equilibrium between dissolution and deposition of silica (catalyzed by OH^- ion) exists in an excess of water (Eq. 1.1.1).



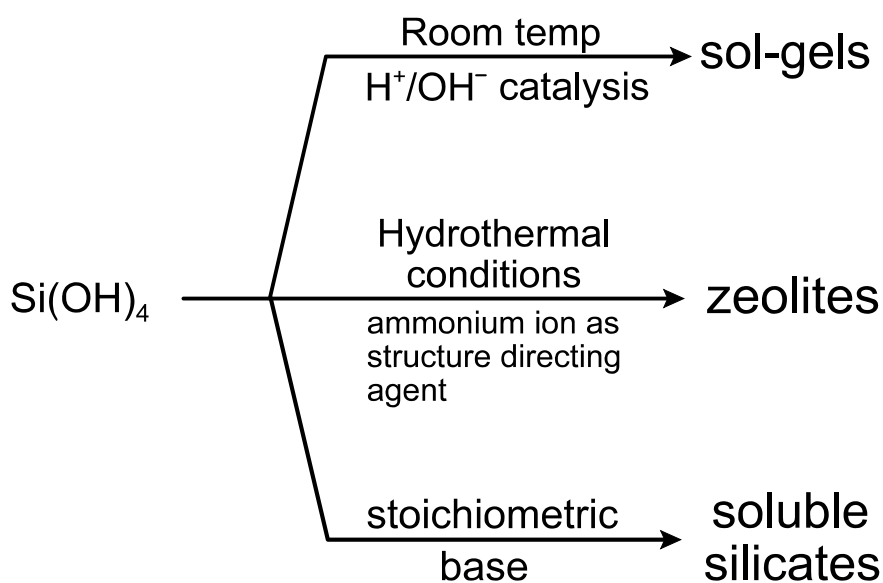
As long as the concentration of $\text{Si}(\text{OH})_4$ is lower than the equilibrium solubility of silica, the $\text{Si}(\text{OH})_4$ remains as monomer for a long time in water at 25 °C. (In neutral water, the equilibrium solubility of silica is estimated to be about 120 ppm for silica gel, 70 - 80 ppm for vitreous silica, and much less for quartz and other crystalline species.)¹ At higher concentrations, self-condensation of monomers, forming siloxane (Si-O-Si) linkages, occurs rapidly. This leads to the formation of polysilicic acids of low molecular weights (up to about 100 000), and consecutively larger polymeric species as colloidal particles (Eq. 1.1.2). This self-condensation is catalyzed by hydroxide ion (i.e., higher rate is expected at pH > 7 where silicic acids exist in their negative charged form, silicate ions).²



This richness in aqueous chemistry of monosilicic acid opens up the syntheses of many useful siliceous materials (**Scheme 1.1.1**) of which uses range from ceramics, adsorbents, catalysts, molecular sieves (zeolites), to inorganic catalyst supports.

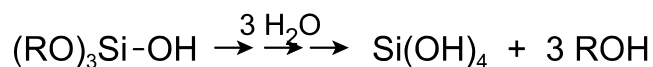
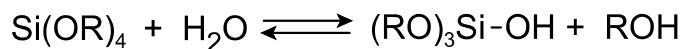
In sol-gel chemistry, other sources (than silica) leading to the formation of silicic acids are also used. Examples are reactive silicon compounds, such as chloro- and alkoxy silanes. With the use of catalytic amounts of acid or base at high Si concentration in solution, a series of hydrolysis reactions followed by condensation of silanols to form solids take place at room temperature (**Scheme 1.1.2**). Reactions of Si-Cl and Si-OR groups with water are very similar, leading to the formation of silanol groups, Si-OH, with hydrochloric acid or alcohol by-products, respectively, although Si-Cl groups are more reactive than Si-OR groups. The formed Si-OH groups are unstable and condense to form siloxane (Si-O-Si) linkages.

In zeolite syntheses, certain quarternary ammonium ions have long been used as structure directing agents (SDA) in the crystallization of Si-rich zeolites;³ later they

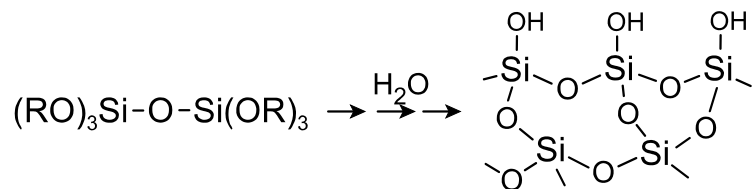


Scheme 1.1.1 Syntheses of many useful siliceous materials from monosilicic acid

Hydrolysis

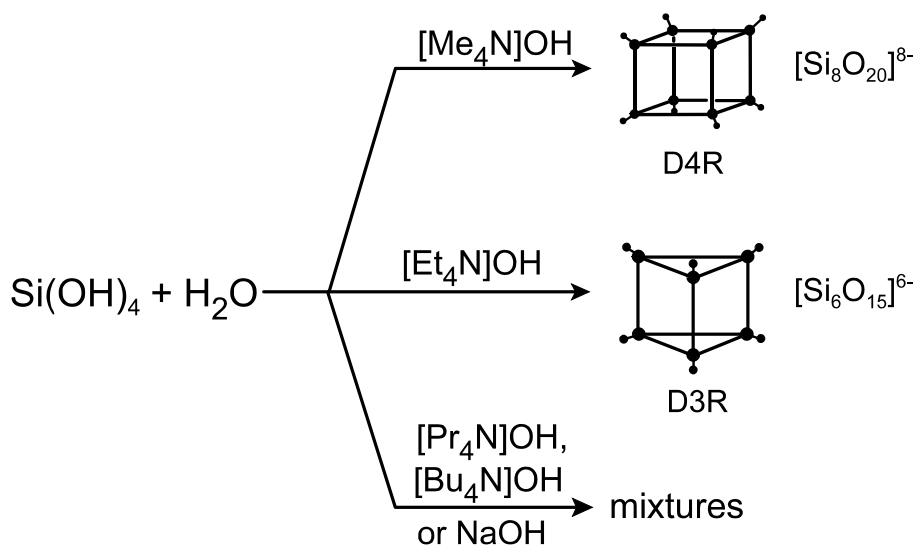


Condensation



Scheme 1.1.2 Hydrolysis and condensation of an alkoxy silane

were adopted to the synthesis of soluble silicates. Under hydrothermal (150 - 300 °C) conditions and in the presence of a structure directing agent, the crystalline metastable products (zeolites) are formed. In the presence of high concentrations of certain tetraalkylammonium ions and dilute silicate solutions, however, hydrolysis and condensation of alkoxy silanes can lead to the formation of only one dominant soluble silicate species⁴⁻²¹ (**Scheme 1.1.3**). In the presence of tetramethylammonium ion, NMe_4^+ , and tetraethylammonium ion, NEt_4^+ , the double-four-ring (D4R) and the double-three-ring (D3R) silicate oligomers are preferentially formed, respectively.^{4, 7, 13, 17, 18, 20, 21} In contrast to these cases, the effect of SDA favoring the formation of a single species is not observed when tetrapropylammonium ion (NPr_4^+), tetra(n-butyl)ammonium ion (NBu_4^+), or sodium ion is present as the counterion. In such cases, mixtures of silicate species are detected in the reaction solution.^{4, 7, 13, 17, 18, 20, 21}



Scheme 1.1.3 Role of certain tetraalkylammonium ions as structure directing agents

1.2 Spherosilicates

Spherosilicates — $[(\text{SiO}_{3/2})\text{O}]_n^{n-}$, $n = 6, 8, 10, 12, 14$ — are silicate species with double-ring structures, such as the cubic oligomer $[\text{Si}_8\text{O}_{20}]^{8-}$ D4R, and the trigonal prismatic hexamer $[\text{Si}_6\text{O}_{15}]^{6-}$ D3R (see **Scheme 1.1.3**). Of the many spherosilicates that have been observed, only a few may be conveniently prepared in large scale and obtained in pure form.

Another class of chemicals, with similar structure but quite different in their chemistry from spherosilicates, is polyhedral oligosilsesquioxanes (POSS). Polyhedral oligosilsesquioxanes are polyhedral clusters with an even number of silicon atoms (i.e., $(\text{RSiO}_{3/2})_n$ with $\text{R} = \text{H}$ or an organic group, $n = \text{even integer}$).²² Structurally, POSS differ from spherosilicates by having a nonpolar organic group bound directly to each skeletal silicon instead of a terminal oxygen. Furthermore, while spherosilicates are commonly prepared from tetrafunctional silicon monomers (e.g., $\text{Si}(\text{OEt})_4$), POSS are prepared from trifunctional silicon monomers (e.g., RSiCl_3 or $\text{RSi}(\text{OMe})_3$). The Si-R ($\text{R} = \text{H}$ or an

organic group) functionality in POSS is much less reactive and more soluble in organic solvents than the Si-O functionality in spherosilicates.

For our study, the D4R spherosilicate $[\text{Si}_8\text{O}_{20}]^{8-}$ (**Figure 1.2**) was selected for the following reasons: it can be conveniently synthesized in large quantities from starting materials available at low cost; it is relative simple to characterize (due to its high symmetry); and it is quite chemically robust.

1.3 Olefin Polymerization

Polyolefins—including low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polypropylene (PP)—form an important class of materials among thermoplastic resins. In 2000, the total production of polyolefins (22 million tons) accounted for 66% of thermoplastic resins produced in the US.²³ Applications of polyolefins benefit from their low cost and a wide range of product properties (e.g., flexibility, impact strength, optical clarity, processibility).

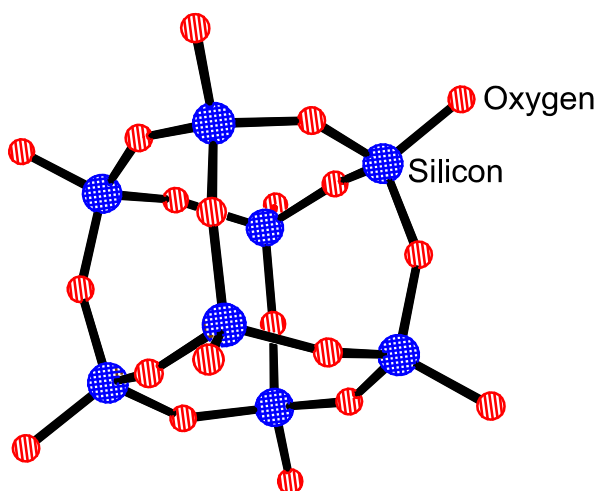


Figure 1.2 D4R spherosilicate $[\text{Si}_8\text{O}_{20}]^{8-}$

Their typical uses range from blown film for bags and packaging (LDPE, LLDPE), shrink-wrap (LLDPE), squeeze bottles (LDPE, HDPE), wire and cable coatings, carpet backing, pipe and conduit, adhesives and sealants, medical devices, to automotive and appliance parts (HDPE, PP).²⁴⁻²⁷

The industrial production of polyethylene (PE) began in 1933 using a free radical initiator (e.g., peroxide and oxygen). The free radical initiated polymerization requires high pressure (> 50 bar) and temperature ($250 - 300$ °C), and produces only low-density polyethylene (LDPE).²⁸ LDPE is polyethylene with both long chain and short chain branches. Its density is below 0.94 g cm^{-3} .²⁹ In the early 1950's, the first production of linear (i.e., non-branching) polyethylene was made possible by using transition metal catalysts. Through the use of Phillips-type catalyst (a molybdenum or chromium oxide chemically bound to silica or alumina support), linear polyethylene with no long chain branching (HDPE, density above 0.94 g cm^{-3})²⁹ was produced. With the introduction of a higher 1-olefin (normally a $C_4 - C_8$ 1-olefin, e.g., 1-butene, 1-hexene) as a comonomer, linear polyethylene with short chain branches (LLDPE) was produced. (The number of branches per molecule and the number of carbon atoms per branch depend on the amount and nature of the comonomer.) The drawback from using Phillips-type catalysts, however, lies in the broad distribution of individual polymer molecules in polymer chains. This contributes to broad molecular weight distribution (MWD) and determines the properties of the resin. In terms of polymerization processes, all polymerizations catalyzed by transition metal catalysts were achieved at much less requiring conditions (pressure < 50 bar and temperature $80 - 180$ °C for Phillips-type catalysts),²⁸ compared to a free-radical initiated polymerization. Different initiation and catalytic systems used in their production are compared in **Table 1.3**.

An improvement in catalytic activity and the ability to polymerize higher 1-olefins

Table 1.3 Comparison of free radical initiation and catalytic systems used in olefin polymerization

Mechanism	Initiator or catalyst	Process	Product	Current industrial use and ongoing improvement
free radical	peroxide and oxygen, by ICI Co. in 1933	high P, high T	LDPE - highly branched	use in LDPE production
coordination	molybdenum or chromium oxide on silica or alumina (heterogeneous catalysts), by AMOCO, Phillips Co. during 1951- 2 ^{30, 31}	low P, low T	HDPE, LLDPE - broad MWD (>10)	production of > 1/3 of PE's sold worldwide ³²
coordination	early transition metal complex and an aluminum alkyl cocatalyst (mainly heterogeneous catalysts; Ziegler-Natta, ZN, catalysts) during 1953 - 4 ³³	low P, room temp	PE's , <i>i</i> -PP - more than one MW ranges, broad MWD's - heterogeneous distribution of comonomers	the majority of PE's and PP productions ³⁴

Table 1.3 (continued)

Mechanism	Initiator or catalyst	Process	Product	Current industrial use and ongoing improvement
coordination	metallocene catalysts (MC) or related complexes of early transition metals (esp. Group 4) and a cocatalyst ^{35, 36} (Single-site catalysts, SSC)	low P, room temp	PE's, <i>i</i> -PP, and new polymers (<i>s</i> -PP, <i>s</i> -PS, cycloolefin polymers, styrene copolymers) - narrow MWD and homogeneous distribution of comonomers - incorporation of various comonomers - control of MW, stereoregularity, and comonomer content by varying ligands on MC	use in LLDPE, HDPE, PP, and copolymer productions <u>Improvements</u> - alkylaluminoxanes as cocatalysts, by Sinn and Kaminsky in 1980 ^{33, 37} - chiral bridged (<i>ansa</i> -) MC for stereocontrolled polymerization, by Hans H. Brintzinger - Late transition metal and non-Cp complexes for the polymerization of heteroatom-containing olefins, by Maurice Brookhart

(or α -olefins) with controlled stereoregularity were found with the use of Ziegler-Natta catalysts for which Karl Ziegler (Germany) and Giulio Natta (Italy) shared Nobel Prize in 1963. (Ziegler-Natta catalysts are usually mixtures of a high valent early transition metal halide or oxyhalide complex as a catalyst, and an alkylaluminum reagent as a cocatalyst. The most important and most thoroughly studied Ziegler-Natta catalysts are combinations of titanium trihalides (e.g., various forms of TiCl_3) or tetrahalides (e.g., TiCl_4) with trialkylaluminum compounds.) Further developments on Ziegler-Natta catalyst systems, through the addition of an appropriate Lewis base, an inorganic support (e.g., MgCl_2) and an electron donor, led to even higher catalytic activities ($> 50 \text{ kg PP/g Ti}\cdot\text{h}$) and high stereospecificity for isotactic polypropylene (*i*-PP, isotactic index $> 90\%$).^{38, 39} The removal of catalysts and the separation of stereo isomers were no longer needed. However, due to the presence of multiple active sites in Ziegler-Natta catalyst systems (multi-site catalysts, MSC), wide MWD and broad composition distributions of polymer products were observed.²⁹

Another breakthrough in olefin polymerization occurred when Kaminsky and Sinn discovered drastically enhanced catalytic activities (10,000 times) of metallocene-based catalysts (MC), by the addition of small amount of water to the trialkylaluminum cocatalyst.^{33, 37} It was already known that trialkylaluminums react with water to produce alkylaluminumoxanes,⁴⁰ leading to their use as cocatalysts in olefin polymerization. With metallocene-based catalysts, narrow MWD and homogeneous composition distributions were observed, as all the active sites behave in the same way during homopolymerization and copolymerization. Consequently, metallocene-based catalysts are called single-site catalysts (SSC).²⁹ Additionally, metallocene catalysts enable the catalyst design (e.g., by varying ligands on the metal) for tailored polyolefins. Various comonomers can be incorporated and several new polymers, i.e., syndiotactic

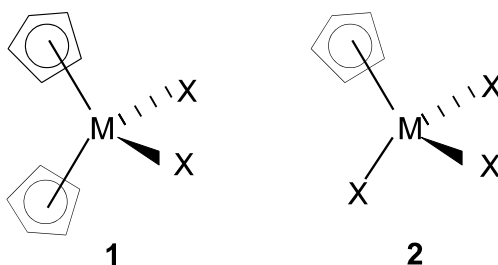
polypropylene (s-PP), syndiotactic polystyrene (s-PS), cycloolefin polymers, and styrene copolymer, can be obtained.²⁹

1.4 Olefin Polymerization Catalyzed by Metallocene-based Catalysts

Metallocene-based catalyst systems are composed of a catalyst precursor and a cocatalyst. In general, the catalyst precursor is a metallocene or a half-sandwich complex of a Group-4 metal (Ti, Zr, or Hf). The metallocene complex (**1**, Cp_2MX_2) consists of two aromatic five-membered ring systems, e.g., cyclopentadienyl (Cp) or substituted cyclopentadienyl ligands, and two other ligands (X) which are normally alkyl or chloride ligands, giving rise to the 16 valence electron count for the metal center. Half-sandwich complexes (**2**, CpMX_3), on the other hand, are composed of only one such aromatic five-membered ring and three other ligands. Having only one η^5 ring within the coordination sphere of the metal produces less sterically hindered 12-electron metal center. Cocatalysts used in olefin polymerization are normally main-group organometallic compounds, among which methylaluminoxane (MAO) is the most reactive.

1.4.1 Mechanism of Olefin Polymerization Catalyzed by MC-MAO Catalyst System

It is important to note that while the mechanism presented below explains both



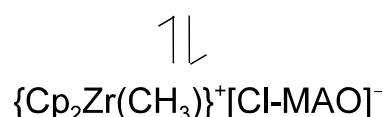
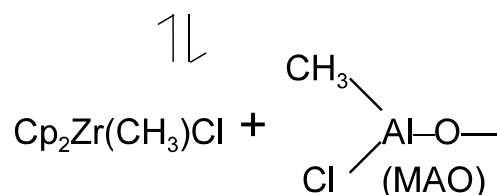
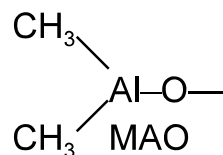
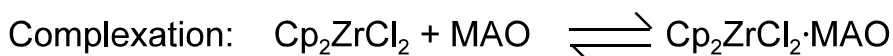
the polymerization of α -olefins and the polymerization of vinyl aromatic olefins (e.g., styrene), their active catalysts are thought to be different. The metal center of active catalysts in α -olefin polymerization is tetravalent, M(IV) where M = Ti, Zr, or Hf. On the other hand, the active catalyst in styrene polymerization is a trivalent metal, usually Ti(III), formed by the reduction of Ti(IV).^{41, 42} In the CpTiCl₃-MAO catalyst system, metal centers of active catalysts were proposed to be [CpTi^{IV}Me₂]⁺ for α -olefin polymerization, and [CpTi^{III}Me]⁺ for styrene polymerization, respectively.^{43, 44} The followings are mechanistic steps that apply to both α -olefin and styrene polymerization.

1.4.1.1 Initiation Step

Due to the lack of knowledge of exact composition and structure of MAO^{35, 45} and its use in large excess to activate metallocene catalyst precursors, the structure of their active species in olefin polymerization is still unknown. **Scheme 1.4.1.1** represents a simplified activation mechanism of zirconocene dichloride by MAO.^{46, 47}

When Cp₂ZrCl₂ is treated with MAO, either the free trimethyl aluminum (TMA) in MAO⁴⁸ or the MAO itself^{49, 50} rapidly alkylates Cp₂ZrCl₂ forming a monomethyl complex, Cp₂Zr(CH₃)Cl.^{48, 51} Kaminsky *et. al.* proposed that excess MAO leads to further alkylation, forming a dimethyl complex, Cp₂Zr(CH₃)₂.⁵¹ Based on several studies,^{49, 50, 52-54} it is generally assumed that some of the Al centers in MAO have an exceptionally high propensity to abstract Cl⁻ from Cp₂Zr(CH₃)Cl, to form {Cp₂Zr(CH₃)}⁺[Cl-MAO]⁻. Furthermore, some Al centers abstract CH₃⁻ of Cp₂Zr(CH₃)₂, forming {Cp₂Zr(CH₃)}⁺[CH₃-MAO]⁻. Nevertheless, in the overall activation mechanism, it is generally accepted that Cp₂ZrCl₂ is monoalkylated and that MAO abstracts Cl⁻ from the resulting Cp₂Zr(CH₃)Cl to form a catalytically active species.⁴⁸

As for the possibility of “free” TMA (contained in MAO) being the actual



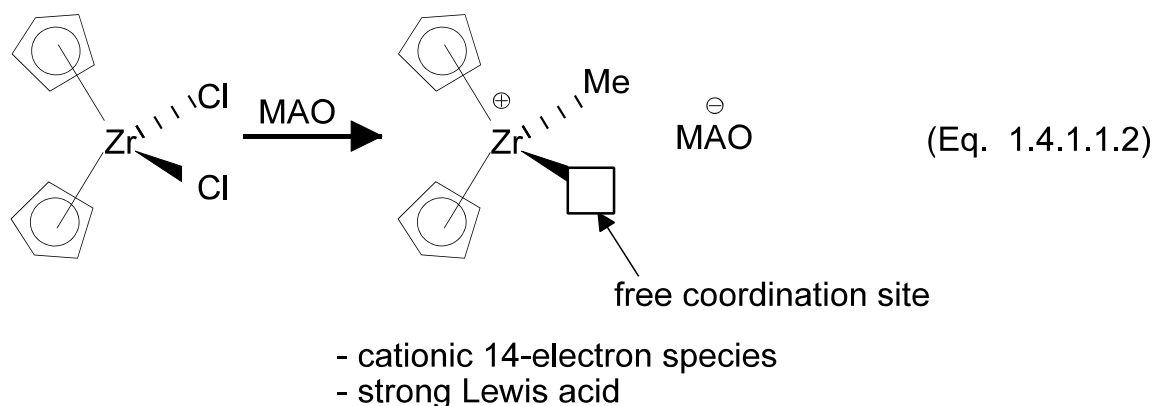
Scheme 1.4.1.1 Activation mechanism of Cp_2ZrCl_2 by MAO

cocatalyst in metallocene–MAO catalyst system, comparative NMR studies of $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{Cl} + \text{TMA}$ and $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{Cl} + \text{MAO}$ reactions done by Tritto *et. al.* show that MAO is a superior alkylating agent and has a greater capacity to produce and stabilize cation-like complexes.^{49, 50} Unlike MAO activation, the equilibrium involved with TMA lies far to the left in Eq. 1.4.1.1.1.⁵⁵ MAO is a significantly stronger Lewis acid, and the resulting counterion is far less coordinating than that of TMA. Therefore, “free” TMA is not the actual cocatalyst in metallocene–MAO catalyst systems.⁵⁶



It is worth mentioning that the alkide or chloride abstraction of metallocene catalyst precursors by MAO, not only leads to the formation of cationic species, but also

frees up a vacant site on the metal, thereby, generating an electron-deficient/coordinatively unsaturated cationic complex⁵⁷ (Eq. 1.4.1.1.2).⁵⁸ MAO not only protects the highly active cationic species by acting as a scavenger of Lewis base poisons, but its bulky anionic cage also weakly coordinates and stabilizes the cationic active center. The proposed model for the actual catalyst is, therefore, a contact ion pair $\{\text{Cp}_2\text{Zr}(\text{CH}_3)\}^+[\text{CH}_3\text{-MAO}]^-$.⁵⁹ This may be the reason that the lifetime of metallocene-MAO catalysts is much longer than metallocenes activated by other cocatalysts, especially perfluorolaryl boranes and conventional trityl borate salts. Without the knowledge on the exact structure of MAO, it is unclear on how many coordination sites are involved in each MAO cage and how many MAO cages coordinate to one metallocene cationic center. Nevertheless, under these circumstances, large excess of MAO is required, presumably, to provide sufficient “active” MAO cages.



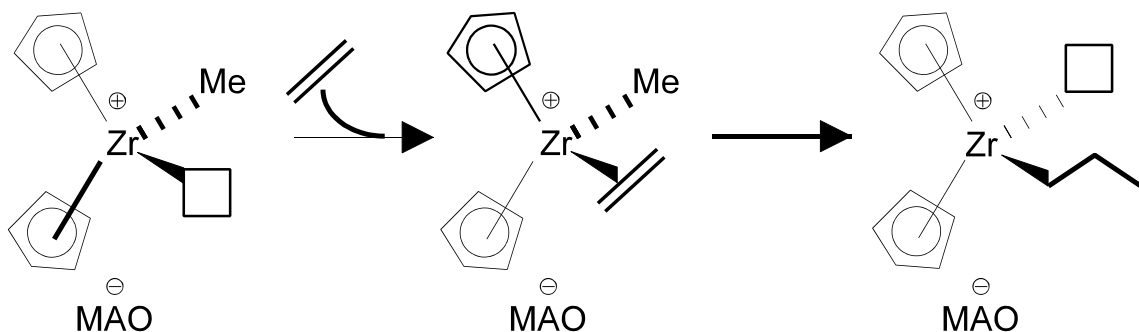
1.4.1.2 Propagation Step

The weak coordination of MAO anion to the cationic center (strong Lewis acid) allows the coordination of olefins (weak Lewis bases). A review by Alt and Köppl⁵⁸ demonstrates the use of bulky ligands at the transition metal in maintaining a certain

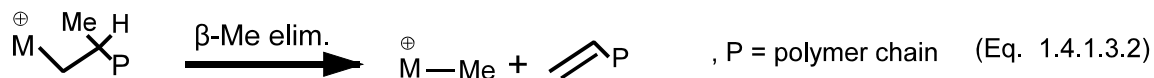
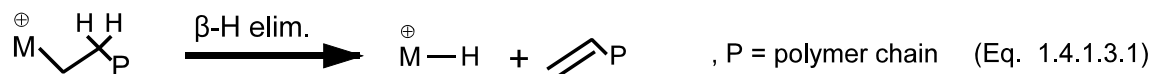
distance between transition metal cation and MAO anion and, thus, increasing the catalyst activities by factors of 5 or 6. After the coordination of an olefin which occupies the vacant coordination site of the transition metal, chain propagation^{60, 61} proceeds with ethylene insertion into the metal–carbon bond (or alkyl migration to the ethylene ligand), generating a new vacant coordination site at the former position of the alkyl ligand (**Scheme 1.4.1.2**).⁶² Stereo- and regio- control of vinyl olefin polymerization is thought to occur at this stage. In the case of prochiral olefins, the stereochemistry of polymerization is largely influenced by the symmetry of the transition metal catalyst; and as polymer chain grows further, the stereochemistry is also controlled by the presence (or absence) of bulky substituents on the ligand of transition metal,⁶³⁻⁶⁵ as well as the symmetry at the chain end of growing polymer.⁶⁶

1.4.1.3 Chain Termination and Chain Transfer

In metallocene-catalyzed olefin polymerization, termination of polymer chain can occur through β -hydrogen elimination (Eq. 1.4.1.3.1)⁶⁷ or β -methyl elimination (Eq. 1.4.1.3.2).^{68, 69} Both types of elimination generate an olefin-terminated polymer chain and



Scheme 1.4.1.2 Propagation step in the polymerization of ethylene



a metal hydride or a metal alkyl, both of which are still active catalytic centers. The olefin-terminated polymer chain can recoordinate to the transition metal catalyst and long-chain branching can occur. Depending on the nature of metallocene, alumoxane, and polymerization condition, polymer chain can also transfer to aluminum,^{69, 70} monomer,^{71, 72} or hydrogen,⁷² resulting in lower molecular weights of polyolefins. Resconi *et al.*⁷³ reported that in propylene polymerization catalyzed by Cp₂ZrCl₂-MAO (at 0 and 50 °C) and Cp₂HfCl₂-MAO (at 50 °C), all chain termination occurred through β -hydrogen elimination, with no chain transfer to aluminum at all.

1.4.2 Reaction Parameters

In the polymerization of olefins by metallocene-based catalysts, the components of the reaction are a catalyst precursor, a cocatalyst, an α -olefin monomer, and a solvent, in most cases. There are also other parameters that can affect the catalyst activity, as well as properties of polyolefins produced. This section lists the parameters that are related to the present study and how they affect catalyst activity, molecular weight and molecular weight distribution (MWD) of polyolefins.

1.4.2.1 Catalyst Precursor

Among metallocenes, the central metal plays the most important role affecting catalyst activity. Several studies on ethylene polymerization of Group-4 metallocene alkyl-methylaluminoxane (MAO) and Group-4 metallocene chloride-MAO catalyst

systems have clearly shown that highest catalytic activities are observed with zirconocenes (especially at temperatures over 50 °C), while hafnocenes have the lowest activities.^{70, 74-77} Titanocene catalysts are more reactive at low temperatures and decomposed at high temperatures (above 50 °C).⁷⁸ Decomposition of Ti(IV) catalysts may be due to reduction of the active Ti(IV) to the inactive Ti(III) (by trimethylaluminum present in the cocatalyst MAO) especially at high temperatures. The stability of Zr(IV) towards reduction makes its complexes exhibit exceptionally high activities.^{43, 44}

Due to the sterically less crowded and electronically less saturated nature of half-sandwich complexes, they were expected to have higher catalyst activities, with respect to metallocenes. However, the comparative experiment on a metallocene, Cp_2ZrCl_2 , and a half-sandwich complex, CpZrCl_3 , exhibited their almost identical activities at a high catalyst concentration (48 μM Zr).⁷⁰ At a low concentration (3.8 μM Zr), the activity of CpZrCl_3 was much less than that of Cp_2ZrCl_2 .

Compared between Group-4 metallocene halides and their alkyl analogs, several studies showed that halide complexes have higher catalytic activities than analogs without halide ligands.^{74, 75, 78} The aromatic five-membered ring systems allow the modification of catalyst activity and the molecular weight and polydispersity of polymer, by varying the aromatic ring (e.g., cyclopentadienyl, indenyl, or fluorenyl) or substituents on them. Alt *et. al.*⁵⁸ demonstrated the following order of activities for various aromatic rings: $(\text{Ind})_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > (\text{Flu})_2\text{ZrCl}_2$ where Ind = indenyl, Cp = cyclopentadienyl, Flu = fluorenyl. Countless other studies were conducted to investigate the interplay of electronic and steric effects of substituents on aromatic five-membered rings. It is generally accepted that electron donating substituents (e.g., alkyls) lead to increased catalyst activities. The steric effect of substituents is not always predictable. In most cases, the increase in steric bulk of substituents decreases catalyst activities and

increase the polymer molecular weight. This has been explained as resulting from the bulky group hindering the approach of the incoming monomer as well as hindering various chain transfer agents.^{35, 58, 70} Depending largely on the position of substituents relative to the active center, substituents can promote the separation of the active catalyst-cocatalyst ion pair, generating a very Lewis-acidic metal center and this leads to dramatic increase in catalyst activities.⁵⁸

As for the effect of catalyst concentration, Chien and Wang⁷⁰ reported that the activity of the Cp_2ZrCl_2 -MAO catalyst is inversely proportional to the Zr complex concentration. This was interpreted as due to the decrease in bimolecular deactivation at low Zr concentrations. The variation of activity with Hf complex concentration is less pronounced.

In styrene polymerization, it has been suggested that the active catalysts are trivalent (usually Ti^{3+} formed by the reduction of Ti^{4+}).^{41, 42} The order of catalytic activities in styrene polymerization is, therefore, often opposite the order observed in α -olefin polymerizations. Among tetravalent Group-4 metal complexes, titanium-containing complexes have been reported to have higher catalytic activities in styrene polymerization than their analogous zirconium-containing complexes,^{79, 80} due to the lower stability of Ti(IV) towards reduction. Titanium-containing complexes were also found to be highly syndiospecific, yielding only syndiotactic polystyrene, whereas catalysts containing other transition metals (i.e., Zr(IV), Hf(IV), V(IV), Co(III), Ni(II)) yielded mostly atactic polystyrene.⁸⁰ Among cyclopentadienyl-containing Ti(IV) complexes, monocyclopentadienyl complexes have been reported to be at least 70 times more reactive than their metallocene analogs under identical polymerization conditions.^{79, 80} Ishihara *et. al.* reported effects of alkoxide and chloride ligands on catalytic activities of Cp^*TiR_3 (R = alkoxide or chloride ligands); however, no specific

trend were observed.⁷⁹

1.4.2.2 Cocatalyst

The role of cocatalysts in olefin polymerization is multifaceted: they react with catalyst precursors to form active catalysts; an appropriate cocatalyst stabilizes the active catalyst for the desired kinetic/thermodynamic profile of reaction. Upon activation, the cocatalyst becomes anion that can form a complex with catalyst cation and the nature of the catalytically active cation-anion complex significantly influences the molecular weight and the stereoregularity of polyolefin produced.⁵⁶ The following discussion describes the various types of cocatalysts used in metallocene-catalyzed olefin polymerization.

1) Aluminum alkyls

Aluminum alkyls mentioned here include aluminum trialkyls (AlR_3 , e.g., $\text{R} = \text{Me}$, Et) and alkylaluminum chlorides (e.g., AlR_2Cl). Although aluminum alkyls are important cocatalysts in Ziegler-Natta coordination polymerization catalysis,⁸¹⁻⁸⁶ metallocene–aluminum alkyl catalysts are limited by their inability to activate the polymerization of propylene and higher α -olefins.⁵⁶ With Ti- or Zr-based metallocene–aluminum alkyl catalysts, low-to-medium activities with rapid catalyst deactivation were reported in ethylene polymerization, producing polyethylene with narrow molecular weight distributions.^{87, 88}

2) Alkylaluminumoxanes

Alkylaluminumoxanes are oligomeric compounds consisting of $-\text{Al}(\text{R})\text{O}-$ subunits, prepared by controlled and partial hydrolysis of alkyl aluminum compounds. The most commonly used aluminum alkyls are trimethylaluminum (AlMe_3), triethylaluminum (AlEt_3), and triisobutylaluminum ($\text{Al}(i\text{-Bu})_3$). Of the various aluminumoxanes available,

methylaluminoxane (MAO) is the most reactive cocatalyst in transition-metal catalyzed olefin polymerization.⁸⁹

Methylaluminoxane, $[-\text{Al}(\text{Me})-\text{O}-]_n$ (MAO), prepared by controlled hydrolysis of AlMe_3 and typically having $n \approx 5 - 20$, affords highly active catalysts for polymerizing ethylene, propylene, and higher α -olefins when combined with Group-4 metallocenes.⁹⁰ Despite its effectiveness as a cocatalyst, the exact composition and structure of MAO remain largely unknown.^{35, 45} Proposed structures for MAO include one-dimensional linear chains (**1**) or cyclic rings (**2**) which contain three-coordinate Al centers, two-dimensional structures (e.g., **3**), and three-dimensional clusters (e.g., **4**) which contain four-coordinate Al centers in six- and four-membered rings and three-coordinate peripheral Al atoms^{59, 91} (**Figure 1.4.2.2**).⁵⁶ Up to date, structure **4** is the most widely accepted model for active MAO species.

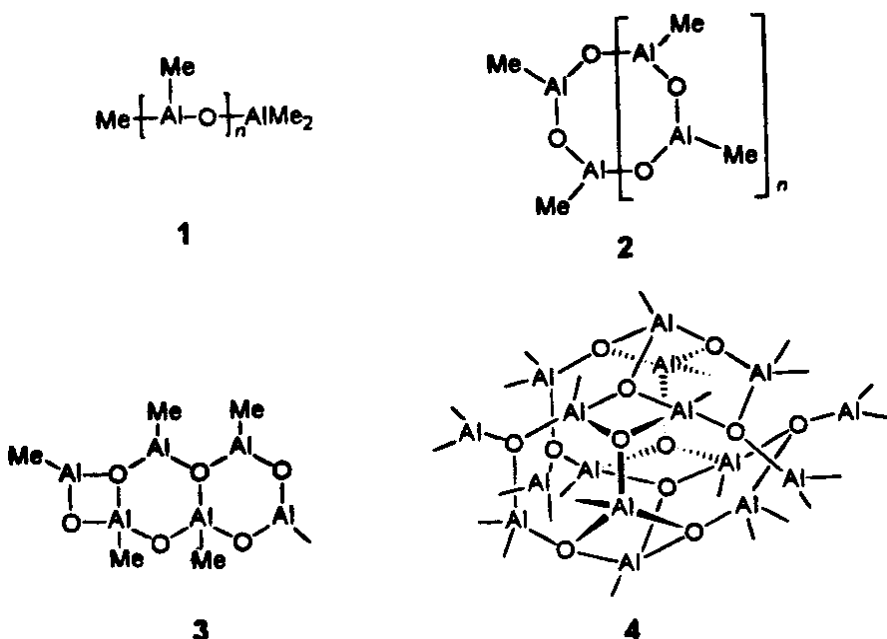


Figure 1.4.2.2 Proposed model structures of MAO

Growing evidence suggests that MAO functions as a Lewis acidic alkide abstractor^{53, 55} (similar to perfluoroarylboranes) as well as an alkylating agent. Through an analysis of their thermochemical data, Marks *et. al.* have indicated that the interaction of MAO with both conventional metallocenes and “constrained geometry” complexes is significantly less exothermic than for perfluoroarylboranes. That is, MAO is not as strong as a Lewis acid as $B(C_6F_5)_3$.⁵⁷ The use of conventional MAO is limited by its low solubility in aliphatic solvents as well as its poor stability in solution. Modified methylaluminoxanes (MMAO from Akzo-Nobel), prepared by controlled hydrolysis of a mixture of trimethylaluminum and triisobutylaluminum, exhibit improved solution storage stability as well as solubility in aliphatic solvents. It can also be produced at lower cost and still provides high polymerization efficiency.⁵⁶

A well-known problem in the preparation of MAO is the presence of residual trimethylaluminum in the MAO product or trialkylaluminum species in the MMAO product.^{35, 45, 92, 93} Several studies have shown that catalyst activity and polymer molecular weight decrease as the amount of free aluminum trialkyls increases.^{35, 75, 94-96} To solve this problem, a new process has been developed for preparing MAO substantially free of trimethylaluminum (“PMAO-IP” from Akzo-Nobel) using nonhydrolytic means.⁹⁷ The PMAO-IP is claimed to exhibit higher catalytic activity in ethylene polymerization of *rac*-ethylenebis(indenyl)zirconium dichloride, compared to conventional MAO's.⁵⁶

Despite the success of MAO in promoting high-activity metallocene-mediated olefin polymerization, it also exhibits several disadvantageous features. High MAO : catalyst precursor ratios (100 to 10 000 : 1) are generally required for obtaining acceptable polymerization activity, which raises issues of the high cost of the cocatalyst and the high ash content (Al_2O_3) of the product polymer. The intrinsically complicated

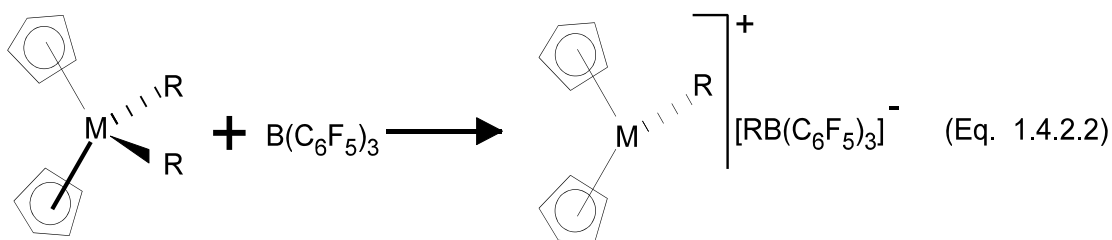
structural features of MAO as well as the large excess of MAO required in the activation process prevent full characterization of the catalytically active species. The overall activation process and the nature of the resulting active species are therefore not well understood.

Effects of the amount of MAO on catalyst activities were compared between a Group-4 metallocene, Cp_2ZrCl_2 , and its corresponding half-sandwich complex, CpZrCl_3 , in ethylene polymerization.⁷⁰ In the case of Cp_2ZrCl_2 -MAO catalyst system with Al/Zr ratios varying from 500 to 90 000, the reaction kinetic profile and catalyst activity are only slightly dependent on [MAO]. On the other hand, the activity of CpZrCl_3 -MAO system is more dependent on [MAO]; a five-fold increase of [MAO] (from Al/Zr of 1 000 to 5 000) doubles the catalyst activity.

In styrene polymerization, increasing the Al:Ti ratio (by increasing [MAO]) resulted in an increase in the yield of polystyrene but a decrease in its molecular weight, implying that MAO not only played a role in generating active species but also acted as a chain transfer agent.⁹⁸

3) Perfluoroaryl boranes

The strong Lewis acidity of tris(pentafluorophenyl)borane, $\text{B}(\text{C}_6\text{F}_5)_3$, allows its use in abstracting alkylidene anions from metallocene alkyls and therefore acts as an efficient activator for metallocene alkyl catalyst precursors in olefin polymerization



(Eq. 1.4.2.2).⁹⁹⁻¹⁰¹ The research groups of Marks and Piers have developed a number of perfluoroaryl boranes with very high Lewis acidity and sterically demanding structures, several of which exhibit significantly higher olefin polymerization efficiency than those based on $B(C_6F_5)_3$.⁵⁶ Although this class of cocatalysts can be used to activate metallocene alkyls in stoichiometric amounts with comparable catalytic activities to those activated with large excesses of MAO, their disadvantages are their high prices and the incorporation of fluorine into polymers, which can cause problems when polyolefins are thermally decomposed.⁵⁸

4) Trityl, ammonium borate, and aluminate salts

The trityl cation Ph_3C^+ is a powerful alkylidene and hydride-abstracting reagent, and ammonium cations of the formula, $HNRR'_2^+$ can readily cleave M–R bonds via facile protonolysis. In combination with noncoordinating/weakly coordinating anions, $M(C_6F_5)_4^-$ (M = B, Al), trityl and ammonium borate and aluminate activators have been developed into highly efficient activators for metallocene and related metal alkyls in olefin polymerization.⁵⁶ Major drawbacks in using $B(C_6F_5)_4^-$ as the anion in activating species are that they have low solubility in hydrocarbons, as well as low thermal stability, resulting in very short catalytic lifetimes.¹⁰² Chen and Marks have given a comprehensive review on the syntheses and use of new borate anions, in place of $B(C_6F_5)_4^-$, and their improved solubility, thermal stability, while maintaining high catalytic efficiency when used in combination with metallocene alkyls.⁵⁶

1.4.2.3 Monomer

Due to the same fundamental basis in the mechanism of Ziegler-Natta and metallocene catalyzed olefin polymerizations, relative reactivities of olefin monomers in polymerization with Ziegler-Natta catalysts are used as a guideline for their relative

reactivities with metallocene catalysts. Compared to the reactivity of propylene which is set as a standard (reactivity = 1), ethylene and styrene have their relative reactivities as 20 and ca. 0.1, respectively.¹⁰³ A point worth mentioning is that, although styrene is a very reactive monomer in radical and cationic polymerization reactions, it exhibits very modest reactivity with Ziegler-Natta (and metallocene) catalysts.

The effect of monomer concentration on ethylene polymerization was studied on Cp_2ZrCl_2 -MAO catalyst system.⁷⁰ Although rate of polymerization is proportional to monomer concentration, the overall catalyst activity, in the unit of kg PE/(mole monomer·mole Zr·h), is not affected by the monomer concentration. Furthermore, as expected, both the molecular weight and molecular weight distribution ($\text{MWD} = M_w/M_n$) of polyethylene increase with increasing monomer concentration.

1.4.2.4 Temperature

It is common among transition-metal catalyzed olefin polymerization for there to be an optimum temperature range for maximum activity, below or above which the activity of catalyst decreases. At the optimum temperature, the maximum catalyst activity was explained as a result of relatively high rates of propagation and relatively low rates of deactivation of the catalyst. Above the optimum temperature, rates of propagation as well as deactivation increase, and below the optimum temperature, rates of propagation as well as deactivation decrease, and as a net result, low activities of catalyst were observed.³⁵ Several studies reported high ethylene polymerization activities of zirconocene alkyl and chloride catalyst systems at temperatures above 50 °C, while Ti-based catalysts were reported to be more reactive at lower temperatures.^{35, 70, 74, 94}

With Zr-based catalysts, temperatures of polymerization have direct effects on polymer molecular weights which decrease monotonically with increasing

temperatures.^{70, 74, 94} This phenomenon was explained by high rates of chain transfer deactivation mechanisms at high temperatures, resulting in shorter polymer chains and thus lower molecular weights. On the contrary, Hf catalysts show a smaller dependence of polymer molecular weights on temperatures.³⁵

Activities of styrene polymerization catalyzed by CpTiCl_3 and Cp^*TiCl_3 were found to be generally dependent on time, temperature, and Al:Ti ratio; the systems having an optimal polymerization temperature of 50 °C, above and below which the activities decreased.⁹⁸

1.4.2.5 Time

Reaction time has no pronounced effect on polymer molecular weight and MWD unless the time spent is shorter than ten minutes and catalyst has a slow activation profile. An example of a slow activation catalyst system is CpZrCl_3 (in comparison to Cp_2ZrCl_2). Ethylene polymerization study on CpZrCl_3 showed a slight decrease of polyethylene molecular weights when the polymerization time was less than 10 minutes.⁷⁰ As for catalyst activities, the reported values of catalyst activities increase with shorter polymerization time.

1.4.3 Silica-supported Metallocene–MAO Catalysts and Their Homogeneous Catalyst Models

Immobilization of metallocene-based catalysts on solid supports, resulting in heterogeneous metallocenes, is normally done with the aim to combine the desired features of homogeneous with heterogeneous catalysts. The advantage of homogeneous metallocenes, including their single active sites and the ability to control polymer microstructure, is preserved in combination with the property of supported

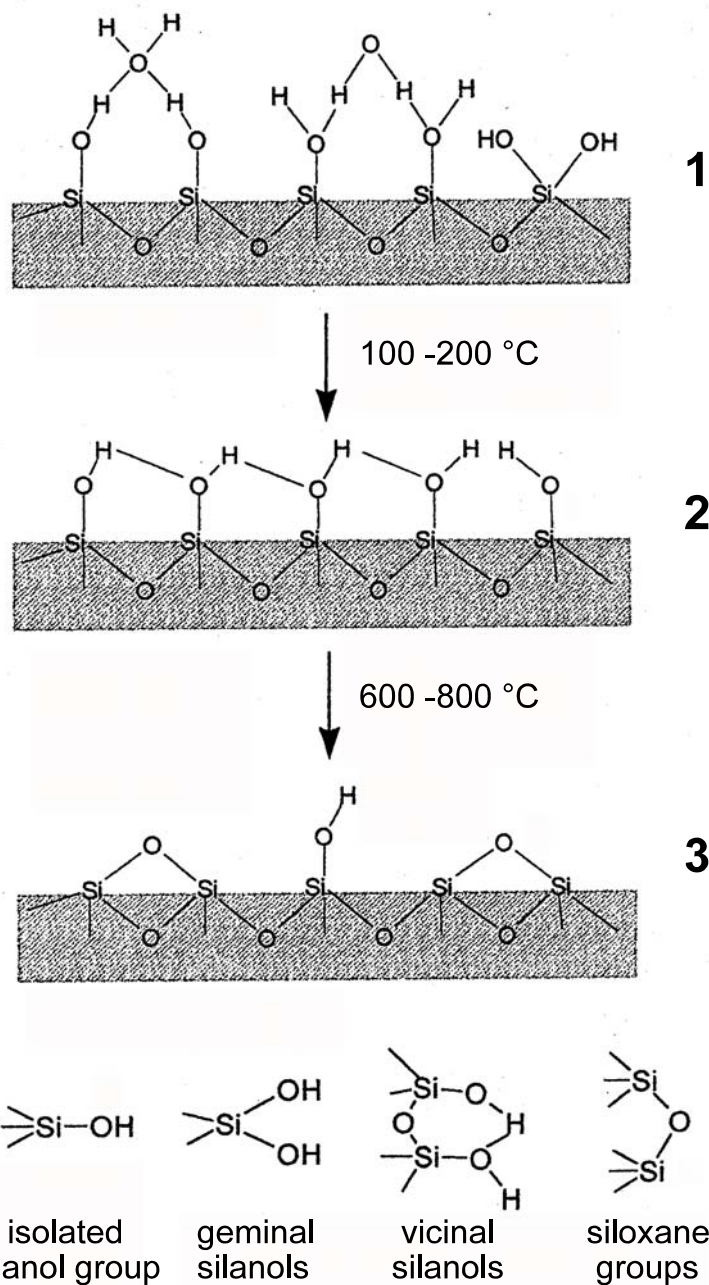
catalysts (good polymer morphology, little reactor fouling, high powder density).

