

Faculty of Chemistry AMU

Bachelor Thesis

Cyclotetrasiloxanes modified with silsesquioxanes – – synthesis and characterization 2020

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Thesis performed in the Department of Organometallic Chemistry under the supervision of prof. UAM dr hab. Beata Dudziec

Summary: Silicon compounds play a very important function in different areas of chemistry due to their physicochemical properties, which include being hybrid compounds and thus affect many directions of application. Among them, the Cyclosiloxanes and silsesquioxanes that are used in this work are classical examples of those systems. Both have an inorganic core of Si-O-Si bonds with organic substituents at silicon atoms, resulting in different structures. The project presents basic literature on the chemistry of cyclosiloxanes and silsesquioxanes, the main methods of functionalization, and in the experimental part, the synthesis of T_8 type silsesquioxanes and the catalytic reactivity of the Si-H compound in the hydrosilylation of tetravinylcyclotetrasiloxane is demonstrated.

Keywords: *Cyclosiloxanes; Silsesquioxanes; Functionalization; Condensation reaction; Hydrolysis; Catalytic process; Hydrosilylation.*

1. Introduction

Silicon-based compounds have an important role in the development of new chemical reagents and polymers due to their high thermal and chemical stabilities, variety of framework structures, and the introduction of organic substituents with Si-C bonds. These organosilicon compounds can be used as building blocks to produce polymers with organic or siloxane linkers, and also as the basic structural units of crystalline silica materials [1][2]. In this work two main families of silicon materials are used: cyclosiloxanes and silsesquioxanes.

1.1. Cyclosiloxanes

Cyclosiloxanes are substances that have an inorganic backbone structure of alternating silicon and oxygen atoms in a closed-loop, giving it a cyclic structure. They may have organic substituents attached to each silicon atom. Some of the most widely used cyclosiloxanes are: octamethylcyclotrisiloxane (D₃), decamethylcyclotetrasiloxane (D₄) and dodecamethylcyclopentasiloxane (D₅) (Figure 1) [3]. They usually exist as a mixture of two or more stereoisomers. For example, 2,4,6,8tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane exists as four stereoisomers *all-cis*, *all-trans*, *cis-trans-cis* and *cis-cis-trans* (Figure 2) [4].

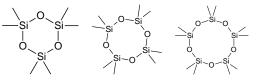


Figure 1: Structure of D₃, D₄ and D₅ cyclosiloxanes.

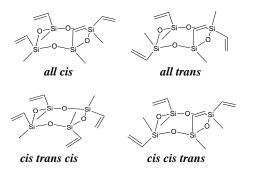


Figure 2: Possible stereoisomers of 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane.

They are generally synthesized in a hydrolytic condensation of organochlorosilanes or organoalkoxy-silanes with two and three reactive groups (Figure 3) [5].

Figure 3: General scheme of linear and cyclic siloxanes synthesis.

Functionalized cyclosiloxanes are used as the basic substrates for anionic and cationic ring-opening polymerization [6]. This reaction is one of the most important routes for obtaining high molecular weight polysiloxanes. It has some advantages over the polycondensation methods, for example, better reaction conditions enabling controlling of reactive end groups, which allows a better oversee the molecular size [7]. The methods of functionalization will be discussed later.

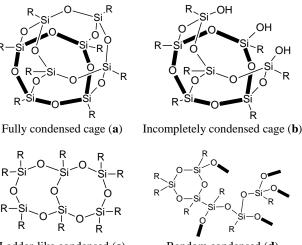
Cyclosiloxanes are mainly used as intermediates or basic raw materials in the production of silicone rubbers, gels, and resins. Silicones are characterized by their ability to function in conditions that would destroy conventional organic materials. They have applications in many sectors such as transport, construction industry, electronics, energy, healthcare, industrial processes, and food industry [8].

1.2. Silsesquioxanes

Polyhedral Oligomeric Silsesquioxanes (POSS®)¹ are molecular models of "silica" that have various inorganic Si-O-Si rings in a three-dimensional structure, connected with organic substituents and are represented by the empirical formula (RSiO_{3/2})_n. In this formula, R can be hydrogen, alkyl, aryl, or different organically modified functional groups [9]. For that reason, they have often been described as having hybrid (organicinorganic) properties, some from the chemically inert and thermally stable inorganic Si-O-Si part and others from the reactive and easily modified R-Si part [10]. Due to these properties they have applications as liquid crystals, porous materials, ionic liquids, functional coating materials, light-emitting diode materials, and mainly nanocomposites (as their modifiers and nanofillers) [11].