Amorphous and porous silica gels (SiO_2) are the most commonly used supports for metallocene/MAO catalysts due to their high surface area and porosity. They are also mechanically robust and chemically stable under reaction and processing conditions.¹⁰⁴⁻¹⁰⁶ As a result of immobilization, the MAO/metallocene molar ratio can be decreased by approximately 2 orders of magnitude, compared to homogeneous systems.^{105, 107}

1.4.3.1 Chemical Properties of Silica Surface and Silica-supported Metallocene-MAO Catalysts

The surface of pure silica gel is covered with silanol (Si-OH) groups. They are mostly found as geminal or isolated pairs (**1, Scheme 1.4.3.1.1**).¹⁰⁸ The hydroxylated surface is hydrophilic and easily adsorbs moisture from the air. By heating silica to the temperature of 100 - 200 °C, physically adsorbed water can be removed. At the same time, partial dehydroxylation occurs, decreasing the number of hydroxyl (OH) groups. The remaining OH groups are either hydrogen-bonded to vicinal silanols or nonhydrogen-bonded (isolated silanol) (**2, Scheme 1.4.3.1.1**).¹⁰⁸ As the temperature is raised further, the number of hydroxyl groups decreases continuously. At 600 - 800 °C, only isolated silanol groups remain and the surface is hydrophobic (**3, Scheme 1.4.3.1.1**).¹⁰⁸

Three methods of supporting a metallocene were suggested by Kaminsky:¹⁰⁹ (1) adsorption of MAO onto the support followed by the addition of metallocene; (2) immobilization of metallocene on the support followed by contact with MAO in the polymerization reactor; (3) immobilization of metallocene on the support followed by treatment with MAO, producing a catalyst that does not require additional MAO during



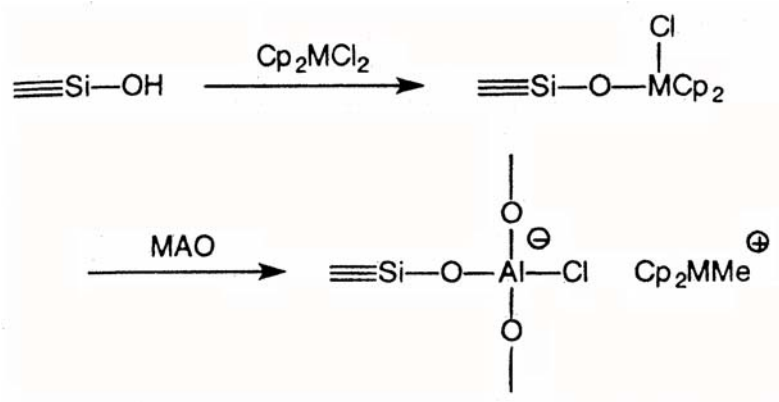
Scheme 1.4.3.1.1 Dehydration of a silica gel surface¹⁰⁸

polymerization. According to Kaminsky, method (1) excludes direct interaction of support and metallocene and therefore performs similarly to a homogeneous catalyst. Catalysts (2) and (3) behave similarly, but (3) requires a lower Al/Zr ratio and is more convenient

to use since no additional MAO is required during the polymerization.

Upon the adsorption of metallocenes Cp_2MCl_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) onto silica, the metallocene reacts with residual hydroxyl groups to form $\equiv\text{Si}-\text{O}-\text{M}(\text{Cl})\text{Cp}_2$ groups (**Scheme 1.4.3.1.2**).¹¹⁰ The study by Blitz and co-workers indicated that the majority of reactions between metallocenes and silica surfaces occurs through isolated silanol groups (even in the presence of vicinal silanols) and the order of reactivity with silica surfaces is $\text{Cp}_2\text{HfCl}_2 > \text{Cp}_2\text{ZrCl}_2 \gg \text{Cp}_2\text{TiCl}_2$.¹¹¹ In the presence of a cocatalyst, the metallocene catalyst on silica surface is activated. When MAO¹¹² or an aluminum alkyl¹¹³ is used as a cocatalyst, several studies have shown that the desorption of metallocenes (Cp_2MCl_2 , $\text{M} = \text{Ti}, \text{Zr}$) from silica surface may be involved in the formation of the active species ($\equiv\text{Si}-\text{O}-\text{Al}(\text{O}^-)_2\text{Cl}^- \text{Cp}_2\text{MMe}^+$) (**Scheme 1.4.3.1.2**). The desorption of significant amounts of half-sandwich complexes (CpMCl_3 , $\text{M} = \text{Ti}^{114}, \text{Zr}^{115}$) from silica surface in the presence of MAO catalysts was also reported.

The desorption of metallocene-based catalysts from silica supports raises questions on their applications as heterogeneous catalysts in olefin polymerization. In



Scheme 1.4.3.1.2 Adsorption and activation of metallocene on silica surface¹¹⁰

case of ethylene polymerization by metallocene catalysts on surfaces of mesoporous (pore diameters 20 - 500 Å) silica-based materials, shape- and size-controlled polyethylene was reported as formed in constrained geometries (i.e., inside mesopores of silica).^{116, 117} However, with respect to the desorption of significant amounts of metallocene catalysts, it is believed that ethylene polymerization in these studies occurred not only in the confined space mentioned, but in bulk solution of the reaction mixture as well.

1.4.3.2 Homogeneous Catalyst Models for Silica-supported Metallocenes

The use of appropriate homogeneous catalyst systems as models for corresponding silica-supported metallocenes provides a major advantage in a wide range of powerful techniques one can use in characterization and mechanistic study. Several metallasiloxanes (i.e., organosilicon compounds containing Si-O-M bonds)^{118, 119}, including silsesquioxane-stabilized Group 4 metal half-sandwich complexes (e.g., $[\text{Si}_8\text{O}_{12}(\text{c-C}_6\text{H}_{11})_7]\text{ZrCp}^*$ where Cp^* is $\eta^5\text{-C}_5\text{Me}_5$ by Feher¹²⁰; $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{MCp}^*\text{Cl}_2$ and $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{TiCp}^*\text{R}_2$ where Cp^* is $\eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2$, M is Ti or Zr, and R is CH_2Ph or Me, reported by Duchateau *et. al.*^{121, 122}) have been used as models for silica-supported systems in α -olefin polymerization.

In this study we reported the synthesis, characterization, and olefin polymerization of both metallocene and half-sandwich complexes of sphaerosilicate with the general formula, $\text{Si}_8\text{O}_{20}(\text{MCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ (M = Ti, Zr; Cp = $\eta^5\text{-C}_5\text{H}_5$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), respectively.

Chapter 2

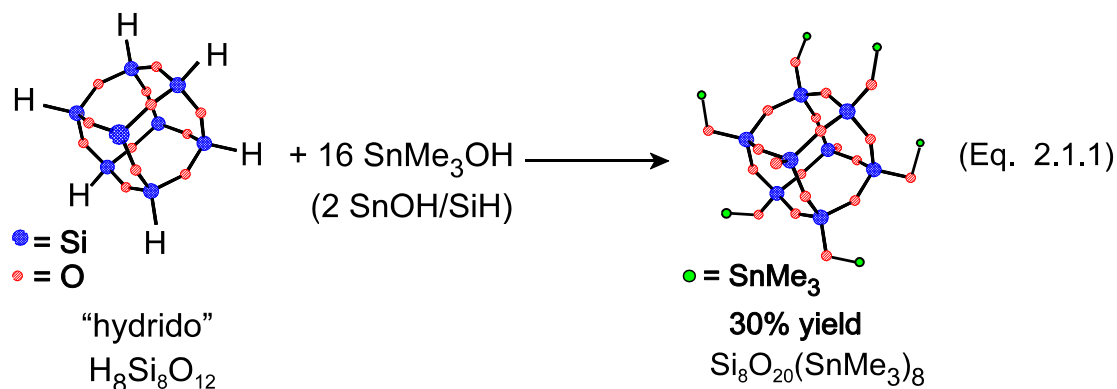
Synthesis and Exchange Reaction of Octa(trimethyltin)

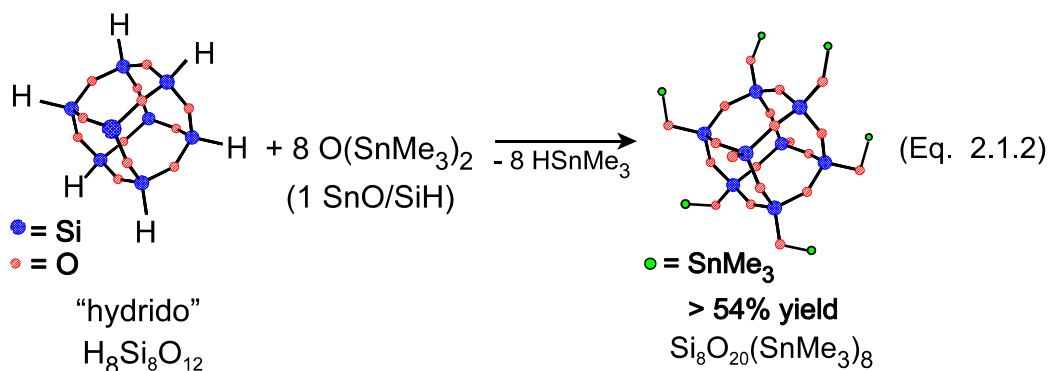
Cuboctameric Spherosilicate, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

2.1 Introduction to $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

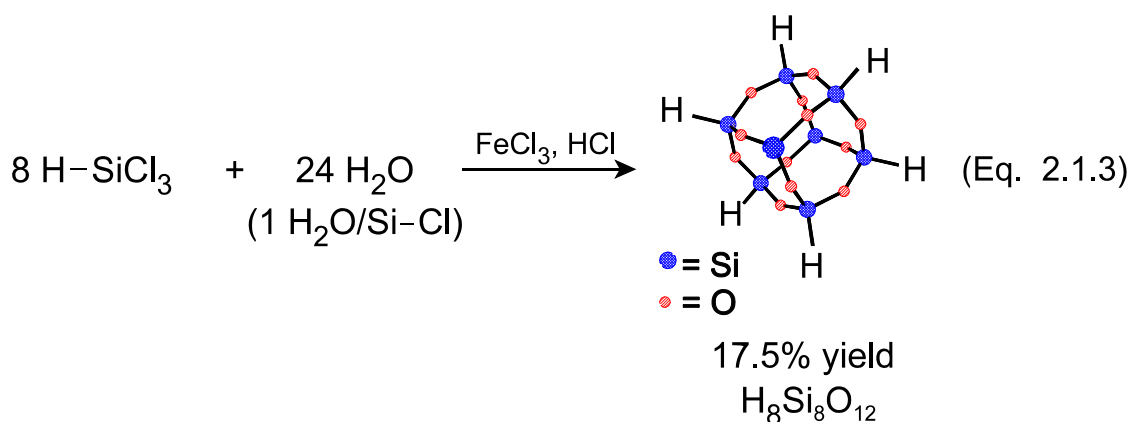
The exchange reaction between metal or nonmetal chlorides with labile functional groups (e.g., SbMe_4 , SnMe_3 , Ti) on cuboctameric spherosilicates is a synthetically useful route towards various derivatives of new spherosilicates.^{123, 124} Among a few spherosilicates with labile functional groups, the octa(trimethyltin) derivative, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was selected for this study.

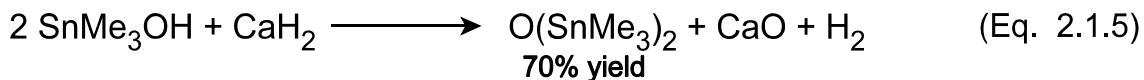
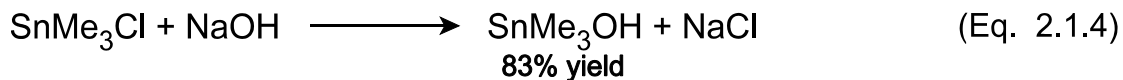
Two methods have been reported in the literature for the synthesis of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$; both of them used the hydridospherosiloxane $\text{H}_8\text{Si}_8\text{O}_{12}$ as the starting material. With the use of excess trimethyltin hydroxide, SnMe_3OH , the research group led by Klemperer reported the preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in 30% yield (Eq. 2.1.1, with two (front and back) H and SnMe_3 groups omitted in the illustrations for the clarity of the structure).¹²⁵ In a similar manner to the tin hydroxide, its anhydride, $\text{O}(\text{SnMe}_3)_2$, was used by Feher *et. al.* to convert the hydrido- starting material, $\text{H}_8\text{Si}_8\text{O}_{12}$, to the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in fair yield (54% after recrystallization from hexane) (Eq. 2.1.2).¹²⁴



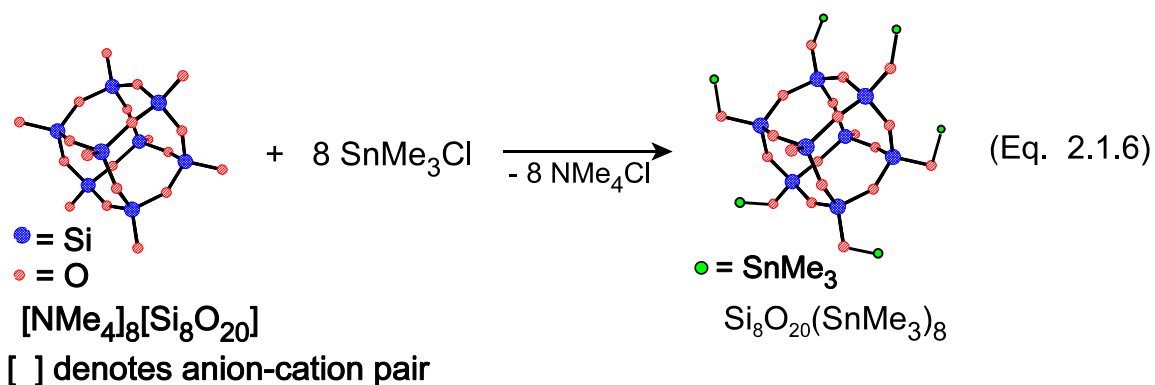


Although Feher *et al.* reported the preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, this preparative reaction is limited by the unavailability of its reactants. The hydrido- reactant, $\text{H}_8\text{Si}_8\text{O}_{12}$, could be prepared in no higher than 17.5% yield from the controlled hydrolysis and condensation of HSiCl_3 (Eq. 2.1.3)¹²⁶, while the stannylating agent, $\text{O}(\text{SnMe}_3)_2$, must be prepared in two steps from an expensive starting material, SnMe_3Cl (Eq. 2.1.4 and 2.1.5).^{127, 128} The formation of each mole of $\text{O}(\text{SnMe}_3)_2$ requires at least two moles of SnMe_3Cl . Furthermore, in the final reaction with the silicate cube, one equivalent of tin is lost as trimethyltin hydride, although it is possible to recycle this to the anhydride. The preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ via the reaction between $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{O}(\text{SnMe}_3)_8$ can, therefore, be very lengthy and costly.

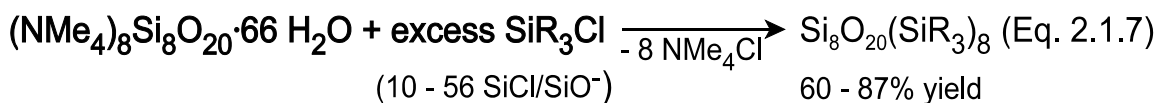




An alternative approach to be demonstrated here is the preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ by the direct reaction between “bare” octaanion $[\text{Si}_8\text{O}_{20}]^{8-}$ in $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}$, and the chlorostannane, SnMe_3Cl (Eq. 2.1.6).



The cubic sphaerosilicate octaanion may be prepared as a highly hydrated tetramethylammonium salt, $[\text{NMe}_4]_8[\text{Si}_8\text{O}_{20}] \cdot 66 \text{H}_2\text{O}$. In its silylation or stannylation, the solvated water molecules always compete with the sphaerosilicate $[\text{Si}_8\text{O}_{20}]^{8-}$ itself. As a result, large excesses (10 to 56 equivalents) of silylating reagents are normally required to attain acceptable yields of desired products (Eq. 2.1.7).¹²⁹⁻¹³¹ Our approach, therefore, involves the removal of solvated water molecules from the cubic octamer prior to its stannylation by SnMe_3Cl . This dehydration of cubic octamer was hoped to decrease the required amount of SnMe_3Cl to close to its stoichiometric amount, while still obtaining a



satisfactory yield of the product.

2.2 Experimental Section

Tetramethylammonium hydroxide (25% by weight NMe_4OH in water from Aldrich), tetraethylorthosilicate ($\text{Si}(\text{OEt})_4$ or TEOS from Acros), acetone (Fisher), dimethylformamide (Fisher), dimethylchlorosilane ($\text{Cl-Si}(\text{Me})_2\text{H}$ from Acros), chloromethyldimethylchlorosilane ($\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$, Acros), vinyltrimethylchlorosilane ($\text{Cl-Si}(\text{Me})_2\text{CH=CH}_2$, Acros), trimethyltin chloride (99% SnMe_3Cl , Aldrich), and trimethylchlorosilane (98% Cl-SiMe_3 , Acros) were used without further purification. Trimethyltin chloride, SnMe_3Cl , was kept and used under a nitrogen atmosphere in a dry box. Group 4 metal chlorides, including chlorotitanium triisopropoxide (97% $\text{CpTi}(\text{OC}_3\text{H}_7)_3$, Strem), cyclopentadienyltitanium trichloride (99% CpTiCl_3 , Strem), cyclopentadienylzirconium trichloride (min. 98% CpZrCl_3 , Strem), and pentamethylcyclopentadienylzirconium chloride (99% Cp^*ZrCl_3 , Strem), were stored and used under a nitrogen atmosphere in a dry box. Prior to their use in exchange reactions with $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, chlorotitanium triisopropoxide (m.p. 34 - 36 °C) and pentamethylcyclopentadienylzirconium chloride were purified by sublimation at 0.050 mm Hg, in warm water bath (for $\text{CpTi}(\text{OC}_3\text{H}_7)_3$) and at 170 °C (for Cp^*ZrCl_3), respectively. Diethyl ether (Na/K), hexanes (Na/K), methylene chloride (CaH_2) and THF (Na) were dried and freshly collected prior to their use. Solvents to be vapor transferred were degassed by pumping during repeated freeze-thaw cycles.

Benzene- d_6 was dried over Na/K alloy, vapor transferred (0.050 mm Hg), stored, and used under nitrogen atmosphere in dry box for the NMR analysis of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$. ^1H NMR spectra were acquired on either a Bruker AC 250 MHz or a Varian Mercury 300 MHz spectrometer. ^{29}Si solid state NMR (SSNMR) data were acquired on a Varian

INOVA 400 solid state NMR spectrometer using cross polarization-magic angle spinning (CPMAS) experiment with a relaxation delay of 3 s. Hydrated and dehydrated cubic octamer samples were spun at 3.5 kHz and 5.5 kHz, respectively. In working up the data, a line broadening of 20 Hz was applied. Except for the hydrated cubic octamer samples, all other solid state NMR samples were packed into NMR rotors under a dry nitrogen atmosphere. ^1H NMR chemical shifts were referenced internally to benzene- d_6 (δ 7.15) or chloroform- d (δ 7.26). The cubic octamer silicic acid trimethylsilyl ester, $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, was used as an external reference for ^{29}Si -NMR (δ 12.4 and -108.6).

The dehydration of cubic octamer and the handling of dehydrated cubic octamer, including its silylations and stannylation, were performed using standard Schlenk techniques and a dry box. While silylated products were chemically stable and could be handled in air and moisture, all treatments of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ were performed under a dry nitrogen atmosphere.

2.2.1 Preparation and Dehydration of $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}\cdot 66\text{H}_2\text{O}$

Hydrated cubic octamer, $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}\cdot 66\text{H}_2\text{O}$, was prepared based on a procedure reported by Harrison *et. al.* as follows:¹³² the 25% aqueous NMe_4OH solution (32 mL, 89.2 mmol) was placed in a polyethylene bottle to which was added water (44 mL); this makes the total amount of water 68 mL. TEOS (20 mL, 87.9 mmol, *ca.* 1 eq/ NMe_4OH) was then added dropwise. After the addition of TEOS was finished, acetone (80 mL), was added and the solution was stirred overnight. The colorless crystalline product precipitated out of solution and was filtered without washing. (Acetone could be used to wash the precipitate. However, some other solvents, including the 5:2 V/V *i*-PrOH/ H_2O used in another method of preparation, dissolved the precipitate and plugged up the filter during the wash.) The colorless crystalline product,

(NMe₄)₈Si₈O₂₀·66 H₂O, (19.06 g, F.W. 2326.85, 74.5% yield) gradually lost the waters of hydration and changed its appearance to dull white solid if left uncovered in air. Its dehydration for the removal of most hydrated waters was done by heating under vacuum (80 °C, 0.050 mm Hg) for 12 h. Upon dehydration, the cubic octamer changed from clear colorless crystals to pale yellowish white solid, accompanied by 42% weight loss. The identification of the cubic octamer by ²⁹Si solid state NMR was done before and after dehydration.

2.2.2 Silylations of Dehydrated Cubic Octamer

Silylations of “dehydrated” cubic octamer were done by a modified procedure based on Yuchs’ method for the silylation of “hydrated” cubic octamer.¹³⁰ Various silylating agents, including Cl–Si(Me)₂H, Cl–Si(Me)₂CH₂Cl, and Cl–Si(Me)₂CH=CH₂, were used; their product yields were compared to those from the reaction with the hydrated cubic octamer. In a typical procedure for the silylation of dehydrated cubic octamer by Cl–Si(Me)₂H, distilled hexane (20 mL) and *N,N*-dimethylformamide (40 mL) were added to the dehydrated cubic octamer (1.5 g (NMe₄)₈Si₈O₂₀·12 H₂O, F.W. 1354.02, 1.1 mmol cubic octamer or 8.8 mmol SiO[–] reaction sites). Under a nitrogen atmosphere, dimethylchlorosilane, Cl–Si(Me)₂H (3.8 mL, 35 mmol, 4 equivalents per SiO[–] reaction site), was added to the cubic octamer suspension. The white turbid reaction mixture was stirred at room temperature for 1 h, during which time some heat evolved from the reaction was noted. The reaction mixture was then stirred at 0 °C in an ice bath and 50 mL of cold distilled water was added dropwise to hydrolyze unreacted silylating agent and to allow the complete formation of siloxane. The reaction mixture was removed from the ice bath and warmed to room temperature. (Undistilled) hexane was added to increase the volume of organic layer before the extraction. The organic

layer was washed with distilled water until acid free. It was then dried over magnesium sulfate and filtered. Solvents were removed from the filtrate in a rotatory evaporator, yielding white solid as a crude product. The crude product was washed with ethanol a few times to yield the white crystalline pure (based on $^1\text{H-NMR}$) $\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8$ (0.71 g, F.W. 1017.98, 64% yield).

The silylation of dehydrated cubic octamer by other silylating agents (i.e., $\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$ and $\text{Cl-Si}(\text{Me})_2\text{CH}=\text{CH}_2$) followed the same procedure as above, except replacing the dimethylchlorosilane $\text{Cl-Si}(\text{Me})_2\text{H}$, by $\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$ (4.6 mL, 35 mmol, 4 equivalents per SiO^- reaction site), or $\text{Cl-Si}(\text{Me})_2\text{CH}=\text{CH}_2$ (4.8 mL, 35 mmol, 4 equivalents per SiO^- reaction site). In each of these silylations, the crude product after the solvent removal by rotatory evaporation was white solid in a high boiling, yellow liquid (which was the siloxane formed by the hydrolysis of excess silylating agent). After ethanol washes, pure white solid was obtained as $\text{Si}_8\text{O}_{20}[\text{Si}(\text{Me})_2\text{CH}_2\text{Cl}]_8$ (0.62 g, F.W. 1405.75, 40% yield), or $\text{Si}_8\text{O}_{20}[\text{Si}(\text{Me})_2\text{CH}=\text{CH}_2]_8$ (0.65 g, F.W. 1226.28, 48% yield) from each of the above silylations, respectively. All silylation products were characterized by ^1H NMR in chloroform-*d*.

2.2.3 Stannylation of Dehydrated Cubic Octamer: Synthesis of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

Dehydrated cubic octamer $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}\cdot 12\text{H}_2\text{O}$ (2.0 g, F.W. 1354.02, 1.5 mmol cube or 12 mmol SiO^- reaction sites), and trimethyltinchloride, SnMe_3Cl (7.88 g, 39.2 mmol, 3.3 SnCl/SiO^- reaction site), were weighed to a Schlenk vessel in a dry box. Under nitrogen flow, distilled hexanes (96 mL), and distilled THF (72 mL) were poured through a pouring spout to the reactants. The reaction mixture was stirred at room temperature for 3 h 20 min. The amount “light” precipitate suspended in solution may be taken as a rough indication of how the reaction is proceeding. The $[\text{Si}_8\text{O}_{20}]^{8-}$ reactant is a

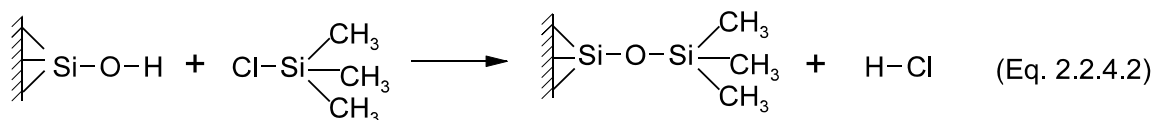
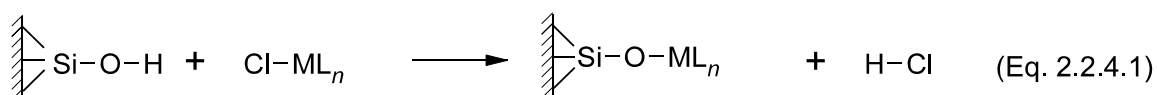
dense solid in the reaction mixture and quickly falls to the bottom of the reaction flask when stirring is halted. The NMe_4Cl side product is a less dense, flocculent solid which remains suspended in the solution immediately after the stirring is halted. The reaction was worked up by the removal of volatiles under vacuum at room temperature. Any heating of the reaction mixture was avoided, until most of the solvents was removed and white damp solid was obtained. The white solid was evacuated for another 30 min to 1 h at 50 – 60 °C (warm water bath) to remove the residual SnMe_3Cl . A white, dry, powdery solid, which is the mixture of primarily $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and NMe_4Cl , was obtained.

The product $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was extracted from the solid residue (white dry powdery solid) by using hot hexanes three times. In each extraction, a generous amount of hot hexanes was poured to the reaction mixture and the reaction mixture was left in contact with hot hexane solvent for at least 4 - 5 min to dissolve as much of the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ as possible. The extracted solution was then filtered through a cotton-plugged pouring spout while it was still warm. (As the filtered solution cooled down to room temperature, some white small crystals might be observed.) After three extractions in hot hexanes, the combined filtered solution was concentrated by removing hexanes under vacuum. (At room temperature, some colorless needle-shaped crystals might begin to grow.) The crystallization of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was allowed to come to completion by keeping the concentrated $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ /hexanes solution at 5 °C overnight. The next day, the mother liquor was cannulated away from colorless needle-shaped crystals and the crystals were washed three times with small amount of freshly distilled, cold hexanes. X-ray and NMR analyses of this material revealed the presence of two waters of hydration. The $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ to be used for further reaction was dried under 0.050 mm Hg at 90 °C for 18 h, yielding pure, non-solvated $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (1.44 g, F.W. 1855.19, 53%) as white powder. The product with two water molecules in the crystal was

soluble in several organic solvents, including benzene, chloroform, dichloromethane, and THF. It was characterized by ^1H -NMR in benzene- d_6 and single crystal X-ray diffraction.

2.2.4 Exchange Reactions of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with Silyl Chlorides and Group 4 Metal Chlorides

Silanol groups ($\equiv\text{Si}-\text{OH}$) on the surface of glass react with reagents containing M-Cl bonds (e.g., Cp_2TiCl_2 and Cp_2ZrCl_2) (Eq. 2.2.4.1). We prevented this undesired side reaction (between metal chloride reagents and glassware surfaces) by converting the reactive silanol group ($\equiv\text{Si}-\text{O}-\text{H}$) to the more stable and less reactive $\equiv\text{Si}-\text{O}-\text{SiMe}_3$ group prior to the use in exchange reactions. Practically, all glasswares used, including NMR tubes and glass pipets, were treated with THF, chlorotrimethylsilane (ClSiMe_3), and triethylamine. THF functioned as a solvent. The silylating agent, ClSiMe_3 , reacted with surface silanol groups, forming stable $\equiv\text{Si}-\text{O}-\text{SiMe}_3$ groups on glass surface and HCl (Eq. 2.2.4.2), which was neutralized by the base, triethylamine. The glassware was then washed and dried prior to use.



Exchange reactions of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with excesses of silyl chlorides ($\text{Cl}-\text{Si}(\text{Me})_2\text{H}$, $\text{Cl}-\text{SiMe}_3$, $\text{Cl}-\text{Si}(\text{Me})_2\text{CH}_2\text{Cl}$, and $\text{Cl}-\text{Si}(\text{Me})_2\text{CH}=\text{CH}_2$) were studied by ^1H -NMR in NMR-scaled reactions in benzene- d_6 . Larger-scaled reactions were later performed in THF. A typical procedure for the reaction of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with

trimethylchlorosilane, Cl-SiMe_3 , at 50-mg scale is as follows: to $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (50 mg, 0.027 mmol, 0.22 mmol SnMe_3 reaction sites), Cl-SiMe_3 (0.10 mL, 0.77 mmol, 3.6 equivalents per SnMe_3 reaction site) and freshly distilled THF were added under a nitrogen atmosphere. The resulting clear colorless reaction mixture was stirred at room temperature for half an hour, after which it was worked up by volatile removal under 0.050 mm Hg vacuum. The crude product from the reaction was analyzed by $^1\text{H-NMR}$ in benzene- d_6 . In the exchange reaction of $\text{Cl-Si(Me)}_2\text{H}$, $\text{Cl-Si(Me)}_2\text{CH}_2\text{Cl}$, and $\text{Cl-Si(Me)}_2\text{CH=CH}_2$, trimethylchlorosilane (Cl-SiMe_3) was replaced by $\text{Cl-Si(Me)}_2\text{H}$ (30 μL , 0.28 mmol, 1.3 eq), $\text{Cl-Si(Me)}_2\text{CH}_2\text{Cl}$ (30 μL , 0.23 mmol, 1.1 eq), and $\text{Cl-Si(Me)}_2\text{CH=CH}_2$ (40 μL , 0.29 mmol, 1.2 eq), respectively. Crude products were washed with ethanol if further purification was required.

In the same manner, exchange reactions of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with excesses of Group 4 metal chlorides ($\text{CITi(OC}_3\text{H}_7)_3$, CpTiCl_3 , CpZrCl_3 , and Cp^*ZrCl_3 , where Cp is C_5H_5 and Cp^* is C_5Me_5) were studied by $^1\text{H-NMR}$ in NMR-scaled reactions in benzene- d_6 . The procedure for the reaction of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with chlorotitanium triisopropoxide, $\text{CITi(OC}_3\text{H}_7)_3$, at 50-mg scale is as follows: $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (50 mg, 0.027 mmol, 0.22 mmol SnMe_3 reaction sites) and $\text{CITi(OC}_3\text{H}_7)_3$ (63 mg, 0.24 mmol, 1.1 equivalents per SnMe_3 reaction site) were weighed into a Schlenk vessel in a dry box. Under 0.050 mm Hg, dry THF was vapor transferred to the reaction vessel. The reaction mixture was stirred for half an hour at room temperature (under static vacuum); during this time, the reaction mixture gradually changed its appearance from clear colorless to cloudy white solution. The reaction was worked up by volatile removal under 0.050 mm Hg, yielding white powdery crude product, which was analyzed by $^1\text{H-NMR}$ in benzene- d_6 .

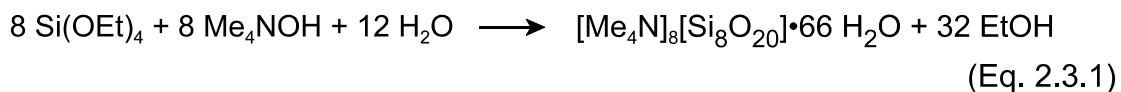
The reaction of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ with cyclopentadienyltitanium trichloride, CpTiCl_3 , at 100-mg scale was done in THF, diethyl ether, and methylene chloride. $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

(100 mg, 0.054 mmol, 0.44 mmol SnMe₃ reaction sites) and CpTiCl₃ (115 mg, 0.52 mmol, 1.2 equivalents per SnMe₃ reaction site) were weighed into a Schlenk vessel in a dry box. Under 0.050 mm Hg, dry solvent was vapor transferred to the reaction vessel. The reaction mixture was stirred for 10 min at room temperature (under static vacuum); during this time, the reaction mixture rapidly changed its appearance from clear neon yellow to gel-like yellow precipitate in clear colorless solution. The reaction was worked up by volatile removal under 0.050 mm Hg vacuum, yielding neon yellow crystals (33 mg), which were insoluble in benzene-*d*₆ and chloroform-*d*.

Exchange reactions of Si₈O₂₀(SnMe₃)₈ with CpZrCl₃ and Cp⁺ZrCl₃ at 100-mg scale were done in THF. The procedure for the reaction of CpTiCl₃ was followed, but CpZrCl₃ (170 mg, 0.63 mmol, 1.4 equivalents per SnMe₃ reaction site) or Cp⁺ZrCl₃ (168 mg, 0.50 mmol, 1.1 equivalents per SnMe₃ reaction site) was used in place of CpTiCl₃ and the reaction time of 30 min was applied. A white precipitate was observed immediately in the reaction mixture of CpZrCl₃. A violet-black fine solid was gradually formed in the reaction of Cp⁺ZrCl₃. After volatile removal, crude reaction mixtures were analyzed by ¹H-NMR in benzene-*d*₆.

2.3 Preparation and Dehydration of (NMe₄)₈Si₈O₂₀·66 H₂O

The hydrated cubic octamer, (NMe₄)₈Si₈O₂₀·66 H₂O, was prepared by the hydrolysis and condensation of Si(OEt)₄ in the presence of the template quarternary ammonium ion, NMe₄⁺ (Eq. 2.3.1). Barnes identified the presence of 66 molecules of hydrogen bonded water by the single crystal X-Ray analysis of the freshly prepared



cubic octamer. Its elemental analysis and ^1H NMR spectrum also revealed the presence of large amount of solvated water, *ca.* 60 ± 5 water molecules.¹³³ Its ^{29}Si solid state NMR spectrum showed only one sharp signal at -98.61 ppm (**Figure 2.3.1**) which is in good agreement with its reported chemical shift of -98.6 ppm. The observation of a single ^{29}Si signal also indicates that there is only one type of magnetically equivalent Si atoms in a Q^3 (i.e., $-\text{Si}(\text{OSi})_3$) environment with the reported chemical shift around -100 ppm.

In the dehydration of cubic octamer, there are two factors to be considered. One is the chemical stability of cubic octamer under dehydration conditions; the second is the amount of removed water to be achieved. Barnes and Williams reported on the 20-hour dehydration of hydrated cubic octamer under vacuum at elevated temperatures.¹³⁴⁻¹³⁶ Based on this study, the chemical stability of cubic octamer under thermal treatment will be discussed first.

At temperatures of dehydration from 70 to 90 °C, 90% of the weight loss occurred during the first 10 h and most of the volatiles removed was water. The final 10% of the weight loss occurred during the last 10 h; trace amounts of methanol and trimethylamine were detected in the volatiles and solid soluble in water (i.e., cubic octamer) was obtained. On the other hand, when cubic octamer was heated at higher temperatures (100 – 120 °C), significant amounts of methanol and trimethylamine were detected as volatiles. Some insoluble solid material was obtained; its ^{29}Si NMR signal (around -98.6 ppm) was significantly broadened (over 50 ppm wide), indicating the condensation between cuboctameric cages. At even higher temperature, 140 °C, only insoluble solid material was obtained after 20 h. A mechanism explaining the dehydration of cubic octamer at elevated temperatures was then suggested by Barnes and Williams (**Scheme 2.3**). Upon heating above 70 °C and as hydrogen-bonded water shells are removed from around the cubic octamer, the overall negative charge on

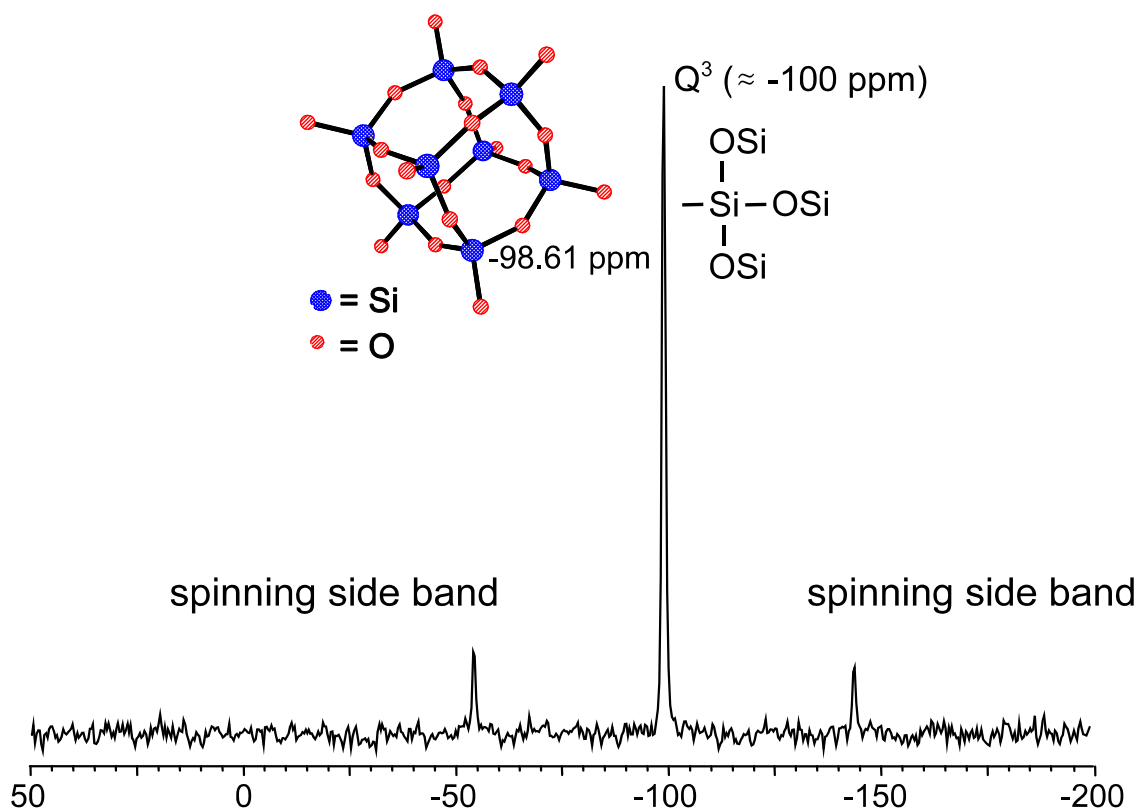
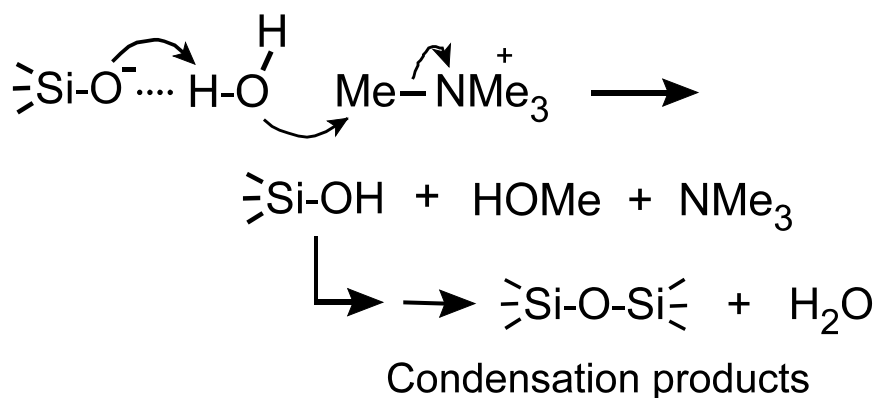


Figure 2.3.1 ^{29}Si solid state NMR spectrum of $[\text{Me}_4\text{N}][\text{Si}_8\text{O}_{20}]\cdot 66 \text{ H}_2\text{O}$



Scheme 2.3 Dehydration of cubic octamer at > 70 °C

[Si₈O₂₀] units became more densely concentrated. In order to reduce this developing negative charge, the cubic octamer must become protonated. The protonation of ≡Si-O⁻ by water (forming silanol groups) is followed by attack of hydroxide ion on the NMe₄⁺ counterion in a Hofmann-elimination type reaction. As a result, methanol and trimethylamine are formed. The silanol groups can then condense together in an intermolecular condensation with the loss of water, thereby cross-linking, individual cubes and eventually producing insoluble silicates.

As expected, Williams observed the amount of removed water and % weight loss increase with the increasing temperature. In order to maximize the amount of water removed while minimizing the condensation of cubic octamers, Williams suggested the optimum condition for the dehydration of cubic octamer as 90 °C for 20 h under vacuum.¹³⁴ Under this condition, 98.6% of water was removed and the cubic octamer was characterized by ¹H-NMR to be (NMe₄)_{4.5}Si₈O₂₀·1 H₂O.

In this present study, a different set of conditions for dehydration were employed. All cubic octamer used for the preparation of Si₈O₂₀(SnMe₃)₈ was dehydrated at 80 °C under a vacuum of 0.050 mm Hg for 12 h. These conditions were not as harsh and were

expected to remove less water than the optimum condition (90 °C heating) suggested by Williams. Under the dehydration condition of 80 °C, 0.050 mm Hg for 12 h, 42% weight loss, accounted for ~54 molecules of water removed (per cubic octamer unit), was observed (**Table 2.3**). This calculation of 54 waters removed was based on the assumption that the cubic octamer being weighed before the dehydration had the formula $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20} \cdot 66 \text{ H}_2\text{O}$ (i.e., no loss of water occurred before the thermal dehydration). It is possible that the actual formula of the “hydrated” cubic octamer might have less than 66 waters to begin with. The actual formula of the “dehydrated” cubic octamer might contain less than 12 molecules of water. The ^{29}Si solid state NMR was employed to confirm the chemical identity of cubic octamer after thermal dehydration (**Figure 2.3.2**). The signal of cubic octamer around -98 ppm was broadened a little bit. Upon testing its solubility, all of the “dehydrated” cubic octamer dissolved in water.

2.4 Silylations of Dehydrated Cubic Octamer

Since there are literature reports on silylations of hydrated cubic octamer, silylations of “dehydrated” cubic octamer were done in order to study effects that

Table 2.3 Calculation of removed water from the weight loss of cubic octamer

Formula	F.W.
$(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}$	1137.84
1 H_2O	18.02
$(\text{NMe}_4)_8\text{Si}_8\text{O}_{20} \cdot 66 \text{ H}_2\text{O}$	2326.85
Wt. Loss (42% of original formula, $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20} \cdot 66 \text{ H}_2\text{O}$)	977.28
54 H_2O	973.08
$(\text{NMe}_4)_8\text{Si}_8\text{O}_{20} \cdot 12 \text{ H}_2\text{O}$ (54 waters removed from 66)	1354.02

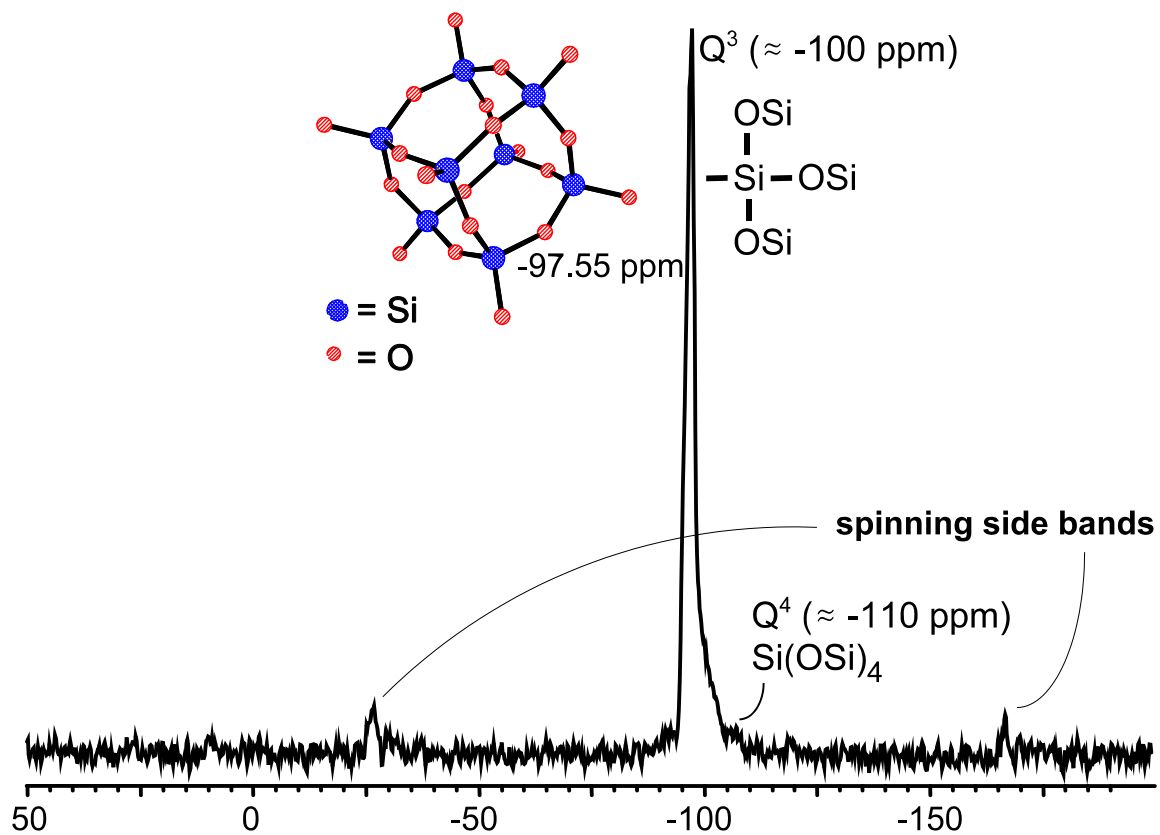


Figure 2.3.2 ^{29}Si solid state NMR spectrum of cubic octamer dehydrated at 80 °C

dehydration has on further reactions of the cubic octamer. Various silylating reagents, including $\text{Cl-Si}(\text{Me})_2\text{H}$, $\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$, and $\text{Cl-Si}(\text{Me})_2\text{CH=CH}_2$, were used, yielding various silylated cubic octamers (Eq. 2.4). **Table 2.4** lists equivalents of silylating reagents used (i.e., number of SiCl/SiO^- reaction site) and percent yields of products from silylations of both hydrated and dehydrated cubic octamers. It is worth mentioning here that, despite a claim in the literature¹³² that only five fold excess (per Si corner) of the silylating reagent $\text{ClSi}(\text{Me})_2\text{H}$ was necessary to silylate all eight SiO^- functions of the hydrated cubic octamer, $[\text{NMe}_4]_8\text{Si}_8\text{O}_{20}\cdot 60 \text{ H}_2\text{O}$, to give $\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8$ in > 80% yield, our calculation, based on the reported experimental procedure, indicates that a ten fold excess of the silylating reagent was actually employed.

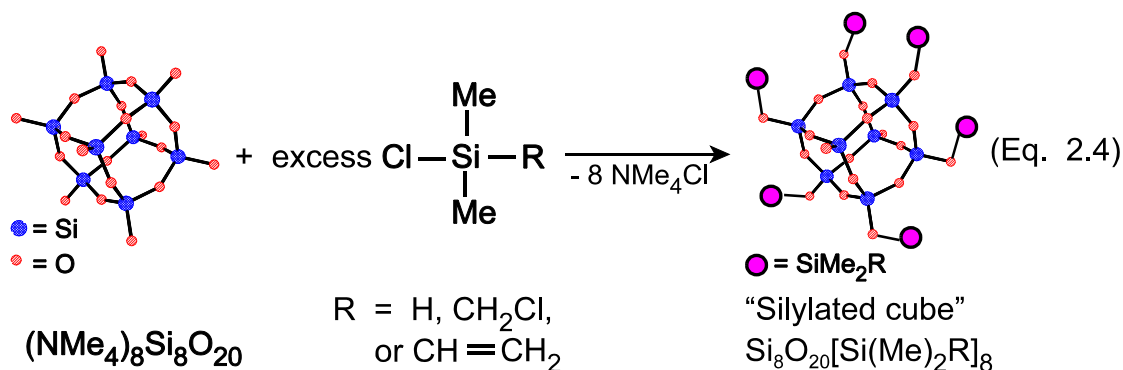


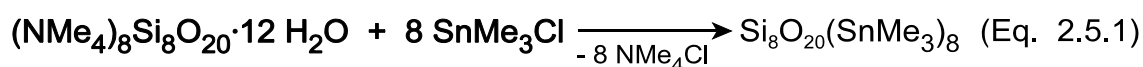
Table 2.4 Conditions and yields of silylations of cubic octamer

Silylaing reagents	Eq used, % yield (Hydrated cubic octamer)	Eq used, % yield (Dehydrated cubic octamer)
$\text{Cl-Si}(\text{Me})_2\text{H}$	10, 83% ¹³²	4, 64%
$\text{O}(\text{SiMe}_2\text{CH}_2\text{Cl})_2$ and $\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$	8, 47% ¹³¹	–
$\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$	–	4, 40%
$\text{Cl-Si}(\text{Me})_2\text{CH=CH}_2$	56, 87% ¹³⁰ 12, 60% ¹²⁹	4, 48%

Although Agaskar reported using as low as 8 equivalents of the silylating reagents, $\text{O}(\text{SiMe}_2\text{CH}_2\text{Cl})_2$ and $\text{Cl-Si}(\text{Me})_2\text{CH}_2\text{Cl}$, yielding 47% of the $\text{Si}_8\text{O}_{20}[\text{Si}(\text{Me})_2\text{CH}_2\text{Cl}]_8$ product, the reported procedure, involving the mixing of three separately prepared reagent solutions, is less convenient than the procedure we have developed. In silylations of dehydrated cubic octamer, it was found that the amount of silylating reagents could be decreased more than two fold (i.e., from 10 – 56 equivalents to 4 equivalents), while product yields were maintained at no less than 40%. Silylations of dehydrated cubic octamer that could be done at small excess of silylating reagents led us to believe that similar improvements could be made in the preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (i.e., with a small excess of stannylating reagent).

2.5 Stannylation of Dehydrated Cubic Octamer: Synthesis of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

The stannylation of dehydrated cubic octamer with trimethyltinchloride (Eq. 2.5.1) is a sensitive reaction; several parameters, including the preparative method of the cubic octamer starting material, could influence the product yield. In the present study, various stannylation conditions were attempted on the cubic octamer dehydrated at 80 °C and 0.050 mm Hg for 12 h. By calculation from the 42% weight loss (i.e., 54 water molecules being removed), the cubic octamer represented the formula $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20} \cdot 12 \text{H}_2\text{O}$. The optimum stannylation condition, with maximum product yield, was reported in the experimental section (Section 2.2.3).



When the stannylation was first attempted following the same procedure as the silylation (i.e., in hexanes/*N,N*-dimethylformamide mixed solvents, followed by

hexanes/water extraction), the yield of the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ product was very low, most probably due to the low solubility of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in hexanes at room temperature. Since the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ product had high solubility in dichloromethane, the extraction of reaction mixture in dichloromethane/water was also attempted. However, the extracting solvent combined with *N,N*-dimethylformamide (DMF) failed to form separate organic and aqueous layers (even after a large quantity of sodium chloride was added to increase the density of the aqueous layer). The work-up of the stannylation by the removal of volatiles under vacuum (0.050 mm Hg) was found to take a very long time and excessive heating was necessary to remove the condensing DMF (boiling point 153.0 °C). Since overheating of the product, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, in reaction mixtures could potentially lead to undesirable reactions (e.g., hydrolysis and then condensation of $-\text{OSnMe}_3$ groups) or its decomposition, this work-up procedure was not pursued.

Different mixed solvents were then used for the stannylation. Since the presence of polar solvent(s) was essential to help solubilize the spherosilicate reactant, $[\text{Si}_8\text{O}_{20}]^{8-}$, THF was used in place of DMF, as a polar aprotic solvent. The choice of aprotic solvents is also important, since this reaction is of $\text{S}_{\text{N}}2$ type (Eq. 2.5.2). Protic solvents (and, strictly speaking, highly polar solvents) can solvate and stabilize the anionic reactant, $[\text{Si}_8\text{O}_{20}]^{8-}$, lowering the reaction rate significantly. **Table 2.5** summarizes attempted stannylation conditions and their product yields after purification.

Comparison between stannylation in pure THF and in hexanes/DMF mixed solvent, under the similar temperatures and reaction times (-10 followed by -5 °C, over

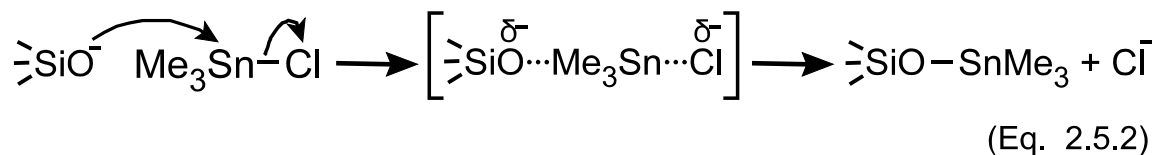


Table 2.5 Conditions and yields of stannylation of dehydrated cubic octamer

Solvent	SnMe ₃ Cl, eq/rxn site	Temp, °C	Time	% Yield
THF	3.3	-10 °C (1 h 30 min), then -5 °C (2 h)		8
1:1 V/V hexanes : DMF (with difficulties in working up reactions)	3.3	-10 °C (1 h 40 min), then -5 °C (2 h)		19
		room	2 h 40 min	25
		70	1 h 30 min	14
		70	14 h 30 min	43
4:3 V/V hexanes : THF	1.7	room	3 h 20 min	20
	5.5	room	3 h 20 min	39
	3.3 (0.5 g-cube reaction)	room	3 h 20 min	52
	3.3 (1 g-cube reaction)	room	3 h 20 min	47
	3.3 (2 g-cube reaction)	room	3 h 20 min	53

about 3 h), the reaction in hexanes/DMF gave a higher product yield (i.e., 19% versus 8%). On the other hand, when compared to the reaction in hexanes/THF, under approximately the same temperature and time (room temperature for about 3 h), the reaction in hexanes/DMF yielded a lower product yield (i.e., 25% versus 52%). The increase in product yields as less polar solvents were used (order of polarity: THF > hexanes/DMF > hexanes/THF) is consistent with the lowering of reaction rates by solvation in S_N2 reactions. Temperatures and amounts of stannylating reagent used also affected the product yield. Despite our expectation that larger excesses of stannylating reagent would keep increasing product yields, there seemed to be a threshold (even at as low as 5.5 equivalents) where product yields would not increase regardless of larger excesses of stannylating reagent.

Since the stannylated product, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, had low solubility in hexanes at room temperature, reaction mixtures were worked up by extraction in generous amounts of boiling hexanes three times. Other work-up procedures, including Soxhlet extraction and extraction in dichloromethane, were also investigated. Soxhlet extraction of reaction mixtures in hexanes for one day did not yield more product. Since dichloromethane dissolves the product very well, extraction of reaction mixtures with dichloromethane was attempted, yielding unclean product (mixed with at least two more compounds). Careful recrystallization of product mixtures in hexanes/dichloromethane yielded unclean product as well. From the result of the Soxhlet extraction in hexanes which did not yield any more product, it is likely that reported product yields were not limited by the amount of “extracted” product, but instead by the nature of the stannylation reaction itself. Extracting three times with generous amounts of boiling hexanes dissolved the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ product quantitatively and selectively.

Under the studied conditions, the maximum product yield of 47 to 53% could be obtained from the stannylation of dehydrated cubic octamer (0.5 to 2 g) by 3.3 equivalents of SnMe_3Cl at room temperature for 3 h 20 min. (The cubic octamer was dehydrated at 0.050 mm Hg, 80 °C for 12 h, losing 42% of its weight.) The product yield of about 50% was quite satisfactory, considering that only 3 equivalents of expensive stannylation reagent, SnMe_3Cl , was required and the stannylation had to occur on all eight reaction sites per molecule of cubic octamer. Nevertheless, some drawbacks from this procedure are its reproducibility when applied to cubic octamer synthesized and dehydrated under different conditions, and its inability to be scaled up beyond 2 g of cubic octamer. (When more than 2 g of cubic octamer was used, the product yield dropped drastically.) Under the present study, a large scale preparation of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was not necessary. However, the ongoing research in our group,

applying this compound as a building block for the synthesis of cross-linked highly siliceous materials, does require a large amount of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and further improvements in its synthesis is desirable. Some lessons learned from conditions presented here may suggest the use of less polar solvents (e.g., by increasing hexanes ratio, and/or by using hexanes/diethyl ether) and higher reaction temperature (i.e., in refluxing solvents) in the stannylation. As for the work-up procedure, the currently applied method using hot hexanes in three extractions is likely to suffice.

2.6 Characterization of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

The eight-fold functionalized $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ is a molecule of high symmetry (time averaged O_h symmetry). In the crystal, the eight corners of the cubic structure and their substituents are symmetry related by inversion symmetry located at the center of the Si_8O_{12} cube. The ^1H NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in benzene- d_6 showed one singlet signal for all eight SnMe_3 groups at 0.36 ppm, along with $^{117/119}\text{Sn}$ satellites ($^2J(^{117}\text{Sn}-\text{H}) = 56.64$ Hz and $^2J(^{119}\text{Sn}-\text{H}) = 59.09$ Hz, i.e., $J(^{119}\text{Sn})/J(^{117}\text{Sn}) = 1.04$) (**Figure 2.6.1**, at 200 MHz ^1H resonance). (Tin has several spin $\frac{1}{2}$ isotopes, including ^{115}Sn (0.35% natural abundance), ^{117}Sn (7.61%), and ^{119}Sn (8.58%). Satellites due to coupling by the ^{117}Sn and ^{119}Sn isotopes can be observed in the ^1H and ^{13}C NMR spectra and it will be noted that the ratio of $J(^{119}\text{Sn})/J(^{117}\text{Sn})$ should be that of the two magnetogyric ratio, i.e., 1.0462.)¹³⁷ This result is also in good agreement with an earlier report by Feher *et.al.* ($\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in benzene- d_6 : δ 0.362, $J_{\text{Sn}-\text{H}} = 58.2, 59.2$ Hz).¹²⁴

It is also important to point out here that the solvent used for NMR characterization of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ should not be a coordinating solvent. It is well known in tin chemistry that the addition of donor molecules (e.g., DMSO, pyridine) to four-coordinate species, in which the tin atom has at least one electronegative

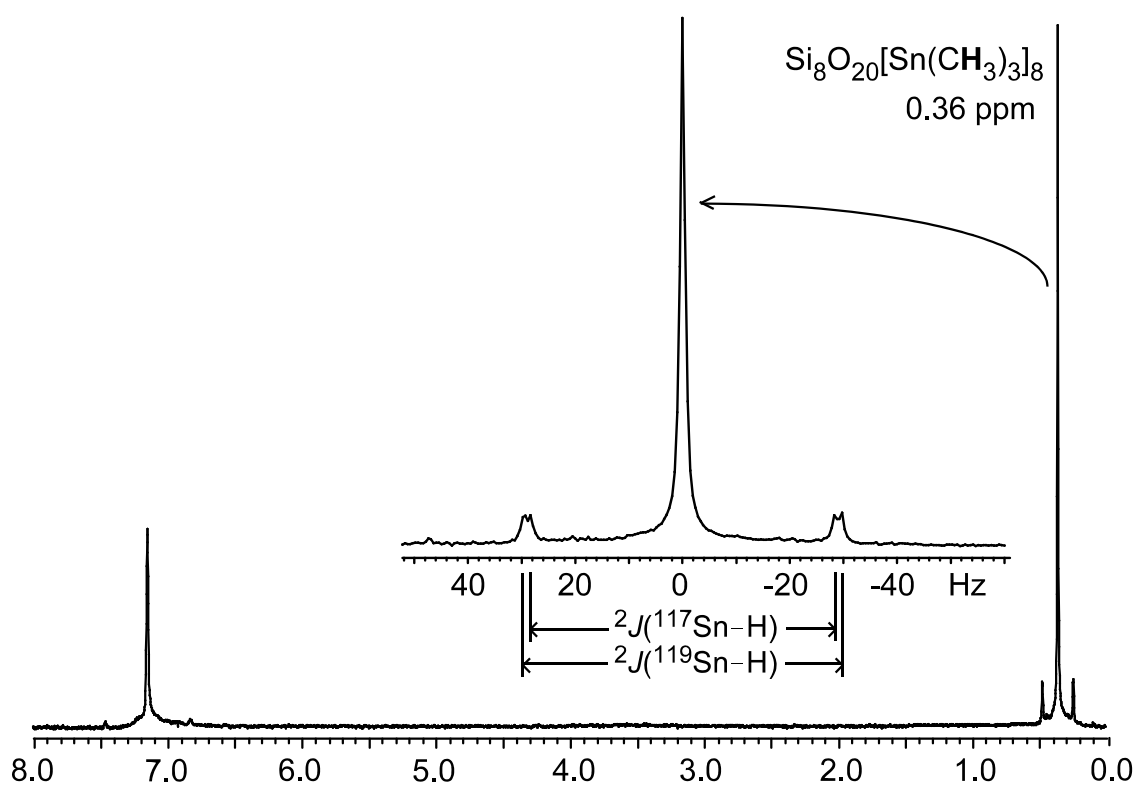


Figure 2.6.1 ^1H NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in $\text{benzene-}d_6$

substituent, can increase the coordination number of tin to five or six.¹³⁸ This effect results in tin shielding (in ^{119}Sn -NMR), by several hundred ppm.¹³⁹ In our case, while ^1H NMR spectra of pure $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ sample showed one clean signal for the methyl protons in noncoordinating solvents, (i.e., deuterated benzene and toluene), more than one signal, centered around 0.36 - 0.41 ppm, was observed in coordinating solvents, (i.e., deuterated chloroform and methanol). (Their ^1H NMR chemical shifts were not affected much by different solvents: δ 0.36 in benzene- d_6 , δ 0.41 in chloroform- d .)

These observations help in understanding how the observed ^1H NMR spectra of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ “cleaned up” after the drying of the sample under vacuum (0.050 mm Hg, 90 °C, 18 h). As we normally took quick ^1H NMR spectra of the “as-prepared” samples of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ outside the dry box (only to confirm their identities), these samples had tendency to absorb moisture from the air. Some of the tin atoms on $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecules might be coordinated to H_2O (possibly in more than one fashion); some might not be. Different environments around methyl protons thus arose, differentiating their methyl signals. Upon dehydration, only noncoordinated SnMe_3 moieties were present and only one signal was observed in ^1H -NMR. Simple ^1H NMR spectra of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ samples, prepared under inert atmosphere, can serve as a useful tool in assuring the dryness of the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ before its further reactions under anhydrous conditions.

$\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ is a molecule of high symmetry. **Figure 2.6.2** illustrates the unique atoms in its X-ray crystal structure. Other atoms in the structure are generated by symmetry related to the inversion center of molecule (**Figure 2.6.3**). To our knowledge, this is the first report on single-crystal X-ray structure data of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$. From the X-ray diffraction study, the presence of solvated water molecules was also confirmed. **Figures 2.6.2 and 2.6.3** show two modes of bonding of waters of solvation to a $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecule. One water molecule is hydrogen bonded to two oxygen atoms

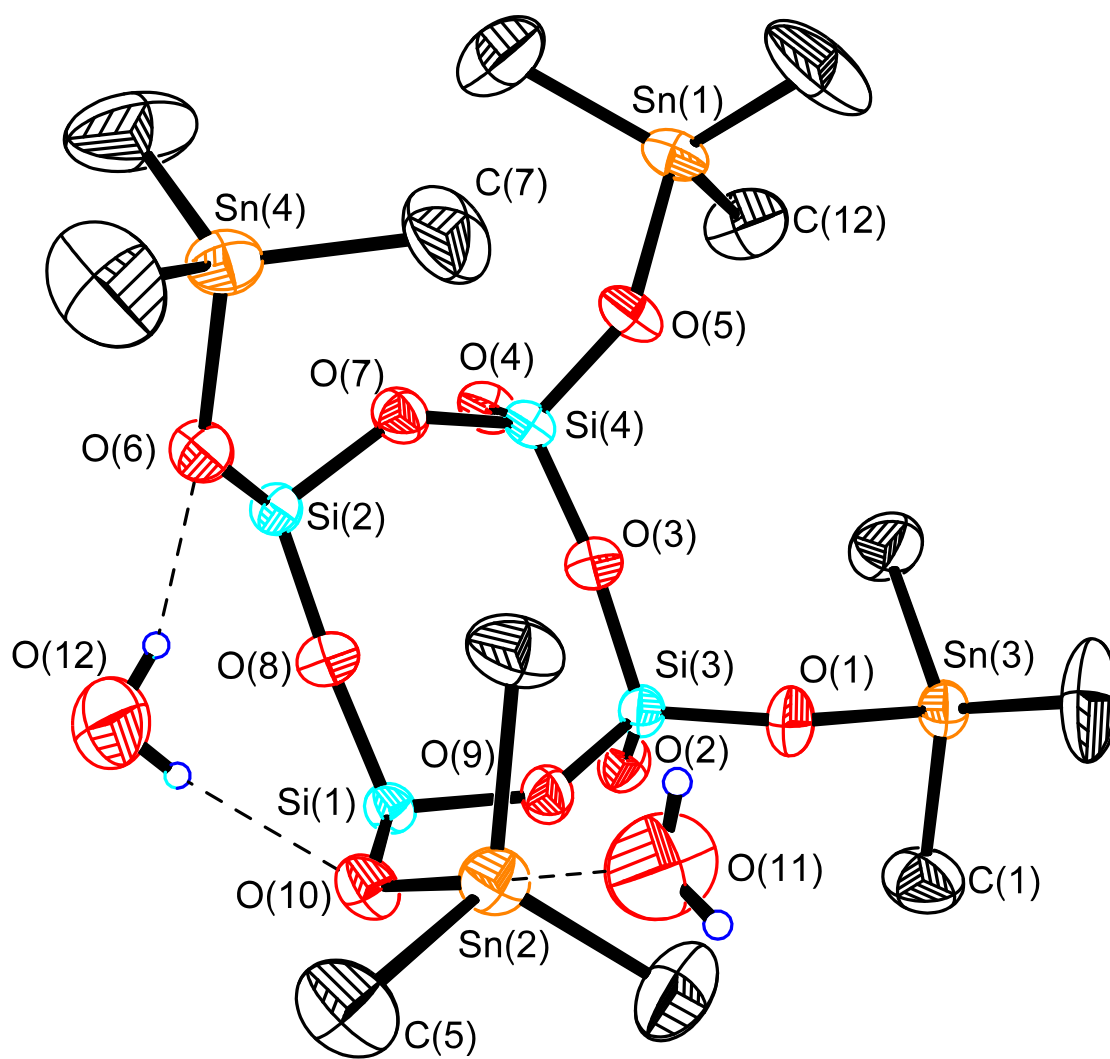


Figure 2.6.2 Unique atoms in the crystal structure of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

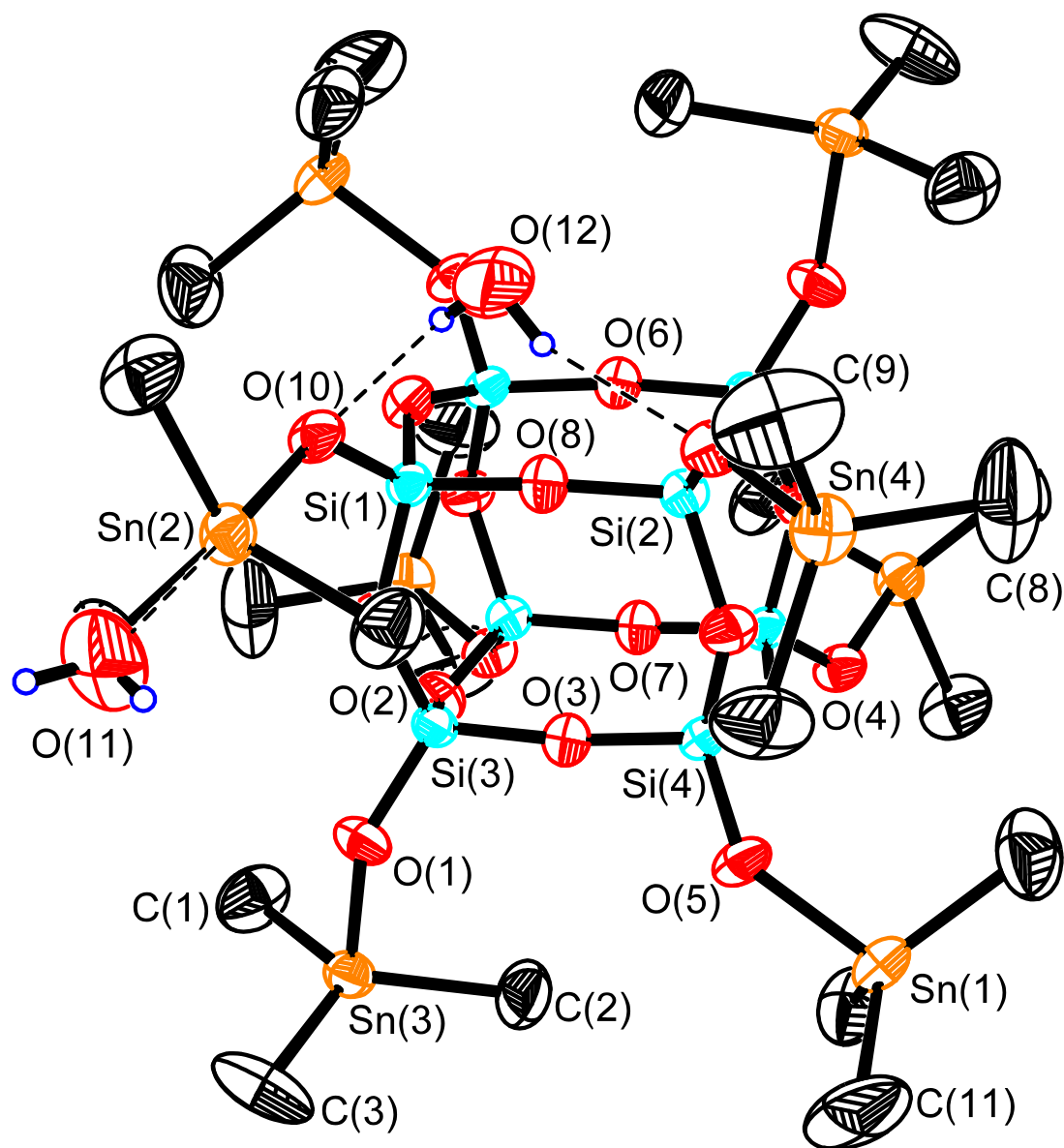


Figure 2.6.3 ORTEP drawing of the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecule along with two waters of solvation

on adjacent OSnMe_3 substituents (see water containing O(12)). A second molecule of water forms a dative bond to a tin atom on one of the two hydrogen bonded OSnMe_3 groups and increases the coordination number of tin to five (see O(11)–Sn(2) in the same figures).

In the context of the overall crystal structure, these waters of solvation are shared between neighboring $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecules. The coordinated water on one $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecule forms hydrogen bonds to oxygen atoms in a neighboring molecule. In **Figure 2.6.4**, the water molecule containing the O(11a) atom is coordinated to the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecule on top and hydrogen bonded to another molecule at the bottom, simultaneously. This collection of inter- and intramolecular hydrogen bonding, in turn, forms planes of hydrogen bonding network in two dimensions. **Figure 2.6.5** shows parallel planes of hydrogen bonding network, one overlapping on top of the other. As can clearly be seen, there is no connection between molecules across planes. **Figure 2.6.6** shows interconnectivity of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecules in the same plane of hydrogen bonding forming a sheet-like arrangement.

2.7 Exchange Reactions of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

The ability of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ to function as a labile source for the sphaerosilicate cubic octamer, $[\text{Si}_8\text{O}_{20}]^{8-}$, was examined by its exchange reactions with both nonmetal and metal chlorides. Among those studied are silyl chlorides, titanium(IV) chlorides, and zirconium(IV) chlorides (**Scheme 2.7.1**).

All exchange reactions between $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and silyl chlorides occurred instantaneously at room temperature, indicated by the immediate formation of silylated products, $\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{X})_8$, and a by-product, Me_3SnCl , in ^1H -NMR spectra. Although these exchange reactions were complete within less than 10 min, half an hour reaction

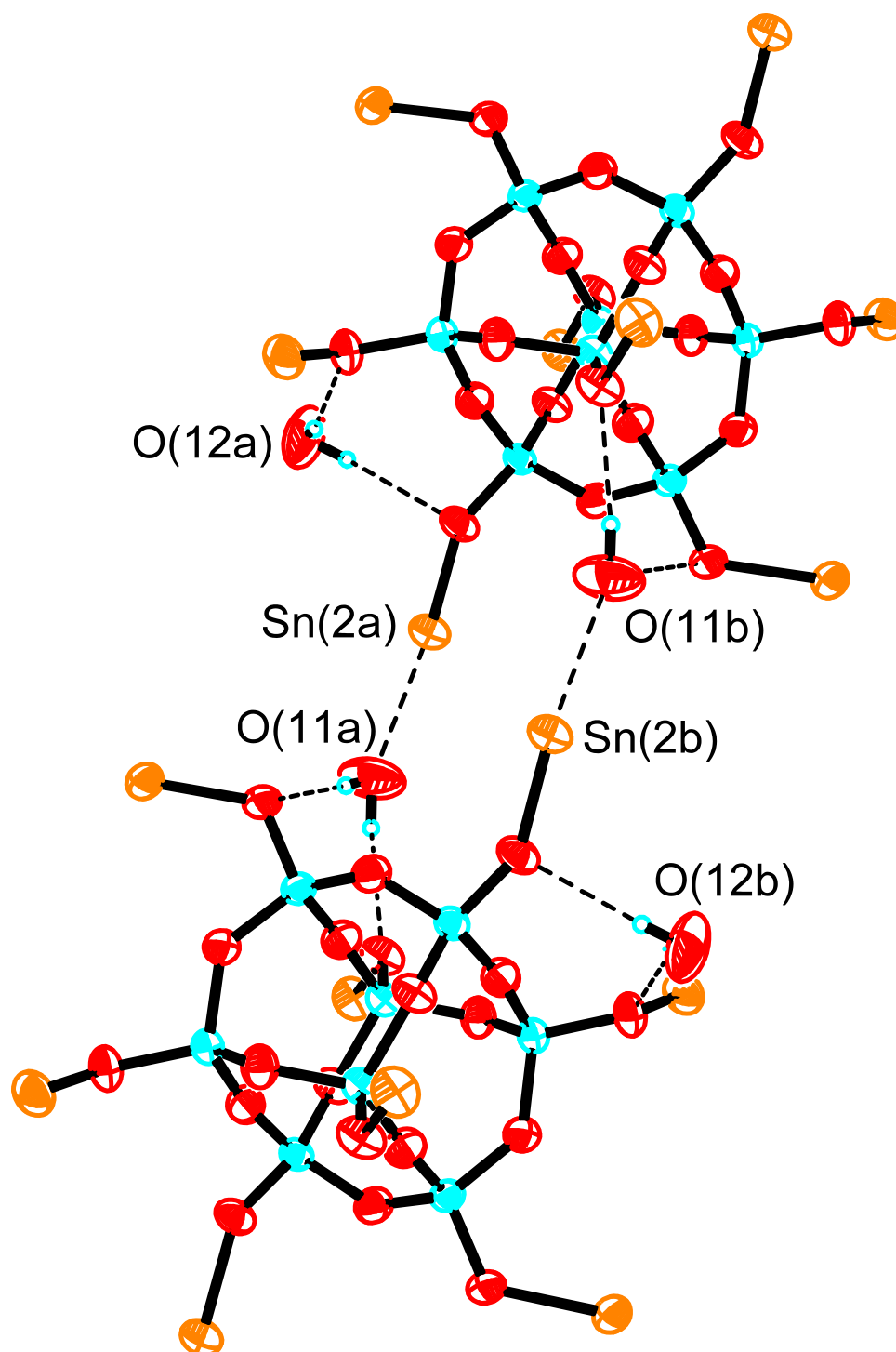


Figure 2.6.4 Interconnection between two $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecules through waters of solvation

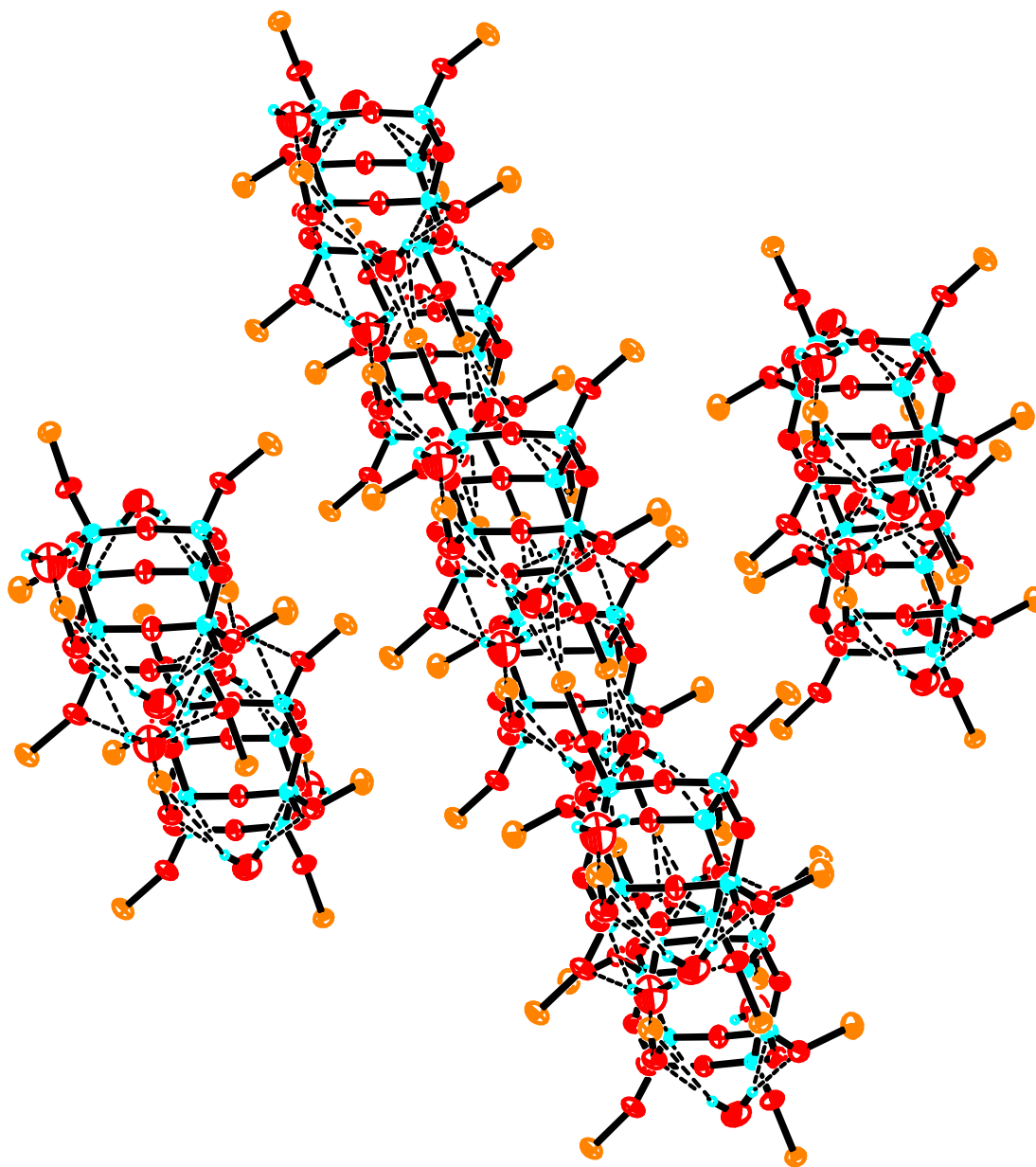


Figure 2.6.5 Crystal lattice of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ in the direction perpendicular to a hydrogen bonding plane

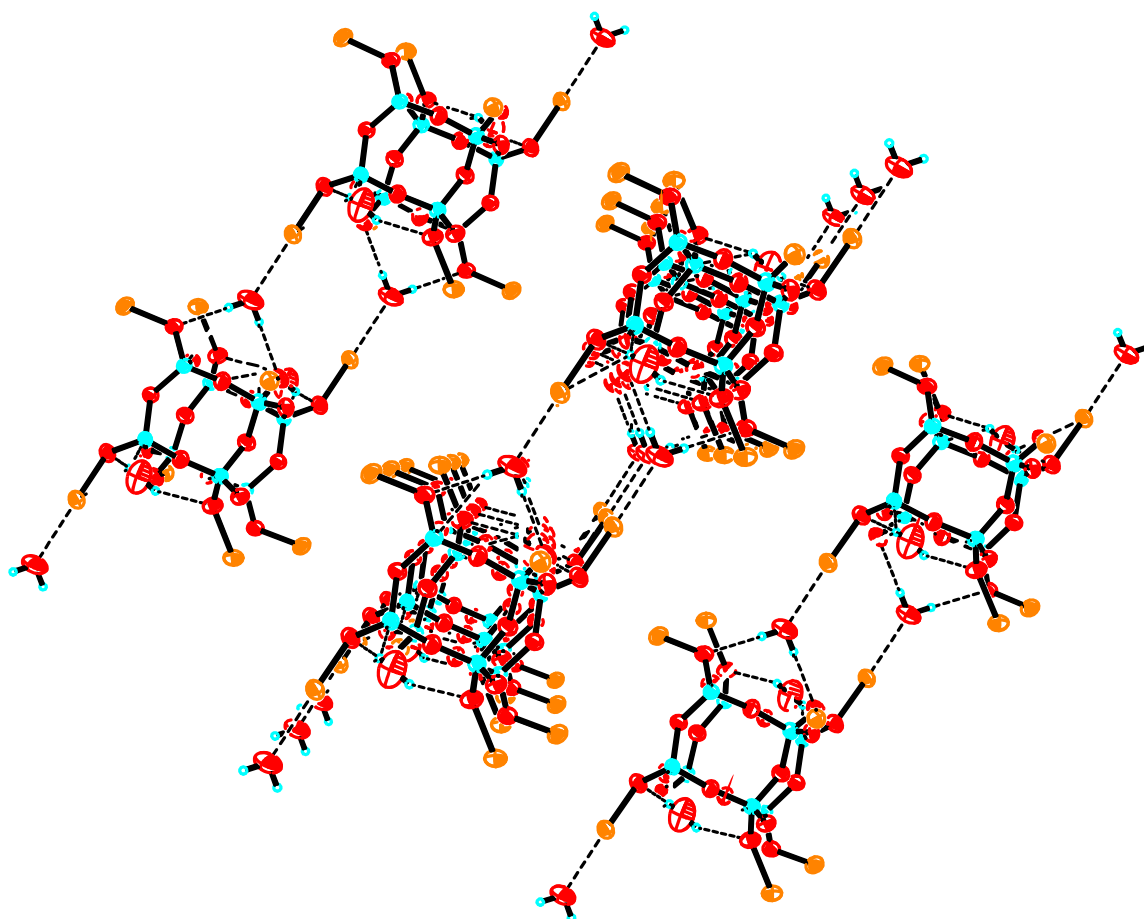
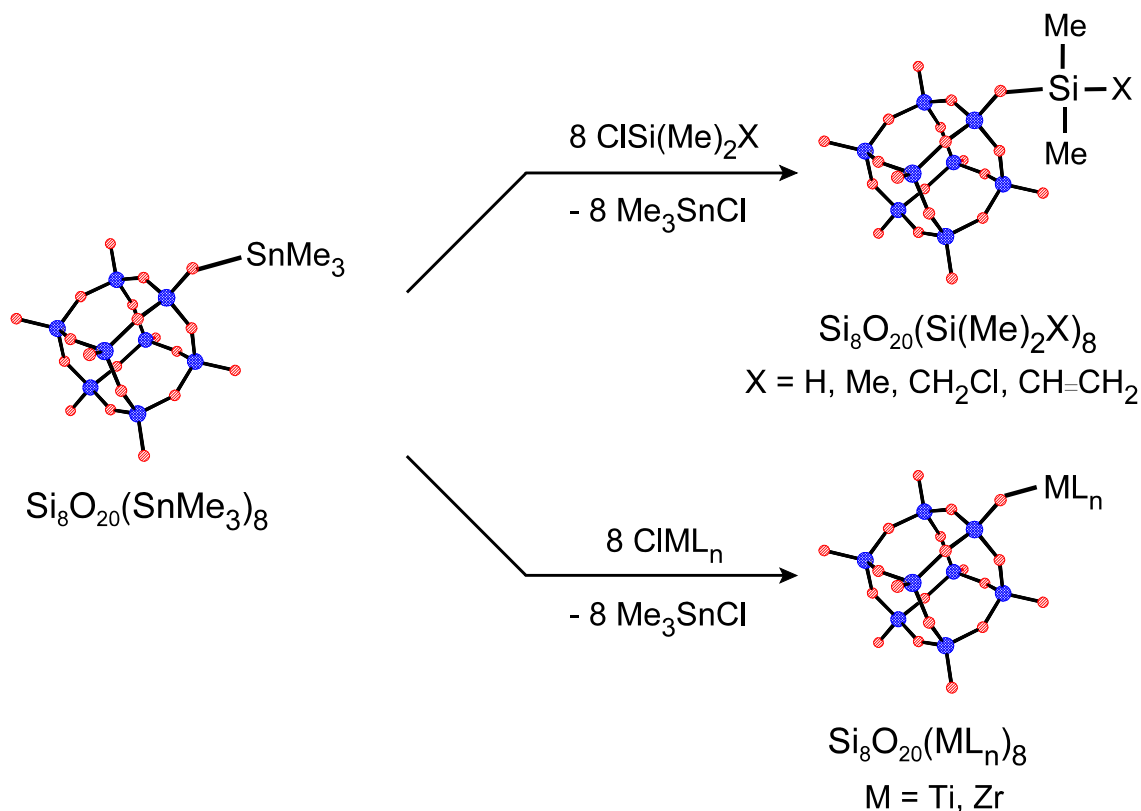


Figure 2.6.6 $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecules interconnected within the same hydrogen bonding plane



Scheme 2.7.1 Exchange reactions of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$

time was allowed in every 50-mg scaled reaction. After removal of the volatiles, pure $\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8$ and $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$ were obtained as crude products at quantitative yields (in 50-mg scaled reactions). Almost quantitative yields of $\text{Si}_8\text{O}_{20}[\text{Si}(\text{Me})_2\text{CH}_2\text{Cl}]_8$ and $\text{Si}_8\text{O}_{20}[\text{Si}(\text{Me})_2\text{CH}=\text{CH}_2]_8$ were obtained after washing with ethanol (to remove excesses of silyl chloride starting materials with high boiling points).

Single crystals of $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$ were obtained. The X-ray structure data and derived structural model are in good agreement with the literature, especially with respect to the observation of disordered SiMe_3 substituents (**Figure 2.7.1**).¹⁴⁰ Crystal structure data of similar derivatives of the cubic octamer, namely $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (from Section 2.6, **Figure 2.7.2**), $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, and $\text{Si}_8\text{O}_{20}\text{Me}_8$,¹⁴¹ are summarized in **Table**

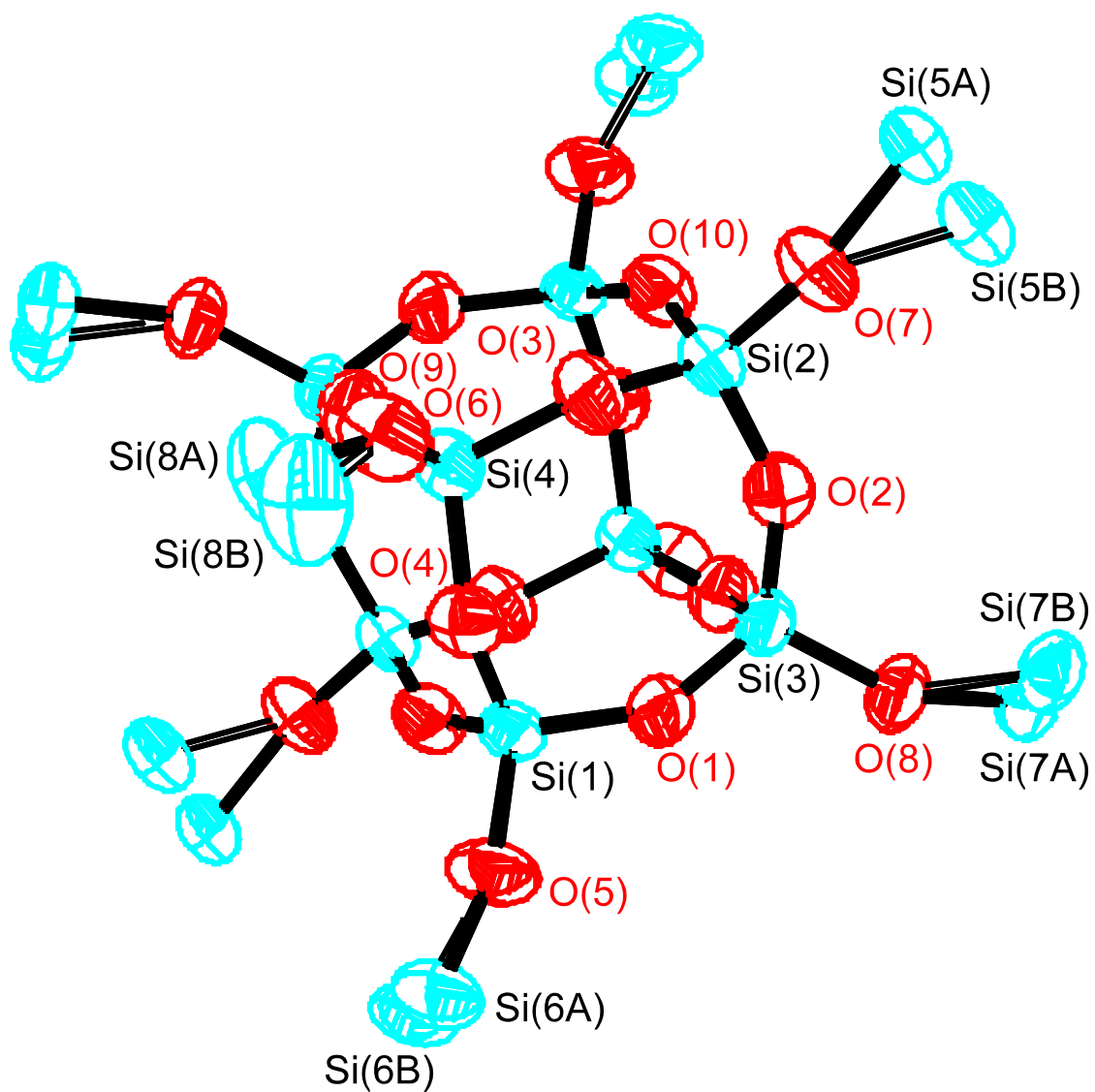


Figure 2.7.1 ORTEP drawing of $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, showing only the Si_8O_{20} core and disorder among pendant SiMe_3 groups. Filled bonds represent major component of disorder

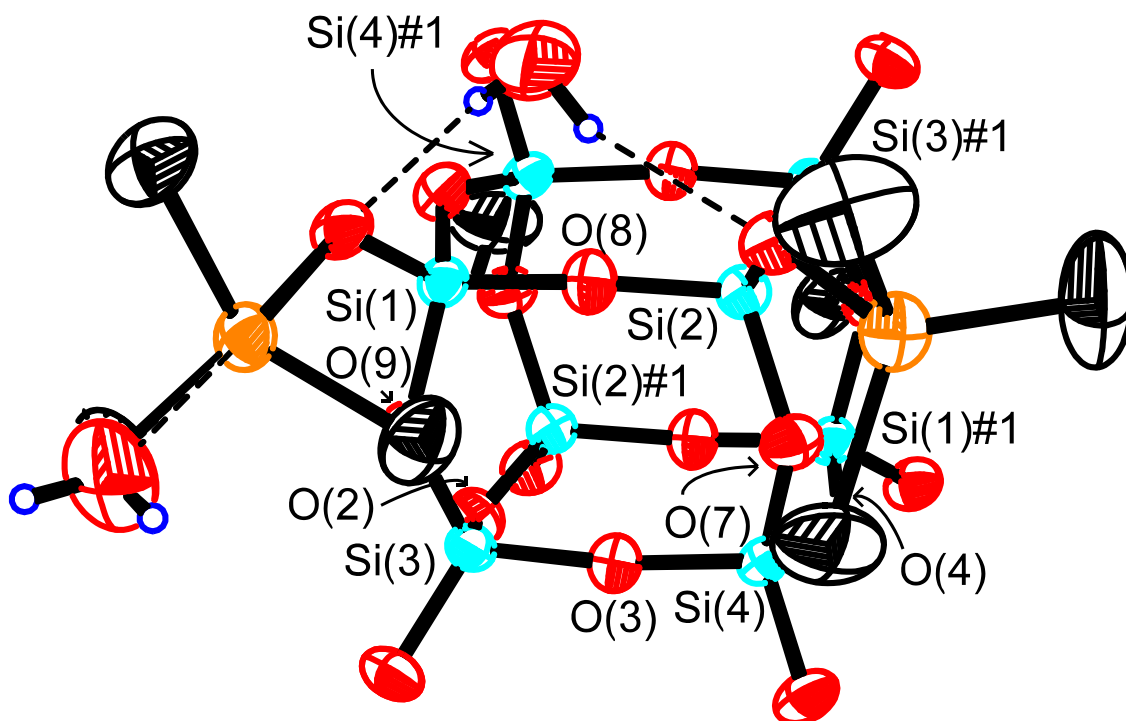


Figure 2.7.2 ORTEP drawing of the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ molecule, with most of the SnMe_3 groups omitted

2.7.1. All of the derivatives have the same crystal system (triclinic) and similar structures (i.e., same Si–O bond lengths). $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, however, showed a unique characteristic in its cubic structure. The cubic core structure in the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was found to be significantly elongated in one direction, while cubic cores in $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, and $\text{Si}_8\text{O}_{20}\text{Me}_8$ were much more symmetric. This elongation of the cubic structure was not a result of any bond elongation (see Si–O bond lengths in **Table 2.7.1**); instead, it occurred through a change in Si–O–Si bond angles around one meridian of the Si_8O_{12} cube (see bolded Si–O–Si angles for $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, **Table 2.7.1**). Although this phenomenon is not unusual among silicate-containing molecules, the bending to this extent (i.e., Si–O–Si bond angle of 171°) is quite an extreme case (see comparison of Si–O–Si bond angles among reported crystal structures of Si_8O_{20} moieties in **Table 2.7.2**).