Silsesquioxane molecules may be referred to as trifunctional siloxanes (T-siloxanes) and denoted as T_nR_n , because they contain a silicon atom bound to three oxygen atoms. The remaining siloxanes moieties are classified as mono- (M), di- (D), and quaternary (Q) [9]. They can be fully (a) or incompletely (b) condensed and have a variety of three-dimensional structures including cages, ladders (c), and random (d) conformations (Figure 4). Silsesquioxanes of random structures do not have many applications in synthesis and do not show very interesting physicochemical properties, because of

that, ladder and cage type are the most employed. On the other hand, the ones that are incompletely condensed, have one or more free Si-OH groups and play an important role of precursors for obtaining more complex silsesquioxane systems to be obtained via condensation reactions [12].



Ladder-like condensed (c)

Random condensed (d)

Figure 4. Possible structures of silsesquioxanes.

For the synthesis of silsesquioxane derivatives, the most important route is the hydrolytic condensation of trifunctional monomers RSiX₃, where R is a chemically stable organic substituent, and X is a highly reactive substituent such as Cl, alkoxy or ethoxy. The silane monomer is hydrolysed to yield a trisilanol monomer that subsequently undergoes self-condensation to produce the Si-O-Si bonds of the silsesquioxane cage (Equation 1,2 and 3). It is catalysed by either acidic or basic media [13].

<i>Hydrolysis</i> : $RSiX_3 + 3 H_2O \rightarrow RSi(OH)_3 + 3 HX$	(1)
Condensation: $3 \text{ RSi}(\text{OH})_3 \rightarrow 3 \text{ RSiO}_{1.5} + 1.5 \text{ H}_2\text{O}$	(2)
Condensation: $RSi(OH)_3 + RSiX_3 \rightarrow RSiO_{1.5} + 3 HX$	(3)

Usually, the cubic T_8 cage is formed as the most thermodynamically stable silsesquioxane cage. The incapacity to form bigger cages (n = 10, 12, 14, and 16) is because the fact that T_8 cage exhibits different physical properties and precipitates before the other cages can form and also considering that the Si₄O₄ rings formed in the T_8 cage are very stable [9].

There are few points to be taken into account when considering the selectivity of the hydrolytic condensation products. The type of R group of the silane (RSiX₃) determines whether a fully condensed or incompletely condensed silsesquioxane will be obtained. If silanes with R groups as tert-butyl, phenyl and cyclohexyl are used, then incompletely condensed silsesquioxanes are isolated. If silanes with smaller groups like methyl or hydrogen are employed, fully condensed silsesquioxane

¹ POSS is a registered trademark of Hybrid Plastics

cages are the only products. The solvent also influences the selectivity of resulting silsesquioxanes obtained. For example, polar solvents and solvents with higher dielectric constant and dipole moment, are able to stabilize incompletely condensed cages by interacting with their OH groups through hydrogen bonding. The nature of the X group must also be considered. For example, Cl groups hydrolyze faster than either OEt or OMe groups [13]. These incompletely condensed cages can be also prepared by ring-opening of fully condensed cages [9].

Monofunctional T_8R_7R' derivatives can also be synthesized from an incompletely condensed silsesquioxane, i.e. $R_7Si_7O_9(OH)_3$, or its sodium salt, $Na_3[R_7Si_7O_9(O)_3]$, making it react with monofunctional trichloro- or trialkoxysilane, often in the presence of a base like NEt₃ or a tetraalkylammoniumhydroxide. (Figure 5) The main advantage of obtaining these derivatives is that with an R group bulky enough, the reactivity of the R' group may be reduced ,and therefore it is more stable and more readily handled than the $T_8R'_8$ analogue [10].

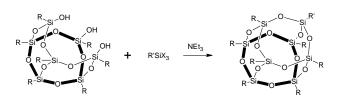


Figure 5. General scheme of the synthesis of monofunctional T_8R_7R' derivatives.

1.3. Methods for modification of Cyclosiloxanes and Silsesquioxanes

direct functionalization The methods for of cyclosiloxanes and silsesquioxanes are limited to stoichiometric reactions at the stage of hydrolytic condensation and catalytic processes as further modifications [10]. For this reason, Si-H and Si-HC=CH₂ vinyl groups are of especial importance. They can be easily converted into many functional groups by different transformations such as metathesis reactions, silvlative coupling, thiol-ene addition. and hydrosilylation [10][13][14][15].

The first two methods, cross-metathesis and silylative coupling, are two types of transition metal-catalyzed reactions that yield mostly the same main products but proceed in the presence of diverse catalytic complexes and via different mechanisms. Silylative coupling of vinylsilanes with olefins proceeds in the presence of complexes possessing or generating in situ [M-H] or [M-Si] reactive species, e.g. [RuHCl(CO)(PCy)₂] and occurs by cleavage of the =C-H bond of the olefin and the C-Si bond of vinylsilanes [16]. In the case of metathesis reaction, the C=C bonds of two olefins are cleaved and rebuilt with different substituents and it is catalyzed by an alkylidene complex, i.e. possessing [M=C] bond, e.g. the first-generation Grubbs' catalyst,

that is also a ruthenium complex of a formula $[(Ru=CHPh)Cl_2(PCy_3)_2]$ [17].

Thiol-ene addition occurs by a free radical mechanism and uses initiators like peroxides or diazo compounds. No metal catalyst, ionic or acid-base active compounds are present in the reaction. The interest in this method concerns the introduction of thioether functions to the product, which may be further modified [18].

Hydrosilylation can be considered the most important approach of functionalization in the chemistry of organosilicon compounds, also of industrial appliance [19], and it is the one used in this work. The basis of this reaction is the addition of terminal Si-H groups to an unsaturated alkene or alkyne group, in the presence of a transition metal catalyst (homogeneous and heterogeneous type). It can occur in two possible ways: α -addition (Markovnikov) or β -addition (anti-Markovnikov) (Figure 6). The anti-Markovnikov addition product is sterically favored and therefore appears as a major product [13]. However, under some conditions (presence of Pd and Ni catalysts) the α -adduct may be also obtained (even regioselectivity) [20].

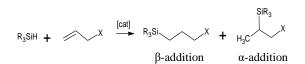


Figure 6. General scheme of a hydrosilylation reaction.

Regarding the catalyst, among the transition metals, the most active are the platinum ones. There are two classes of platinum catalysts; those with Pt(0), e.g. Karstedt's catalyst [Pt2(dvds)3], and those with higher oxidation states, e.g. (+4) like in Speier's catalyst H₂PtCl₆ [13]. Karstedt's type catalyst (Figure 7), the one employed in this work, is obtained by treating hexachloroplatinic acid with vinylsiloxane [20]. This type of catalyst has the advantage of high turnover numbers (>10000), high selectivity and its only drawbacks are from the environmental point of view, besides the fact that they are expensive, and they have limited functional group tolerance. For this reason, several catalysts have been developed to improve these characteristics [21]. For example, other platinum complexes with N-heterocyclic and amino-acyclic carbenes, phosphine Pd-(0) and Pd-(II) complexes, other transition metal (nickel, rhodium, iron, zirconium, ruthenium) complexes such as carbonvls. or photogenerated catalysts. Another option is the immobilization of the transition metal complexes on polymers organic (polystyrene-divinylbenzene, polypropylene), inorganic oxides (silica, molecular sieves), ion exchangers or ionic liquids [20].

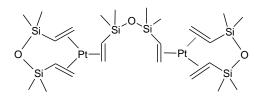


Figure 7. Structure of Karstedt's catalyst.

The hydrosilylation mechanism is derived from studies of chloroplatinic acid as a precursor. In the beginning, the oxidative addition of trisubstituted silanes, HSiR₃, to a metal alkene complex takes place. It is followed by a migratory insertion of the alkene into the M-H bond, and the resulting complex undergoes reductive elimination by Si-C bond formation and regeneration of metal alkene complex in an excess of an alkene. The rate-determining step is the Si-C reductive elimination. There is also a modified mechanism that explains the formation of the unsaturated organosilicon product. It consists of the alkene insertion into the M-Si bond followed by C-H reductive elimination (Figure 8) [22].

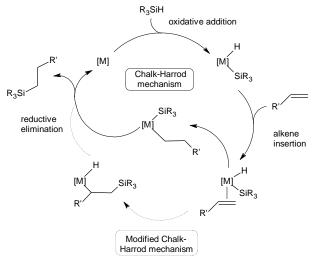


Figure 8. Chalk – Harrod and modified Chalk – Harrod mechanism of transition metal catalyzed hydrosilylation of alkenes

2. Results and Discussion

The synthesis of T_8 type silsesquioxane has been carried out from an incompletely condensed T_7 silsesquioxane with isobutyl groups (1). This process has three stages: condensation – corner capping (product 2), hydrolysis of Si-Cl to Si-OH (product 3), and consecutive condensation of Si-OH with Cl-SiMe₂H (product 4). The resulting product 4 has been subjected to spectroscopic analysis and subsequently to a hydrosilylation reaction with 2,4,6,8–tetravinyl-2,4,6,8tetramethyl-cyclotetrasiloxane. With this last reaction, the reactivity of the reagents and the activity of the catalyst were studied.