Group 4 metal chlorides used in the exchange reaction study with $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ are $\text{ClTi}(\text{OC}_3\text{H}_7)_3$, CpTiCl_3 , CpZrCl_3 , and Cp^*ZrCl_3 ($\text{Cp} = \text{C}_5\text{H}_5$ and $\text{Cp}^* = \text{C}_5\text{Me}_5$). All of these exchange reactions occurred instantaneously, as observed by the immediate formation of the by-product, Me_3SnCl , in ^1H -NMR spectra. The completion of reactions within half an hour was also observed by ^1H -NMR, as the signal of the limiting reactant, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, completely vanished. Gel-like solid products yielded from these reactions were unidentified. The product from the reaction of CpTiCl_3 was completely insoluble in typical NMR solvents (i.e., benzene- d_6 and chloroform- d). Products from reactions of other metal chlorides showed broad NMR signals centered around signals of their proton-containing ligands (i.e., centered around the expected chemical shift of OC_3H_7 , Cp , or Cp^* signal in the molecule). These broad signals were not observed in the spectra of their reactants. Broad ^1H -NMR signals and zero to low solubilities indicate the formation of cross-linked cubic octamers with high molecular weights,

Table 2.7.1 Comparison of crystal structure data for $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, and $\text{Si}_8\text{O}_{20}(\text{Me})_8$

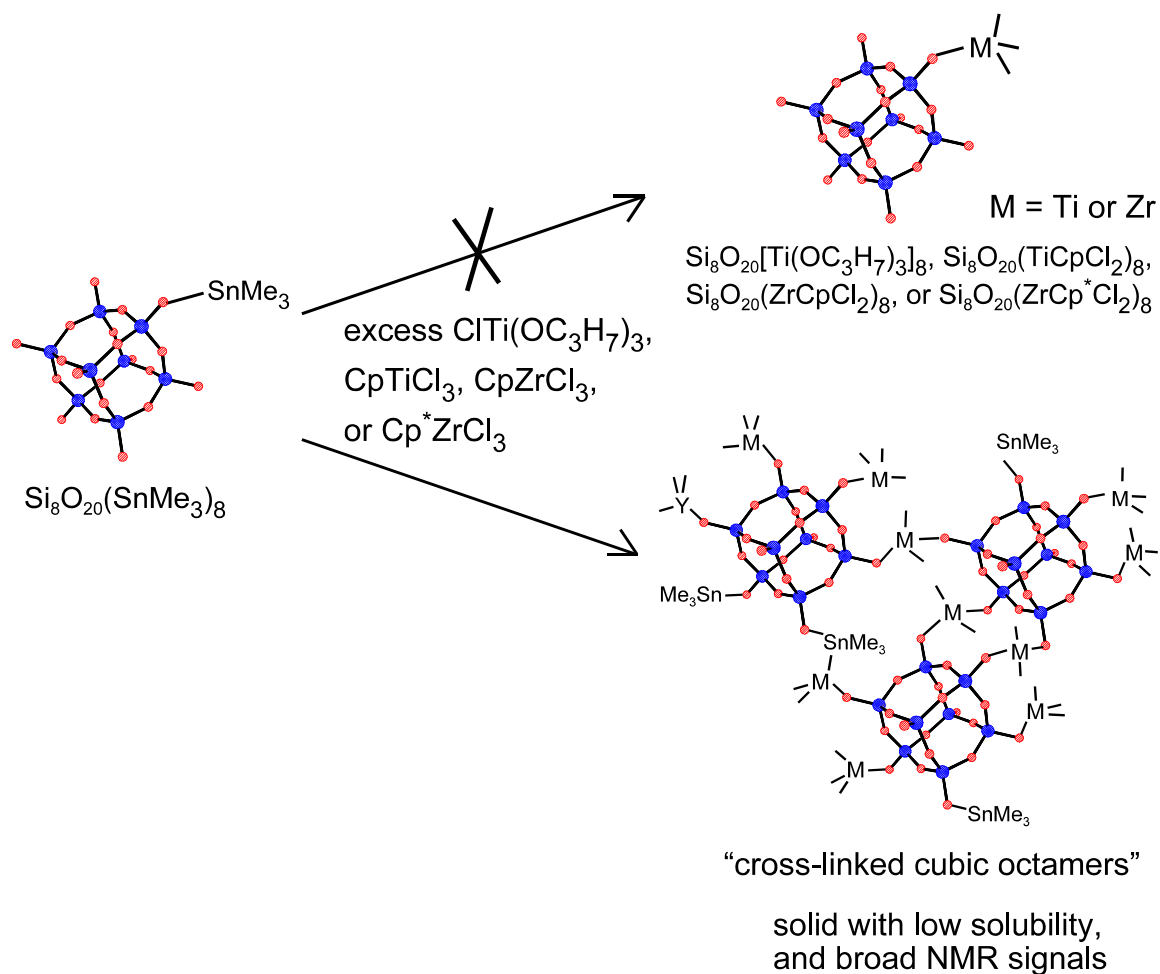
Chemical identity	$\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (Figure 2.7.2)	$\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$	$\text{Si}_8\text{O}_{20}(\text{Me})_8$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Si–O (in cube), Å	min 1.6015(17), max 1.6241(16); avg. 1.6150	min 1.598(3), max 1.611(3)	avg. 1.604
Si–OR (R = SnMe_3 , SiMe_3 , or Me), Å	min 1.5872(16), max 1.5966(16); avg. 1.5913	min 1.581(2), max 1.589(2)	avg. 1.596
Si–O–Si bond angles and Si...Si distances (on the same edge in the cube)	Si(3)–O(2)–Si(2)#1 137.21(11)°, Si(3)...Si(2)#1 3.019 Å; Si(4)–O(4)–Si(1)#1 136.35(10)°, Si(4)...Si(1)#1 3.019 Å; Si(1)–O(9)–Si(3) 140.94(11)°, Si(1)...Si(3) 3.052 Å; Si(2)–O(7)–Si(4) 139.28(11)°, Si(2)...Si(4) 3.037 Å; Si(1)–O(8)–Si(2) 171.10(12)° , Si(1)...Si(2) 3.204 Å; Si(3)–O(3)–Si(4) 172.13(12)° , Si(3)...Si(4) 3.201 Å	Si–O–Si angles: min 147.78(17)°, max 148.12(17)°; Si...Si distances: min 3.076 Å, max 3.094 Å	avg. 148.2°; Si...Si distances were not reported

Table 2.7.2 Comparison of reported Si–O–Si bond angles among known derivatives of cubic octamer

Chemical identity	Si–O (in cube), Å	Si–O–Si (in cube), °
$\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$	1.585 - 1.616(9) ¹⁴⁰	147.2 - 150.5(6) ¹⁴⁰
$\text{Si}_8\text{O}_{20}(\text{SiMe}_2\text{H})_8$	1.599 - 1.607(5) ¹⁴⁰	148.1 - 148.3(3) ¹⁴⁰
$\text{Si}_8\text{O}_{20}(\text{CMe}_2\text{H})_8$	1.586(7) - 1.607(7) ¹⁴²	148.5(5) ¹⁴²
$\text{Si}_8\text{O}_{20}[\text{SiMe}_2(\text{CH}=\text{CH}_2)]_8$	1.597 - 1.608(3) ¹⁴⁰	148.1 - 148.3(3) ¹⁴⁰
$[(\text{CO})_4\text{Co}]_8\text{Si}_8\text{O}_{12}$	1.610(4) - 1.637(4); Si...Si (cube edge) 3.120(1) - 3.164(3) ¹⁴³	147.6(2) - 154.1(3) ¹⁴³
$[\text{NBnMe}_3]_8[\text{Si}_8\text{O}_{20}] \cdot 53.6$ H_2O	1.610(5) - 1.630(6) ¹⁴⁴	148.6(4) - 151.1(3) ¹⁴⁴
$[\text{TMPA}]_4[\text{Si}_8\text{O}_{20}] \cdot 34 \text{ H}_2\text{O}$, TMPA is $[\text{C}_8\text{H}_{20}\text{N}_2]^{2+}$	1.616(2) - 1.628(2) ¹⁴⁵	148.1(2) - 154.3(2) ¹⁴⁵
$[\text{hmbtp}]_2[\text{NEt}_4]_2[\text{Si}_8\text{O}_{20}] \cdot 7$ 0 H_2O , hmbtp is a heterocyclic ammonium (+3) cation	1.613 - 1.638; average 1.626 ¹⁴⁶	143.3 - 160.0; average: 149.8 ¹⁴⁶

instead of the expected single-molecule products (**Scheme 2.7.2**). The cross-linking between two or more cubic octamer cages could occur through reactions of their reactive groups (i.e., Ti–Cl or Zr–Cl, and O–SnMe₃ groups) across cages. No further attempt was made to characterize these low solubility products.

The observation of instantaneous exchange reactions between SnMe₃ groups on the cubic octamer with both nonmetal and metal chlorides ensured the expected function



Scheme 2.7.2 Results from exchange reactions with certain chlorides of Group 4 metal

of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ as a labile source for the sphaerosilicate cubic octamer, $[\text{Si}_8\text{O}_{20}]^{8-}$.

SnMe_3 groups could be replaced by other substituents and various derivatives of cubic octamer could be prepared. Three single-molecule derivatives of cubic octamer, prepared by the exchange reaction of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, will be discussed in Chapter 3.

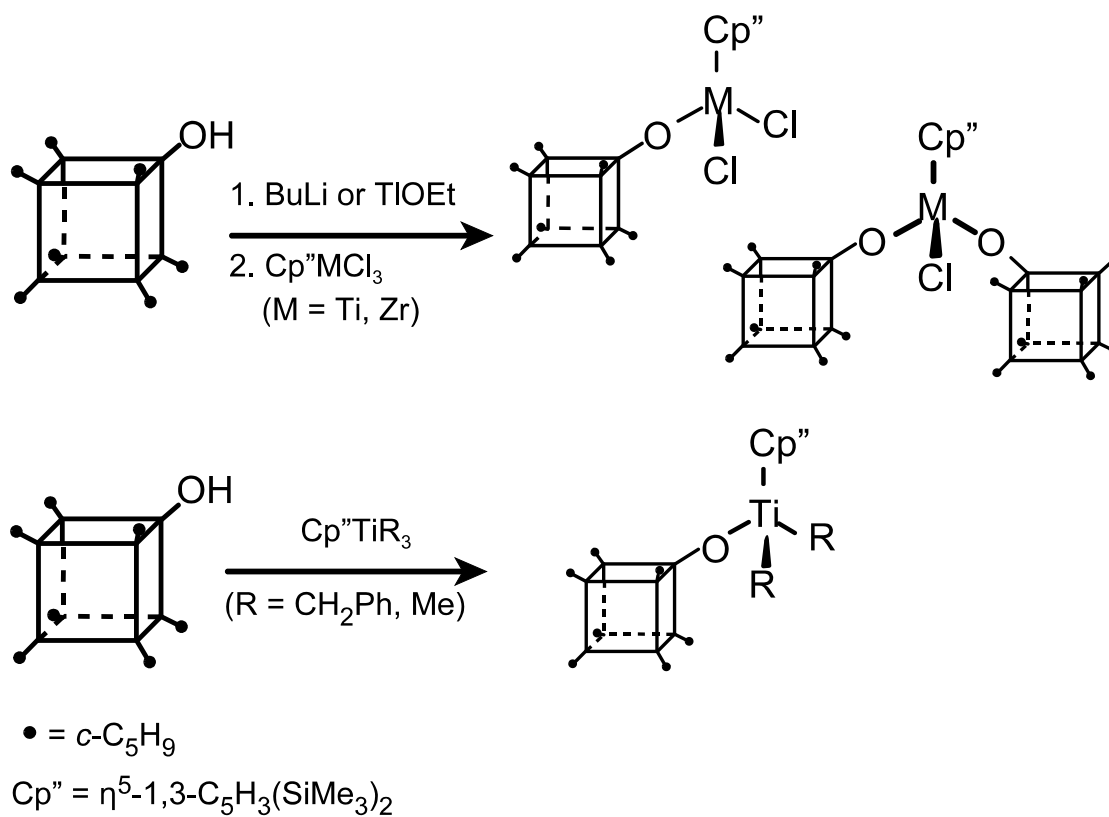
Chapter 3

Syntheses and Olefin Polymerization of Eight-fold Functionalized Metallocene and Half-sandwich Complexes of Cuboctameric Spherosilicate

3.1 Introduction to Chapter 3

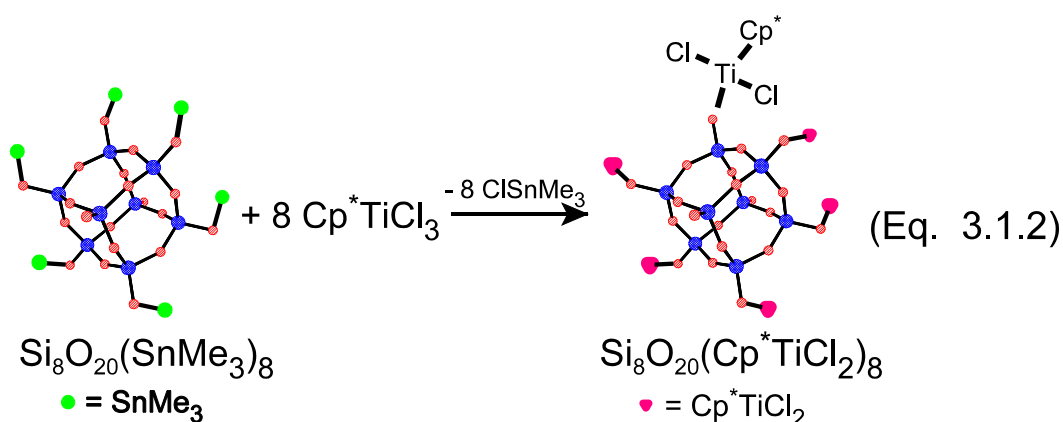
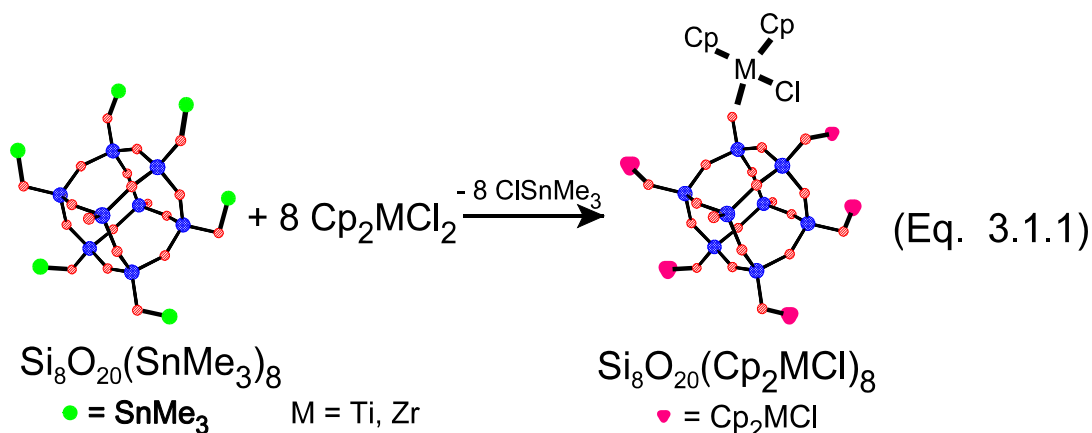
Half-sandwich Group 4 (Ti and Zr) complexes of the cuboctameric spherosilicate have been reported as catalyst models for silica-adsorbed heterogeneous catalyst analogs.^{120-122, 147-150} The complexes that have been prepared are mono-functionalized derivatives of cubic silsesquioxane octamer, representing catalysts adsorbed by their reaction with isolated silanol functionalities as found in partially dehydroxylated silica.¹¹¹ Feher *et. al.* reported the preparation of $(\text{Si}_7\text{O}_{12})(\text{c-C}_6\text{H}_{11})_7\text{ZrCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with a single Zr atom incorporated into the cubic octamer cage.¹²⁰ Duchateau *et. al.* reported the use of a cuboctameric hydroxysilsesquioxane, $\text{Si}_8\text{O}_{12}(\text{c-C}_5\text{H}_9)_7(\text{OH})$, as the starting material for the synthesis of $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{MCp}^*\text{Cl}_2$ and $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{TiCp}^*\text{R}_2$ ($\text{Cp}^* = \eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2$, $\text{M} = \text{Ti or Zr}$, $\text{R} = \text{CH}_2\text{Ph or Me}$) by chloride exchange reaction and protonolysis, respectively (**Scheme 3.1**).^{121, 122} In the chloride exchange reaction (top), the dimeric silsesquioxane $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]_2\text{MCp}^*\text{Cl}$ also formed along with the monomeric product, $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{MCp}^*\text{Cl}_2$.

In a similar manner to the chloride exchange reactions described in the previous chapter, further work indicates facile chloride exchange reactions between both metal and nonmetal chlorides occurs with the trimethyltin group on the spherosilicate $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$. With the use of the eight-fold functionalized $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ as a starting material, chloride exchange reactions occur cleanly on all eight reaction sites, leading to new eight-fold functionalized derivatives of cuboctameric spherosilicate. Examples are syntheses of $\text{Si}_8\text{O}_{20}(\text{MCp}_2\text{Cl})_8$ ($\text{M} = \text{Ti, Zr}$) (Eq. 3.1.1), and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (Eq. 3.1.2) to be described in this chapter.



Scheme 3.1 Syntheses of [Si₈O₁₃(*c*-C₅H₉)₇]MCp''Cl₂ and [Si₈O₁₃(*c*-C₅H₉)₇]TiCp''R₂ by

Duchateau^{121, 122}



3.2 Experimental Section

All manipulations were performed under dry nitrogen atmospheres using a dry box or standard Schlenk techniques. $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was synthesized and dried according to the procedure reported in previous chapter. Bis(cyclopentadienyl)titanium dichloride (97% Cp_2TiCl_2 , Acros) and bis(cyclopentadienyl)zirconium dichloride (99% Cp_2ZrCl_2 , Strem) were checked by ^1H -NMR and used without further purification. Pentamethylcyclopentadienyltitanium trichloride (98% Cp^*TiCl_3 , Strem) was checked by ^1H -NMR and purified by crystallization in methylene chloride/hexanes. Solvents were dried as follows: benzene (Na), *n*-butylchloride (CaH_2), chloroform (molecular sieve),

diethyl ether (Na/K), hexanes (Na/K), methylene chloride (CaH_2), THF (Na), and toluene (Na). In all the syntheses described below, solvents were degassed by pumping during repeated freeze-thaw cycles and vapor transferred under vacuum (0.050 mm Hg) to reaction vessels. All glassware was silylated with chlorotrimethylsilane in order to prevent side reactions between transition metal chlorides and silanol groups on glass surfaces (see Section 2.2.4).

NMR solvents, benzene- d_6 , chloroform- d , and methylene chloride- d_2 (from Cambridge Isotope), were dried over Na/K alloy, molecular sieve, and calcium hydride, respectively. These solvents were vapor transferred (0.050 mm Hg) into clean Teflon vacuum bulbs, stored, and used under nitrogen atmosphere in dry box. ^1H NMR spectra were acquired on either a Bruker AC 250 MHz or a Varian Mercury 300 MHz NMR spectrometer. ^{13}C NMR spectra were acquired on a Bruker Avance 400 MHz NMR spectrometer. ^{29}Si and 2D NMR measurements (HSQC) were recorded on a Varian INOVA 600 NMR spectrometer. All ^{13}C , ^{29}Si , and 2D NMR samples were prepared as saturated solutions although $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ samples have extremely low solubilities in NMR solvents. A paramagnetic relaxation agent, chromium(III) acetylacetonate [$\text{Cr}(\text{acac})_3$], was added. All ^{29}Si NMR spectra were acquired at 119.149 MHz with 45° pulse angle and 2-s relaxation delay, in the presence of ca. 29 mM $\text{Cr}(\text{acac})_3$ (7 mg $\text{Cr}(\text{acac})_3$ in 0.7 mL solvent), as a paramagnetic relaxation time agent. In the HSQC (^{13}C - ^1H) experiment, the coherence selection was obtained using pulsed field gradients along the Z direction. (The data of the indirect dimension were zero filled to be 2 x number of acquired data increments.) The number of collected transients were 16–64 and time increments 256–512. With 1-s relaxation delay at 69 Hz cross polarization, the acquisition time was 0.11 s.

Chemical shifts were referenced internally to benzene- d_6 (^1H -NMR δ 7.15, ^{13}C -

NMR δ 128.0) or chloroform-*d* (residual ^1H -NMR δ 7.26, ^{13}C -NMR δ 77.0) for ^1H - and ^{13}C -NMR. Cubic octamer silicic acid trimethylsilyl ester, $\text{Si}_8\text{O}_{20}(\text{SiMe}_3)_8$, was used as an external reference for ^{29}Si -NMR (δ 12.4 and -108.6 in benzene-*d*₆).

The preparation of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was performed in an H-shaped crystallization chamber, which has two legs as areas for growing crystals and a medium glass fritted disc in the connecting piece (**Figure 3.2.1**). Reacting solids were added to one leg of the H inside the dry box. The apparatus was sealed and removed from the dry box, hooked to a Schlenk line and evacuated. Solvents were vapor transferred to the reacting solids and thawed. The resulted reaction mixture was quickly filtered by passing through the connecting piece, to remove any undissolved particles. The reaction mixture was evacuated briefly before it was set still for crystallization to take place. In vapor-phase mixed solvent systems (e.g., hexanes/methylene chloride vapor diffused solvents), solvent vapor was allowed to slowly diffuse through this glass fritted disc at the connecting piece.

3.2.1 Synthesis of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

The progress of reaction between $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and a large excess of Cp_2TiCl_2 (δ 5.91) in benzene-*d*₆ at 50 °C was followed by ^1H -NMR. At this temperature, the reaction occurred rapidly. After 10 min, several signals of new SnMe_3 -containing intermediates (δ 0.55 - 0.2 ppm) were observed. At 1 h 30 min, the reaction leading to the desired product, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ (δ 6.24), was essentially complete. Even after another hour (total reaction time: 2 h 30 min), no further reaction was observed. A significant amount of golden yellow microcrystalline product was noticed in the NMR tube.

Large-scale preparation of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ was accomplished as follows.

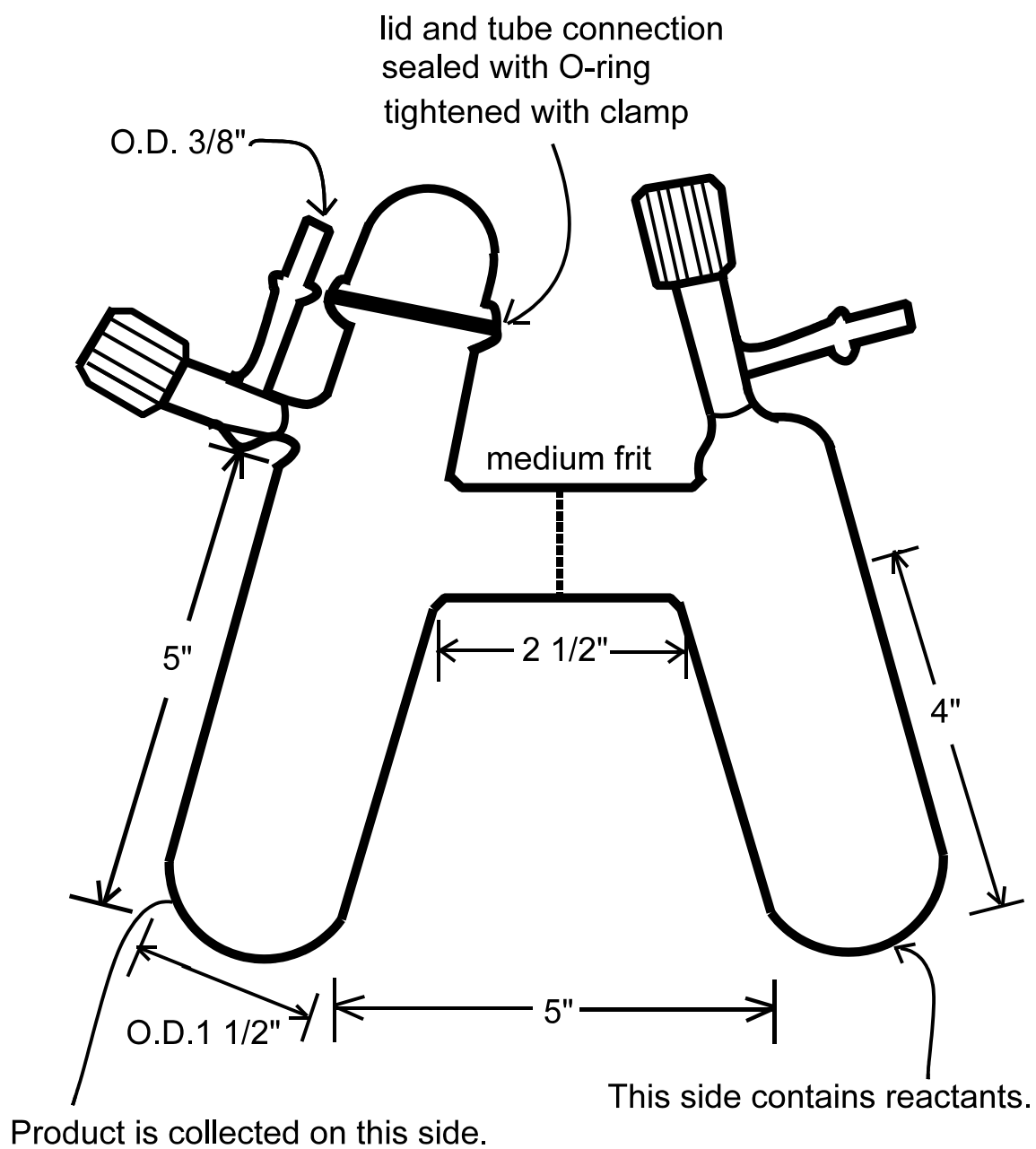


Figure 3.2.1 H-shaped crystallization chamber

$\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (0.47 g, 0.25 mmol, 2.0 mmol SnMe_3 reaction site) was weighed into one side of an H-shaped crystallization vessel (H-tube) and Cp_2TiCl_2 (1.04 g, 4.1 mmol, 2.1 eq/ SnMe_3) was weighed into the other side of the same crystallization vessel. Benzene was vapor transferred into both reactants. While the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ /benzene solution was clear and colorless, the Cp_2TiCl_2 /benzene solution was clear deep red in the presence of some undissolved Cp_2TiCl_2 . The reaction was started when the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ /benzene solution was poured through a medium frit to the Cp_2TiCl_2 /benzene solution. At 50 °C the yellow microcrystal gradually precipitated out of deep red solution. After 2 h, the undissolved Cp_2TiCl_2 crystals disappeared. The reaction was stopped by removing all volatiles after 2 h 30 min. The golden yellow microcrystalline $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ was washed with methylene chloride several times until the orange-red color of Cp_2TiCl_2 was not observed in the wash solution. After the removal of methylene chloride, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ (0.470 g, F.W. 2252.74, 0.21 mmol, 84% yield) was obtained.

$\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ was characterized by ^1H , ^{13}C , ^{29}Si -NMR, single crystal X-ray diffraction, and elemental analysis (EA). Several samples of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ sent for EA (at Robertson Microlit Laboratories, Inc.) were synthesized in THF, dried under vacuum (0.025 mm Hg) for 19 h at room temperature, before being flame sealed (0.025 mm Hg). Simultaneously, analogous samples treated identically were checked by ^1H -NMR to confirm the identity of samples sent for EA.

3.2.2 Synthesis of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

The progress of reaction between $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and a large excess of Cp_2ZrCl_2 (δ 5.86) in benzene- d_6 was followed by ^1H -NMR. Reaction took place immediately even at room temperature, as was evidenced by the expected formation of the ClSnMe_3 (δ

0.22) by-product and the complete loss of the SnMe_3 signal for the $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ starting material (δ 0.36) within 5 min. The formation of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ (δ 6.22) as the major product along with other minor Cp containing products (δ 6.70 to 6.00) was observed as well. The completion of reaction was ensured by heating at 50 °C for 5.5 h after which white precipitate of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ was observed in the NMR solvent.

Large-scale preparation of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ was carried out as follows.

$\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (0.95 g, 0.51 mmol, 4.1 mmol SnMe_3 reaction site) and Cp_2ZrCl_2 (1.60 g, 5.3 mmol, 1.3 eq/ SnMe_3) were weighed under inert atmosphere into the same leg of an H-shaped crystallization vessel (H-tube). Under vacuum, dry *n*-butylchloride (or benzene) was vapor transferred to dissolve solid reactants. Before the reaction was allowed to proceed at higher temperature, the slightly cloudy solution was filtered through a medium glass-fritted disc to another leg of the H-tube. The clear reaction mixture was stirred at 50 °C for 5 h 30 min, even though a lot of white precipitate was observed after a few hours. The reaction was terminated by the removal of volatiles under 0.050 mm Hg at room temperature. The white, crude mixture from the reaction weighed 1.082 g. Almost pure $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ was obtained by repetitive washes with *n*-butylchloride in order to dissolve the excess starting material, Cp_2ZrCl_2 , from the less soluble product, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$. However, during the third wash of the product, the white powder of the $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ product started to dissolve into *n*-BuCl and it is advisable to dry the product under vacuum after a few washes and re-do the wash on dry $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$. The once-dried microcrystalline $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ was much less soluble in any solvent. After the removal of most *n*-butylchloride under vacuum, white fine powder of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ (0.640 g, F.W. 2699.61, 48% yield) with 81% purity (along with residual Cp_2ZrCl_2 , see **Figure 3.4.1**) was obtained. The ^1H -NMR of mother liquor after volatile removal indicated the presence of unreacted Cp_2ZrCl_2 as the major

species and a significant amount of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$. Although benzene could be used as solvent for this reaction, the product obtained from reaction in *n*-BuCl was always more pure.

The $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ sample sent for elemental analysis was synthesized and washed in *n*-butylchloride. The removal of residual *n*-butylchloride was accomplished, without the decomposition of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, by heating the sample at 50 °C at 0.025 mm Hg for 4 h. The sample was flame sealed under 0.025 mm Hg and sent for the elemental analysis at E&R Microanalytical Division, Complete Analysis Laboratories, Inc. (CALI, Parsippany, NJ). (Samples were first sent to Robertson Microlit Laboratories, Inc. and %C were repeatedly reported at ca. 1.5% lower than the calculated value. These samples (from the same synthesis batch) were subsequently analyzed correctly by E&R Microanalytical Division.)

3.2.3 Synthesis of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$

At room temperature, the progress of the reaction between $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and excess Cp^*TiCl_3 was followed by ^1H -NMR in chloroform-*d*. Reaction occurred within 20 min as was evidenced by the formation of the by-product ClSnMe_3 (δ 0.67 in chloroform-*d*). $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ (δ 2.32) started to form after 1 h and the intensity of the signal of starting material $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (δ 0.41) drastically decreased. As time went by, the amount of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ increased, until $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ was used up at 4 h. The reaction was allowed to proceed overnight, after which not much change was observed.

A larger quantity of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was prepared in high purity as microcrystalline product from the reaction between $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ and Cp^*TiCl_3 in hexanes/methylene chloride mixed solvent (1:3 v/v). To $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ (100 mg, 0.0539 mmol, 0.431 mmol SnMe_3 reaction site) and Cp^*TiCl_3 (152 mg, 0.515 mmol, 1.2

eq/ OSnMe_3 reaction sites), 35 mL of methylene chloride was vapor transferred. To the other side of the crystallization chamber, 11 mL of hexanes was cannulated. Before crystallization was allowed to take place in a hexanes-methylene chloride mixture obtained by vapor diffusion at room temperature, the crystallization chamber was evacuated briefly to establish a slight vacuum (0.200 mm Hg). After five days, yellow fine precipitate of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was observed. More precipitate of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was obtained after six days mixed with red needle-shaped crystals of the starting material, Cp^*TiCl_3 . The precipitate was washed with hexanes (3 times or until the wash is colorless). Pure $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ (10 mg, F.W. 2576.79, 7% yield) was normally obtained with small-scaled reaction (100 mg $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ reactant) after five days reaction time and several washes in hexanes, in which a significant amount of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ dissolved. A preparative-scaled reaction (1 g $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ reactant) could be accomplished at the expense of lower purity of the $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ product.

3.2.4 Ethylene and Styrene Polymerizations

Handling of chemicals was done under an inert atmosphere using a dry box and standard Schlenk techniques. Catalyst precursors, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$, were prepared in non-coordinating (i.e., hexanes) or weakly coordinating solvents (i.e., methylenechloride, *n*-butylchloride), according to procedures reported in Section 3.2.1. The polymerization solvent, toluene, was freshly distilled over Na-K alloy before polymerization. The antioxidant for thermal stabilization of polyolefins, IRGANOX[®] 1076 or octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate (CAS number: 2082-79-3, F.W. 531), was obtained from Ciba Specialty Chemicals, Inc.

Cocatalysts, including trimethylaluminum (AlMe_3 , 25 wt % in hexanes), di-*i*-butylaluminum chloride (97% $(\text{C}_4\text{H}_9)_2\text{AlCl}$, Strem), tris(pentafluorophenyl)boron (min. 97% $\text{B}(\text{C}_6\text{F}_5)_3$, Strem), and modified methylaluminoxane type 3A (MMAO-3A, *ca.* 7 wt % Al in toluene, Akzo-Nobel), were used without further purification. MMAO-3A solution was stored at -20 °C and used under nitrogen atmosphere at room temperature. The exact concentration of Al in various lot numbers of MMAO-3A solutions ranged from 6.76 to 7.25 wt %; its exact concentration was analyzed by the company. Since MAO solutions are known to change their compositions with time (i.e., aging), the ethylene polymerization catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{MMAO}$ (300 Al:Ti) at room temperature was performed as a standard “checkpoint” on a regular basis. The reproducibility of catalytic activities under this set of conditions was used as an indication of the activity of MMAO as a function of storage time and of the comparable activities of MMAO from various lots. It is also worth mentioning that MMAO-3A (*ca.* 7 wt %), purchased from Akzo-Nobel, was at least ten times more reactive than methylaluminoxane (MAO, 10 wt % solution in toluene, Aldrich), of which negligible catalytic activities were observed. In this study, catalytic activities obtained by using MMAO-3A as a cocatalyst are reported.

CP grade ethylene (C_2H_4) with 99.5% minimum purity (National Welders) in cylinder size 200 (with 30 lbs. content) was used in ethylene polymerization. Other specifications of this CP grade ethylene are oxygen 10 ppm, carbon monoxide 50 ppm, acetylene 10 ppm, and moisture 75 ppm. Research grade ethylene (minimum purity of 99.99%, oxygen < 5 ppm, carbon monoxide < 1 ppm, acetylene < 1 ppm, and moisture < 5 ppm, in cylinder size 200, from National Welders) was also tested. To our surprise, catalytic activities when research grade ethylene was used were slightly lower than those of CP grade ethylene. In this study, only catalytic activities from CP grade ethylene polymerization were therefore reported. Styrene (> 99.5% $(\text{C}_6\text{H}_5)\text{CH}=\text{CH}_2$ with 10 to 20

ppm *p-tert*-butylcatechol, stabilized p.a. from Acros) was distilled over calcium hydride in vacuo and stored over molecular sieves at 5 °C under a nitrogen atmosphere.

Ethylene polymerizations were carried out in a Parr Series 4560 minireactor with the total volume of 600 mL, maximum working pressure of 3000 psi, and maximum operating temperature of 350 °C. To reduce the magnitude of reactor fouling, a glass liner with silylated inner surface was used (as a reaction vessel) inside the stainless steel reactor. A series 4841 temperature controller and model A1120HC Parr magnetic drives for motor were also employed in controlling the temperature and stirring of the reaction content at a constant speed.

A typical procedure for ethylene polymerization catalyzed by the catalyst precursor $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ is as follows. In a dry box, a $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ solution (ca. 9.4 mM Ti) was prepared by dissolving $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ (33 mg, F.W. 2247.67, 0.12 mmol Ti) in freshly distilled toluene (12.5 mL), yielding a reddish orange, clear solution. (This catalyst precursor solution was used within one week after its preparation. During the period of one week, it was kept at -20 °C under nitrogen atmosphere.) Into a Parr minireactor, freshly distilled toluene (100 mL as a solvent), cocatalyst solution (see **Table 3.2.4.1** for the amount), and $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ solution (2.50 mL of 9.4 mM Ti solution, 23 μmol Ti catalyst precursor) were added, yielding a pale orange, clear solution. (Various orders of catalyst mixing, e.g., catalyst precursor + cocatalyst + solvent, did not affect measured catalytic activities.) The reactor was sealed immediately and brought from the dry box to the reactor set-up. Since we were not equipped with a catalyst addition chamber, the active catalyst was prepared in the manner described above and the reaction was considered to start at the moment the monomer (ethylene gas) was fed into the reactor. The time interval between the mixing of cocatalyst and catalyst precursor and the introduction of monomer was in the range of 5 to 7 min. The

Table 3.2.4.1 Amounts of cocatalysts in ethylene polymerization

Cocatalyst	Reaction condition	Amount added, mL
AlMe_3 (25 wt % in hexanes)	1000 Al:Ti	8.00
$\text{Al}(i\text{-Bu})_2\text{Cl}$	1000 Al:Ti	4.70
$\text{Al}(i\text{-Bu})_2\text{Cl}$, $\text{B}(\text{C}_6\text{F}_5)_3$	1000 Al:6 B: Ti	4.70 mL $\text{Al}(i\text{-Bu})_2\text{Cl}$, 76 mg $\text{B}(\text{C}_6\text{F}_5)_3$
MMAO-3A (ca. 7 wt % Al)	150 Al:Ti	3.50
	250 Al:Ti	5.50
	300 Al:Ti	7.00
	600 Al:Ti	14.00
	1000 Al:Ti	23.4
	ca. 2000 Al:Ti (The exact ratio is 1700 Al:Ti.)	40.0

reaction was stirred at a studied temperature (room temperature or 60 °C) under a constant pressure of ethylene (5.4 atm). A significant increase in temperature was observed as a result of the exothermic nature of polymerization reaction. Temperature readings were recorded. After 30 min, ethylene gas feed was stopped. The reaction mixture was poured into acidified methanol or acidified ethanol (100 mL, 1% V/V HCl/MeOH or 1% V/V HCl/EtOH). The resulted white solid polyethylene (PE) was washed with methanol or ethanol until the wash solution was no longer acidic.

IRGANOX® 1076 in the amount of 0.2% of wet PE mass was added to stabilize the PE before drying at 60 °C for 17 h. The catalytic activity was calculated in the unit of $\text{kg}/(\text{mol}\cdot\text{h}\cdot\text{atm})$, where kg is the mass of dry PE (kilogram PE), mol refers to the amount of catalyst precursor initially added (mole of Ti or Zr), h is the reaction time (hour), and atm is the pressure of ethylene monomer (atmosphere). Each set of

polymerization conditions was repeated at least once and the averaged value of reproducible catalytic activities was reported.

The above procedure was also followed in ethylene polymerization catalyses of other catalyst precursors, by replacing the $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ solution (ca. 9.4 mM Ti) with each of the following catalyst precursor solutions (ca. 9.4 mM Ti or Zr): $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ (38 mg, F.W. 2599.57, in 12.5 mL toluene), $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ (38 mg, F.W. 2576.79, in 12.5 mL toluene), Cp_2TiCl_2 (30 mg in 12.5 mL toluene), Cp_2ZrCl_2 (35 mg in 12.5 mL toluene), and Cp^*TiCl_3 (34 mg in 12.5 mL toluene). All mixed catalyst precursor/cocatalyst solutions were transparent. A change in color was evident only in the case of half-sandwich complexes/MMAO catalyst systems (i.e., $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$ and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$) in which color changed from bright orange to yellow, green, and deep violet indicating the reduction of Ti(IV) to Ti(III) within 5 min.

Styrene polymerizations were performed in round-bottomed flasks with side arms. A typical procedure for styrene polymerization catalyzed by the catalyst precursor $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ is as follows. In a dry box, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ solution (ca. 3.2 mM Ti) was prepared by dissolving $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ (26 mg, F.W. 2576.79, 81 μmol Ti) in freshly distilled toluene (25.0 mL), yielding a bright orange, clear solution. (This catalyst precursor solution was used within one week after its preparation. During the period of one week, it was kept at $-20\text{ }^\circ\text{C}$ under nitrogen atmosphere.) Under nitrogen flow, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ solution (2.5 mL of 3.2 mM Ti solution, 8.1 μmol Ti), and the cocatalyst MMAO-3A (see **Table 3.2.4.2** for the amount) were injected into the reaction flask. The catalyst precursor and cocatalyst were allowed to react for 5 min at room temperature in order to maintain consistency with the ethylene polymerization; during this time, a color change from bright orange to yellow, green, and deep purple was observed. Freshly distilled toluene (25 mL as a solvent) and the monomer styrene (4.4 mL, 38 mmol, 4757

Table 3.2.4.2 Amounts of MMAO-3A in styrene polymerization

Reaction condition	Amount added, mL
100 Al:Ti	0.80
300 Al:Ti	2.40
1000 Al:Ti	8.00

styrene:Ti) were then injected and the reaction was considered starting. After 30 min at a studied temperature (room temperature or 50 °C in a temperature-equilibrated silicon oil bath), the reaction mixture was exposed to air and poured into acidified methanol or acidified ethanol (100 mL, 1% V/V HCl/MeOH or 1% V/V HCl/EtOH). The resulted white solid polystyrene (PS) was washed with methanol or ethanol until the wash solution was no longer acidic. IRGANOX® 1076 at the amount of 0.1% of wet PS mass was added to stabilize the PS before its drying at 60 °C for 17 h. The catalytic activity was calculated in the unit of kg/(mol·h), where kg is the mass of dry PS (kilogram PS), mol is the amount of catalyst precursor initially added (mole of Ti), and h is the reaction time (hour). Each set of polymerization conditions was repeated at least once and the averaged value of reproducible catalytic activities was reported.

The above procedure was followed in styrene polymerization catalyzed by Cp^*TiCl_3 , by replacing the $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ solution (ca. 3.2 mM Ti) with Cp^*TiCl_3 (24 mg in 25.0 mL toluene, ca. 3.3 mM Ti). The appearance and color change in the reaction of Cp^*TiCl_3 were identical to that observed for $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$.

Molecular weights and polydispersities of selected polyethylene and polystyrene samples were analyzed by gel permeation chromatography (GPC). The analyses were performed by Eastman Chemicals, Inc., using a Polymer Labs (PL) 210 GPC system and 1,2,4-trichlorobenzene (TCB) as the solvent. The TCB for the analyses and sample

preparation contained approximately 2 g of 2, 6-di-*tert*-butyl-4-methylphenol (F.W. 220.36) per 4000 mL of TCB as an antioxidant. GPC samples were prepared by dissolving approximately 2.5 mg of polymer resin in about 2 mL of TCB. The samples were dissolved at 160 °C for 4 h in a heater/stirrer and were filtered prior to analysis using glass wool stuffed pipettes in an aluminum block that was maintained at 160 °C. GPC columns and detectors were maintained at 160 °C. The detectors were Viscotek 210R viscometer and PL refractive index detector. The injection loop was 200 μ L and the flow rate was 1.0 mL/min. The column set consisted of three PLgel Mixed B 300 x 7.5 mm columns and one PLgel Mixed B 50 x 7.5 mm column. The system was calibrated using PL narrow molecular weight distribution polystyrenes ranging from 7.5 million to 7 000 g/mol. Molecular weight calculations were performed using the Universal Calibration method, in which a standard calibration plot between a viscometric hydrodynamic volume function ($\log[\eta]M$) and elution volume was used. This standard calibration plot is applicable to any polymer, regardless of its chemical nature or morphological structure.¹⁵¹

The tacticity of representative polystyrene (PS) samples was analyzed by ¹³C-NMR in chloroform-*d* at 50 °C on a Bruker Avance 400 MHz NMR spectrometer. Sample preparation was achieved by gradually dissolving PS resin (64 mg) in chloroform-*d* (0.8 mL) as follows: the first 0.5 mL of chloroform-*d* was added to 20 mg of PS resin in a 0.5-mm NMR tube. After a clear gel-like solution was observed, the rest (44 mg) of the PS was added and shaken well in the solution. The rest 0.3 mL of chloroform-*d* was then added to dissolve the remaining solid PS. The temperature of the obtained homogeneous, clear, gel-like solution was equilibrated at 50 °C before the NMR tube was capped. ¹³C NMR spectra were acquired at 100.653 MHz with 57° pulse angle and 3-s relaxation delay, for 2 000 transients. Exponential multiplication with a line

broadening of 2.0 Hz was applied in working up the data. Chemical shift was referenced internally to chloroform-*d* (^{13}C -NMR δ 77.0).

3.3 Identity of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

Derivatives of cubic octamer eight-fold functionalized by equivalent groups, including $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, are molecules of high symmetry. All eight substitution sites (i.e., $\equiv\text{Si}-\text{O}-$ on eight corners of the cubic structure) and substituents on them are symmetry related. Consequently, they are magnetically equivalent. This drastically simplifies the pattern of NMR spectra for there is only one group of representative signals for eight substitution sites and their substituents.

The magnetically equivalent Cp or $\eta^5\text{-C}_5\text{H}_5$ aromatic rings of the Cp_2Ti groups were detected as a singlet signal in ^1H (δ 6.24 in benzene-*d*₆, **Figure 3.3.1**) and ^{13}C NMR spectra (δ 118.50 in benzene-*d*₆, obtained from an HSQC experiment, **Figure 3.3.2**). The eight-fold functionalization of cubic octamer was confirmed by the presence of only one ^{29}Si NMR signal (δ -106.34 in chloroform-*d*, **Figure 3.3.3**) which can only result from highly symmetric structure. (The broad background signal is resulted from the glass NMR tube.) The observed ^{29}Si NMR chemical shift is similar to the chemical shift of -111.76 ppm (in toluene-*d*₈) reported in a similar compound, $[\text{Si}_8\text{O}_{13}(\text{C-C}_5\text{H}_9)_{17}]\text{TiCp}''\text{Cl}_2$ ($\text{Cp}'' = \eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2$).¹²¹

The sample sent for the elemental analysis (EA) was obtained from the reaction in THF. Its ^1H NMR spectrum confirmed the identity of this specific sample as $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8 \cdot 2 \text{ THF}$. With the molecular formula $\text{C}_{88}\text{Cl}_8\text{H}_{96}\text{O}_{22}\text{Si}_8\text{Ti}_8$, the EA results are in good agreement with the theoretical values as follow: %C 44.21 (theoretical: 44.09), %H 4.30 (theoretical: 4.04), %N < 0.02 (theoretical: 0.00) .

The overall molecular structure was proven by its single crystal X-ray structure.

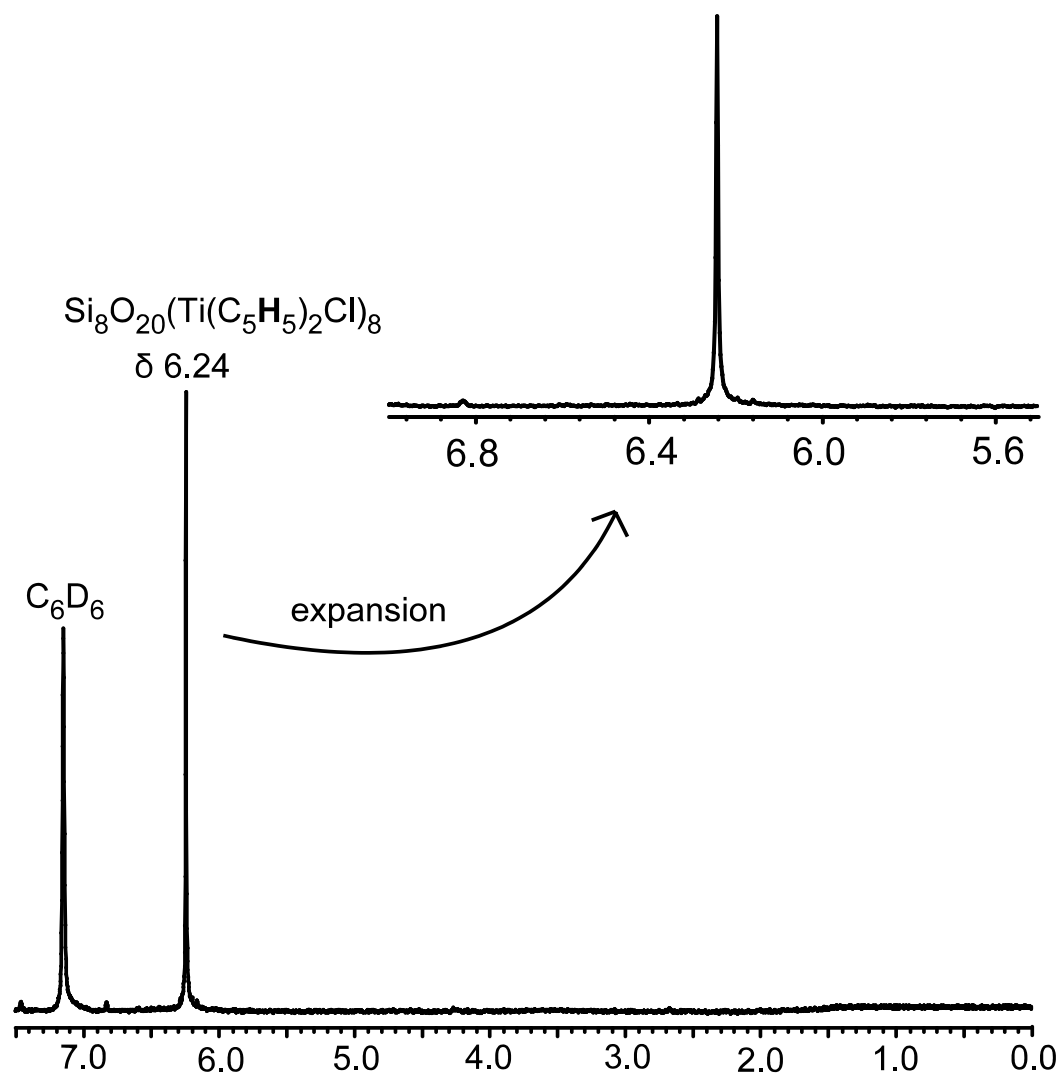


Figure 3.3.1 ^1H NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

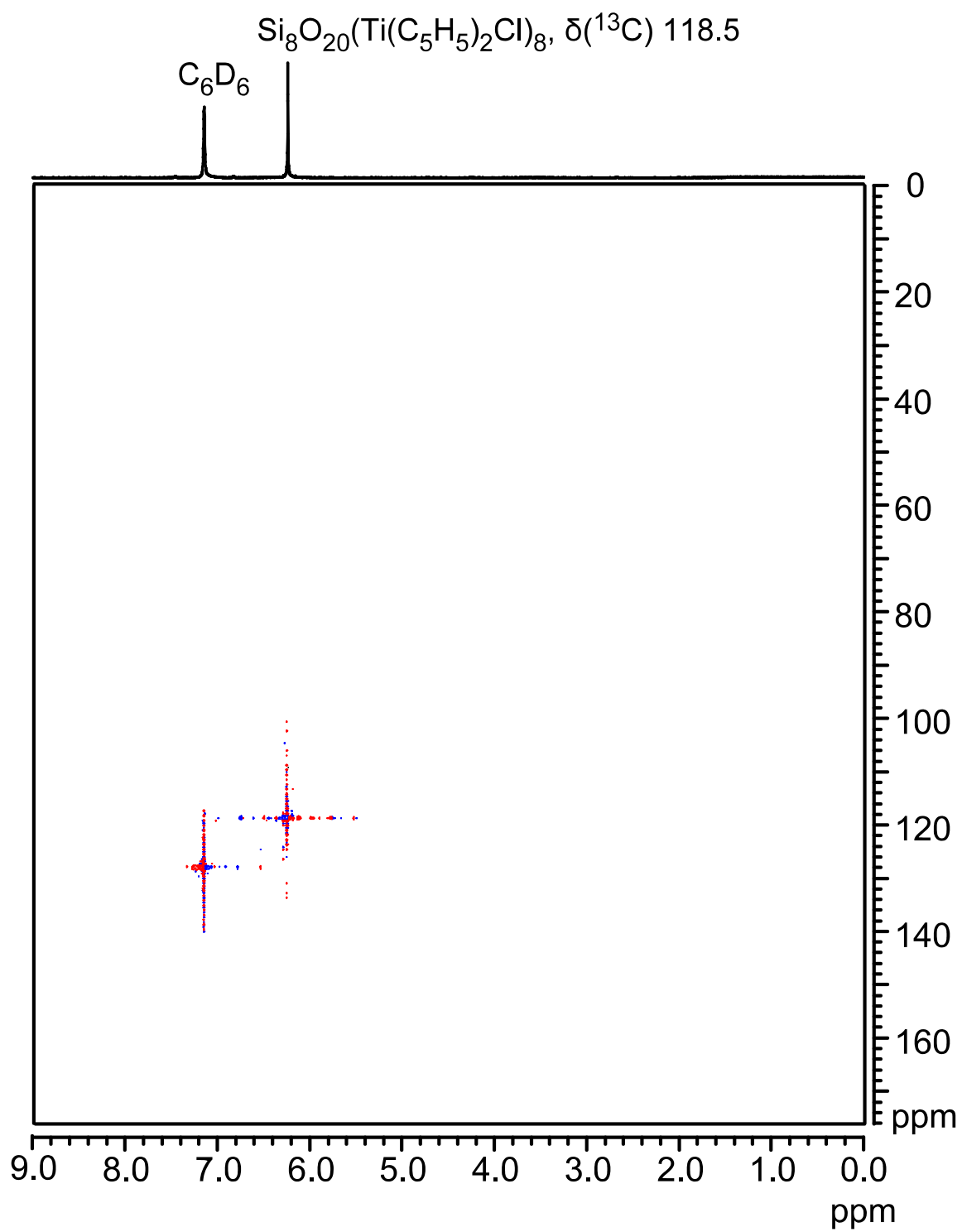


Figure 3.3.2 HSQC spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

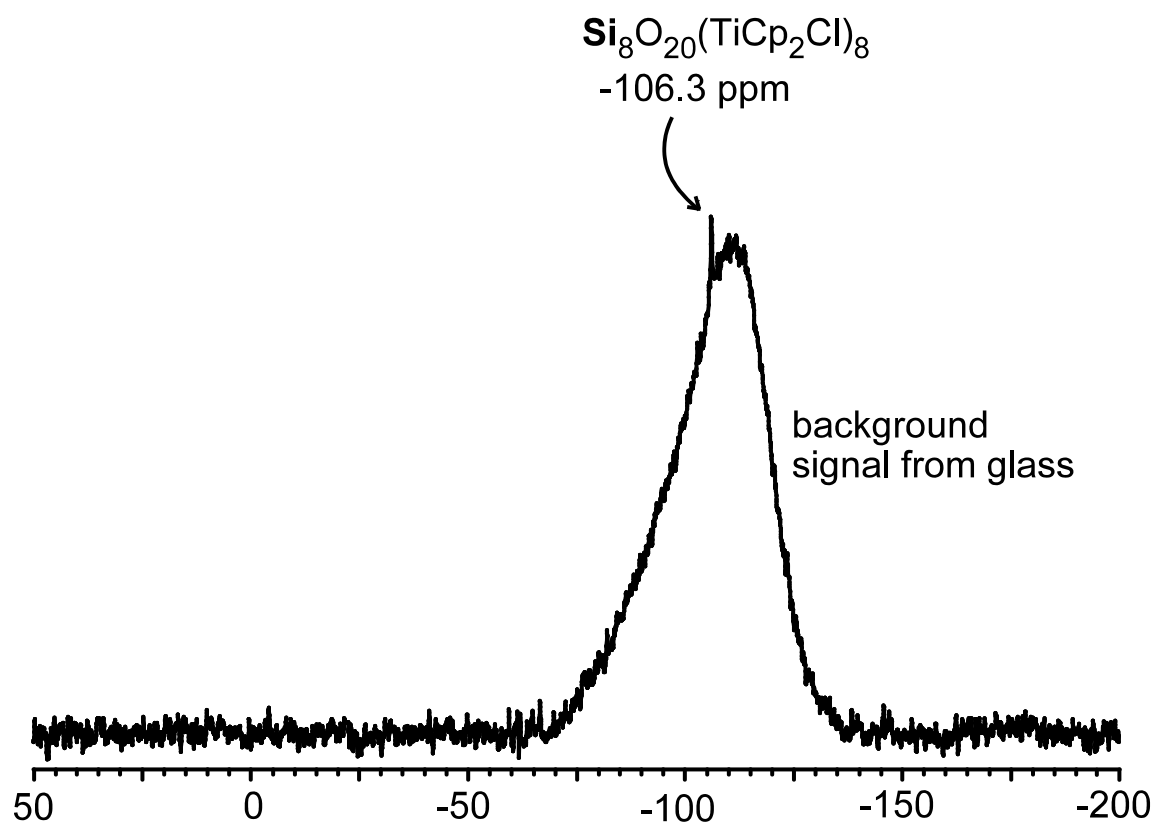
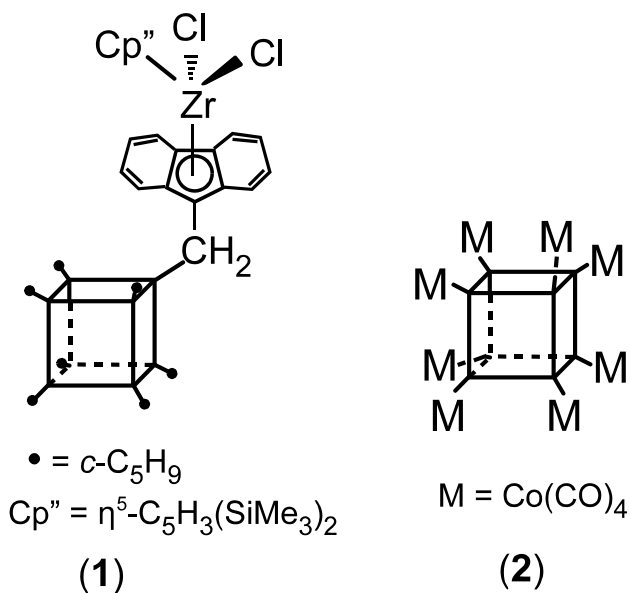


Figure 3.3.3 ^{29}Si NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

In the crystal, two molecules of methylene chloride solvation were observed (**Figures 3.3.4 and 3.3.5**), along with the disorder of both TiCp_2Cl groups and solvated methylene chloride molecules (**Figure 3.3.6**). The crystal packing of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ molecules is shown in **Figure 3.3.7**.

Due to the tendency of this family of molecules to grow poor quality microcrystalline materials, up to date, this is the only single crystal X-ray structure ever acquired of metallocene or half-sandwich complexes coordinated to the cubic octamer. Selected bond distances and bond angles were compared to the corresponding values of molecules with similar structures, which include $[(\text{c-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{-9-Flu})\text{ZrCp}''\text{Cl}_2]$ (**1**)¹⁵², $\text{Si}_8\text{O}_{12}(\text{Co}(\text{CO})_4)_8$ (**2**)¹⁴³, and $\text{Cp}_2\text{TiCl}(\text{OSiPh}_3)$ ¹⁵³ (**Table 3.3**). Bond distances and bond angles in the cubic octamer cage and in the titanocene moieties of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ are normal within reported ranges.



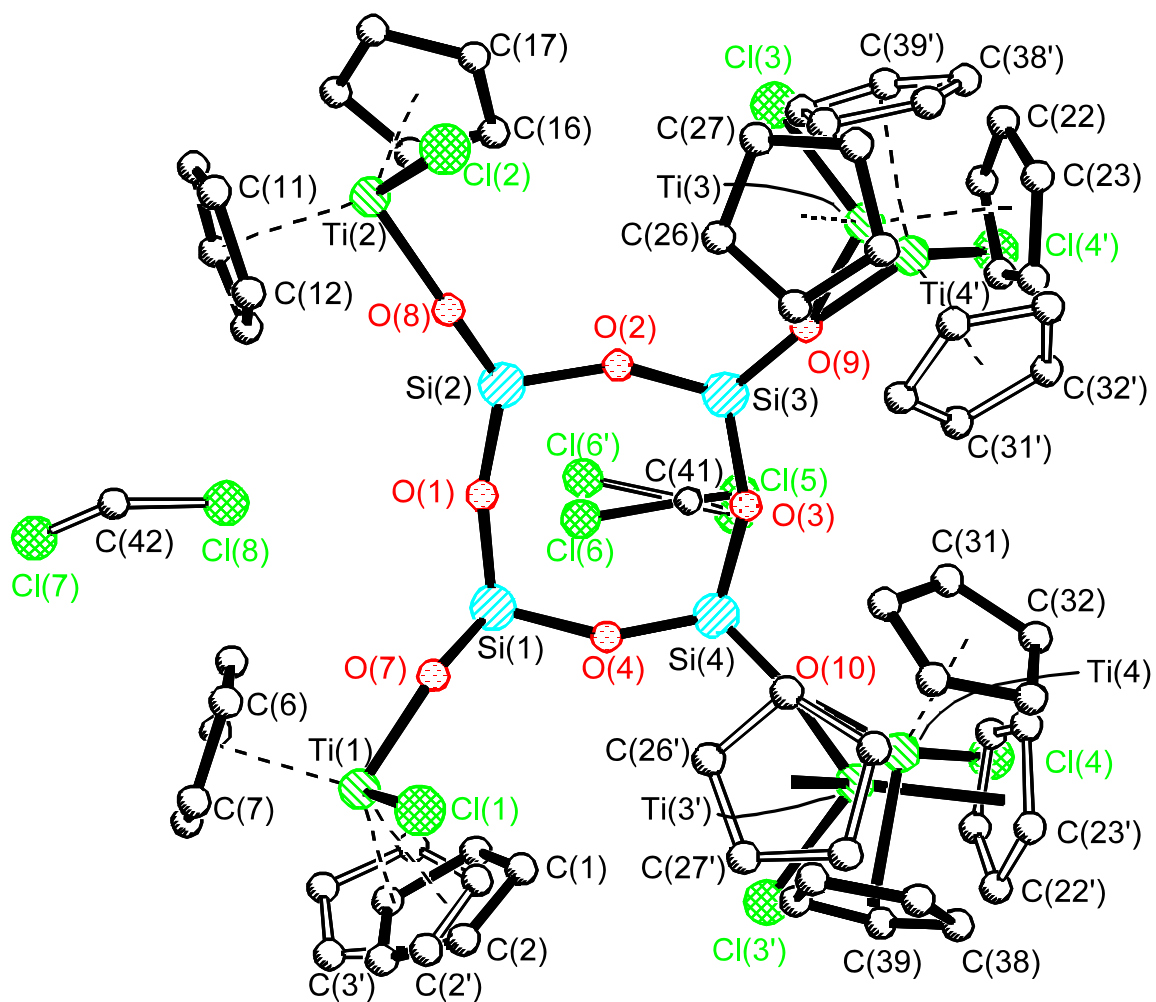


Figure 3.3.4 View showing atom numbering system of a unique part of the $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ molecule (Inversion symmetry generates the rest of the molecule.)
C(41) and C(42) are methylene chloride solvates

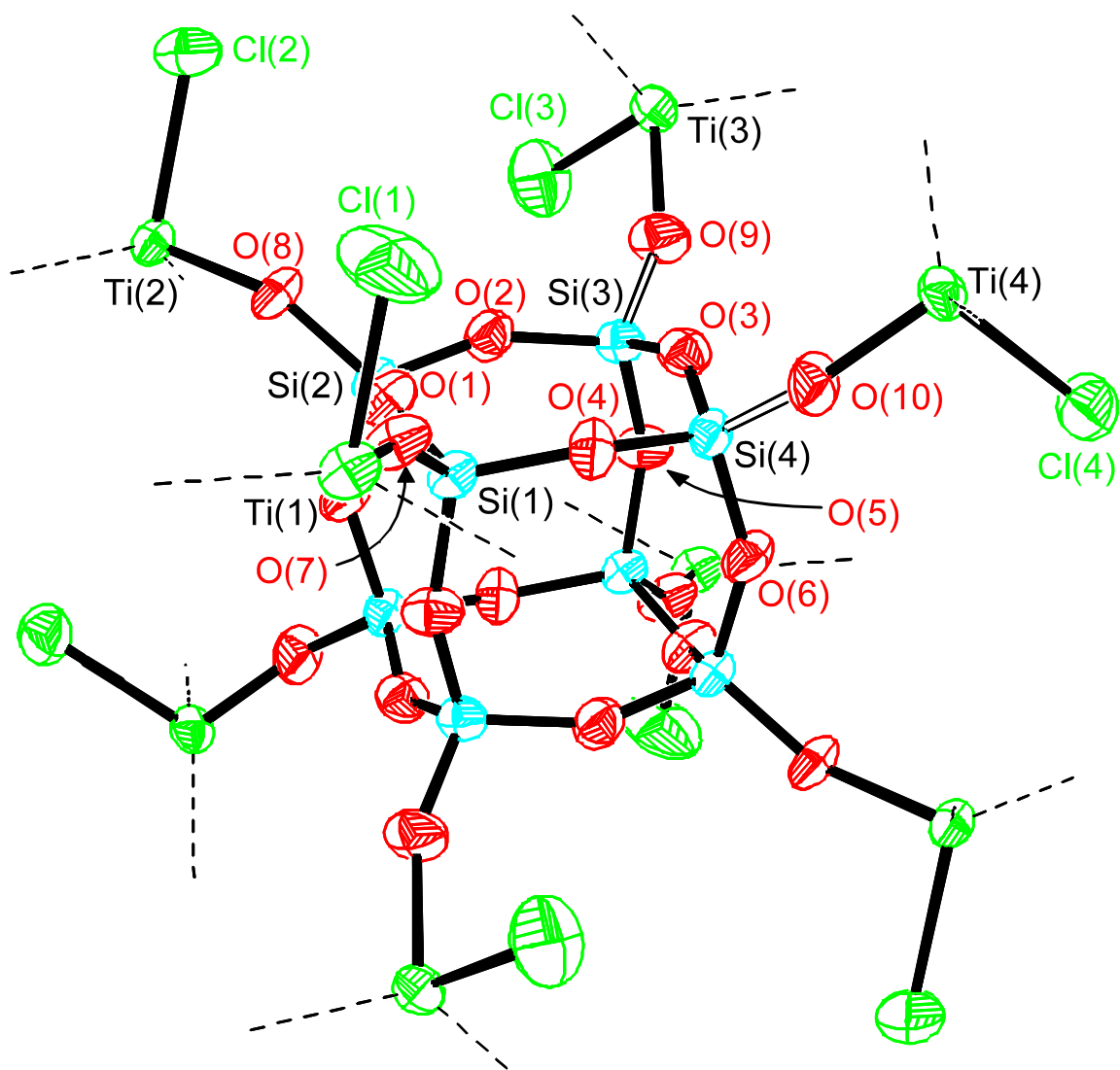


Figure 3.3.5 ORTEP drawing of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ (Disorder not shown here)

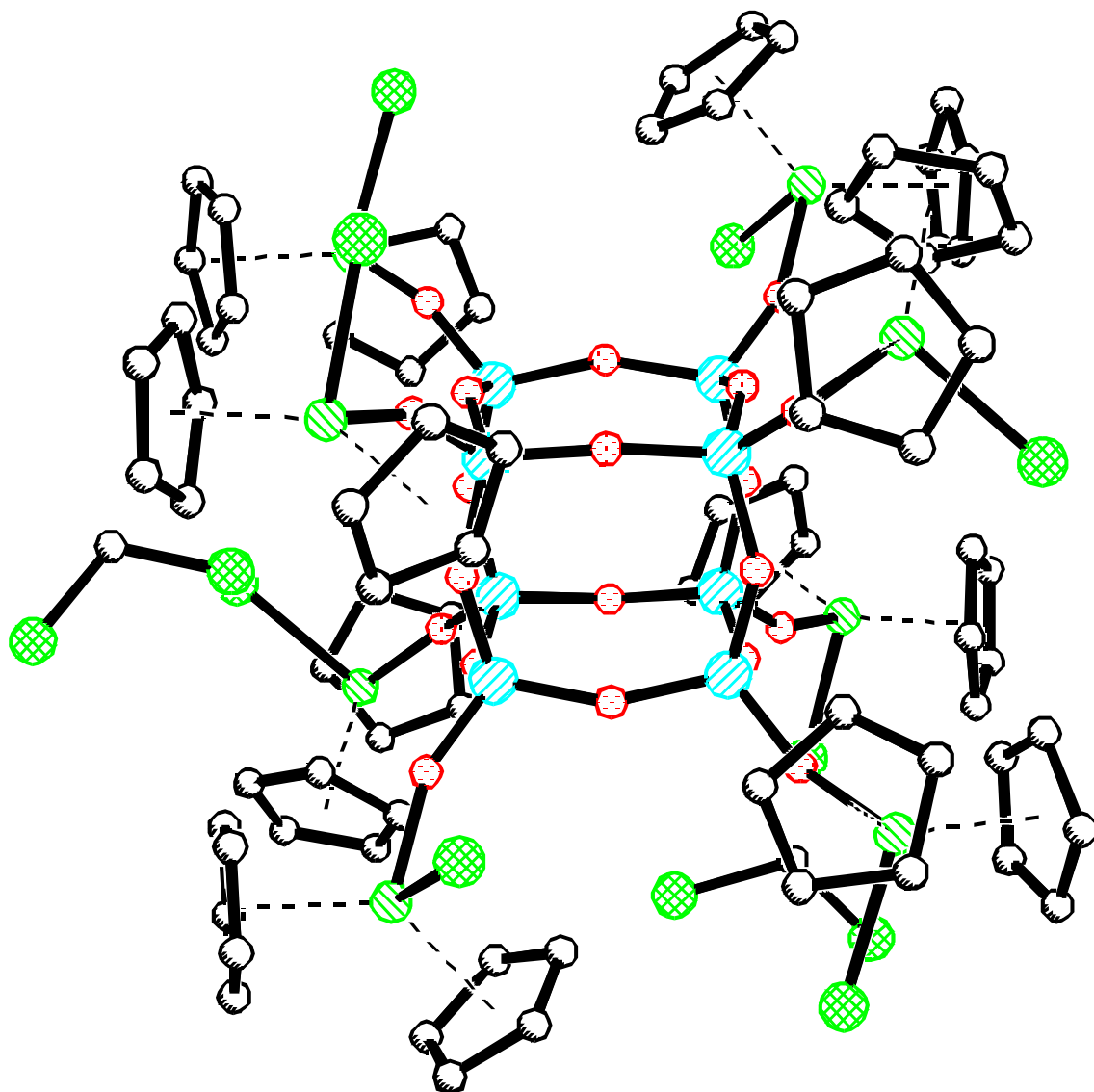


Figure 3.3.6 Stick-and-ball presentation of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ showing the disorder of TiCp_2Cl groups

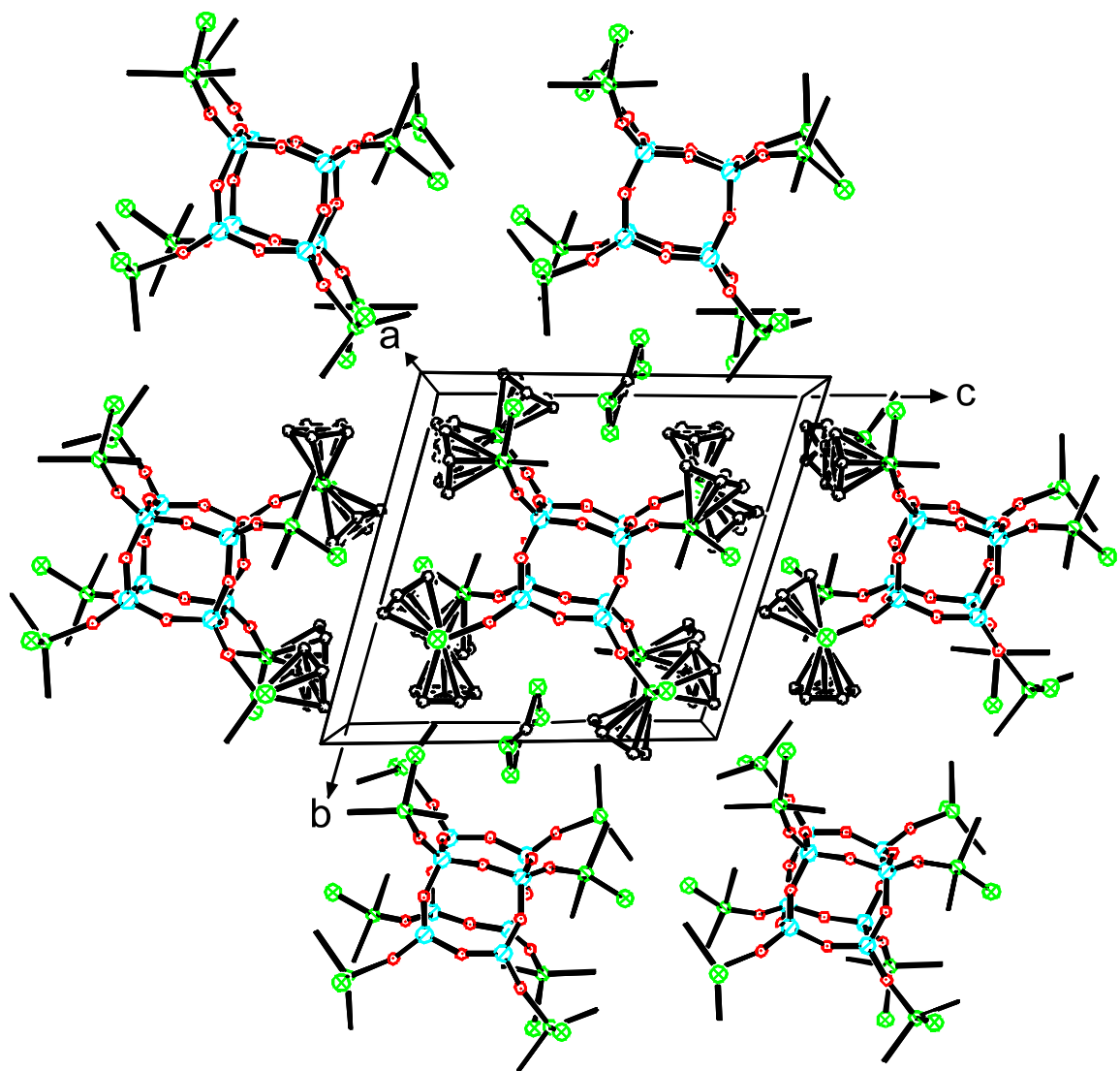
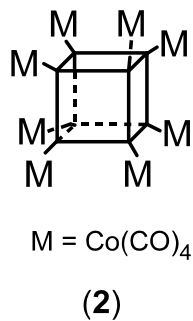
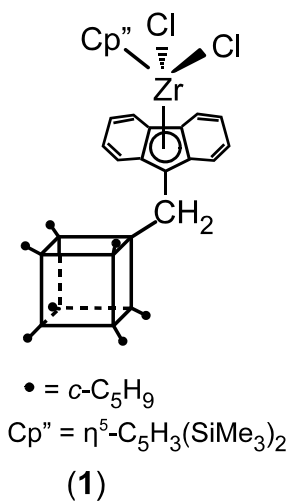


Figure 3.3.7 Packing of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ molecules in the crystal structure

Table 3.3 Comparison of selected bond distances and bond angles in $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and molecules with similar structures

Formula	$\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$	$[(\text{c-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{CH}_2\text{-9-Flu})\text{ZrCp}''\text{Cl}_2]$ by Duchateau ¹⁵²	$\text{Si}_8\text{O}_{12}(\text{Co}(\text{CO})_4)_8$ by Jutzi ¹⁴³	$\text{Cp}_2\text{TiCl}(\text{OSiPh}_3)$ by Dehnicke ¹⁵³
Si–O (in cube), Å	min 1.583(3), max 1.595(4)	min 1.607(5), max 1.635(6)	min 1.610(4), max 1.637(4)	N/A
Si–O–Si bond angles	min 144.8(2)°, max 151.6(2)°	min 147.3(4)°, max 152.0(4)°	min 147.6(2)°, max 154.1(3)°	N/A
Ti–O, Å	min 1.818(4), max 1.838(3)	N/A	N/A	avg. 1.842(4)
Si–O (not in cube), Å	min 1.550(4), max 1.573(3)	N/A	N/A	avg. 1.615(4)
Si–O–Ti	min 154.5(2)°, max 163.9(3)°	N/A	N/A	avg. 164.5(2) °
Ti–Cl, Å	min 2.3064(18), max 2.348(3)	N/A	N/A	avg. 2.388(2)



3.4 Identity of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

The identity of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ was confirmed by ^1H , ^{13}C , ^{29}Si NMR, and elemental analysis (EA). Its ^1H (δ 6.22 in benzene- d_6 , **Figure 3.4.1**), ^{13}C (δ 115.12 in benzene- d_6 obtained by HSQC experiment, **Figure 3.4.2**), and ^{29}Si NMR (δ -105.75 in benzene- d_6 , **Figure 3.4.3**) confirmed the presence of one type of magnetically equivalent ($=\text{SiO}$) ZrCp_2Cl grouping in the complex. This is also in good agreement with the reported ^{29}Si chemical shift of a similar compound, $[\text{Si}_8\text{O}_{13}(\text{c-C}_5\text{H}_9)_7]\text{ZrCp}^*\text{Cl}_2$ ($\text{Cp}^* = \eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2$), at -111.40 ppm (in THF- d_8)¹²². From the ^1H -NMR of the sample sent for elemental analysis (see **Figure 3.4.1**), its identity is $0.81 \text{ Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8 + 0.19 \text{ Cp}_2\text{ZrCl}_2$ which corresponds with the EA result: %C 36.89 (theoretical: 36.96), %H 3.08 (theoretical: 3.10), and %N <0.01 (theoretical: 0.00).

Attempts have been made to grow single crystals of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$. Among solvents attempted (i.e., CH_2Cl_2 and its slow removal to increase the solution concentration, CH_2Cl_2 /hexanes vapor mixture, benzene, $n\text{-BuCl}$, THF), toluene was found to be a good candidate the growth of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ single crystals (by very slow crystal growth). In the present study, after the reaction mixture was allowed to equilibrate at room temperature overnight, nice fine crystals growing together (not single crystals) were observed. The order of solubility of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ in various solvents are as follow: $\text{CH}_2\text{Cl}_2 \gg$ toluene $\gg n\text{-BuCl} \gg$ hexanes (undissolved) while Cp_2ZrCl_2 dissolves well in all except hexanes.

3.5 Identity of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$

The identity of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was confirmed by ^1H , ^{13}C , and ^{29}Si NMR analyses. Its magnetically equivalent pentamethylcyclopentadienyl (Cp^*) ligand, $\eta^5\text{-C}_5(\text{CH}_3)_5$, was observed as a singlet signal in ^1H -NMR (δ 2.31 in benzene- d_6 , **Figure**

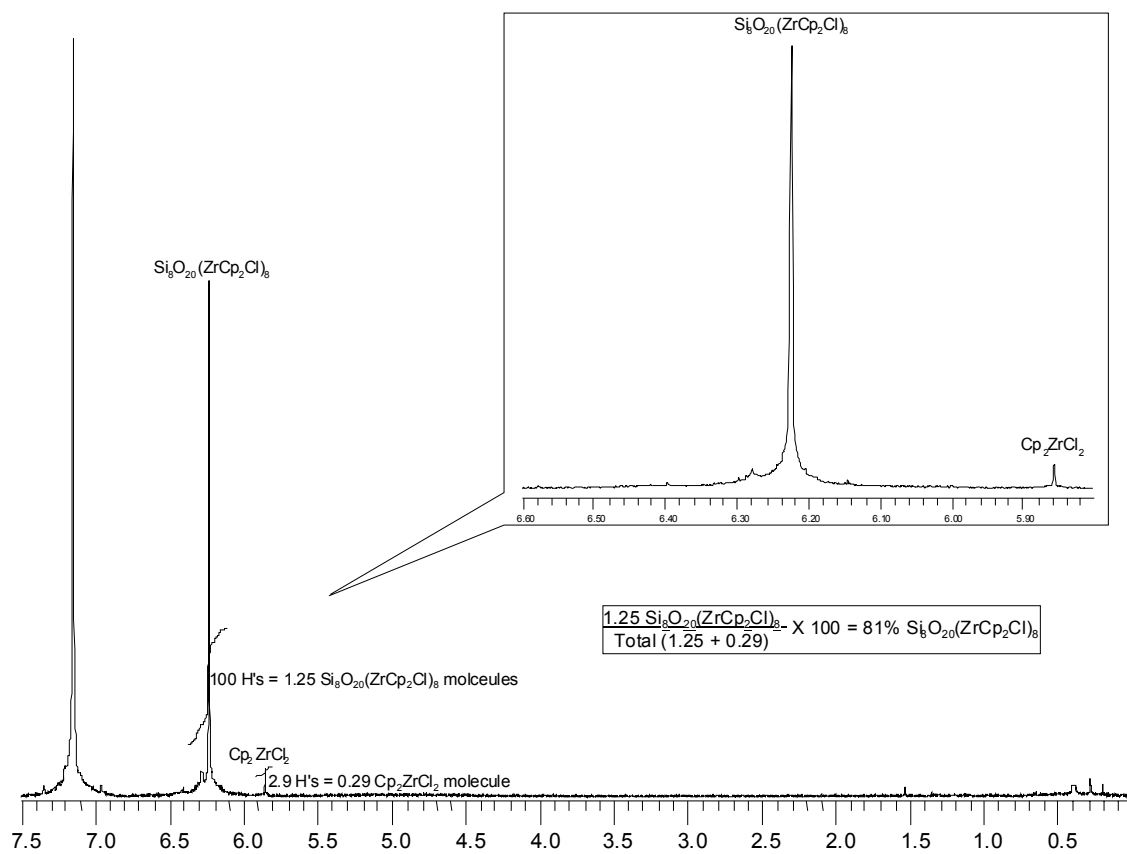


Figure 3.4.1 ^1H NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

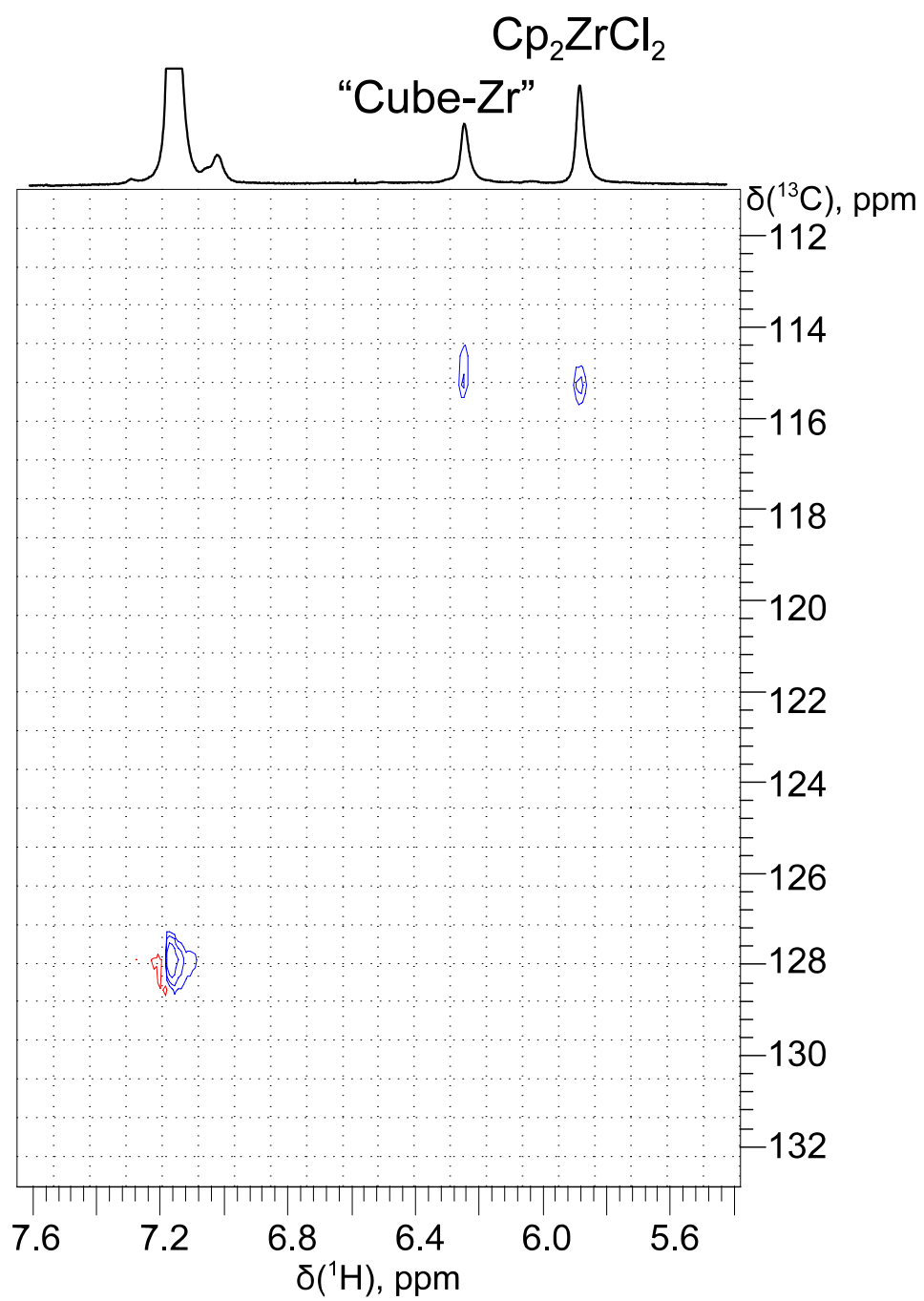


Figure 3.4.2 HSQC NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

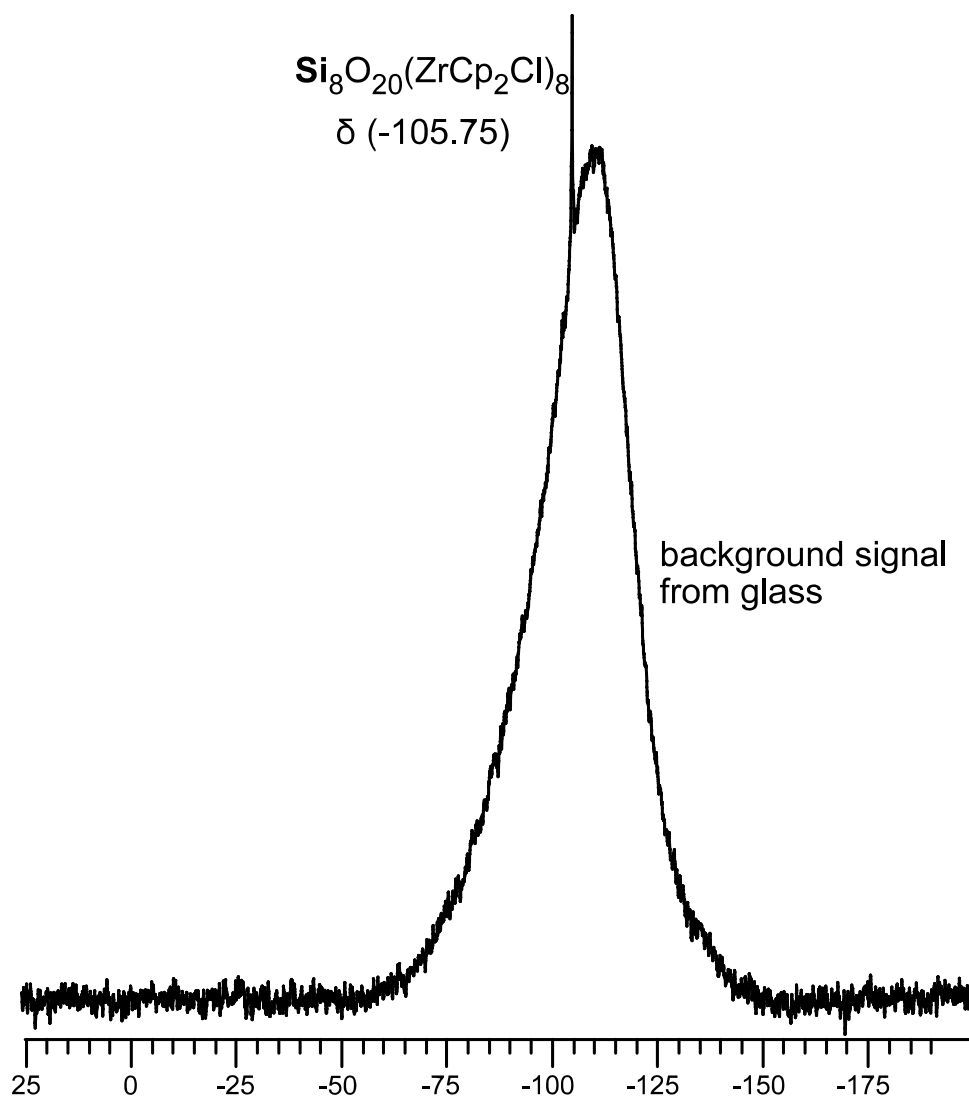


Figure 3.4.3 ^{29}Si -NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

3.5.1), and as two signals for two different types of carbon atoms in ^{13}C -NMR (135.55 ppm for aromatic carbon atoms in Cp^* ring and 13.93 ppm for CH_3 , in benzene- d_6 ,

Figure 3.5.2).

Unlike $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ containing pentamethylcyclopentadienyl ligand (Cp^*) was completely soluble in benzene- d_6 , giving bright orange clear solution. Its ^{29}Si -NMR spectrum with high signal-to-noise ratio was achieved with only 3472 scans. As expected, only one ^{29}Si NMR signal at -111.04 ppm (in benzene- d_6) was observed (**Figure 3.5.3**). The chemical shift of this signal is in good agreement with the reported ^{29}Si NMR chemical shift of a similar compound, $[\text{Si}_8\text{O}_{13}(\text{C}-\text{C}_5\text{H}_9)_7]\text{TiCp}^*\text{Cl}_2$ ($\text{Cp}^* = \eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2$), at -111.76 ppm (in THF- d_8)¹²¹.

3.6 Olefin Polymerization Catalysis

Among α -olefin substrates, ethylene shows the highest catalytic activity and was chosen as a monomer for the study of catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$. Styrene was chosen as another monomer for three reasons. First, styrene is prochiral and its polymerization allows the study of stereocontrol of catalysts. Second, it is easier to measure the exact amount of styrene used in a polymerization reaction; this cannot be achieved easily with gaseous monomers (e.g., propylene). Third the active catalysts in styrene polymerization are different from those in α -olefin polymerizations. It has been suggested that the active catalysts for styrene polymerization are trivalent (usually Ti^{3+} formed by the reduction of Ti^{4+}), whereas the active species for α -olefin polymerizations are tetravalent (e.g., Ti^{4+} or Zr^{4+}).^{41, 42} With the selection of styrene in this study, reducibility of catalyst precursors under polymerization conditions can be investigated.