2.1. Synthesis of T₈ type silsesquioxane derivative

The synthesis consists of three steps. The first one was based on a condensation that was carried out according to the general procedure presented in the experimental section (point 3.4), using the following amounts of compounds: 6.03 g (7.6 mmol) iBuPOSS-3OH (1), 180 ml THF, 3.83 ml (27.4 mmol) triethylamine, 0.91 ml (7.8 mmol) tetrachlorosilane (Figure 9). Product 2 was isolated as a white solid.



Figure 9. Condensation – corner capping of iBuPOSS-3OH (1).

Compound 2 was dissolved in 90 ml of THF and 5 ml of distilled water. After that, the solution was subjected to hydrolysis by refluxing at 65° C under the argon atmosphere for 24 hours (Figure 10). Then, the post-reaction mixture was evaporated under reduced pressure and was subjected to extraction with petroleum ether and ammonium chloride solution. The organic layer was kept, dried with magnesium sulfate and evaporated under reduced pressure. It enabled to obtain product 3 that was isolated as white solid and subjected to spectroscopic analysis.

¹**H NMR** (300 MHz, CDCl₃, δ, ppm): 0.59-0.65 (m, 14H, -C*H*₂- (iBu)); 0.94-0.97 (m, 42H, -C*H*₃ (iBu)); 1.81, 1.92 (m, 7H, -C*H*- (iBu)); 3.73-3.77 (m, 1H, O*H*)

²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -66. 74, -67.84, -67.86 (-Si-iBu); -101,04 (-Si-OH)

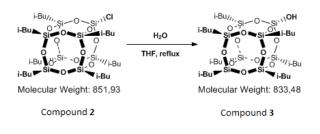


Figure 10. Hydrolysis of Si-Cl to Si-OH.

Compound **3** was subjected to a consecutive condensation reaction carried out according to the general procedure presented in the experimental section (point 3.4), using the following amounts of compounds: 2.02 g (2.4 mmol) iBuPOSS-OH (**3**), 35 ml THF, 0.51 ml (3.6 mmol) triethylamine, 0.30 ml (2.6 mmol) chlorodimethylsilane (Figure 11). The crude product was

dissolved in DCM and precipitated in MeOH, to remove any possible hydrochloride residue. After decantation the solid 4 was dried under reduced pressure with 88% yield and subjected to spectroscopic analysis.

IR (cm⁻¹): 2953.29, 2906.14, 2868.75 ($\bar{\upsilon}$ -C-H); 2138.65 ($\bar{\upsilon}$ Si-H); 1464.67 ($\bar{\upsilon}$ -C-H); 1229.94 ($\bar{\upsilon}$ Si-C); 1104.68 ($\bar{\upsilon}$ Si-O-Si)

¹**H NMR** (300 MHz, CDCl₃, δ, ppm): 0.22 (m, 6H, Si-C*H*₃); 0.59-0.63 (m, 14H, -C*H*₂- (iBu)); 0.94-0.97 (m, 42H, -C*H*₃ (iBu)); 1.79-1.94 (m, 7H, -C*H*- (iBu)); 4.69-4.73 (m, 1H, Si-*H*)

¹³C NMR (100 MHz, CDCl₃, δ, ppm): 0.34 (–SiCH₃); 22.50-22.65, 23.97, 24.01, 25.83, 25.85 (iBu)

²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -2.97 (-SiMe₂H); -66.94, -67.87, -67.89 (-Si-iBu); -109.06 (SiO₄)

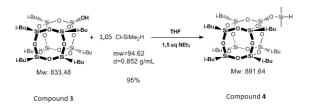


Figure 11. Consecutive condensation of Si-OH with Cl-SiMe2H.

2.2. Verification of catalytic activity of T_8 type silsesquioxanes OSi(Me₂)H group in a hydrosilylation reaction

The hydrosilylation is one of the fundamental processes in the industry of organosilicon compounds, that is why it was the method chosen to check the catalytic activity of the silsesquioxane (4) obtained previously. In this case, the monosubstituted T_8 type of silsesquioxane with Si-H terminal group was reacted with the vinyl groups of the tetravinylsubstituted cyclotetrasiloxane(2,4,6,8-tetravinyl-2,4,6,8-tetramethyl-cyclotetrasiloxane). The whole process was catalyzed by $Pt_2(dvs)_3$, also known as Karstedt's catalyst.

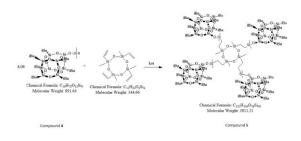


Figure 15. Hydrosilylation reaction scheme between compound 4 and tetravinylsubstituted cyclotetrasiloxane

The procedure for the synthesis of **5** is described as follows. To a 10 mL glass reactor equipped with a condenser and magnetic stirrer, **4** (0.202 g, 0.227 mmol) was placed in argon atmosphere along with toluene (6 ml) and 2,4,6,8 tetravinyl- 2,4,6,8 tetramethyl-

cyclotetrasiloxane (19.4 µl, 0.056 mmol). It was heated at 40°C and Pt₂(dvs)₃ solution (51.35 μ l, 2.246x10⁻⁴ mmol) was added (Figure 15). The reaction mixture was kept at 95°C to obtain complete Si-H consumption - that was verified using the FTIR analysis and changes in the surface areas of band $\bar{\upsilon} = 2200 \text{ cm}^{-1}$ characteristic for stretching vibrations of Si-H bond - (usually 24h). After the reaction completion, it was transferred to a flask, washed with toluene and evaporated under reduced pressure. A crude product 5 was obtained as a white solid which was later transferred onto column (silica gel 60) to remove any possible catalyst residue, using CHCl₃. The obtained solution was evaporated under reduced pressure. The crude product was dissolved in DCM and precipitated in MeOH. After evaporation of MeOH, 5 was isolated as white solid, with 95% yield and subjected to spectroscopic analysis.

IR (cm⁻¹): 2952.94, 2925.63, 2906.59, 2869.87 (ῡ -C-H); 1464.46 (ῡ -C-H); 1228.54 (ῡ Si-C); 1076.68 (ῡ Si-O-Si)

¹**H NMR** (300 MHz, CDCl₃, δ, ppm): 0.10- 0.12 (m, 24H, -Si(C*H*₃)₂); 0.14- 0.15 (m, 8H, -C*H*₂-); 0.49 (m, 12H, -C*H*₃ (D₄^{Vi})); 0.59 - 0.63 (m, 56H, -C*H*₂- (iBu)); 0.73 - 0.75 (m, 4H, -C*H*₂-); 0.95 -0.97 (m, 168H, -C*H*₃ (iBu)); 1.15 - 1.17 (m, 4H, -C*H*₂-); 1.80- 1.92 (m, 28H, -C*H*- (iBu))

¹³C NMR (100 MHz, CDCl₃, δ , ppm): -0.86 (-Si(CH₃)₂); -0.70 (-SiCH₃ (D₄^{Vi})); 6.66 – 9.62 (CH₂-CH₂); 22.10, 22.57, 22.60, 22.63, 22.68, 24.00, 24.03, 25.87 (iBu)

²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): 12.11, 12.00 (-Si-O); -19.51, -19.61, -19.68, -19.87, -19.96 (-Si-O₂); -67.10, -67.90 (-Si-iBu); -109.65, -109.86, -109.95 (SiO₄)

The spectroscopic analyses spectra of the substrate 2,4,6,8-tetravinyl- 2,4,6,8-tetramethyl-cyclotetrasiloxane are shown below.

IR (cm⁻¹): 3054.90, 2963.24 ($\bar{\upsilon}$ -C-H); 1597.14 ($\bar{\upsilon}$ C=C); 1405.69 ($\bar{\upsilon}$ -C-H vinyl); 1258.91 ($\bar{\upsilon}$ Si-C); 1053.45 ($\bar{\upsilon}$ Si-O-Si)

¹**H NMR** (300 MHz, CDCl₃, δ, ppm): 0.22-0.26 (m, 12H, -C*H*₃); 5.82-5.94 (m, 8H, =C*H*₂); 5.99-6.14 (m, 4H, -C*H*=)

²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -32.45, -32.47, -32.56 (-Si-O₂)

When the spectra of the reagents and the final product (5) are compared, it can be seen that the complete conversion of Si-H bond (4.69 - 4.73 ppm) and vinyl groups (5.82 - 6.14 ppm) in the ¹H NMR spectrum of the product was obtained.