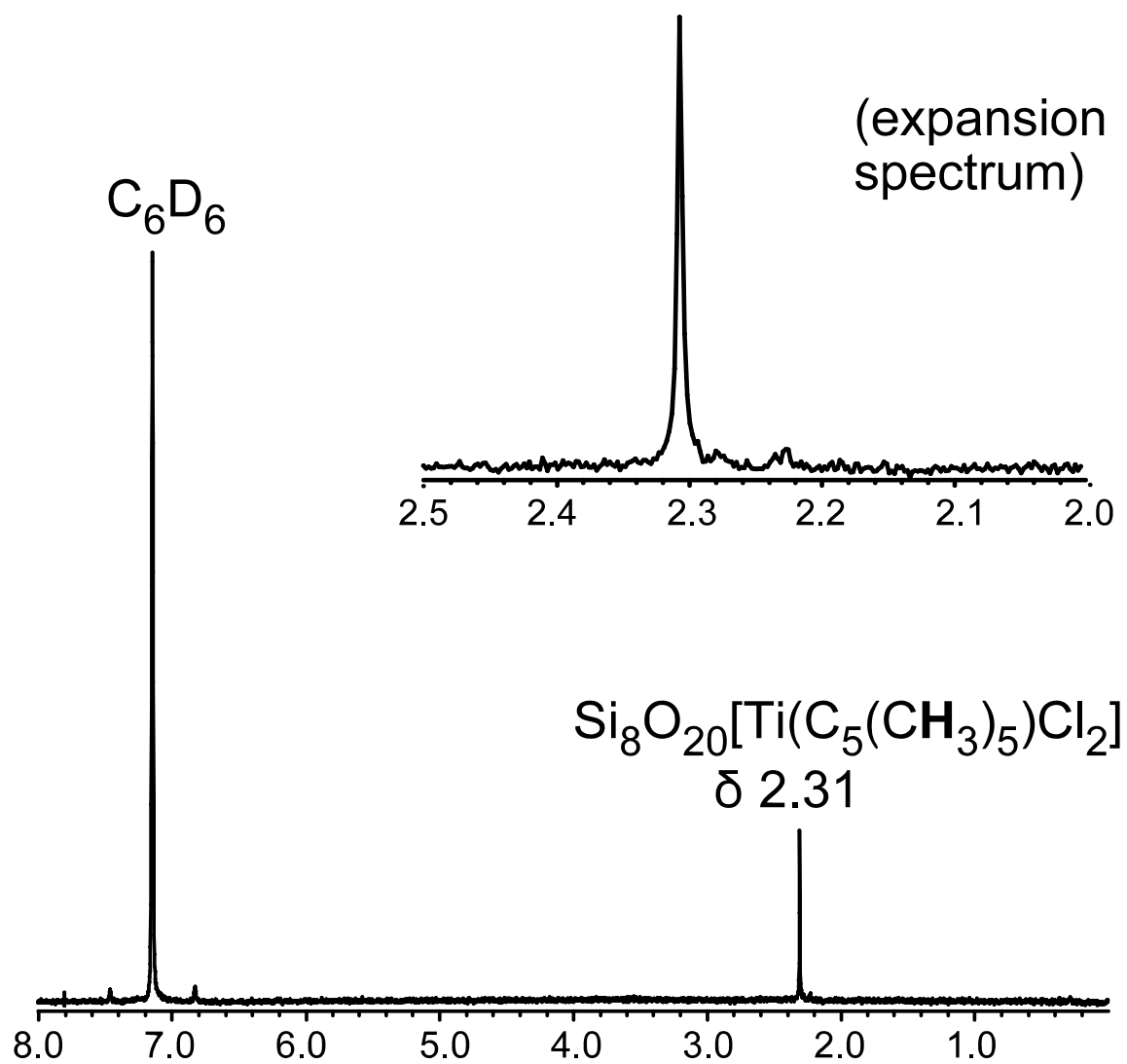


Figure 3.5.1 ^1H NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$

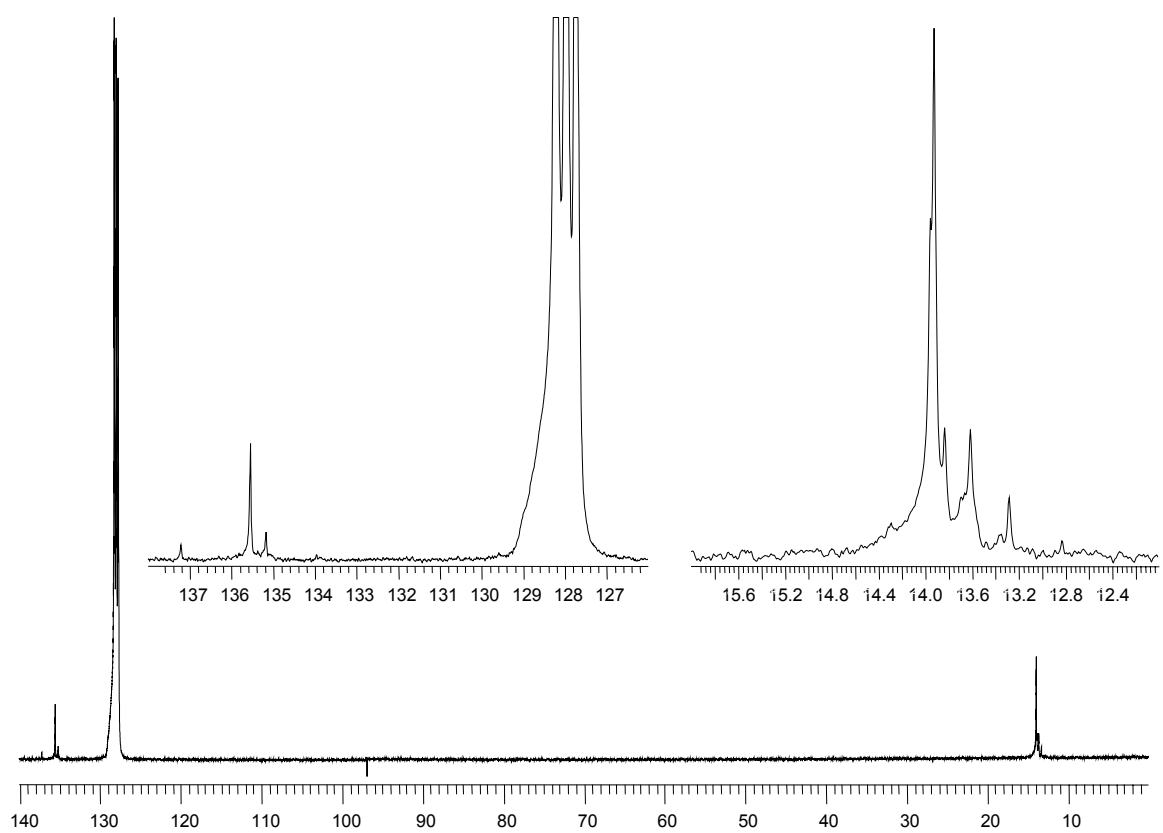


Figure 3.5.2 ^{13}C NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$

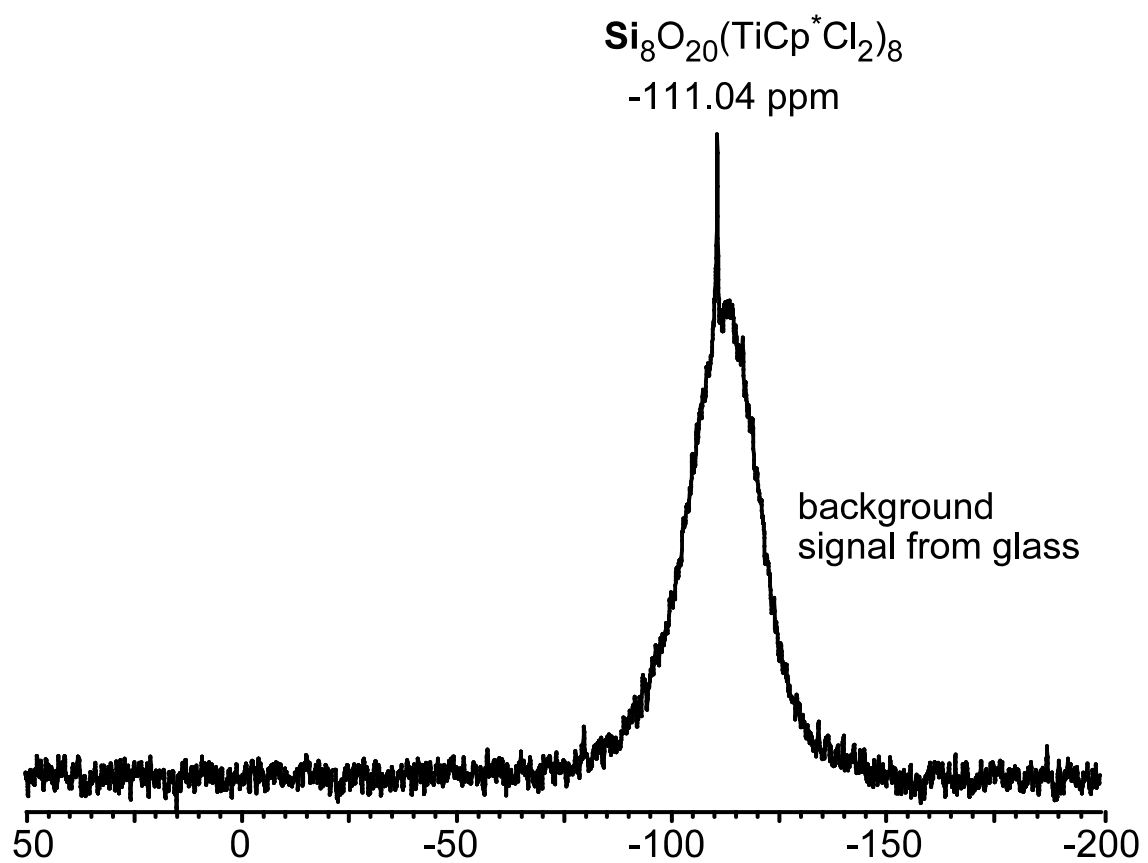


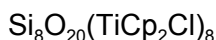
Figure 3.5.3 ^{29}Si NMR spectrum of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$

Under the reaction conditions investigated for ethylene and styrene polymerization, the new catalyst precursors, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$, were compared to the analogous standard catalyst precursors, Cp_2TiCl_2 , Cp_2ZrCl_2 , and Cp^*TiCl_3 , respectively. In order to assure the effect of catalyst precursors on catalytic activities, we also performed blank polymerization runs of ethylene and styrene in the absence of any catalyst precursors. As expected, no polymerization of ethylene or styrene was observed in the absence of catalyst precursor, even in the presence of cocatalysts.

Among cyclopentadienyl-containing Group 4 complexes used in styrene polymerization catalysis, monocyclopentadienyl complexes have been reported to be more reactive than their bis(cyclopentadienyl) (i.e., metallocene) analogs under identical polymerization conditions.^{79, 80} In our study, similar results to these findings were observed. Negligible amount of polystyrene was obtained when metallocene complexes, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, Cp_2TiCl_2 , and Cp_2ZrCl_2 , were used as catalyst precursors. On the other hand, monocyclopentadienyltitanium(IV) complexes, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ and TiCp^*Cl_3 , yielded significant amounts of polystyrene, for which we report catalytic activities.

3.6.1 Ethylene Polymerization Catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

It is generally accepted that methylaluminoxanes are the most active cocatalysts in α -olefin polymerization catalyses of Group 4 metallocenes.⁹⁰ Different cocatalysts were used with the new metallocene catalyst, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, to examine this behavior (**Table 3.6.1.1**). In the same manner as other metallocenes, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ indeed showed the highest catalytic activity when activated by a methylaluminoxane (MMAO-3A), even when used with smaller molar ratios than aluminum alkyl cocatalysts.

Table 3.6.1.1 Effect of cocatalyst on ethylene polymerization catalyzed by

Cocatalyst	Al:Ti mole ratio	Activity, kg/(mol·h·atm)
no cocatalyst	0	0
AlMe_3	1000	6.7
$\text{Al}(i\text{-Bu})_2\text{Cl}$	1000	41
$\text{Al}(i\text{-Bu})_2\text{Cl}$, $\text{B}(\text{C}_6\text{F}_5)_3$ at 6 B : Ti	1000	68
MMAO-3A	300	126

Note: Reactions were performed using 23 μmol Ti, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min at room temperature.

Catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$ and $\text{Cp}_2\text{TiCl}_2/\text{MMAO}$ were then studied at room temperature and at 60 °C (**Table 3.6.1.2**). Temperature indeed affected catalytic activities of both catalysts; room temperature was observed to give almost doubled catalytic activities, compared to 60 °C. This behavior was nearly identical to that described by Kaminsky.⁷⁸ In his findings, titanocene/MAO catalysts are more reactive at low temperatures and decompose at high temperatures (above 50 °C); this may be due to the reduction of the active Ti(IV) to the inactive Ti(III) at high temperatures.⁷⁸

In terms of the effectiveness of the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$) compared to the standard catalyst ($\text{Cp}_2\text{TiCl}_2/\text{MMAO}$), both of them showed similar catalytic activities and similar exotherms at both room temperature and 60 °C. (No conclusion could be drawn on any quantitative relationship between the temperature rise in an exotherm and its corresponding catalytic activity.) The polyethylene (PE) produced by using the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$) had less desirable properties (i.e., lower molecular weight and broader molecular weight distribution,

Table 3.6.1.2 Effect of temperature on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and Cp_2TiCl_2

Catalyst precursor	Temperature	Activity, kg/(mol·h·atm)	M_w of PE, kg/mol	M_w/M_n
$\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$	room temperature, 29 to 62 °C (33 °C rise)	126	254	3.5
	61 to 96 °C (35 °C rise)	69	—	—
Cp_2TiCl_2	room, temperature, 27 to 69 °C (42 °C rise)	130	457	2.4
	60 to 101 °C (41 °C rise)	87	—	—

Note: Reactions were performed using 23 μmol Ti, 300 Al (MMAO-3A):Ti mole ratio, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min.

(M_w/M_n) than the PE produced by the standard catalyst ($\text{Cp}_2\text{TiCl}_2/\text{MMAO}$). The chromatogram from GPC analysis of polyethylenes is illustrated in **Figure 3.6.1**. Overall, there was no obvious improvement in the catalytic performance of the new catalyst over the standard catalysts.

3.6.2 Ethylene Polymerization Catalyzed by $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

Catalytic activities of the new catalyst ($\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8/\text{MMAO}$) and a standard catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{MMAO}$) were studied at room temperature and at 60 °C (**Table 3.6.2.1**). Due to the high thermal stability of Zr(IV), high catalytic activities of zirconocenes at high temperature, especially above 50 °C, were anticipated.^{43, 44} High catalytic activity of the standard catalyst at 60 °C was indeed observed, while this behavior was not as obvious with the new catalyst. The catalytic activity of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8/\text{MMAO}$ at 60 °C (176 kg/(mol·h·atm)) was not significantly higher than

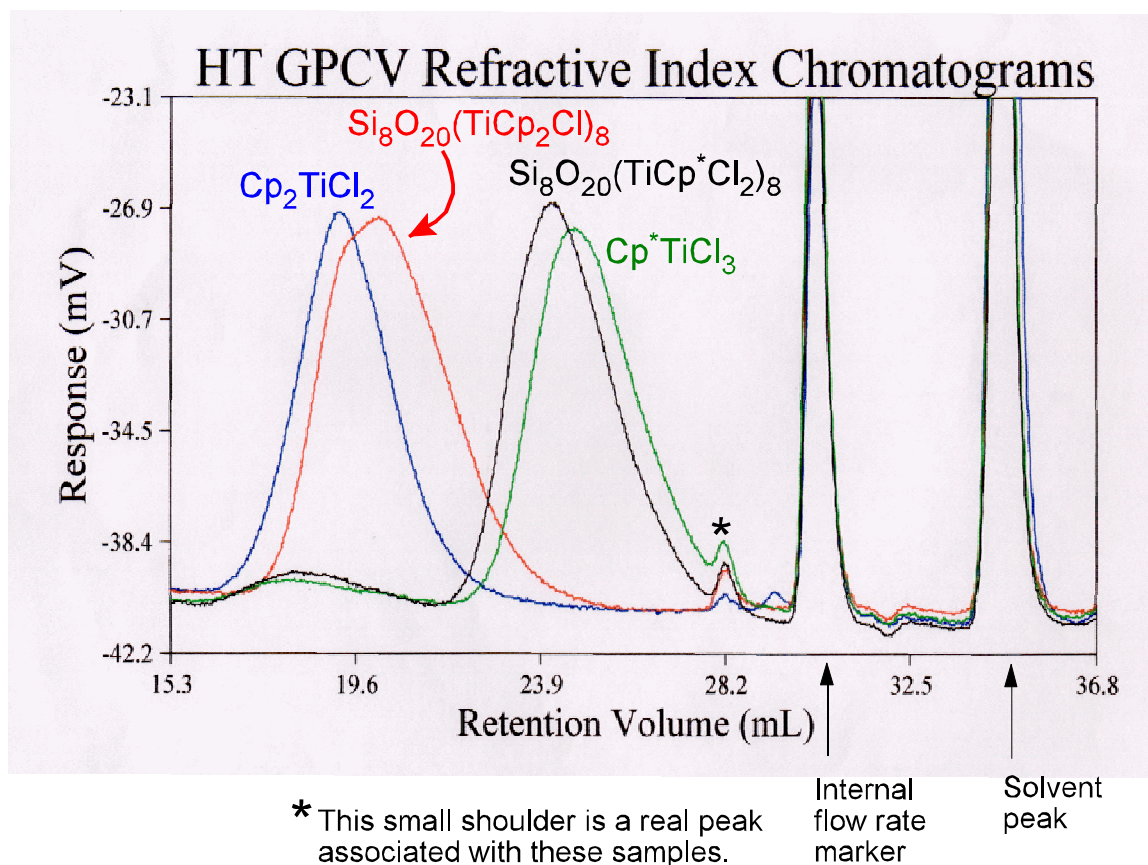


Figure 3.6.1 Chromatogram of PE samples produced from catalyses by the following catalyst precursors: Cp_2TiCl_2 , $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$, and Cp^*TiCl_3 ,

Table 3.6.2.1 Effect of temperature on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ and Cp_2ZrCl_2

Catalyst precursor	Temperature	Activity, kg/(mol·h·atm)	M_w of PE, kg/mol	M_w/M_n
$\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$	room temperature,	160	51.3	17.57
	27 to 68 °C (41 °C rise)			
	60 to 104 °C (44 °C rise)	176	—	—
Cp_2ZrCl_2	room temperature,	122	79.4	17.76
	27 to 69 °C (42 °C rise)			
	60 to 115 °C (55 °C rise)	204	—	—

Note: Reactions were performed using 23 μmol Zr, 300 Al (MMAO-3A):Zr mole ratio, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min.

that at room temperature (160 kg/(mol·h·atm)).

Although the catalytic activity of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8/\text{MMAO}$ was slightly higher than that of $\text{Cp}_2\text{ZrCl}_2/\text{MMAO}$ at room temperature, the relative order of their activities was reversed at higher temperature. The polyethylene (PE) produced by using the new catalyst ($\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8/\text{MMAO}$) had lower molecular weight but approximately the same polydispersity index ($\text{PDI} = M_w/M_n$) as the PE produced by the standard catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{MMAO}$). The chromatogram from GPC analysis is shown in **Figure 3.6.2**. (We did not investigate the cause of unusually large PDI observed, $M_w/M_n \sim 18$. Normally PDI of polyethylenes produced by the catalysis of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ is ≤ 3 .⁷⁰) Overall, no obvious improvement in the catalytic performance was observed from the new catalyst ($\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8/\text{MMAO}$), compared to the standard catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{MMAO}$).

Chien *et. al.* reported that catalytic activities of Cp_2ZrCl_2 were only slightly

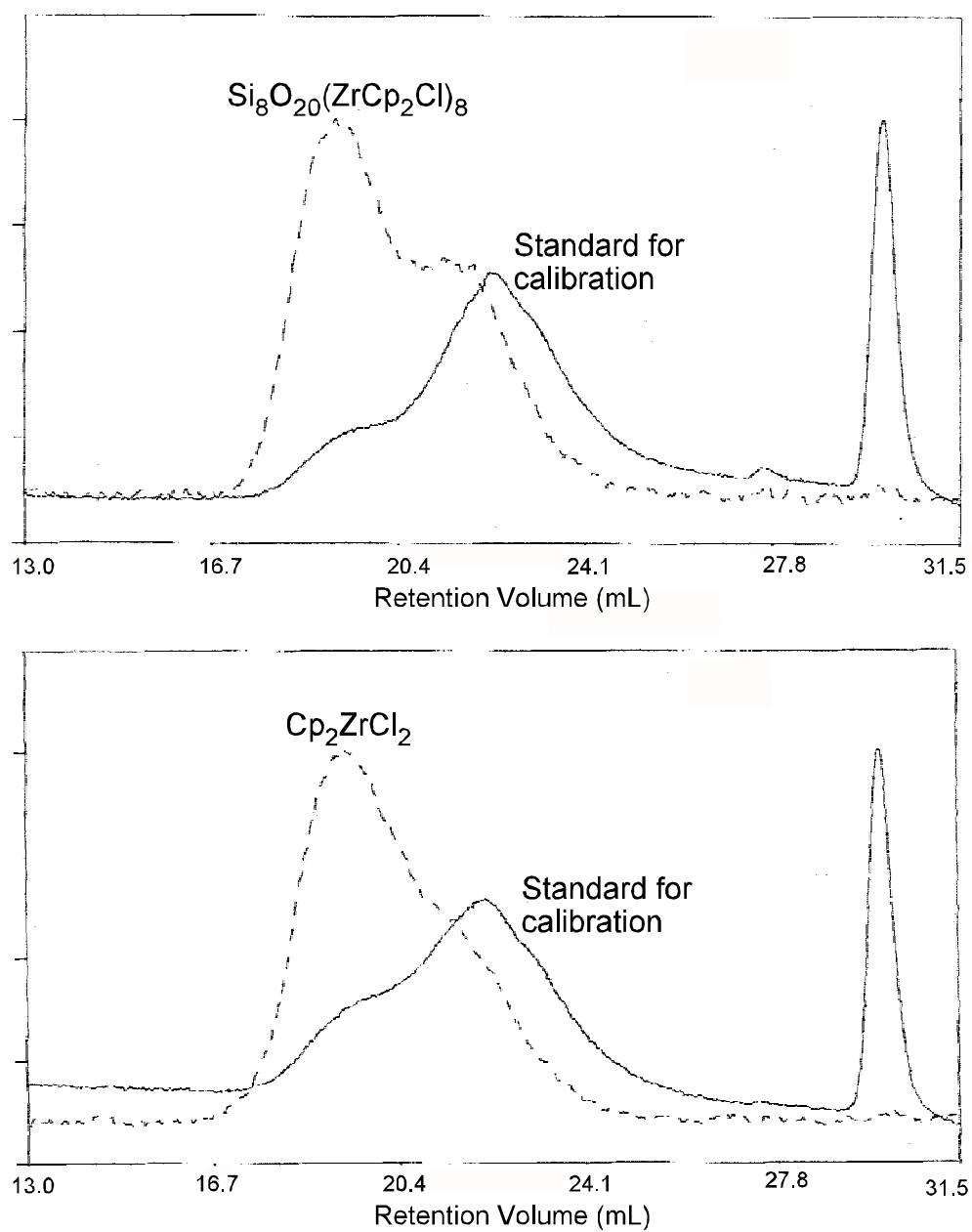


Figure 3.6.2 Chromatograms of PE samples produced from catalyses by $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ and Cp_2ZrCl_2

dependent on concentrations of the cocatalyst MAO used (as opposed to its monocyclopentadienyl analog, CpZrCl_3 , on which more influences of $[\text{MAO}]$ were observed).⁷⁰ This behavior of metallocene was also observed when various excesses of MMAO-3A were used to activate $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ (**Table 3.6.2.2**). Despite the ten-fold increase in the amount of MMAO-3A (from 150 to 2000 Al:Zr), the catalytic activity of $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$ increased only slightly.

3.6.3 Ethylene Polymerization Catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$

The effect of cocatalysts on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ was investigated both in the absence, and in the presence of a cocatalyst, namely trimethylaluminum (AlMe_3 at 250 and 1000 Al:Ti) and MMAO-3A (at 250 Al:Ti). Under the set of conditions studied (i.e., 24 μmol Ti, 5.4 atm ethylene, 30 min, room temperature), the only active cocatalyst yielding polyethylene at 46 kg

Table 3.6.2.2 Effect of the amount of MMAO-3A on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$

Catalyst precursor	Al:Zr mole ratio	Temperature, °C	Activity, kg/(mol·h·atm)
$\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$	0 (no cocatalyst)	27 constant	0
	150	27 to 56	149
	300	27 to 67	160
	600	27 to 75	163
	1000	27 to 91	165
	2000	29 to 64	182

Note: Reactions were performed using 23 μmol Zr, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min at room temperature.

PE/(mol Ti·h·atm) activity, was MMAO-3A. Trimethylaluminum, even at as much as 1000 Al:Ti, failed to give any polyethylene. MMAO-3A was used as a cocatalyst for all of the following ethylene polymerization catalyses of $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$.

Table 3.6.3.1 summarizes results from catalytic ethylene polymerizations at two different temperatures. Results from the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8/\text{MMAO}$) were compared to those from its analogous standard catalyst ($\text{Cp}^+\text{TiCl}_3/\text{MMAO}$). At 60 °C, activities of both catalysts dropped to about 1/3 of their activities at room temperature. This may be due to the reduction of the active Ti(IV) to the inactive Ti(III) at a high temperature.⁷⁸ It is also noteworthy to mention that the three fold decrease in catalytic activities of monocyclopentadienyltitanium(IV) complexes (i.e., $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8/\text{MMAO}$ and $\text{Cp}^+\text{TiCl}_3/\text{MMAO}$) at 60 °C was larger than that observed with metallocenes. (See

Table 3.6.3.1 Effect of temperature on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$ and Cp^+TiCl_3

Catalyst precursor	Temperature	Activity, kg/(mol·h·atm)	M_w of PE, kg/mol	M_w/M_n
$\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$	room temperature, 30 to 43 °C (13 °C rise)	46	1,107 and 6.8 (bimodal)	3.2 and 3.9
	60 to 83 °C (23 °C rise)	16	—	—
Cp^+TiCl_3	room temperature, 31 to 40 °C (9 °C rise)	26	1,121 and 4.3 (bimodal)	4.3 and 3.0
	60 to 82 °C (22 °C rise)	9	—	—

Note: Reactions were performed using 24 µmol Ti, 250 Al (MMAO-3A):Ti mole ratio, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min.

Section 3.6.1 and **Table 3.6.1.2** for the data on the two fold decrease in catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$ and $\text{Cp}_2\text{TiCl}_2/\text{MMAO}$ at 60 °C, compared to room temperature.)

In general, catalytic activities of monocyclopentadienyltitanium(IV) complexes, ($\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$ and $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$) were also about an order of magnitude lower than those of titanocenes ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$ and $\text{Cp}_2\text{TiCl}_2/\text{MMAO}$), under similar ethylene polymerization conditions. (See **Table 3.6.1.2** for catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8/\text{MMAO}$ and $\text{Cp}_2\text{TiCl}_2/\text{MMAO}$.) This could be an indication of more reducibility of monocyclopentadienyltitanium(IV) complexes than titanocenes, leading to lower catalytic activities observed in α -olefin polymerizations. Zhu *et. al.* also reported higher concentrations of the inactive Ti(III) formed in $\text{CpTiCl}_3/\text{MAO}$ catalytic system than in the presence of $\text{Cp}_2\text{TiCl}_2/\text{MAO}$, under similar conditions.⁴³

Comparing between the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$) and the standard catalyst ($\text{Cp}^*\text{TiCl}_3/\text{MMAO}$), catalytic activities of the new catalyst were about two times higher than activities of the standard catalyst, both at room temperature and at 60 °C. Two molecular weight ranges of polyethylene (PE) were obtained from both catalysts. One molecular weight range was extremely high (> 1 million g/mol); another was extremely low (in the magnitude of 1000's g/mol). Overall, molecular weight ranges and polydispersities (M_w/M_n) of PE produced from both catalysts were very similar, while catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$ were about twice those of the standard catalyst, $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$.

Chien *et. al.* reported the dependence of catalytic activities of a monocyclopentadienyl complex (CpZrCl_3) on the concentration of MAO.⁷⁰ Indeed, this is what we observed with the catalyst $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$ (**Table 3.6.3.2**). Catalytic activities of this monocyclopentadienyltitanium(IV) complex were raised five fold as the

Table 3.6.3.2 Effect of the amount of MMAO-3A on ethylene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ and Cp^*TiCl_3

Catalyst precursor	Al:Ti mole ratio	Temperature, °C	Activity, kg/(mol·h·atm)
$\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$	100	27 to 31 (4 °C rise)	15
	250	30 to 43 (13 °C rise)	46
	1000	27 to 34 (7 °C rise)	70
Cp^*TiCl_3	250	31 to 40 (9 °C rise)	26
	1000	27 to 31 (4 °C rise)	23

Note: Reactions were performed using 24 μmol Ti, in 100 mL toluene, under 5.4 atmosphere of ethylene for 30 min at room temperature.

amount of MMAO-3A was increased from 100 to 1000 Al:Ti.

3.6.4 Styrene Polymerization Catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$

Catalytic activities of the new catalyst, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$, and the standard catalyst, $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$, in styrene polymerization were studied at room temperature and at 50 °C (**Table 3.6.4.1**). Reaction temperature had a large impact on activities of both catalysts. At 50 °C, the catalytic activity of the new catalyst increased by more than ten times its activity at room temperature. This large increase in catalytic activity may have resulted from the formation of the active Ti(III) species in styrene polymerization, from the reduction of Ti(IV), at high temperatures.⁷⁸ Activities of styrene polymerization catalyzed by Cp^*TiCl_3 were actually reported as having an optimal reaction temperature of 50 °C, above and below which activities decreased.⁹⁸

Among the two catalysts studied, catalytic activity of the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$) was as high as four times that of the standard catalyst, at the

Table 3.6.4.1 Effect of temperature on styrene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ and Cp^*TiCl_3

Catalyst precursor	Temperature, °C	Activity, kg/(mol·h)	M_w of PS, kg/mol	M_w/M_n	Tacticity of PS
$\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$	room	18	–	–	syndiotactic
	50	222	105.9	1.96	syndiotactic
Cp^*TiCl_3	room	17	–	–	syndiotactic
	50	54	36.2	1.63	syndiotactic

Note: Reactions were performed using 8.1 μmol Ti, 4700 styrene:100 Al (MMAO-3A):1

Ti mole ratio, in 25 mL toluene for 30 min.

optimal temperature (60 °C). Polystyrene obtained from this catalyst had higher molecular weight than the polystyrene obtained by using the standard catalyst, while low polydispersity index ($M_w/M_n \approx 2$) was also maintained (**Figure 3.6.4.1**). In term of stereocontrol of catalysts, both the new and standard catalysts are highly syndiospecific, producing only syndiotactic polystyrene (sPS). **Figures 3.6.4.2** and **3.6.4.3** are ^{13}C NMR spectra of polystyrenes produced by the catalysis of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$ and $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$, respectively. Both spectra showed identical signals to those reported for syndiotactic polystyrene,¹⁵⁴ especially its single, sharp aromatic carbon signal at 145.27 ppm.¹⁵⁵ In both spectra, signals observed around 30 ppm are assigned to the antioxidant, IRGANOX® 1076, which was added for thermal stability of polymer resins upon the work up of polymerization reactions (see **Figure 3.6.4.4** for the ^{13}C NMR spectrum of IRGANOX® 1076.)

Ishihara *et. al.* reported increased activities of CpTiCl_3 as the Al (MAO):Ti ratio increased.⁹⁸ Both the new catalyst ($\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO}$) and the standard catalyst

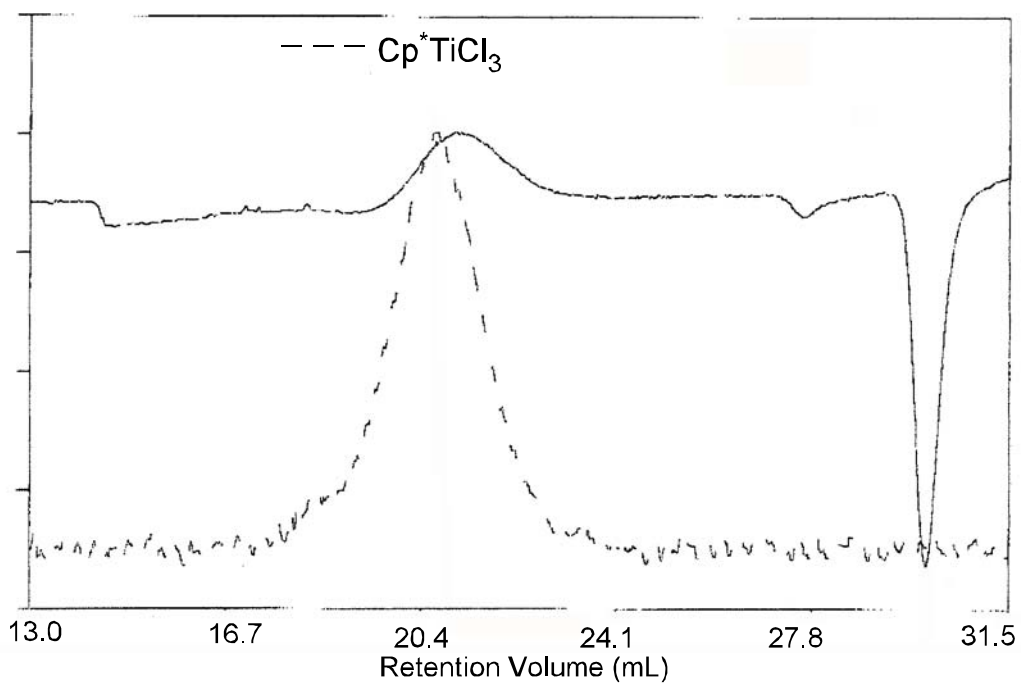
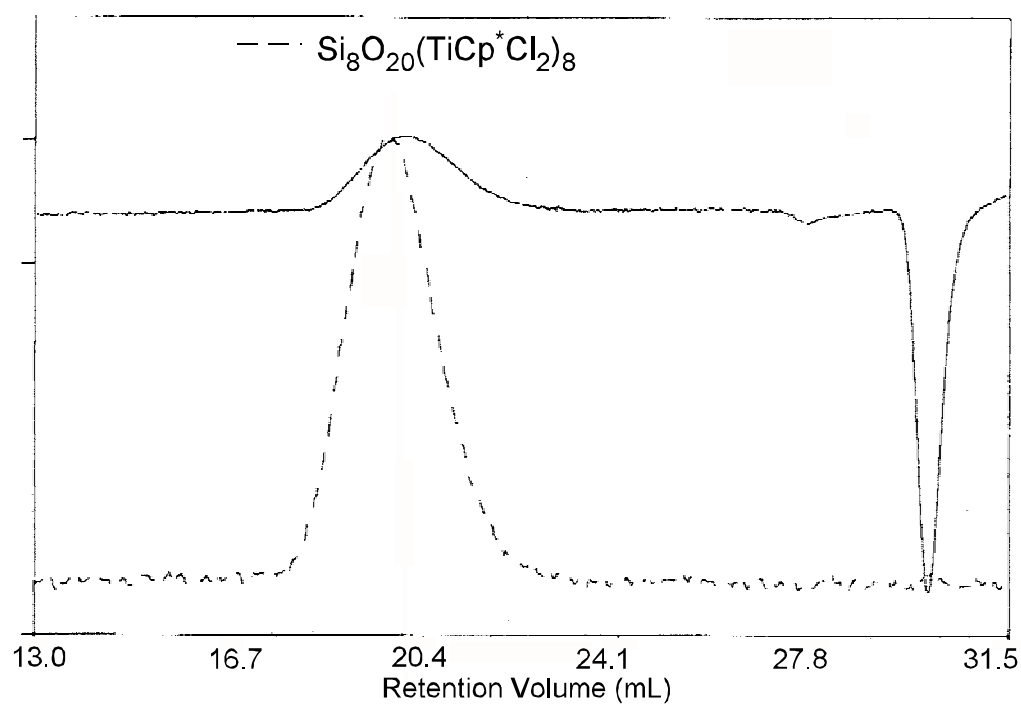


Figure 3.6.4.1 GPC traces of PS produced by catalyses of $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ and Cp^*TiCl_3

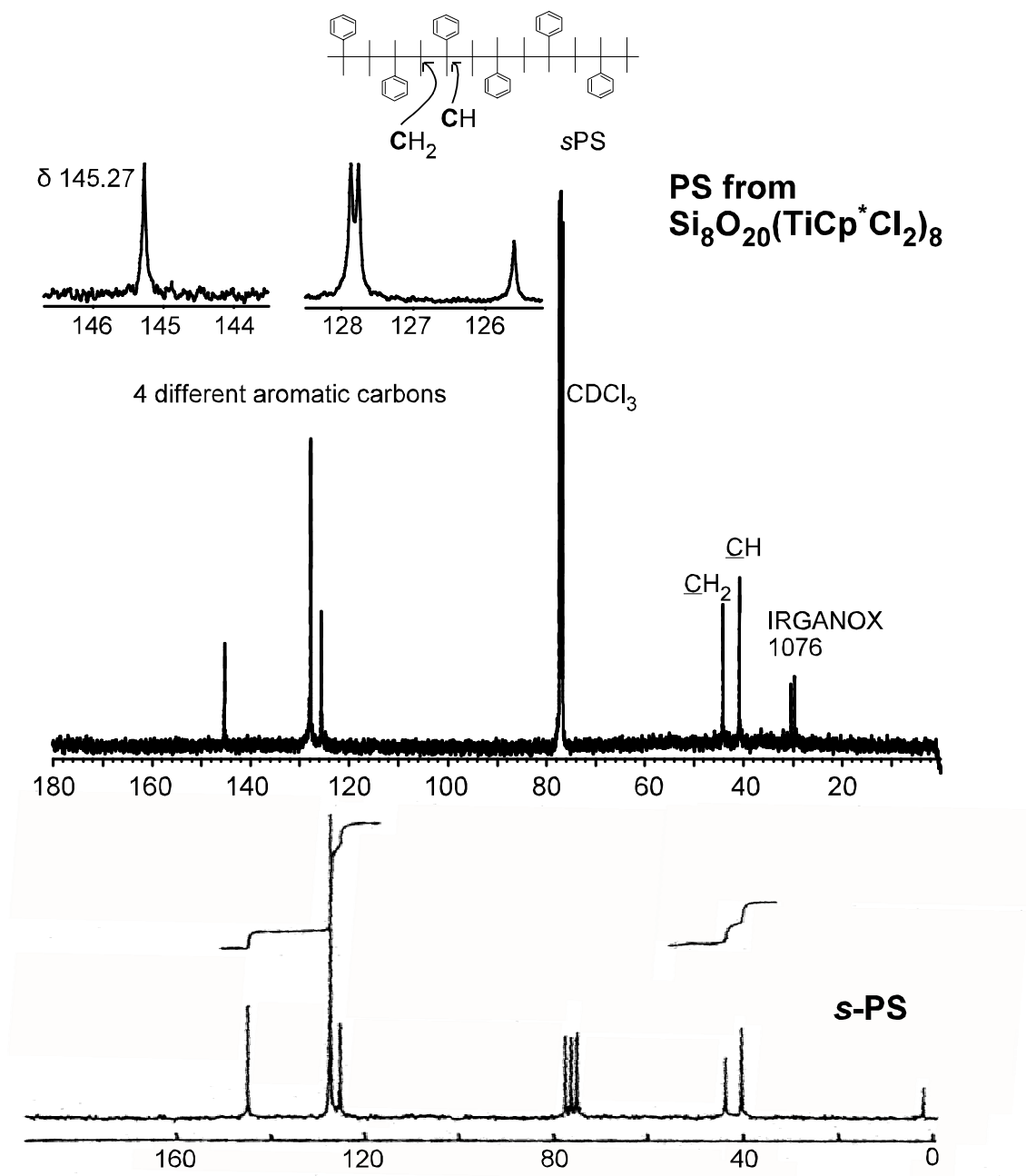


Figure 3.6.4.2 ^{13}C NMR spectrum of polystyrene produced with the catalyst

$\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8/\text{MMAO-3A}$, compared to the literature report by Soga *et. al.*¹⁵⁴

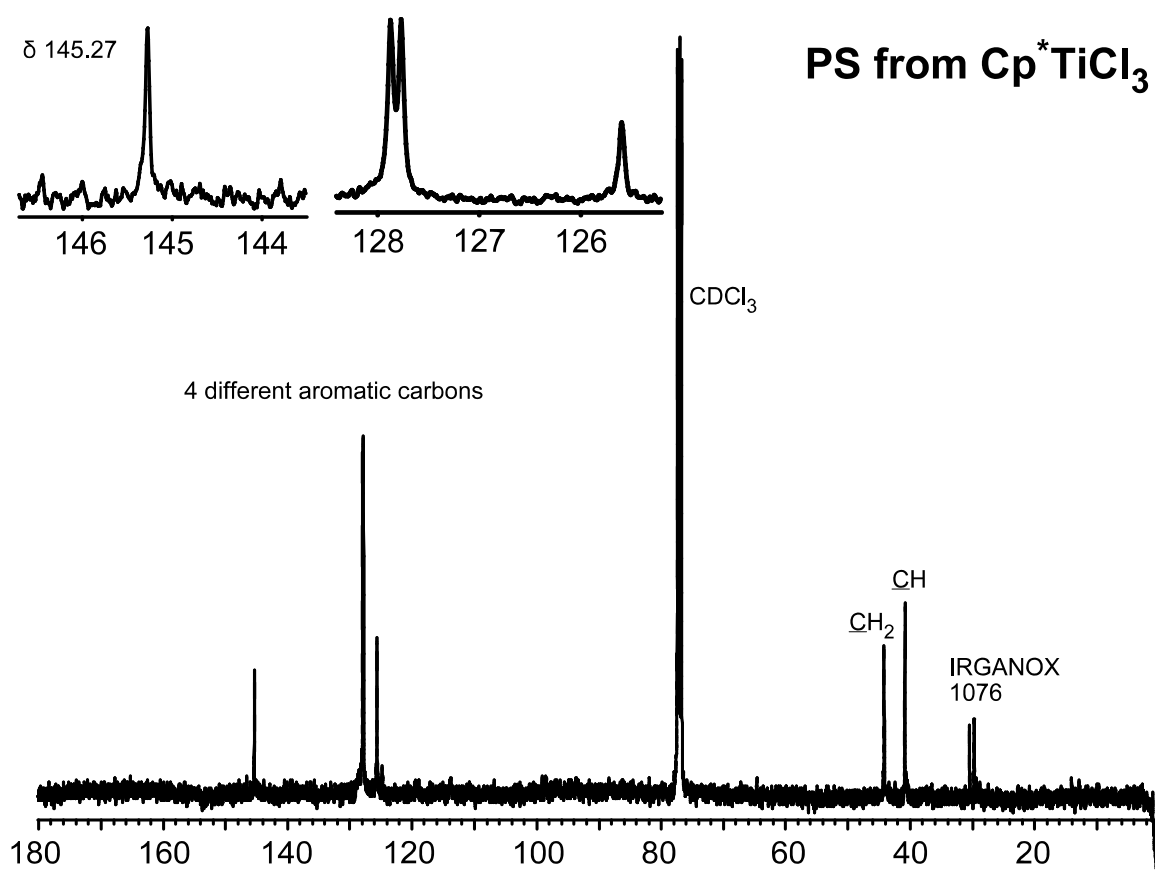
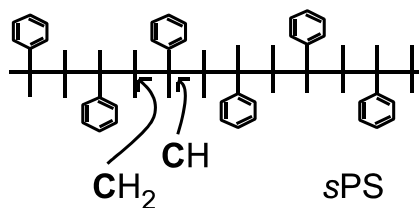


Figure 3.6.4.3 ^{13}C NMR spectrum of polystyrene produced with the catalyst $\text{Cp}^*\text{TiCl}_3/\text{MMAO-3A}$

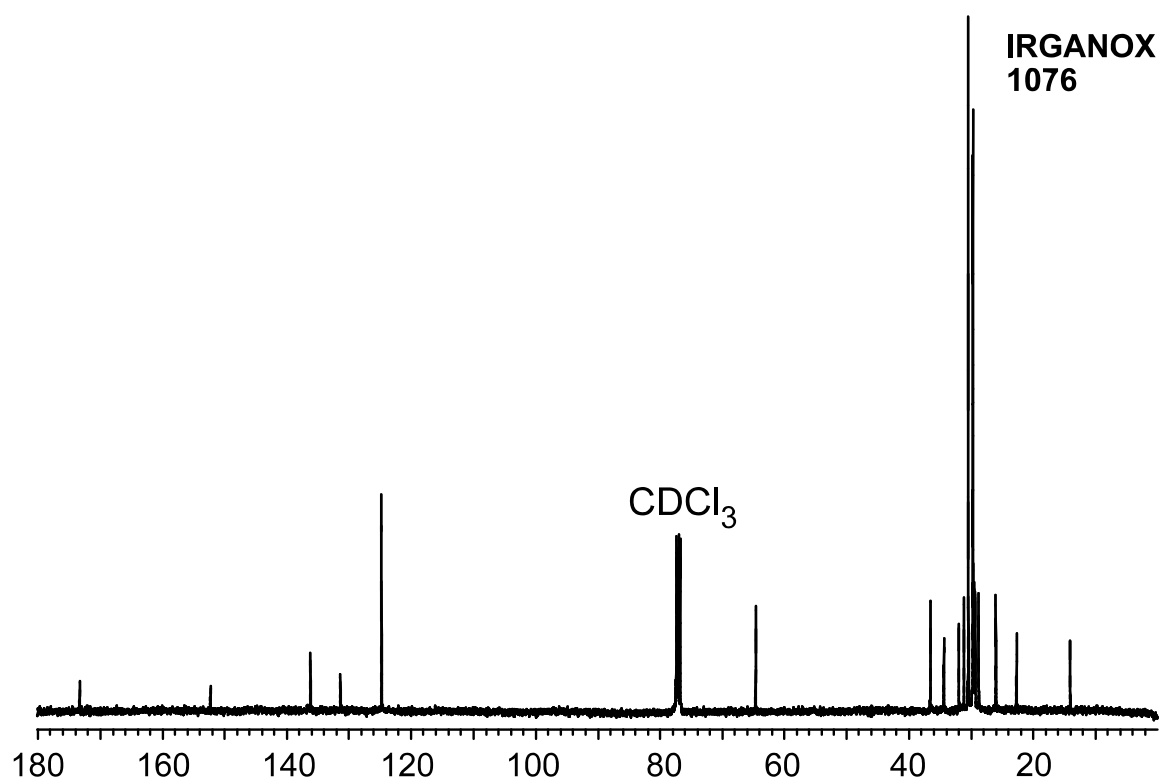


Figure 3.6.4.4 ^{13}C NMR spectrum of IRGANOX[®] 1076

($\text{Cp}^*\text{TiCl}_3/\text{MMAO}$) in our study exhibited this behavior (**Table 3.6.4.2**). With the standard catalyst, this was more obvious as the whole reaction mixture was solidified with gel-like polystyrene (at 1000 Al:Ti). On the other hand, the increase in activity of the new catalyst appeared to be leveling off at this Al:Ti ratio.

3.6.5 Summary on the Performance of New Catalysts in Olefin Polymerization

All new catalysts synthesized ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$) are active catalysts for ethylene polymerization when activated by a cocatalyst, MMAO. Catalytic activities of metallocene complexes ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$) were similar to that observed for their standard catalyst analogs (i.e., TiCp_2Cl_2 , and ZrCp_2Cl_2 , respectively) at both high and room temperatures. On the other hand, the half-sandwich complex, $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$, showed a two-fold increase in catalytic activity, compared to the standard catalyst TiCp^*Cl_3 (at both temperatures).

Table 3.6.4.2 Effect of the amount of MMAO-3A on styrene polymerization catalyzed by $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$ and Cp^*TiCl_3

Catalyst precursor	Al:Ti mole ratio	Activity, kg/(mol·h)
$\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$	100	222
	300	300
	1000	358
Cp^*TiCl_3	100	54
	300	309
	1000	1311 (gel)

Note: Reactions were performed using 8.1 μmol Ti, 4700 styrene:Ti mole ratio, in 25 mL toluene for 30 min at 50 °C.

Properties of polyethylenes produced from new catalysts were either similar to or less desirable (i.e., lower M_w or broader M_w/M_n) than those produced from standard catalysts.

The observed similar catalytic activities between new and standard catalysts may result from the detachment of active catalyst fragments from the cuboctametric cage through the breaking of the Si–O–M (M = Ti, Zr) bond. This supports the observation of the desorption of metallocene catalysts¹¹³ and half-sandwich complexes^{114, 115} from silica surface in the presence of an alkylaluminum. Duchateau's study on half-sandwich Group 4 silsesquioxane complexes also reported this leaching of the catalyst when MAO was used as a cocatalyst.¹²²

As for styrene polymerization, the only active catalyst is the half-sandwich complex, $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$, activated by MMAO. Its catalytic activity was about four times that of the standard catalyst TiCp^+Cl_2 at its optimal temperature (60 °C). Desirable properties of polystyrene product (high M_w , $M_w/M_n \approx 2$, stereocontrolled syndiotactic polystyrene) were also obtained.

Chapter 4

Conclusions

The chemically robust cubic sphaerosilicate octaanion was prepared as a highly hydrated tetramethylammonium salt, $(\text{NMe}_4)_8\text{Si}_8\text{O}_{20}\cdot 66 \text{ H}_2\text{O}$, in large quantities from low-cost starting materials. The removal of solvated water molecules (i.e., dehydration) from this sphaerosilicate by heating under vacuum (80 °C, 0.050 mm Hg) for 12 h resulted in 42% weight loss while maintaining the identity of the cubic cage. After dehydration, the reaction of the cubic sphaerosilicate octaanion with various silylating and stannylating reagents could be performed cleanly using small excesses (3 - 4 eq/ SiO^- reaction site) of these reagents. The stannylation product, $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, obtained at 53% yield was a particularly useful starting material for the preparation of many other derivatives of the cubic octamer.

The chloride exchange reaction between excesses of metal or nonmetal chloride with the SnMe_3 functionality on $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ occurred spontaneously, leading to the formation of eight-fold functionalized cubic octamer. Results from these exchange reactions confirmed the capability of $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$ to function as a labile source for the sphaerosilicate cubic octamer, $[\text{Si}_8\text{O}_{20}]^{8-}$. In the case that more than one reactive chloride ligands were present on each metal center, continuing exchange reactions of these chlorides between cuboctameric cages (i.e., cross-linking of cages) were also observed, forming oligomers of functionalized cuboctameric sphaerosilicates (i.e. cross-linked sphaerosilicates).

From chloride exchange reactions of specific Group 4 metal chlorides (Cp_2TiCl_2 , Cp_2ZrCl_2 , and Cp^*TiCl_3) with $\text{Si}_8\text{O}_{20}(\text{SnMe}_3)_8$, eight-fold functionalized Group 4 complexes of cubic octamer, containing only one cuboctameric cage, were obtained. The formulas of these products are $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^*\text{Cl}_2)_8$,

respectively. The single crystal X-ray structure of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ is reported and is the only single crystal X-ray structure ever obtained for metallocene or half-sandwich complexes coordinated to the cubic octamer.

Catalytic activities of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$, $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, and $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$ in ethylene and styrene polymerizations were studied under various conditions. While both metallocene (i.e., $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$) and half-sandwich (i.e., $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$) Group 4 complexes of cubic octamer were active in ethylene polymerization, the half-sandwich complex was the only active catalyst in styrene polymerization.

Catalytic activities of metallocene complexes ($\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$) in ethylene polymerization were similar to those of standard catalysts (TiCp_2Cl_2 and ZrCp_2Cl_2). Less desirable properties (i.e., lower M_w or broader M_w/M_n) were observed among polyethylenes produced by the catalyses of $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$ and $\text{Si}_8\text{O}_{20}(\text{ZrCp}_2\text{Cl})_8$, than those produced from standard catalysts. Similar catalytic activities between metallocene derivatives of cuboctameric spherosilicate and standard catalysts may serve as models for the desorption of metallocene catalysts from silica surface by their reactions with aluminum alkyls.

The half-sandwich complex, $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$, showed slight increases (2 – 4 times) in catalytic activity compared to the standard catalyst TiCp^+Cl_3 in ethylene and styrene polymerizations. Both polyethylene and polystyrene prepared had desirable properties (high M_w , narrow M_w/M_n) similar to those observed with the standard catalyst. In styrene polymerization, $\text{Si}_8\text{O}_{20}(\text{TiCp}^+\text{Cl}_2)_8$ was found to be highly syndiospecific, producing only syndiotactic polystyrene.

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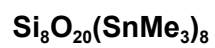
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APPENDICES

APPENDIX A

Crystal Structure Data for the Octa(trimethyltin) Cuboctameric Spherosilicate,



STRUCTURE DETERMINATION SUMMARY

Table A.1 Crystal data and structure refinement

Chemical formula	$C_{24}H_{80}O_{24}Si_8Sn_8$	
Formula weight	1927.12	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 11.2046(6)$ Å, $b = 12.0644(6)$ Å, $c = 12.3545(6)$ Å,	$\alpha = 86.6650(10)^\circ$ $\beta = 81.8930(10)^\circ$ $\gamma = 85.4890(10)^\circ$
Volume	$1646.35(14)$ Å ³	
Z	1	
Density (calculated)	1.944 Mg/m ³	
Absorption coefficient	3.187 mm ⁻¹	
F(000)	928	
Crystal size	$0.5 \times 0.4 \times 0.4$ mm ³	
Theta range for data collection	1.67 to 28.28°	
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 16$, $-15 \leq l \leq 16$	
Reflections collected	17832	
Independent reflections	7705 [R(int) = 0.0240]	
Completeness to $\theta = 28.28^\circ$	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7705 / 5 / 317	
Goodness-of-fit on F^2	1.135	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0634$	
R indices (all data)	$R_1 = 0.0267$, $wR_2 = 0.0647$	
Largest diff. peak and hole	0.363 and -1.802 e.Å ⁻³	

Table A.2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sn(1)	414(1)	7301(1)	1781(1)	41(1)
Sn(2)	6883(1)	3219(1)	3852(1)	39(1)
Sn(3)	5723(1)	8900(1)	2196(1)	35(1)
Sn(4)	1666(1)	2275(1)	2783(1)	44(1)
Si(4)	2974(1)	5841(1)	1149(1)	27(1)
Si(2)	3756(1)	3377(1)	1037(1)	27(1)
Si(1)	6461(1)	3878(1)	1309(1)	26(1)
Si(3)	5673(1)	6353(1)	1422(1)	27(1)
O(9)	6380(2)	5161(1)	1654(1)	34(1)
O(10)	7051(2)	3076(1)	2187(1)	36(1)
O(5)	1970(2)	6450(2)	2005(1)	37(1)
O(4)	2768(1)	6228(1)	-96(1)	34(1)
O(6)	3253(2)	2363(1)	1817(1)	37(1)
O(1)	5764(2)	7184(1)	2352(1)	37(1)
O(2)	6240(2)	6874(1)	238(1)	34(1)
O(7)	2906(1)	4505(1)	1307(1)	35(1)
O(3)	4287(1)	6138(1)	1362(1)	36(1)
O(8)	5113(1)	3544(1)	1237(1)	35(1)
C(1)	7420(3)	9114(3)	1260(4)	70(1)
C(2)	4168(3)	9177(3)	1389(4)	70(1)
C(3)	5588(5)	9098(3)	3889(3)	88(1)
C(6)	4980(3)	3489(3)	4183(3)	63(1)
C(5)	7771(3)	1646(3)	4192(3)	68(1)
C(12)	944(3)	8679(3)	748(3)	67(1)
C(4)	7884(4)	4608(4)	3957(3)	74(1)
C(7)	1456(4)	3704(4)	3730(3)	85(1)
C(10)	-545(4)	6104(4)	1149(4)	84(1)
C(9)	1955(5)	783(4)	3712(4)	106(2)
C(8)	421(4)	2221(6)	1653(4)	118(2)
C(11)	-252(5)	7704(5)	3418(4)	111(2)
O(11)	6597(3)	3196(3)	6141(2)	86(1)
O(12)	5562(3)	1101(2)	2147(3)	82(1)

Table A.3 Bond lengths [Å] and angles [°]

Sn(1)-O(5)	1.9978(15)	C(8)-Sn(4)-C(7)	115.6(2)
Sn(1)-C(12)	2.108(3)	O(5)-Si(4)-O(3)	109.43(10)
Sn(1)-C(10)	2.112(4)	O(5)-Si(4)-O(7)	110.08(9)
Sn(1)-C(11)	2.125(4)	O(3)-Si(4)-O(7)	108.17(9)
Sn(2)-O(10)	2.0549(16)	O(5)-Si(4)-O(4)	110.45(9)
Sn(2)-C(4)	2.108(4)	O(3)-Si(4)-O(4)	109.87(9)
Sn(2)-C(6)	2.117(3)	O(7)-Si(4)-O(4)	108.80(9)
Sn(2)-C(5)	2.120(3)	O(6)-Si(2)-O(8)	109.07(9)
Sn(3)-O(1)	2.0648(16)	O(6)-Si(2)-O(7)	109.82(9)
Sn(3)-C(3)	2.102(3)	O(8)-Si(2)-O(7)	109.85(9)
Sn(3)-C(1)	2.108(3)	O(6)-Si(2)-O(2)#1	110.70(9)
Sn(3)-C(2)	2.122(3)	O(8)-Si(2)-O(2)#1	108.78(9)
Sn(4)-O(6)	2.0032(16)	O(7)-Si(2)-O(2)#1	108.60(9)
Sn(4)-C(9)	2.107(4)	O(10)-Si(1)-O(8)	109.90(9)
Sn(4)-C(8)	2.115(4)	O(10)-Si(1)-O(9)	110.64(9)
Sn(4)-C(7)	2.118(4)	O(8)-Si(1)-O(9)	108.17(9)
Si(4)-O(5)	1.5966(16)	O(10)-Si(1)-O(4)#1	111.19(9)
Si(4)-O(3)	1.6015(17)	O(8)-Si(1)-O(4)#1	107.51(9)
Si(4)-O(7)	1.6194(17)	O(9)-Si(1)-O(4)#1	109.33(9)
Si(4)-O(4)	1.6241(16)	O(1)-Si(3)-O(3)	110.75(10)
Si(2)-O(6)	1.6001(16)	O(1)-Si(3)-O(9)	111.20(9)
Si(2)-O(8)	1.6040(16)	O(3)-Si(3)-O(9)	107.61(9)
Si(2)-O(7)	1.6204(16)	O(1)-Si(3)-O(2)	110.27(9)
Si(2)-O(2)#1	1.6210(16)	O(3)-Si(3)-O(2)	107.83(9)
Si(1)-O(10)	1.5902(15)	O(9)-Si(3)-O(2)	109.07(9)
Si(1)-O(8)	1.6095(16)	Si(3)-O(9)-Si(1)	140.94(11)
Si(1)-O(9)	1.6211(16)	Si(1)-O(10)-Sn(2)	128.23(10)
Si(1)-O(4)#1	1.6277(17)	Si(4)-O(5)-Sn(1)	130.40(10)
Si(3)-O(1)	1.5872(16)	Si(4)-O(4)-Si(1)#1	136.35(10)
Si(3)-O(3)	1.6066(17)	Si(2)-O(6)-Sn(4)	129.26(10)
Si(3)-O(9)	1.6176(16)	Si(3)-O(1)-Sn(3)	127.15(9)
Si(3)-O(2)	1.6216(17)	Si(2)#1-O(2)-Si(3)	137.21(11)
O(4)-Si(1)#1	1.6277(17)	Si(4)-O(7)-Si(2)	139.28(11)
O(2)-Si(2)#1	1.6211(16)	Si(4)-O(3)-Si(3)	172.13(12)
		Si(2)-O(8)-Si(1)	171.10(12)
O(5)-Sn(1)-C(12)	104.17(11)	Symmetry transformations used to generate equivalent atoms #1: -x+1,-y+1,-z	
O(5)-Sn(1)-C(10)	102.72(13)		
C(12)-Sn(1)-C(10)	118.00(17)		
O(5)-Sn(1)-C(11)	100.29(15)		
C(12)-Sn(1)-C(11)	114.1(2)		
C(10)-Sn(1)-C(11)	114.4(2)		
O(10)-Sn(2)-C(4)	101.42(12)		
O(10)-Sn(2)-C(6)	98.94(10)		
C(4)-Sn(2)-C(6)	116.28(17)		
O(10)-Sn(2)-C(5)	95.87(11)		
C(4)-Sn(2)-C(5)	115.67(17)		
C(6)-Sn(2)-C(5)	121.29(16)		
O(1)-Sn(3)-C(3)	94.15(12)		
O(1)-Sn(3)-C(1)	100.48(11)		
C(3)-Sn(3)-C(1)	117.00(19)		
O(1)-Sn(3)-C(2)	98.00(11)		
C(3)-Sn(3)-C(2)	120.2(2)		
C(1)-Sn(3)-C(2)	117.72(17)		
O(6)-Sn(4)-C(9)	101.88(15)		
O(6)-Sn(4)-C(8)	103.11(15)		
C(9)-Sn(4)-C(8)	115.1(3)		
O(6)-Sn(4)-C(7)	106.05(13)		
C(9)-Sn(4)-C(7)	113.1(2)		

Table A.4 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

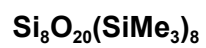
	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sn(1)	30(1)	44(1)	45(1)	0(1)	0(1)	8(1)
Sn(2)	41(1)	45(1)	32(1)	1(1)	-10(1)	1(1)
Sn(3)	39(1)	31(1)	36(1)	-6(1)	-6(1)	-3(1)
Sn(4)	41(1)	52(1)	36(1)	6(1)	3(1)	-10(1)
Si(4)	24(1)	28(1)	26(1)	-1(1)	-1(1)	4(1)
Si(2)	28(1)	25(1)	27(1)	2(1)	-2(1)	-3(1)
Si(1)	27(1)	26(1)	25(1)	1(1)	-6(1)	2(1)
Si(3)	30(1)	25(1)	26(1)	-4(1)	-6(1)	-1(1)
O(9)	37(1)	29(1)	39(1)	-5(1)	-12(1)	2(1)
O(10)	42(1)	35(1)	30(1)	2(1)	-11(1)	10(1)
O(5)	34(1)	45(1)	30(1)	-3(1)	1(1)	12(1)
O(4)	32(1)	41(1)	27(1)	1(1)	-3(1)	5(1)
O(6)	38(1)	30(1)	39(1)	6(1)	4(1)	-5(1)
O(1)	53(1)	30(1)	30(1)	-7(1)	-10(1)	-3(1)
O(2)	38(1)	36(1)	29(1)	-2(1)	-4(1)	-8(1)
O(7)	33(1)	29(1)	39(1)	0(1)	1(1)	-1(1)
O(3)	30(1)	39(1)	40(1)	-4(1)	-7(1)	-2(1)
O(8)	30(1)	39(1)	36(1)	2(1)	-6(1)	-6(1)
C(1)	50(2)	58(2)	99(3)	2(2)	8(2)	-8(2)
C(2)	56(2)	53(2)	108(3)	-6(2)	-39(2)	7(2)
C(3)	162(5)	63(2)	41(2)	-16(2)	-3(2)	-35(3)
C(6)	47(2)	89(3)	49(2)	-1(2)	2(1)	7(2)
C(5)	82(2)	66(2)	53(2)	16(2)	-18(2)	18(2)
C(12)	60(2)	53(2)	88(3)	22(2)	-21(2)	-4(2)
C(4)	85(3)	88(3)	57(2)	-11(2)	-14(2)	-36(2)
C(7)	93(3)	87(3)	67(2)	-23(2)	26(2)	-4(2)
C(10)	71(2)	73(3)	114(4)	9(2)	-31(2)	-27(2)
C(9)	138(4)	73(3)	89(3)	41(2)	26(3)	0(3)
C(8)	62(3)	223(7)	77(3)	-23(4)	-20(2)	-28(3)
C(11)	99(3)	152(5)	66(3)	-28(3)	22(2)	47(3)
O(11)	85(2)	140(3)	33(1)	-14(1)	0(1)	-19(2)
O(12)	78(2)	30(1)	142(3)	4(1)	-34(2)	2(1)

Table A.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
H(1A)	7844	8399	1136	105
H(1B)	7883	9553	1648	105
H(1C)	7307	9487	570	105
H(2A)	4371	8982	639	105
H(2B)	3884	9948	1416	105
H(2C)	3546	8726	1746	105
H(3A)	4808	8898	4238	131
H(3B)	5686	9860	4018	131
H(3C)	6206	8627	4184	131
H(6A)	4725	4170	3813	95
H(6B)	4742	3539	4957	95
H(6C)	4609	2881	3928	95
H(5A)	8185	1355	3523	102
H(5B)	7186	1143	4521	102
H(5C)	8344	1727	4686	102
H(12A)	1474	9093	1090	101
H(12B)	242	9150	618	101
H(12C)	1358	8424	64	101
H(4A)	8671	4491	3541	111
H(4B)	7965	4702	4708	111
H(4C)	7471	5263	3668	111
H(7A)	2179	3767	4050	128
H(7B)	785	3636	4300	128
H(7C)	1309	4355	3269	128
H(10A)	-166	5936	426	126
H(10B)	-1363	6394	1121	126
H(10C)	-542	5438	1614	126
H(9A)	2676	378	3387	159
H(9B)	1278	339	3726	159
H(9C)	2042	951	4446	159
H(8A)	806	2415	930	177
H(8B)	-260	2740	1846	177
H(8C)	152	1484	1670	177
H(11A)	218	7279	3910	167
H(11B)	-1082	7532	3585	167
H(11C)	-193	8484	3499	167
H(1)	5930(20)	3150(40)	6560(30)	97(16)
H(2)	7010(40)	3240(40)	6670(30)	107(17)
H(4)	4910(30)	1510(40)	2270(50)	160(30)
H(3)	6030(30)	1610(30)	2110(40)	97(16)

APPENDIX B

Crystal Structure Data for the Octa(trimethylsilyl) Cuboctameric Spherosilicate,



STRUCTURE DETERMINATION SUMMARY

Table B.1 Crystal data and structure refinement

Chemical formula	$C_{24}H_{72}O_{20}Si_{16}$	
Formula weight	2422.61	
Temperature	198(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 10.868(2)$ Å,	$\alpha = 76.97(3)^\circ$
	$b = 10.880(2)$ Å,	$\beta = 80.75(3)^\circ$
	$c = 13.497(3)$ Å,	$\gamma = 83.57(3)^\circ$
Volume	1529.8(5) Å ³	
Z	1	
Density (calculated)	1.227 Mg/m ³	
Absorption coefficient	0.388 mm ⁻¹	
F(000)	600	
Crystal size	0.2 x 0.2 x 0.2 mm ³	
Theta range for data collection	1.90 to 22.55/	
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 0, -14 ≤ l ≤ 14	
Reflections collected	4425	
Independent reflections	4430 [R(int) = 0.0230]	
Completeness to theta = 22.55/	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4030 / 0 / 392	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2σ(I)]	R1 = 0.0477, wR2 = 0.1249	
R indices (all data)	R1 = 0.0578, wR2 = 0.1345	
Largest diff. peak and hole	0.303 and -0.325 e.Å ⁻³	

Table B.2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	1847(1)	1194(1)	10369(1)	43(1)
Si(2)	-1427(1)	1639(1)	8787(1)	44(1)
Si(3)	1388(1)	940(1)	8235(1)	46(1)
Si(4)	-968(1)	1893(1)	10921(1)	44(1)
O(1)	1938(2)	1291(2)	9158(2)	57(1)
O(2)	-26(2)	1541(2)	8207(2)	58(1)
O(3)	-1433(2)	2131(2)	9820(2)	56(1)
O(4)	532(2)	1849(2)	10781(2)	54(1)
O(5)	2951(2)	1889(3)	10580(2)	71(1)
O(6)	-1565(2)	3002(2)	11474(2)	65(1)
O(7)	-2275(2)	2609(2)	8064(2)	62(1)
O(8)	2221(2)	1498(3)	7185(2)	64(1)
O(9)	-1406(2)	567(2)	11602(2)	56(1)
O(10)	-1955(2)	260(2)	9057(2)	55(1)
Si(5A)	-3279(3)	2660(3)	7273(2)	61(1)
C(4A)	-4752(11)	2034(19)	7977(9)	156(7)
C(6A)	-3550(40)	4300(30)	6710(30)	230(20)
C(5)	-2542(6)	1703(6)	6317(5)	117(2)
Si(5B)	-2521(3)	3142(3)	6857(2)	61(1)
C(4B)	-1294(12)	4151(11)	6155(9)	115(4)
C(6B)	-4000(20)	4040(20)	6840(20)	141(10)
Si(6A)	3710(5)	2686(6)	11076(2)	69(1)
C(2A)	3200(20)	4320(12)	10771(16)	203(9)
C(3A)	5245(13)	2610(40)	10530(30)	300(20)
C(1)	3301(9)	2108(9)	12510(5)	172(3)
Si(6B)	4114(4)	1924(9)	11203(3)	75(2)
C(2B)	5091(13)	455(19)	11279(13)	150(8)
C(3B)	5030(40)	3090(70)	10700(20)	476(12)
Si(7A)	2674(3)	1283(5)	6008(2)	61(1)
C(7A)	3490(20)	2690(20)	5351(17)	197(12)
C(8A)	3705(11)	-182(11)	6062(9)	149(5)
C(9A)	1326(15)	1040(18)	5447(14)	145(7)
Si(7B)	2214(7)	1948(8)	5943(3)	63(2)
C(7B)	3702(19)	2400(40)	5360(30)	88(8)
C(8B)	1136(18)	3322(17)	5623(13)	115(7)
C(9B)	1710(40)	640(30)	5510(30)	180(20)
Si(8A)	-1607(11)	3782(12)	12370(9)	64(2)
C(10)	-525(9)	3032(8)	13224(5)	164(3)
C(11A)	-1770(70)	5422(18)	11720(20)	330(40)
C(12A)	-2980(30)	3570(30)	13221(16)	185(12)
Si(8B)	-1349(11)	4030(10)	12107(9)	88(2)
C(11B)	-2850(30)	4680(40)	12620(30)	330(30)
C(12B)	-250(30)	5086(16)	11480(14)	194(12)

Table B.3 Bond lengths [Å] and angles [°]

Si(1)-O(5)	1.581(2)	C(1)-Si(6B)	1.886(8)
Si(1)-O(10)#1	1.597(3)	Si(6B)-C(3B)	1.66(4)
Si(1)-O(4)	1.598(3)	Si(6B)-C(2B)	1.810(18)
Si(1)-O(1)	1.601(2)	Si(7A)-C(9A)	1.823(13)
Si(2)-O(7)	1.589(2)	Si(7A)-C(7A)	1.83(2)
Si(2)-O(2)	1.600(3)	Si(7A)-C(8A)	1.838(11)
Si(2)-O(3)	1.600(2)	Si(7B)-C(7B)	1.75(2)
Si(2)-O(10)	1.611(3)	Si(7B)-C(8B)	1.81(2)
Si(3)-O(8)	1.587(3)	Si(7B)-C(9B)	1.82(2)
Si(3)-O(1)	1.600(2)	Si(8A)-C(12A)	1.73(3)
Si(3)-O(9)#1	1.603(3)	Si(8A)-C(10)	1.782(12)
Si(3)-O(2)	1.605(3)	Si(8A)-C(11A)	1.81(2)
Si(4)-O(6)	1.583(2)	C(10)-Si(8B)	1.933(12)
Si(4)-O(9)	1.603(3)	Si(8B)-C(12B)	1.735(17)
Si(4)-O(3)	1.603(2)	Si(8B)-C(11B)	1.80(2)
Si(4)-O(4)	1.607(3)		
O(5)-Si(6A)	1.575(3)	O(5)-Si(1)-O(10)#1	109.71(15)
O(5)-Si(6B)	1.635(4)	O(5)-Si(1)-O(4)	109.90(14)
O(6)-Si(8B)	1.609(10)	O(10)#1-Si(1)-O(4)	109.24(14)
O(6)-Si(8A)	1.619(11)	O(5)-Si(1)-O(1)	109.09(15)
O(7)-Si(5A)	1.633(3)	O(10)#1-Si(1)-O(1)	109.53(14)
O(7)-Si(5B)	1.655(3)	O(4)-Si(1)-O(1)	109.35(14)
O(8)-Si(7B)	1.638(5)	O(7)-Si(2)-O(2)	109.43(15)
O(8)-Si(7A)	1.646(3)	O(7)-Si(2)-O(3)	109.28(14)
O(9)-Si(3)#1	1.603(3)	O(2)-Si(2)-O(3)	109.50(14)
O(10)-Si(1)#1	1.597(3)	O(7)-Si(2)-O(10)	109.84(14)
Si(5A)-C(6A)	1.79(3)	O(2)-Si(2)-O(10)	108.77(14)
Si(5A)-C(4A)	1.842(13)	O(3)-Si(2)-O(10)	110.01(14)
Si(5A)-C(5)	1.865(6)	O(8)-Si(3)-O(1)	108.86(14)
C(5)-Si(5B)	1.874(6)	O(8)-Si(3)-O(9)#1	110.08(14)
Si(5B)-C(6B)	1.79(2)	O(1)-Si(3)-O(9)#1	109.73(14)
Si(5B)-C(4B)	1.825(12)	O(8)-Si(3)-O(2)	109.45(15)
Si(6A)-C(3A)	1.711(17)	O(1)-Si(3)-O(2)	109.75(14)
Si(6A)-C(2A)	1.776(16)	O(9)#1-Si(3)-O(2)	108.95(14)
Si(6A)-C(1)	1.892(8)	O(6)-Si(4)-O(9)	109.60(15)

Table B.3 Bond lengths [Å] and angles [°]

O(6)-Si(4)-O(3)	108.93(14)	C(9A)-Si(7A)-C(8A)	106.2(7)
O(9)-Si(4)-O(3)	109.41(14)	C(7A)-Si(7A)-C(8A)	112.5(9)
O(6)-Si(4)-O(4)	110.20(14)	O(8)-Si(7B)-C(7B)	108.8(12)
O(9)-Si(4)-O(4)	108.90(14)	O(8)-Si(7B)-C(8B)	111.8(7)
O(3)-Si(4)-O(4)	109.79(14)	C(7B)-Si(7B)-C(8B)	106.3(13)
Si(3)-O(1)-Si(1)	148.07(17)	O(8)-Si(7B)-C(9B)	107.1(12)
Si(2)-O(2)-Si(3)	148.12(17)	C(7B)-Si(7B)-C(9B)	114.1(18)
Si(2)-O(3)-Si(4)	147.78(17)	C(8B)-Si(7B)-C(9B)	108.8(16)
Si(1)-O(4)-Si(4)	148.06(16)	O(6)-Si(8A)-C(12A)	110.6(12)
Si(6A)-O(5)-Si(1)	161.3(3)	O(6)-Si(8A)-C(10)	109.9(7)
Si(6A)-O(5)-Si(6B)	32.04(15)	C(12A)-Si(8A)-C(10)	98.7(11)
Si(1)-O(5)-Si(6B)	151.1(4)	O(6)-Si(8A)-C(11A)	104.4(13)
Si(4)-O(6)-Si(8B)	147.3(4)	C(12A)-Si(8A)-C(11A)	104.1(17)
Si(4)-O(6)-Si(8A)	150.4(4)	C(10)-Si(8A)-C(11A)	128(2)
Si(8B)-O(6)-Si(8A)	16.7(5)	Si(8A)-C(10)-Si(8B)	13.7(5)
Si(2)-O(7)-Si(5A)	141.7(2)	O(6)-Si(8B)-C(12B)	114.6(7)
Si(2)-O(7)-Si(5B)	143.9(2)	O(6)-Si(8B)-C(11B)	108.7(10)
Si(5A)-O(7)-Si(5B)	36.92(12)	C(12B)-Si(8B)-C(11B)	117.3(15)
Si(3)-O(8)-Si(7B)	143.4(3)	O(6)-Si(8B)-C(10)	103.3(6)
Si(3)-O(8)-Si(7A)	142.7(2)	C(12B)-Si(8B)-C(10)	102.3(8)
Si(7B)-O(8)-Si(7A)	29.2(2)	C(11B)-Si(8B)-C(10)	109.3(13)
Si(4)-O(9)-Si(3)#1	149.72(17)		
Si(1)#1-O(10)-Si(2)	149.41(16)		
O(7)-Si(5A)-C(6A)	105.3(10)		
O(7)-Si(5A)-C(4A)	110.4(4)		
C(6A)-Si(5A)-C(4A)	109.8(15)		
O(7)-Si(5A)-C(5)	107.2(3)		
C(6A)-Si(5A)-C(5)	112.7(14)		
C(4A)-Si(5A)-C(5)	111.2(6)		
Si(5A)-C(5)-Si(5B)	32.33(13)		
O(7)-Si(5B)-C(6B)	109.0(10)		
O(7)-Si(5B)-C(4B)	110.2(4)		
C(6B)-Si(5B)-C(4B)	109.3(11)		
O(7)-Si(5B)-C(5)	105.9(3)		
C(6B)-Si(5B)-C(5)	110.2(8)		
C(4B)-Si(5B)-C(5)	112.2(5)		
O(5)-Si(6A)-C(3A)	109.4(10)		
O(5)-Si(6A)-C(2A)	110.9(7)		
C(3A)-Si(6A)-C(2A)	104.4(16)		
O(5)-Si(6A)-C(1)	105.1(3)		
C(3A)-Si(6A)-C(1)	119.2(13)		
C(2A)-Si(6A)-C(1)	107.8(8)		
Si(6B)-C(1)-Si(6A)	27.18(17)		
O(5)-Si(6B)-C(3B)	115.1(17)		
O(5)-Si(6B)-C(2B)	109.9(6)		
C(3B)-Si(6B)-C(2B)	107(3)		
O(5)-Si(6B)-C(1)	102.9(4)		
C(3B)-Si(6B)-C(1)	110.2(15)		
C(2B)-Si(6B)-C(1)	111.3(7)		
O(8)-Si(7A)-C(9A)	109.8(6)		
O(8)-Si(7A)-C(7A)	104.4(8)		
C(9A)-Si(7A)-C(7A)	115.0(11)		
O(8)-Si(7A)-C(8A)	108.9(4)		

Symmetry transformations used to generate equivalent atoms #1: -x,-y,-z+2

Table B.4 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Si(1)	42(1)	48(1)	45(1)	-17(1)	-11(1)	-13(1)
Si(2)	50(1)	44(1)	41(1)	-11(1)	-17(1)	1(1)
Si(3)	49(1)	54(1)	34(1)	-9(1)	0(1)	-12(1)
Si(4)	50(1)	43(1)	43(1)	-21(1)	-10(1)	1(1)
O(1)	59(2)	72(2)	43(1)	-13(1)	-5(1)	-20(1)
O(2)	56(2)	65(2)	50(1)	-10(1)	-8(1)	-3(1)
O(3)	68(2)	59(2)	49(1)	-21(1)	-19(1)	4(1)
O(4)	53(1)	57(2)	59(2)	-26(1)	-10(1)	-4(1)
O(5)	60(2)	80(2)	87(2)	-32(2)	-23(1)	-25(1)
O(6)	69(2)	64(2)	75(2)	-44(1)	-18(1)	11(1)
O(7)	71(2)	56(2)	62(2)	-13(1)	-33(1)	11(1)
O(8)	70(2)	81(2)	39(1)	-9(1)	7(1)	-25(1)
O(9)	64(2)	55(2)	51(1)	-15(1)	-2(1)	-7(1)
O(10)	59(2)	54(2)	55(2)	-12(1)	-19(1)	-7(1)
Si(5A)	59(2)	79(2)	46(2)	-5(1)	-22(1)	-1(2)
C(4A)	75(8)	320(20)	83(8)	-36(11)	-13(6)	-51(10)
C(6A)	360(50)	110(15)	230(30)	44(15)	-230(30)	0(20)
C(5)	137(5)	144(5)	96(4)	-59(4)	-34(4)	-19(4)
Si(5B)	71(2)	60(2)	55(2)	-7(1)	-30(2)	0(1)
C(4B)	147(11)	106(8)	86(7)	5(6)	-22(7)	-38(8)
C(6B)	132(12)	109(15)	220(20)	-71(16)	-128(14)	54(12)
Si(6A)	67(2)	76(3)	78(2)	-23(2)	-24(1)	-30(2)
C(2A)	250(20)	95(10)	280(20)	-66(12)	-40(17)	-62(11)
C(3A)	46(8)	500(50)	430(40)	-230(40)	33(13)	-106(16)
C(1)	205(9)	235(10)	94(5)	-68(6)	-35(5)	-14(7)
Si(6B)	50(2)	111(5)	80(2)	-40(3)	-17(2)	-22(2)
C(2B)	76(9)	220(20)	159(15)	-46(13)	-44(9)	36(11)
C(3B)	460(30)	980(50)	108(15)	-170(30)	70(20)	-611
Si(7A)	59(1)	85(2)	37(1)	-14(1)	0(1)	-7(1)
C(7A)	350(30)	176(17)	63(10)	-8(10)	49(14)	-152(18)
C(8A)	138(9)	184(11)	141(9)	-95(9)	-26(7)	58(8)
C(9A)	94(7)	270(20)	95(9)	-75(11)	-41(6)	-3(9)
Si(7B)	76(4)	73(4)	41(2)	-17(2)	4(2)	-22(3)
C(7B)	55(9)	140(20)	62(15)	-22(13)	21(8)	-13(11)
C(8B)	137(15)	121(14)	87(11)	-3(10)	-52(11)	-1(11)
C(9B)	350(60)	127(19)	110(20)	-72(17)	30(30)	-160(30)
Si(8A)	99(4)	53(4)	48(4)	-29(3)	-20(3)	6(3)
C(10)	234(9)	177(7)	107(5)	-38(5)	-80(6)	-31(7)
C(11A)	710(100)	55(10)	180(20)	-37(12)	80(40)	60(30)
C(12A)	230(30)	180(20)	109(14)	-46(15)	58(15)	59(19)
Si(8B)	149(5)	58(3)	68(4)	-37(3)	-10(3)	-7(3)
C(11B)	230(30)	470(60)	400(50)	-390(50)	-150(30)	230(40)
C(12B)	350(30)	95(11)	172(15)	-27(10)	-64(17)	-125(16)

Table B.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$)

	x	y	z	U(eq)
H(4AA)	-4581	1192	8362	234
H(4AB)	-5310	2015	7497	234
H(4AC)	-5132	2568	8437	234
H(6AA)	-2782	4621	6341	341
H(6AB)	-3871	4758	7234	341
H(6AC)	-4150	4396	6236	341
H(5A)	-1722	1366	6467	176
H(5B)	-2480	2230	5639	176
H(5C)	-3046	1020	6352	176
H(4BA)	-516	3645	6078	172
H(4BB)	-1211	4784	6529	172
H(4BC)	-1510	4555	5490	172
H(6BA)	-3984	4772	7121	211
H(6BB)	-4645	3527	7242	211
H(6BC)	-4179	4305	6144	211
H(2AA)	2343	4442	11054	305
H(2AB)	3295	4610	10039	305
H(2AC)	3703	4790	11056	305
H(3AA)	5595	1750	10680	457
H(3AB)	5700	3128	10813	457
H(3AC)	5300	2912	9804	457
H(1A)	2728	2725	12786	257
H(1B)	4047	1983	12828	257
H(1C)	2919	1321	12645	257
H(2BA)	5502	392	10605	226
H(2BB)	4583	-244	11553	226
H(2BC)	5707	436	11720	226
H(3BA)	5434	2994	10030	714
H(3BB)	5654	3071	11133	714
H(3BC)	4539	3888	10637	714
H(7AA)	2912	3430	5338	295
H(7AB)	3814	2620	4660	295
H(7AC)	4162	2762	5709	295
H(8AA)	4413	-119	6387	224
H(8AB)	3988	-306	5378	224
H(8AC)	3254	-886	6450	224
H(9AA)	876	373	5899	218
H(9AB)	1604	814	4796	218
H(9AC)	786	1807	5352	218
H(7BA)	3911	3076	5638	131
H(7BB)	3703	2681	4633	131
H(7BC)	4307	1691	5492	131
H(8BA)	299	3112	5905	172
H(8BB)	1194	3588	4890	172
H(8BC)	1344	3996	5903	172
H(9BA)	913	416	5883	277
H(9BB)	2313	-81	5632	277
H(9BC)	1656	882	4790	277
H(10A)	230	2746	12838	245
H(10B)	-884	2322	13697	245

Table B.5 (Continued)

	x	y	z	U(eq)
H(10C)	-338	3625	13599	245
H(11A)	-1025	5626	11244	501
H(11B)	-1889	5950	12214	501
H(11C)	-2476	5562	11352	501
H(12A)	-2984	2708	13585	277
H(12B)	-3682	3786	12849	277
H(12C)	-3032	4115	13702	277
H(11D)	-3258	5187	12061	490
H(11E)	-2738	5207	13075	490
H(11F)	-3355	4011	12980	490
H(12D)	-566	5639	10900	290
H(12E)	509	4625	11249	290
H(12F)	-79	5577	11944	290

APPENDIX C

Crystal Structure Data for the Octa(bis(cyclopentadienyl) monochloro titanium(IV))

Cuboctameric Spherosilicate, $\text{Si}_8\text{O}_{20}(\text{TiCp}_2\text{Cl})_8$

STRUCTURE DETERMINATION SUMMARY

Table C.1 Crystal data and structure refinement

Chemical formula	C ₈₂ H ₈₄ Cl ₁₂ O ₂₀ Si ₈ Ti ₈
Formula weight	2507.74
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 13.5224(5)$ Å, $b = 13.9471(6)$ Å, $c = 14.0575(6)$ Å, $\alpha = 102.0180(10)^\circ$, $\beta = 99.8730(10)^\circ$, $\gamma = 107.7360(10)^\circ$
Volume	$2390.06(17)$ Å ³
Z	1
Density (calculated)	1.742 Mg/m ³
Absorption coefficient	1.193 mm ⁻¹
F(000)	1270
Crystal size	$0.2 \times 0.2 \times 0.05$ mm ³
Theta range for data collection	1.84 to 27.50°
Index ranges	$-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	29643
Independent reflections	29643 [R(int) = 0.0000]
Completeness to $\theta = 28.28^\circ$	96.2 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	29643 / 821 / 866
Goodness-of-fit on F ²	3.201
Final R indices [$I > 2\sigma(I)$]	R ₁ = 0.1160, wR ₂ = 0.2540
R indices (all data)	R ₁ = 0.1355, wR ₂ = 0.2572
Largest diff. peak and hole	2.021 and -0.901 e.Å ⁻³

Table C.2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	3958(1)	3907(1)	6077(1)	26(1)
Si(2)	3366(1)	3367(1)	3801(1)	26(1)
Si(3)	3683(1)	5670(1)	3914(1)	29(1)
Si(4)	4281(1)	6211(1)	6199(1)	29(1)
O(1)	3329(2)	3374(2)	4927(3)	36(1)
O(2)	3304(3)	4431(2)	3608(3)	39(1)
O(3)	3710(2)	6083(2)	5066(3)	37(1)
O(4)	4028(3)	5089(2)	6393(3)	38(1)
O(5)	4861(2)	6116(3)	3776(3)	36(1)
O(6)	5536(2)	6734(2)	6363(2)	37(1)
Ti(1)	3191(1)	2763(1)	7812(1)	34(1)
Cl(1)	1520(1)	2835(2)	7869(2)	93(1)
O(7)	3340(2)	3275(3)	6721(2)	37(1)
C(1)	3690(30)	4592(14)	8590(20)	118(11)
C(2)	3260(30)	4070(20)	9230(20)	159(17)
C(3)	3910(30)	3560(30)	9530(20)	113(15)
C(4)	4758(19)	3730(20)	9056(14)	84(9)
C(5)	4620(20)	4420(20)	8550(20)	73(10)
C(1')	4230(20)	4375(18)	8801(17)	86(10)
C(2')	3719(19)	3870(17)	9405(16)	73(8)
C(3')	4080(13)	3080(20)	9488(15)	58(6)
C(4')	4839(16)	3090(30)	8928(17)	75(9)
C(5')	4938(14)	3910(30)	8543(15)	88(11)
C(6)	2036(7)	1037(6)	6895(8)	101(3)
C(7)	2366(9)	1042(6)	7843(10)	120(4)
C(8)	3427(11)	1286(7)	8112(8)	136(4)
C(9)	3822(8)	1463(7)	7267(11)	126(5)
C(10)	2917(10)	1238(6)	6546(7)	105(3)
Ti(2)	1747(1)	1271(1)	1969(1)	31(1)
Cl(2)	51(1)	1397(1)	1681(2)	80(1)
O(8)	2391(2)	2407(3)	3069(2)	37(1)
C(11)	705(5)	-420(5)	2011(6)	69(2)
C(12)	1054(6)	179(5)	2970(6)	68(2)
C(13)	2116(6)	484(5)	3258(6)	78(2)
C(14)	2462(6)	91(5)	2449(8)	81(3)
C(15)	1548(7)	-487(5)	1676(6)	87(3)
C(16)	2635(7)	2558(5)	1221(5)	75(2)
C(17)	1697(7)	1943(8)	554(6)	100(3)
C(18)	1733(6)	950(7)	266(5)	89(3)
C(19)	2722(6)	972(6)	768(5)	73(2)
C(20)	3232(5)	1947(6)	1358(5)	71(2)
Ti(3)	1783(1)	5961(1)	2270(1)	32(1)
Cl(3)	2372(3)	5126(2)	987(2)	72(1)
O(9)	2921(3)	6041(3)	3247(3)	46(1)
C(21)	2726(10)	7417(9)	1750(13)	85(4)
C(22)	1721(11)	7084(9)	1246(8)	67(4)
C(23)	1119(8)	7216(8)	1895(13)	85(5)
C(24)	1804(17)	7645(10)	2860(11)	133(9)

Table C.2 (Continued)

	x	y	z	U(eq)
C(25)	2771(13)	7758(9)	2717(12)	128(7)
C(26)	907(7)	4288(7)	2482(8)	56(3)
C(27)	385(8)	4277(7)	1574(8)	70(3)
C(28)	-58(7)	5008(9)	1687(10)	81(4)
C(29)	149(9)	5491(8)	2683(11)	88(4)
C(30)	756(8)	5035(8)	3172(7)	77(4)
Ti(4)	3285(1)	7797(1)	7535(1)	32(1)
Cl(4)	4715(2)	9339(2)	7708(2)	58(1)
O(10)	3901(3)	6913(3)	6963(3)	45(1)
C(31)	2639(7)	7680(7)	5824(6)	49(2)
C(32)	2532(7)	8546(6)	6381(7)	49(2)
C(33)	1809(7)	8231(8)	6927(7)	57(3)
C(34)	1482(7)	7168(8)	6723(7)	58(3)
C(35)	1964(6)	6829(7)	6033(7)	56(3)
C(36)	2675(7)	6908(8)	8667(7)	57(3)
C(37)	2421(8)	7796(10)	8850(7)	70(3)
C(38)	3353(11)	8637(9)	9207(8)	75(4)
C(39)	4205(8)	8286(8)	9285(7)	64(3)
C(40)	3754(9)	7249(10)	9005(9)	98(6)
Ti(3')	3182(3)	7373(3)	7817(3)	32(1)
Cl(3')	4362(6)	7233(5)	9084(5)	72(1)
O(9')	2921(3)	6041(3)	3247(3)	46(1)
C(21')	4377(13)	9124(13)	8210(20)	98(12)
C(22')	3741(18)	9097(14)	8846(13)	86(10)
C(23')	2748(14)	8875(14)	8290(20)	90(10)
C(24')	2730(20)	8701(18)	7272(18)	120(14)
C(25')	3750(20)	8890(16)	7257(17)	128(7)
C(26')	2190(11)	5567(11)	7482(13)	46(5)
C(27')	2161(13)	6040(15)	8400(12)	63(6)
C(28')	1647(15)	6727(15)	8329(16)	78(7)
C(29')	1357(12)	6687(14)	7328(17)	70(7)
C(30')	1663(13)	5950(14)	6826(11)	57(5)
Ti(4')	2051(3)	6558(3)	2583(3)	32(1)
Cl(4')	3411(4)	7971(4)	2435(5)	58(1)
O(10')	3901(3)	6913(3)	6963(3)	45(1)
C(31')	2304(11)	7376(12)	4260(10)	45(5)
C(32')	1978(12)	7985(11)	3745(12)	48(5)
C(33')	959(13)	7426(14)	3185(12)	58(6)
C(34')	637(11)	6451(14)	3369(13)	58(6)
C(35')	1470(14)	6445(12)	4037(12)	57(5)
C(36')	798(15)	5015(15)	1366(13)	71(7)
C(37')	491(14)	5816(19)	1208(13)	82(8)
C(38')	1270(20)	6450(17)	888(17)	89(11)
C(39')	2050(15)	6020(20)	808(15)	119(15)
C(40')	1751(16)	5150(19)	1102(17)	83(9)
C(41)	-940(5)	7521(5)	5009(6)	82(2)
Cl(5)	147(8)	8486(11)	4914(12)	105(4)
Cl(6)	-784(10)	6394(9)	5210(20)	110(4)
C(41')	-940(5)	7521(5)	5009(6)	82(2)

Table C.2 (Continued)

	x	y	z	U(eq)
Cl(5')	223(9)	8529(9)	5173(17)	109(5)
Cl(6')	-865(11)	6306(8)	4728(13)	81(3)
C(42)	4356(15)	10093(13)	4980(20)	160(16)
Cl(7)	5233(6)	9563(7)	5319(6)	148(3)
Cl(8)	4843(3)	11320(4)	4975(4)	85(1)

Table C.3 Bond lengths [Å] and angles [°]

Si(1)-O(7)	1.561(3)	Ti(2)-C(11)	2.369(6)
Si(1)-O(4)	1.585(3)	Ti(2)-C(12)	2.378(6)
Si(1)-O(5)#1	1.586(3)	Ti(2)-C(16)	2.383(6)
Si(1)-O(1)	1.592(4)	C(11)-C(15)	1.328(8)
Si(2)-O(8)	1.573(3)	C(11)-C(12)	1.346(8)
Si(2)-O(6)#1	1.585(3)	C(12)-C(13)	1.329(8)
Si(2)-O(2)	1.588(3)	C(13)-C(14)	1.374(8)
Si(2)-O(1)	1.589(3)	C(14)-C(15)	1.388(8)
Si(3)-O(9)	1.550(4)	C(16)-C(17)	1.348(8)
Si(3)-O(2)	1.583(3)	C(16)-C(20)	1.361(8)
Si(3)-O(5)	1.585(3)	C(17)-C(18)	1.378(9)
Si(3)-O(3)	1.592(4)	C(18)-C(19)	1.388(8)
Si(4)-O(10)	1.560(3)	C(19)-C(20)	1.333(8)
Si(4)-O(6)	1.583(3)	Ti(3)-O(9)	1.837(4)
Si(4)-O(4)	1.588(3)	Ti(3)-C(23)	2.308(9)
Si(4)-O(3)	1.595(4)	Ti(3)-C(24)	2.312(12)
O(5)-Si(1)#1	1.586(3)	Ti(3)-C(29)	2.316(9)
O(6)-Si(2)#1	1.585(3)	Ti(3)-C(30)	2.323(8)
Ti(1)-O(7)	1.838(3)	Ti(3)-Cl(3)	2.330(3)
Ti(1)-C(1')	2.25(2)	Ti(3)-C(28)	2.338(9)
Ti(1)-C(9)	2.279(8)	Ti(3)-C(25)	2.340(11)
Ti(1)-C(2')	2.29(2)	Ti(3)-C(22)	2.347(10)
Ti(1)-C(8)	2.289(8)	Ti(3)-C(21)	2.377(10)
Ti(1)-Cl(1)	2.3064(18)	Ti(3)-C(26)	2.379(8)
Ti(1)-C(5')	2.318(19)	Ti(3)-C(27)	2.398(9)
Ti(1)-C(4)	2.317(19)	C(21)-C(22)	1.308(11)
Ti(1)-C(3)	2.33(3)	C(21)-C(25)	1.328(12)
Ti(1)-C(7)	2.332(7)	C(22)-C(23)	1.343(11)
Ti(1)-C(3')	2.337(19)	C(23)-C(24)	1.395(12)
Ti(1)-C(4')	2.349(19)	C(24)-C(25)	1.324(12)
C(1)-C(5)	1.351(14)	C(26)-C(27)	1.342(10)
C(1)-C(2)	1.356(14)	C(26)-C(30)	1.358(10)
C(2)-C(3)	1.354(15)	C(27)-C(28)	1.327(11)
C(3)-C(4)	1.403(14)	C(28)-C(29)	1.360(11)
C(4)-C(5)	1.358(14)	C(29)-C(30)	1.363(11)
C(1')-C(2')	1.359(13)	Ti(4)-O(10)	1.818(4)
C(1')-C(5')	1.365(14)	Ti(4)-C(34)	2.311(9)
C(2')-C(3')	1.352(15)	Ti(4)-C(36)	2.323(8)
C(3')-C(4')	1.394(13)	Ti(4)-C(33)	2.334(8)
C(4')-C(5')	1.342(14)	Ti(4)-Cl(4)	2.348(3)
C(6)-C(7)	1.329(10)	Ti(4)-C(35)	2.349(8)
C(6)-C(10)	1.339(9)	Ti(4)-C(37)	2.350(8)
C(7)-C(8)	1.334(10)	Ti(4)-C(32)	2.356(8)
C(8)-C(9)	1.421(10)	Ti(4)-C(31)	2.366(8)
C(9)-C(10)	1.353(10)	Ti(4)-C(38)	2.370(10)
Ti(2)-O(8)	1.827(3)	Ti(4)-C(40)	2.401(11)
Ti(2)-C(14)	2.304(6)	Ti(4)-C(39)	2.408(9)
Ti(2)-C(15)	2.322(6)	C(31)-C(32)	1.359(9)
Ti(2)-Cl(2)	2.3266(17)	C(31)-C(35)	1.380(9)
Ti(2)-C(20)	2.331(6)	C(32)-C(33)	1.370(10)
Ti(2)-C(18)	2.337(6)	C(33)-C(34)	1.362(10)
Ti(2)-C(19)	2.359(6)	C(34)-C(35)	1.343(9)
Ti(2)-C(13)	2.364(6)	C(36)-C(40)	1.351(11)
Ti(2)-C(17)	2.368(7)	C(36)-C(37)	1.370(10)
		C(37)-C(38)	1.362(11)

Table C.3 (Continued)

C(38)-C(39)	1.379(11)	O(4)-Si(1)-O(5)#1	108.66(19)
C(39)-C(40)	1.328(11)	O(7)-Si(1)-O(1)	108.12(18)
Ti(3')-Cl(3')	2.262(8)	O(4)-Si(1)-O(1)	109.90(19)
Ti(3')-C(29')	2.277(16)	O(5)#1-Si(1)-O(1)	108.97(18)
Ti(3')-C(28')	2.298(17)	O(8)-Si(2)-O(6)#1	110.37(18)
Ti(3')-C(23')	2.340(17)	O(8)-Si(2)-O(2)	110.3(2)
Ti(3')-C(30')	2.342(16)	O(6)#1-Si(2)-O(2)	108.95(19)
Ti(3')-C(24')	2.35(2)	O(8)-Si(2)-O(1)	108.68(17)
Ti(3')-C(27')	2.344(16)	O(6)#1-Si(2)-O(1)	108.63(19)
Ti(3')-C(22')	2.348(17)	O(2)-Si(2)-O(1)	109.85(18)
Ti(3')-C(25')	2.37(2)	O(9)-Si(3)-O(2)	110.8(2)
Ti(3')-C(26')	2.366(14)	O(9)-Si(3)-O(5)	109.70(19)
Ti(3')-C(21')	2.367(17)	O(2)-Si(3)-O(5)	108.29(19)
C(21')-C(22')	1.342(14)	O(9)-Si(3)-O(3)	110.1(2)
C(21')-C(25')	1.370(14)	O(2)-Si(3)-O(3)	109.08(18)
C(22')-C(23')	1.341(14)	O(5)-Si(3)-O(3)	108.74(18)
C(23')-C(24')	1.395(14)	O(10)-Si(4)-O(6)	108.97(19)
C(24')-C(25')	1.331(14)	O(10)-Si(4)-O(4)	109.44(19)
C(26')-C(27')	1.335(13)	O(6)-Si(4)-O(4)	108.72(19)
C(26')-C(30')	1.361(13)	O(10)-Si(4)-O(3)	111.7(2)
C(27')-C(28')	1.354(13)	O(6)-Si(4)-O(3)	108.47(18)
C(28')-C(29')	1.379(13)	O(4)-Si(4)-O(3)	109.48(19)
C(29')-C(30')	1.334(13)	Si(2)-O(1)-Si(1)	144.8(2)
Ti(4')-C(31')	2.311(14)	Si(3)-O(2)-Si(2)	151.6(2)
Ti(4')-Cl(4')	2.325(6)	Si(3)-O(3)-Si(4)	145.7(2)
Ti(4')-C(35')	2.329(15)	Si(1)-O(4)-Si(4)	151.1(2)
Ti(4')-C(33')	2.335(16)	Si(3)-O(5)-Si(1)#1	149.4(2)
Ti(4')-C(32')	2.336(15)	Si(4)-O(6)-Si(2)#1	149.3(2)
Ti(4')-C(34')	2.348(15)	O(7)-Ti(1)-C(1')	88.0(5)
Ti(4')-C(36')	2.383(18)	O(7)-Ti(1)-C(9)	93.2(3)
Ti(4')-C(37')	2.387(16)	C(1')-Ti(1)-C(9)	124.2(8)
Ti(4')-C(38')	2.39(2)	O(7)-Ti(1)-C(2')	121.0(5)
Ti(4')-C(40')	2.42(2)	C(1')-Ti(1)-C(2')	34.8(5)
Ti(4')-C(39')	2.45(2)	C(9)-Ti(1)-C(2')	125.8(7)
C(31')-C(32')	1.346(12)	O(7)-Ti(1)-C(8)	129.0(3)
C(31')-C(35')	1.368(12)	C(1')-Ti(1)-C(8)	121.7(7)
C(32')-C(33')	1.358(13)	C(9)-Ti(1)-C(8)	36.2(3)
C(33')-C(34')	1.390(13)	C(2')-Ti(1)-C(8)	101.7(6)
C(34')-C(35')	1.340(13)	O(7)-Ti(1)-Cl(1)	98.11(12)
C(36')-C(37')	1.351(13)	C(1')-Ti(1)-Cl(1)	99.8(8)
C(36')-C(40')	1.371(13)	C(9)-Ti(1)-Cl(1)	134.9(3)
C(37')-C(38')	1.358(14)	C(2')-Ti(1)-Cl(1)	84.1(6)
C(38')-C(39')	1.377(14)	C(8)-Ti(1)-Cl(1)	113.9(4)
C(39')-C(40')	1.333(14)	O(7)-Ti(1)-C(5')	85.0(5)
C(41)-Cl(5)	1.710(10)	C(1')-Ti(1)-C(5')	34.7(4)
C(41)-Cl(6)	1.722(11)	C(9)-Ti(1)-C(5')	89.8(9)
C(42)-Cl(7)	1.633(13)	C(2')-Ti(1)-C(5')	57.1(6)
C(42)-Cl(8)	1.637(13)	C(8)-Ti(1)-C(5')	97.6(9)
	Angle (°)	Cl(1)-Ti(1)-C(5')	134.5(9)
O(7)-Si(1)-O(4)	110.5(2)	O(7)-Ti(1)-C(4)	105.9(5)
O(7)-Si(1)-O(5)#1	110.70(18)	C(1')-Ti(1)-C(4)	34.9(7)
		C(9)-Ti(1)-C(4)	92.8(9)

Table C.3 (Continued)

C(2')-Ti(1)-C(4)	41.1(7)	C(5)-C(4)-C(3)	103.6(12)
C(8)-Ti(1)-C(4)	87.6(9)	C(5)-C(4)-Ti(1)	76.5(13)
Cl(1)-Ti(1)-C(4)	124.9(8)	C(3)-C(4)-Ti(1)	72.7(13)
C(5')-Ti(1)-C(4)	21.4(6)	C(1)-C(5)-C(4)	111.5(12)
O(7)-Ti(1)-C(3)	131.3(7)	C(1)-C(5)-Ti(1)	73.2(13)
C(1')-Ti(1)-C(3)	43.3(8)	C(4)-C(5)-Ti(1)	70.0(12)
C(9)-Ti(1)-C(3)	111.2(12)	C(2')-C(1')-C(5')	107.8(12)
C(2')-Ti(1)-C(3)	15.1(9)	C(2')-C(1')-Ti(1)	74.2(11)
C(8)-Ti(1)-C(3)	87.0(10)	C(5')-C(1')-Ti(1)	75.3(11)
Cl(1)-Ti(1)-C(3)	93.3(9)	C(3')-C(2')-C(1')	107.8(13)
C(5')-Ti(1)-C(3)	55.1(7)	C(3')-C(2')-Ti(1)	74.9(11)
C(4)-Ti(1)-C(3)	35.2(4)	C(1')-C(2')-Ti(1)	71.0(11)
O(7)-Ti(1)-C(7)	128.8(3)	C(2')-C(3')-C(4')	108.5(12)
C(1')-Ti(1)-C(7)	142.8(6)	C(2')-C(3')-Ti(1)	71.1(11)
C(9)-Ti(1)-C(7)	57.5(3)	C(4')-C(3')-Ti(1)	73.2(10)
C(2')-Ti(1)-C(7)	110.0(6)	C(5')-C(4')-C(3')	106.4(11)
C(8)-Ti(1)-C(7)	33.6(3)	C(5')-C(4')-Ti(1)	72.0(10)
Cl(1)-Ti(1)-C(7)	82.1(3)	C(3')-C(4')-Ti(1)	72.2(10)
C(5')-Ti(1)-C(7)	130.1(9)	C(4')-C(5')-C(1')	109.4(11)
C(4)-Ti(1)-C(7)	115.6(8)	C(4')-C(5')-Ti(1)	74.6(10)
C(3)-Ti(1)-C(7)	99.6(8)	C(1')-C(5')-Ti(1)	69.9(11)
O(7)-Ti(1)-C(3')	140.6(5)	C(7)-C(6)-C(10)	105.3(9)
C(1')-Ti(1)-C(3')	57.0(5)	C(7)-C(6)-Ti(1)	71.9(5)
C(9)-Ti(1)-C(3')	92.8(7)	C(10)-C(6)-Ti(1)	72.9(4)
C(2')-Ti(1)-C(3')	34.0(4)	C(6)-C(7)-C(8)	111.4(8)
C(8)-Ti(1)-C(3')	68.8(7)	C(6)-C(7)-Ti(1)	75.3(4)
Cl(1)-Ti(1)-C(3')	104.8(4)	C(8)-C(7)-Ti(1)	71.5(5)
C(5')-Ti(1)-C(3')	56.2(5)	C(7)-C(8)-C(9)	107.2(8)
C(4)-Ti(1)-C(3')	34.8(7)	C(7)-C(8)-Ti(1)	75.0(5)
C(3)-Ti(1)-C(3')	18.9(9)	C(9)-C(8)-Ti(1)	71.5(4)
C(7)-Ti(1)-C(3')	86.4(7)	C(10)-C(9)-C(8)	103.0(8)
O(7)-Ti(1)-C(4')	113.2(5)	C(10)-C(9)-Ti(1)	76.1(5)
C(1')-Ti(1)-C(4')	57.4(6)	C(8)-C(9)-Ti(1)	72.3(5)
C(9)-Ti(1)-C(4')	71.4(9)	C(6)-C(10)-C(9)	112.8(9)
C(2')-Ti(1)-C(4')	57.4(5)	C(6)-C(10)-Ti(1)	74.2(4)
C(8)-Ti(1)-C(4')	66.2(9)	C(9)-C(10)-Ti(1)	69.9(5)
Cl(1)-Ti(1)-C(4')	138.9(5)	O(8)-Ti(2)-C(14)	101.0(3)
C(5')-Ti(1)-C(4')	33.4(4)	O(8)-Ti(2)-C(15)	133.5(3)
C(4)-Ti(1)-C(4')	22.6(6)	C(14)-Ti(2)-C(15)	34.9(2)
C(3)-Ti(1)-C(4')	46.0(9)	O(8)-Ti(2)-Cl(2)	97.24(12)
C(7)-Ti(1)-C(4')	97.0(9)	C(14)-Ti(2)-Cl(2)	135.35(18)
C(3')-Ti(1)-C(4')	34.6(4)	C(15)-Ti(2)-Cl(2)	108.6(2)
Si(1)-O(7)-Ti(1)	155.8(2)	O(8)-Ti(2)-C(20)	86.3(2)
C(5)-C(1)-C(2)	107.1(13)	C(14)-Ti(2)-C(20)	89.8(3)
C(5)-C(1)-Ti(1)	74.0(14)	C(15)-Ti(2)-C(20)	102.6(3)
C(2)-C(1)-Ti(1)	72.7(10)	Cl(2)-Ti(2)-C(20)	132.0(2)
C(3)-C(2)-C(1)	107.8(14)	O(8)-Ti(2)-C(18)	134.7(2)
C(3)-C(2)-Ti(1)	71.5(13)	C(14)-Ti(2)-C(18)	102.2(4)
C(1)-C(2)-Ti(1)	74.2(10)	C(15)-Ti(2)-C(18)	83.0(3)
C(2)-C(3)-C(4)	109.6(14)	Cl(2)-Ti(2)-C(18)	92.9(2)
C(2)-C(3)-Ti(1)	75.0(13)	C(20)-Ti(2)-C(18)	55.5(2)
C(4)-C(3)-Ti(1)	72.1(12)	O(8)-Ti(2)-C(19)	118.5(2)

Table C.3 (Continued)

C(14)-Ti(2)-C(19)	77.1(3)	C(15)-C(11)-Ti(2)	71.6(4)
C(15)-Ti(2)-C(19)	74.9(3)	C(12)-C(11)-Ti(2)	73.9(3)
Cl(2)-Ti(2)-C(19)	127.2(2)	C(13)-C(12)-C(11)	109.5(7)
C(20)-Ti(2)-C(19)	33.02(19)	C(13)-C(12)-Ti(2)	73.1(4)
C(18)-Ti(2)-C(19)	34.4(2)	C(11)-C(12)-Ti(2)	73.1(4)
O(8)-Ti(2)-C(13)	78.0(2)	C(12)-C(13)-C(14)	107.6(6)
C(14)-Ti(2)-C(13)	34.2(2)	C(12)-C(13)-Ti(2)	74.3(4)
C(15)-Ti(2)-C(13)	56.3(3)	C(14)-C(13)-Ti(2)	70.5(4)
Cl(2)-Ti(2)-C(13)	114.5(2)	C(13)-C(14)-C(15)	106.5(6)
C(20)-Ti(2)-C(13)	113.1(3)	C(13)-C(14)-Ti(2)	75.3(4)
C(18)-Ti(2)-C(13)	135.8(3)	C(15)-C(14)-Ti(2)	73.3(4)
C(19)-Ti(2)-C(13)	110.3(3)	C(11)-C(15)-C(14)	107.8(7)
O(8)-Ti(2)-C(17)	106.0(3)	C(11)-C(15)-Ti(2)	75.5(4)
C(14)-Ti(2)-C(17)	133.2(3)	C(14)-C(15)-Ti(2)	71.8(4)
C(15)-Ti(2)-C(17)	116.6(3)	C(17)-C(16)-C(20)	107.5(7)
Cl(2)-Ti(2)-C(17)	78.0(2)	C(17)-C(16)-Ti(2)	72.9(4)
C(20)-Ti(2)-C(17)	55.4(3)	C(20)-C(16)-Ti(2)	71.2(4)
C(18)-Ti(2)-C(17)	34.1(2)	C(16)-C(17)-C(18)	107.6(7)
C(19)-Ti(2)-C(17)	56.5(3)	C(16)-C(17)-Ti(2)	74.1(4)
C(13)-Ti(2)-C(17)	166.7(3)	C(18)-C(17)-Ti(2)	71.7(4)
O(8)-Ti(2)-C(11)	124.7(2)	C(17)-C(18)-C(19)	108.1(7)
C(14)-Ti(2)-C(11)	56.0(2)	C(17)-C(18)-Ti(2)	74.2(4)
C(15)-Ti(2)-C(11)	32.9(2)	C(19)-C(18)-Ti(2)	73.7(4)
Cl(2)-Ti(2)-C(11)	80.12(18)	C(20)-C(19)-C(18)	106.0(7)
C(20)-Ti(2)-C(11)	135.2(3)	C(20)-C(19)-Ti(2)	72.4(4)
C(18)-Ti(2)-C(11)	100.5(3)	C(18)-C(19)-Ti(2)	72.0(4)
C(19)-Ti(2)-C(11)	105.1(3)	C(19)-C(20)-C(16)	110.8(7)
C(13)-Ti(2)-C(11)	55.0(2)	C(19)-C(20)-Ti(2)	74.6(4)
C(17)-Ti(2)-C(11)	126.6(3)	C(16)-C(20)-Ti(2)	75.3(4)
O(8)-Ti(2)-C(12)	91.7(2)	O(9)-Ti(3)-C(23)	132.0(4)
C(14)-Ti(2)-C(12)	55.5(2)	O(9)-Ti(3)-C(24)	97.8(5)
C(15)-Ti(2)-C(12)	55.0(2)	C(23)-Ti(3)-C(24)	35.2(3)
Cl(2)-Ti(2)-C(12)	83.70(18)	O(9)-Ti(3)-C(29)	114.3(4)
C(20)-Ti(2)-C(12)	144.2(3)	C(23)-Ti(3)-C(29)	77.7(4)
C(18)-Ti(2)-C(12)	133.4(3)	C(24)-Ti(3)-C(29)	83.5(5)
C(19)-Ti(2)-C(12)	128.4(3)	O(9)-Ti(3)-C(30)	84.0(3)
C(13)-Ti(2)-C(12)	32.55(19)	C(23)-Ti(3)-C(30)	110.0(4)
C(17)-Ti(2)-C(12)	155.8(3)	C(24)-Ti(3)-C(30)	103.2(5)
C(11)-Ti(2)-C(12)	32.95(19)	C(29)-Ti(3)-C(30)	34.2(3)
O(8)-Ti(2)-C(16)	79.2(2)	O(9)-Ti(3)-Cl(3)	92.66(16)
C(14)-Ti(2)-C(16)	123.3(3)	C(23)-Ti(3)-Cl(3)	114.4(4)
C(15)-Ti(2)-C(16)	130.5(3)	C(24)-Ti(3)-Cl(3)	134.7(3)
Cl(2)-Ti(2)-C(16)	100.0(2)	C(29)-Ti(3)-Cl(3)	130.9(3)
C(20)-Ti(2)-C(16)	33.5(2)	C(30)-Ti(3)-Cl(3)	121.7(3)
C(18)-Ti(2)-C(16)	55.6(2)	O(9)-Ti(3)-C(28)	138.1(3)
C(19)-Ti(2)-C(16)	55.7(2)	C(23)-Ti(3)-C(28)	78.2(4)
C(13)-Ti(2)-C(16)	140.5(3)	C(24)-Ti(3)-C(28)	101.6(6)
C(17)-Ti(2)-C(16)	33.0(2)	C(29)-Ti(3)-C(28)	34.0(3)
C(11)-Ti(2)-C(16)	156.1(3)	C(30)-Ti(3)-C(28)	55.6(3)
C(12)-Ti(2)-C(16)	170.5(3)	Cl(3)-Ti(3)-C(28)	99.2(4)
Si(2)-O(8)-Ti(2)	154.5(2)	O(9)-Ti(3)-C(25)	79.7(3)
C(15)-C(11)-C(12)	108.6(7)	C(23)-Ti(3)-C(25)	55.1(4)

Table C.3 (Continued)

C(24)-Ti(3)-C(25)	33.1(3)	C(24)-C(23)-Ti(3)	72.6(6)
C(29)-Ti(3)-C(25)	116.1(6)	C(25)-C(24)-C(23)	104.4(10)
C(30)-Ti(3)-C(25)	127.9(6)	C(25)-C(24)-Ti(3)	74.6(8)
Cl(3)-Ti(3)-C(25)	108.2(5)	C(23)-C(24)-Ti(3)	72.3(6)
C(28)-Ti(3)-C(25)	132.2(5)	C(24)-C(25)-C(21)	111.3(11)
O(9)-Ti(3)-C(22)	128.4(4)	C(24)-C(25)-Ti(3)	72.3(8)
C(23)-Ti(3)-C(22)	33.5(3)	C(21)-C(25)-Ti(3)	75.2(7)
C(24)-Ti(3)-C(22)	56.7(4)	C(27)-C(26)-C(30)	107.1(8)
C(29)-Ti(3)-C(22)	106.7(5)	C(27)-C(26)-Ti(3)	74.5(5)
C(30)-Ti(3)-C(22)	140.8(5)	C(30)-C(26)-Ti(3)	71.0(5)
Cl(3)-Ti(3)-C(22)	82.6(3)	C(28)-C(27)-C(26)	109.0(9)
C(28)-Ti(3)-C(22)	93.1(4)	C(28)-C(27)-Ti(3)	71.2(5)
C(25)-Ti(3)-C(22)	54.1(4)	C(26)-C(27)-Ti(3)	72.9(5)
O(9)-Ti(3)-C(21)	96.4(4)	C(27)-C(28)-C(29)	109.2(9)
C(23)-Ti(3)-C(21)	54.8(3)	C(27)-C(28)-Ti(3)	76.2(6)
C(24)-Ti(3)-C(21)	55.7(4)	C(29)-C(28)-Ti(3)	72.1(6)
C(29)-Ti(3)-C(21)	132.3(4)	C(30)-C(29)-Ti(3)	73.2(5)
C(30)-Ti(3)-C(21)	158.7(4)	C(26)-C(30)-C(29)	108.8(8)
Cl(3)-Ti(3)-C(21)	79.5(3)	C(26)-C(30)-Ti(3)	75.5(5)
C(28)-Ti(3)-C(21)	125.2(4)	C(29)-C(30)-Ti(3)	72.6(5)
C(25)-Ti(3)-C(21)	32.7(3)	O(10)-Ti(4)-C(34)	108.6(3)
C(22)-Ti(3)-C(21)	32.1(3)	O(10)-Ti(4)-C(36)	97.8(3)
O(9)-Ti(3)-C(26)	85.8(2)	C(34)-Ti(4)-C(36)	83.2(3)
C(23)-Ti(3)-C(26)	131.1(3)	O(10)-Ti(4)-C(33)	133.1(3)
C(24)-Ti(3)-C(26)	136.3(4)	C(34)-Ti(4)-C(33)	34.1(3)
C(29)-Ti(3)-C(26)	56.2(3)	C(36)-Ti(4)-C(33)	101.3(3)
C(30)-Ti(3)-C(26)	33.5(3)	O(10)-Ti(4)-Cl(4)	95.37(14)
Cl(3)-Ti(3)-C(26)	88.2(3)	C(34)-Ti(4)-Cl(4)	133.4(3)
C(28)-Ti(3)-C(26)	54.9(3)	C(36)-Ti(4)-Cl(4)	133.4(3)
C(25)-Ti(3)-C(26)	158.5(5)	C(33)-Ti(4)-Cl(4)	101.5(3)
C(22)-Ti(3)-C(26)	144.8(4)	O(10)-Ti(4)-C(35)	78.8(2)
C(21)-Ti(3)-C(26)	167.6(4)	C(34)-Ti(4)-C(35)	33.5(2)
O(9)-Ti(3)-C(27)	116.3(3)	C(36)-Ti(4)-C(35)	102.0(3)
C(23)-Ti(3)-C(27)	108.5(4)	C(33)-Ti(4)-C(35)	55.6(3)
C(24)-Ti(3)-C(27)	134.0(6)	Cl(4)-Ti(4)-C(35)	124.4(2)
C(29)-Ti(3)-C(27)	55.3(3)	O(10)-Ti(4)-C(37)	131.8(3)
C(30)-Ti(3)-C(27)	54.7(3)	C(34)-Ti(4)-C(37)	76.1(3)
Cl(3)-Ti(3)-C(27)	76.3(3)	C(36)-Ti(4)-C(37)	34.1(3)
C(28)-Ti(3)-C(27)	32.5(3)	C(33)-Ti(4)-C(37)	77.4(3)
C(25)-Ti(3)-C(27)	163.5(4)	Cl(4)-Ti(4)-C(37)	116.2(3)
C(22)-Ti(3)-C(27)	112.3(4)	C(35)-Ti(4)-C(37)	107.2(4)
C(21)-Ti(3)-C(27)	139.8(5)	O(10)-Ti(4)-C(32)	112.4(2)
C(26)-Ti(3)-C(27)	32.6(2)	C(34)-Ti(4)-C(32)	56.6(3)
Si(3)-O(9)-Ti(3)	159.0(3)	C(36)-Ti(4)-C(32)	135.1(3)
C(22)-C(21)-C(25)	107.9(10)	C(33)-Ti(4)-C(32)	34.0(2)
C(22)-C(21)-Ti(3)	72.7(6)	Cl(4)-Ti(4)-C(32)	77.6(2)
C(25)-C(21)-Ti(3)	72.1(7)	C(35)-Ti(4)-C(32)	55.7(3)
C(21)-C(22)-C(23)	108.8(9)	C(37)-Ti(4)-C(32)	109.5(3)
C(21)-C(22)-Ti(3)	75.2(6)	O(10)-Ti(4)-C(31)	80.7(2)
C(23)-C(22)-Ti(3)	71.7(5)	C(34)-Ti(4)-C(31)	56.6(3)
C(22)-C(23)-C(24)	107.7(9)	C(36)-Ti(4)-C(31)	135.8(3)
C(22)-C(23)-Ti(3)	74.8(5)	C(33)-Ti(4)-C(31)	56.1(3)

Table C.3 (Continued)

Cl(4)-Ti(4)-C(31)	90.4(2)	C(37)-C(36)-Ti(4)	74.0(5)
C(35)-Ti(4)-C(31)	34.0(2)	C(38)-C(37)-C(36)	108.1(8)
C(37)-Ti(4)-C(31)	130.7(3)	C(38)-C(37)-Ti(4)	74.1(5)
C(32)-Ti(4)-C(31)	33.4(2)	C(36)-C(37)-Ti(4)	71.9(5)
O(10)-Ti(4)-C(38)	135.0(3)	C(37)-C(38)-C(39)	108.9(8)
C(34)-Ti(4)-C(38)	104.1(4)	C(37)-C(38)-Ti(4)	72.4(5)
C(36)-Ti(4)-C(38)	56.2(3)	C(39)-C(38)-Ti(4)	74.7(6)
C(33)-Ti(4)-C(38)	90.6(4)	C(40)-C(39)-C(38)	104.6(9)
Cl(4)-Ti(4)-C(38)	83.5(3)	C(40)-C(39)-Ti(4)	73.7(6)
C(35)-Ti(4)-C(38)	137.5(4)	C(38)-C(39)-Ti(4)	71.7(6)
C(37)-Ti(4)-C(38)	33.5(3)	C(39)-C(40)-C(36)	113.0(9)
C(32)-Ti(4)-C(38)	111.3(4)	C(39)-C(40)-Ti(4)	74.3(6)
C(31)-Ti(4)-C(38)	144.2(4)	C(36)-C(40)-Ti(4)	70.3(6)
O(10)-Ti(4)-C(40)	84.3(3)	Cl(3')-Ti(3')-C(29')	131.1(6)
C(34)-Ti(4)-C(40)	116.2(4)	Cl(3')-Ti(3')-C(28')	98.2(6)
C(36)-Ti(4)-C(40)	33.2(3)	C(29')-Ti(3')-C(28')	35.1(4)
C(33)-Ti(4)-C(40)	131.0(3)	Cl(3')-Ti(3')-C(23')	111.8(7)
Cl(4)-Ti(4)-C(40)	105.2(3)	C(29')-Ti(3')-C(23')	78.8(7)
C(35)-Ti(4)-C(40)	128.5(4)	C(28')-Ti(3')-C(23')	78.3(7)
C(37)-Ti(4)-C(40)	54.0(3)	Cl(3')-Ti(3')-C(30')	122.4(5)
C(32)-Ti(4)-C(40)	163.0(3)	C(29')-Ti(3')-C(30')	33.5(4)
C(31)-Ti(4)-C(40)	159.3(4)	C(28')-Ti(3')-C(30')	55.8(5)
C(38)-Ti(4)-C(40)	53.4(3)	C(23')-Ti(3')-C(30')	110.8(7)
O(10)-Ti(4)-C(39)	102.2(3)	Cl(3')-Ti(3')-C(24')	138.2(6)
C(34)-Ti(4)-C(39)	131.9(3)	C(29')-Ti(3')-C(24')	77.1(8)
C(36)-Ti(4)-C(39)	56.3(3)	C(28')-Ti(3')-C(24')	96.0(10)
C(33)-Ti(4)-C(39)	124.1(4)	C(23')-Ti(3')-C(24')	34.6(4)
Cl(4)-Ti(4)-C(39)	77.2(3)	C(30')-Ti(3')-C(24')	97.9(7)
C(35)-Ti(4)-C(39)	158.4(3)	Cl(3')-Ti(3')-C(27')	75.1(4)
C(37)-Ti(4)-C(39)	55.9(3)	C(29')-Ti(3')-C(27')	57.0(5)
C(32)-Ti(4)-C(39)	138.6(3)	C(28')-Ti(3')-C(27')	33.9(4)
C(31)-Ti(4)-C(39)	167.4(3)	C(23')-Ti(3')-C(27')	109.7(7)
C(38)-Ti(4)-C(39)	33.5(3)	C(30')-Ti(3')-C(27')	55.0(5)
C(40)-Ti(4)-C(39)	32.1(3)	C(24')-Ti(3')-C(27')	129.6(9)
Si(4)-O(10)-Ti(4)	163.9(3)	Cl(3')-Ti(3')-C(22')	82.1(5)
C(32)-C(31)-C(35)	106.7(7)	C(29')-Ti(3')-C(22')	109.7(8)
C(32)-C(31)-Ti(4)	72.9(5)	C(28')-Ti(3')-C(22')	96.8(7)
C(35)-C(31)-Ti(4)	72.3(5)	C(23')-Ti(3')-C(22')	33.2(4)
C(31)-C(32)-C(33)	108.2(8)	C(30')-Ti(3')-C(22')	143.0(8)
C(31)-C(32)-Ti(4)	73.7(5)	C(24')-Ti(3')-C(22')	57.3(5)
C(33)-C(32)-Ti(4)	72.1(5)	C(27')-Ti(3')-C(22')	117.1(7)
C(34)-C(33)-C(32)	108.2(8)	Cl(3')-Ti(3')-C(25')	116.7(8)
C(34)-C(33)-Ti(4)	72.0(5)	C(29')-Ti(3')-C(25')	108.0(9)
C(32)-C(33)-Ti(4)	73.9(5)	C(28')-Ti(3')-C(25')	128.2(9)
C(35)-C(34)-C(33)	107.6(8)	C(23')-Ti(3')-C(25')	54.4(5)
C(35)-C(34)-Ti(4)	74.8(5)	C(30')-Ti(3')-C(25')	119.2(8)
C(33)-C(34)-Ti(4)	73.9(5)	C(24')-Ti(3')-C(25')	32.8(4)
C(34)-C(35)-C(31)	109.2(8)	C(27')-Ti(3')-C(25')	162.1(9)
C(34)-C(35)-Ti(4)	71.7(5)	C(22')-Ti(3')-C(25')	55.5(5)
C(31)-C(35)-Ti(4)	73.7(5)	Cl(3')-Ti(3')-C(26')	88.8(5)
C(40)-C(36)-C(37)	104.9(8)	C(29')-Ti(3')-C(26')	56.8(5)
C(40)-C(36)-Ti(4)	76.5(6)	C(28')-Ti(3')-C(26')	56.0(5)

Table C.3 (Continued)

C(23')-Ti(3')-C(26')	132.4(5)	C(31')-Ti(4')-C(32')	33.7(3)
C(30')-Ti(3')-C(26')	33.6(3)	Cl(4')-Ti(4')-C(32')	76.8(4)
C(24')-Ti(3')-C(26')	131.0(7)	C(35')-Ti(4')-C(32')	56.1(4)
C(27')-Ti(3')-C(26')	32.9(3)	C(33')-Ti(4')-C(32')	33.8(3)
C(22')-Ti(3')-C(26')	149.8(7)	C(31')-Ti(4')-C(34')	56.7(5)
C(25')-Ti(3')-C(26')	150.2(8)	Cl(4')-Ti(4')-C(34')	132.4(5)
Cl(3')-Ti(3')-C(21')	85.0(6)	C(35')-Ti(4')-C(34')	33.3(3)
C(29')-Ti(3')-C(21')	130.7(6)	C(33')-Ti(4')-C(34')	34.5(4)
C(28')-Ti(3')-C(21')	129.2(6)	C(32')-Ti(4')-C(34')	56.9(5)
C(23')-Ti(3')-C(21')	54.4(4)	C(31')-Ti(4')-C(36')	136.7(6)
C(30')-Ti(3')-C(21')	152.4(8)	Cl(4')-Ti(4')-C(36')	131.8(5)
C(24')-Ti(3')-C(21')	56.1(5)	C(35')-Ti(4')-C(36')	102.5(6)
C(27')-Ti(3')-C(21')	147.4(8)	C(33')-Ti(4')-C(36')	103.2(7)
C(22')-Ti(3')-C(21')	33.1(4)	C(32')-Ti(4')-C(36')	136.8(7)
C(25')-Ti(3')-C(21')	33.6(4)	C(34')-Ti(4')-C(36')	84.4(7)
C(26')-Ti(3')-C(21')	172.5(6)	C(31')-Ti(4')-C(37')	131.9(6)
C(22')-C(21')-C(25')	108.1(13)	Cl(4')-Ti(4')-C(37')	115.5(6)
C(22')-C(21')-Ti(3')	72.7(9)	C(35')-Ti(4')-C(37')	107.0(7)
C(25')-C(21')-Ti(3')	73.1(11)	C(33')-Ti(4')-C(37')	79.4(6)
C(23')-C(22')-C(21')	106.6(12)	C(32')-Ti(4')-C(37')	111.6(6)
C(23')-C(22')-Ti(3')	73.1(9)	C(34')-Ti(4')-C(37')	76.6(6)
C(21')-C(22')-Ti(3')	74.3(9)	C(36')-Ti(4')-C(37')	32.9(4)
C(22')-C(23')-C(24')	110.6(13)	C(31')-Ti(4')-C(38')	145.6(7)
C(22')-C(23')-Ti(3')	73.7(9)	Cl(4')-Ti(4')-C(38')	83.2(6)
C(24')-C(23')-Ti(3')	73.0(11)	C(35')-Ti(4')-C(38')	136.9(8)
C(25')-C(24')-C(23')	104.2(13)	C(33')-Ti(4')-C(38')	91.3(8)
C(25')-C(24')-Ti(3')	74.4(12)	C(32')-Ti(4')-C(38')	112.7(7)
C(23')-C(24')-Ti(3')	72.4(11)	C(34')-Ti(4')-C(38')	103.8(8)
C(24')-C(25')-C(21')	110.3(14)	C(36')-Ti(4')-C(38')	54.6(5)
C(24')-C(25')-Ti(3')	72.8(13)	C(37')-Ti(4')-C(38')	33.0(4)
C(21')-C(25')-Ti(3')	73.2(10)	C(31')-Ti(4')-C(40')	158.0(7)
C(27')-C(26')-C(30')	106.9(11)	Cl(4')-Ti(4')-C(40')	104.7(6)
C(27')-C(26')-Ti(3')	72.7(8)	C(35')-Ti(4')-C(40')	128.1(8)
C(30')-C(26')-Ti(3')	72.2(8)	C(33')-Ti(4')-C(40')	133.2(6)
C(26')-C(27')-C(28')	109.0(12)	C(32')-Ti(4')-C(40')	165.1(6)
C(26')-C(27')-Ti(3')	74.4(8)	C(34')-Ti(4')-C(40')	117.3(7)
C(28')-C(27')-Ti(3')	71.2(9)	C(36')-Ti(4')-C(40')	33.1(4)
C(27')-C(28')-C(29')	107.7(12)	C(37')-Ti(4')-C(40')	54.1(5)
C(27')-C(28')-Ti(3')	74.9(9)	C(38')-Ti(4')-C(40')	53.5(5)
C(29')-C(28')-Ti(3')	71.6(9)	C(31')-Ti(4')-C(39')	168.5(7)
C(30')-C(29')-C(28')	106.3(12)	Cl(4')-Ti(4')-C(39')	77.5(5)
C(30')-C(29')-Ti(3')	75.9(10)	C(35')-Ti(4')-C(39')	157.1(7)
C(28')-C(29')-Ti(3')	73.3(9)	C(33')-Ti(4')-C(39')	124.3(8)
C(29')-C(30')-C(26')	110.0(12)	C(32')-Ti(4')-C(39')	139.3(8)
C(29')-C(30')-Ti(3')	70.5(9)	C(34')-Ti(4')-C(39')	131.4(6)
C(26')-C(30')-Ti(3')	74.2(8)	C(36')-Ti(4')-C(39')	54.6(5)
C(31')-Ti(4')-Cl(4')	91.1(4)	C(37')-Ti(4')-C(39')	54.7(5)
C(31')-Ti(4')-C(35')	34.3(3)	C(38')-Ti(4')-C(39')	33.0(4)
Cl(4')-Ti(4')-C(35')	125.4(5)	C(40')-Ti(4')-C(39')	31.7(4)
C(31')-Ti(4')-C(33')	56.1(4)	C(32')-C(31')-C(35')	107.9(11)
Cl(4')-Ti(4')-C(33')	99.6(5)	C(32')-C(31')-Ti(4')	74.2(8)
C(35')-Ti(4')-C(33')	55.8(5)	C(35')-C(31')-Ti(4')	73.6(8)

Table C.3 (Continued)

C(31')-C(32')-C(33')	107.8(11)
C(31')-C(32')-Ti(4')	72.1(8)
C(33')-C(32')-Ti(4')	73.0(8)
C(32')-C(33')-C(34')	108.6(11)
C(32')-C(33')-Ti(4')	73.2(8)
C(34')-C(33')-Ti(4')	73.3(8)
C(35')-C(34')-C(33')	106.1(11)
C(35')-C(34')-Ti(4')	72.6(9)
C(33')-C(34')-Ti(4')	72.2(8)
C(34')-C(35')-C(31')	109.6(11)
C(34')-C(35')-Ti(4')	74.1(9)
C(31')-C(35')-Ti(4')	72.1(8)
C(37')-C(36')-C(40')	106.9(12)
C(37')-C(36')-Ti(4')	73.7(9)
C(40')-C(36')-Ti(4')	75.1(11)
C(36')-C(37')-C(38')	107.8(12)
C(36')-C(37')-Ti(4')	73.4(9)
C(38')-C(37')-Ti(4')	73.6(10)
C(37')-C(38')-C(39')	108.9(13)
C(37')-C(38')-Ti(4')	73.3(9)
C(39')-C(38')-Ti(4')	76.0(11)
C(40')-C(39')-C(38')	106.2(12)
C(40')-C(39')-Ti(4')	73.0(13)
C(38')-C(39')-Ti(4')	71.0(11)
C(39')-C(40')-C(36')	110.2(13)
C(39')-C(40')-Ti(4')	75.3(13)
C(36')-C(40')-Ti(4')	71.8(11)
Cl(5)-C(41)-Cl(6)	118.7(7)
Cl(7)-C(42)-Cl(8)	116.2(12)

Symmetry transformations used to generate
equivalent atoms #1: -x+1,-y+1,-z+1

Table C.4 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	27(1)	29(1)	23(1)	12(1)	9(1)	4(1)
Si(2)	25(1)	25(1)	22(1)	3(1)	7(1)	2(1)
Si(3)	28(1)	33(1)	30(1)	16(1)	8(1)	11(1)
Si(4)	29(1)	25(1)	30(1)	1(1)	14(1)	7(1)
O(1)	34(2)	37(2)	29(2)	7(2)	12(2)	2(2)
O(2)	40(2)	32(2)	38(2)	9(2)	0(2)	8(2)
O(3)	33(2)	41(2)	39(2)	11(2)	13(2)	14(2)
O(4)	44(2)	29(2)	40(2)	8(2)	19(2)	10(2)
O(5)	29(2)	45(2)	38(2)	21(2)	13(2)	12(2)
O(6)	27(2)	36(2)	37(2)	-3(2)	11(2)	2(2)
Ti(1)	33(1)	40(1)	30(1)	16(1)	13(1)	6(1)
Cl(1)	65(1)	112(2)	150(2)	70(2)	69(1)	52(1)
O(7)	29(2)	48(2)	33(2)	25(2)	11(2)	1(2)
C(1)	210(30)	43(11)	71(17)	-39(10)	-8(19)	54(15)
C(2)	160(30)	230(30)	45(16)	-67(18)	-14(19)	100(30)
C(3)	160(30)	90(20)	19(11)	26(14)	9(16)	-58(18)
C(4)	68(15)	108(19)	20(9)	-2(12)	-8(9)	-24(14)
C(5)	80(19)	52(13)	41(12)	17(10)	11(13)	-39(11)
C(1')	120(20)	33(11)	70(20)	8(11)	-26(17)	5(15)
C(2')	81(15)	81(18)	16(11)	-14(10)	7(11)	-9(14)
C(3')	37(9)	95(17)	43(10)	43(11)	3(7)	9(10)
C(4')	34(9)	150(30)	50(12)	50(16)	11(8)	35(14)
C(5')	46(10)	150(30)	23(10)	36(15)	-9(7)	-27(12)
C(6)	85(6)	45(5)	132(9)	-5(5)	43(7)	-21(4)
C(7)	149(10)	64(6)	199(13)	78(8)	119(10)	42(7)
C(8)	171(11)	126(9)	175(12)	117(9)	44(10)	92(9)
C(9)	94(7)	83(7)	256(16)	68(9)	97(9)	65(6)
C(10)	149(9)	41(5)	120(8)	-6(5)	68(8)	26(6)
Ti(2)	29(1)	27(1)	29(1)	3(1)	6(1)	5(1)
Cl(2)	37(1)	69(1)	113(2)	-2(1)	-1(1)	21(1)
O(8)	29(2)	37(2)	29(2)	-3(2)	10(2)	-4(2)
C(11)	55(4)	41(4)	93(6)	13(4)	25(4)	-5(3)
C(12)	69(5)	63(5)	73(5)	35(4)	33(4)	5(4)
C(13)	79(6)	70(5)	80(6)	47(5)	-3(5)	14(5)
C(14)	58(5)	50(5)	163(9)	61(5)	34(6)	32(4)
C(15)	116(7)	29(4)	119(8)	17(4)	45(6)	22(4)
C(16)	120(7)	50(4)	49(5)	23(4)	38(5)	9(5)
C(17)	130(8)	120(8)	55(6)	57(6)	17(6)	33(7)
C(18)	99(7)	98(7)	24(4)	0(4)	11(4)	-17(5)
C(19)	79(5)	81(5)	41(4)	-3(4)	30(4)	10(4)
C(20)	64(5)	91(6)	42(4)	15(4)	29(4)	-1(4)
Ti(3)	36(1)	35(1)	31(1)	14(1)	10(1)	15(1)
Cl(3)	98(2)	71(2)	57(2)	13(1)	39(2)	36(2)
O(9)	41(2)	52(2)	51(2)	31(2)	6(2)	17(2)
C(21)	59(8)	74(9)	167(14)	74(10)	65(9)	40(7)
C(22)	96(11)	66(8)	59(8)	42(7)	21(8)	39(8)
C(23)	56(7)	53(7)	191(15)	74(10)	58(9)	40(6)
C(24)	310(30)	60(10)	97(13)	51(10)	119(17)	107(15)
C(25)	146(15)	27(6)	155(16)	36(8)	-60(12)	-1(8)

Table C.4 (Continued)

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(26)	45(5)	33(5)	80(8)	28(5)	6(5)	0(4)
C(27)	52(6)	52(7)	88(9)	16(6)	6(6)	2(6)
C(28)	29(6)	99(10)	112(11)	59(9)	13(6)	4(6)
C(29)	93(10)	68(8)	152(14)	62(10)	99(10)	37(8)
C(30)	89(8)	64(7)	53(7)	27(6)	31(6)	-22(6)
Ti(4)	36(1)	31(1)	33(1)	7(1)	16(1)	15(1)
Cl(4)	51(1)	42(1)	84(2)	20(1)	24(1)	12(1)
O(10)	48(2)	39(2)	44(2)	-5(2)	23(2)	14(2)
C(31)	58(6)	67(6)	28(5)	8(4)	6(4)	36(5)
C(32)	64(6)	44(5)	55(6)	24(5)	24(5)	30(5)
C(33)	65(7)	79(8)	47(6)	17(6)	17(5)	52(6)
C(34)	39(5)	86(8)	50(6)	22(6)	14(5)	21(6)
C(35)	40(5)	59(6)	51(6)	3(5)	-9(5)	13(5)
C(36)	44(6)	75(8)	61(7)	38(6)	31(5)	14(6)
C(37)	59(7)	143(11)	48(6)	48(7)	41(6)	61(8)
C(38)	114(11)	59(9)	51(8)	-11(6)	36(8)	37(8)
C(39)	80(8)	52(6)	33(6)	-8(5)	1(5)	6(6)
C(40)	143(13)	163(14)	110(11)	101(11)	117(11)	134(12)
Ti(3')	36(1)	31(1)	33(1)	7(1)	16(1)	15(1)
Cl(3')	98(2)	71(2)	57(2)	13(1)	39(2)	36(2)
O(9')	41(2)	52(2)	51(2)	31(2)	6(2)	17(2)
C(21')	63(15)	32(11)	230(30)	29(16)	120(20)	18(10)
C(22')	120(20)	33(13)	57(18)	-28(11)	-32(17)	15(14)
C(23')	54(15)	36(12)	170(30)	-12(17)	53(18)	20(11)
C(24')	140(30)	47(15)	120(30)	-10(17)	-70(20)	39(18)
C(25')	146(15)	27(6)	155(16)	36(8)	-60(12)	-1(8)
C(26')	33(9)	29(9)	76(14)	11(9)	27(10)	6(7)
C(27')	50(13)	82(16)	58(15)	33(13)	15(11)	16(12)
C(28')	45(13)	90(18)	110(20)	27(17)	42(14)	21(13)
C(29')	14(9)	67(15)	110(20)	29(15)	-15(11)	1(9)
C(30')	50(12)	53(12)	40(12)	5(10)	-9(9)	-3(10)
Ti(4')	36(1)	35(1)	31(1)	14(1)	10(1)	15(1)
Cl(4')	51(1)	42(1)	84(2)	20(1)	24(1)	12(1)
O(10')	48(2)	39(2)	44(2)	-5(2)	23(2)	14(2)
C(31')	36(10)	75(13)	22(9)	-2(9)	4(7)	26(10)
C(32')	63(13)	58(12)	53(12)	25(10)	29(10)	48(11)
C(33')	64(14)	92(17)	42(12)	14(11)	17(10)	59(13)
C(34')	17(9)	85(16)	62(14)	9(12)	23(9)	4(10)
C(35')	75(14)	79(15)	55(13)	42(12)	54(12)	44(12)
C(36')	63(15)	69(15)	46(13)	28(11)	-18(11)	-14(12)
C(37')	37(13)	140(20)	45(14)	-3(15)	-17(10)	36(15)
C(38')	68(18)	100(20)	80(20)	63(18)	-22(17)	5(18)
C(39')	33(14)	230(40)	36(13)	36(19)	7(11)	-40(20)
C(40')	44(14)	130(30)	69(17)	-8(16)	-6(12)	62(17)
C(41)	46(4)	84(5)	97(6)	12(5)	21(4)	6(4)
Cl(5)	60(4)	131(8)	104(6)	59(7)	2(4)	-3(4)
Cl(6)	91(4)	91(4)	133(13)	12(6)	19(7)	29(3)
C(41')	46(4)	84(5)	97(6)	12(5)	21(4)	6(4)
Cl(5')	51(5)	88(6)	141(9)	-28(6)	50(5)	-16(4)
Cl(6')	87(4)	87(4)	73(6)	18(4)	17(5)	40(3)

Table C.4 (Continued)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(42)	140(20)	98(19)	280(40)	70(20)	140(30)	31(16)
Cl(7)	128(6)	141(6)	158(7)	84(6)	-10(5)	20(6)
Cl(8)	66(2)	89(3)	90(3)	23(3)	27(2)	12(2)

Table C.5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$).

	x	y	z	U(eq)
H(1)	3519	5175	8431	142
H(2)	2732	4225	9554	191
H(3)	3809	3138	9995	136
H(4)	5315	3426	9079	101
H(5)	5121	4765	8201	88
H(1')	4206	5045	8732	103
H(2')	3260	4078	9801	88
H(3')	3900	2600	9894	70
H(4')	5260	2642	8854	90
H(5')	5457	4175	8176	106
H(6)	1289	837	6546	121
H(7)	1927	854	8300	143
H(8)	3857	1266	8731	163
H(9)	4538	1556	7178	151
H(10)	2880	1217	5847	126
H(11)	-44	-776	1655	82
H(12)	614	312	3423	82
H(13)	2599	864	3916	94
H(14)	3182	109	2438	98
H(15)	1505	-951	1038	105
H(16)	2868	3311	1501	90
H(17)	1126	2154	255	120
H(18)	1200	351	-246	107
H(19)	3001	405	665	87
H(20)	3963	2203	1769	85
H(21)	3356	7479	1452	102
H(22)	1458	6857	497	80
H(23)	344	7134	1711	102
H(24)	1626	7943	3491	160
H(25)	3579	8087	2943	154
H(26)	1196	3763	2628	67
H(27)	417	3852	948	84
H(28)	-481	5113	1114	97
H(29)	-216	5929	2981	106
H(30)	948	5178	3898	92
H(31)	3053	7647	5327	59
H(32)	2880	9253	6345	58
H(33)	1564	8709	7348	69
H(34)	886	6769	6943	69
H(35)	1786	6097	5684	67
H(36)	2204	6185	8517	68
H(37)	1698	7796	8812	84
H(38)	3477	9382	9410	90
H(39)	4941	8768	9488	77
H(40)	4236	6879	9160	118
H(21')	5150	9399	8469	117
H(22')	3920	9303	9575	103
H(23')	2139	8935	8541	108
H(24')	2145	8605	6713	144
H(25')	4026	8953	6670	154

Table C.5 (Continued)

	x	y	z	U(eq)
H(26')	2452	5000	7289	55
H(27')	2401	5839	8994	75
H(28')	1451	7099	8887	94
H(29')	894	7033	7066	84
H(30')	1483	5703	6098	68
H(31')	2969	7677	4782	55
H(32')	2333	8716	3786	58
H(33')	469	7672	2801	70
H(34')	-49	5885	3082	69
H(35')	1462	5887	4351	68
H(36')	322	4437	1537	85
H(37')	-210	5880	1151	98
H(38')	1296	7014	577	106
H(39')	2672	6171	531	142
H(40')	2034	4586	1076	100
H(41A)	-1510	7316	4382	98
H(41B)	-1209	7831	5564	98
H(41C)	-1190	7629	5631	98
H(41D)	-1490	7550	4462	98
H(42A)	3874	10041	5439	192
H(42B)	3913	9674	4297	192

VITA

Suree Saengkerdsub was born in Thailand in 1973. She grew up in Lopburi, Thailand and graduated with her highschool diploma from St. John's College in 1990. She then went on to Chulalongkorn University in Bangkok Thailand. Under the supervision of Prof. Ratana Magee, her undergraduate research was on the synthesis, characterization, and complexation with late transition metals of a derivative of H₂-salen. She earned a Bachelor of Science Degree in chemistry in 1994. She started her Ph.D. study in the department of chemistry at the University of Tennessee, Knoxville in fall 1995, working under the supervision of Prof. Craig Barnes. In May 2002, she completed the requirements for a Doctor of Philosophy Degree in chemistry.