Looking at the FTIR spectra of product **5**, there is no peak at $\bar{\upsilon} = 2100 \text{ cm}^{-1}$ corresponding to the stretching vibrations of Si-H bond, neither the peaks over 1400 cm⁻¹ corresponding to the C=C and C-H of vinyl group of cyclotetrasiloxane.

In the case of the ²⁹Si NMR spectra, in the cyclotetrasiloxane there is only one type of silicon (secondary D type) and therefore one signal, and in the

silsesquioxane cage area there are three (primary M type, tertiary T type and quaternary Q type). In the product spectra there are four signals and consequently four types of silicon, which is what may be expected when looking at its structure.

Moreover, a few enantiomers may be formed as described in the introduction [23]. As mentioned above, cyclotetrasiloxane has four possible enantiomers: all-cis, all-trans, cis-trans-cis and cis-cis-trans. Different enantiomers could be formed during the formation of product **5** as the substrate D_4^{Vi} is a mixture of isomers, basing on the ¹H and ²⁹Si NMR. In the ¹H NMR spectrum the signals of the H of the bond CH₂-CH₂ are split into different zones (0.14-0.15 ppm, 0.73-0.75 ppm, 1.15-1.17 ppm) and in the ¹³C NMR spectrum there is not a defined two signals from the carbons of this bond (the signals are between 6.66 and 9.62 ppm). In the ²⁹Si NMR spectrum, the signal from the Si of the cyclotetrasiloxane structure (-19 ppm) is split into five peaks. The obtained results, basing on the comparison of the NMR spectra of substrate D_4^{Vi} and product 5, are possible to that the reaction mixture contains also different enantiomers. However, it is still not clear which ones we obtained.

3. Experimental Part

3.1. Materials and methods.

Experimental works, both synthesis and catalytic tests are carried out under argon atmosphere using Schlenk line (vacuum-gas line). Substances used during the research have been purchased: iBuPOSS-3OH in Hybrid Plastics, dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, toluene, n-hexane, methanol, chloroform, ammonium chloride, anhydrous magnesium sulphate, silica gel 60, tetrachlorosilane, chlorodimethylsilane, triethylamine, N,N-diisopropylethylamine, 2,4,6,8-tetravinyl-2,4,6,8-tetramethyl-cyclotetrasiloxane, Karstedt's catalyst in Sigma-Aldrich.

3.2. Nuclear Magnetic Resonance (NMR)

¹H, ¹³C, and ²⁹Si Nuclear Magnetic Resonance (NMR) were performed on Brucker Ultra Shield 600, 400 and 300 spectrometers using CDCl₃ as a solvent. Chemical shifts are reported in ppm with reference to the residual solvent (CHCl₃) peaks for ¹H and ¹³C and to TMS for ²⁹Si.

3.3. FT – IR

Fourier Transform-Infrared (FT-IR) spectra were recorded on a Nicolet iS5 (Thermo Scientific) spectrophotometer equipped with a diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm⁻¹ were collected, to record the spectra in a range of 4000-650 cm⁻¹. Stretching vibrations $\bar{\nu}$ Si-H 2200 cm⁻¹ are checked on the spectrum.

3.4. General condensation procedure

To a Schlenk flask fitted with a magnetic stirrer and a gas inlet cap, the substrate was added and dried under reduced pressure for 1 hour. To the dried substrate, under argon atmosphere, THF was added as a reaction medium. Then the amine was added, and the mixture was cooled in an ice bath. The silane was introduced by dropping to the solution. The reaction mixture became cloudy as a result of hydrochloride formation and consequently [HNEt₃]Cl was observed as a white solid. The mixture was warmed to room temperature and kept at stirring for 24 hours. Then, the post-reaction mixture was subjected to filtration in order to remove the formed triethylamine hydrochloride and washed with THF. The solvent was evaporated under reduced pressure to obtain the raw reaction product.

4. Conclusions

This project aimed to present the synthesis of T_8 type silsesquioxanes, their characteristics as well as verification of catalytic reactivity of hydrogen derivative in the hydrosilylation process with D_4^{Vi} . The T_8 type silsesquioxanes were synthesized from incompletely condensed cages in three steps: condensation, hydrolysis and consecutive condensation. Once synthesized, they applied a hydrosilylation reaction have with 2,4,6,8-tetravinyl-2,4,6,8-tetramethyl-cyclotetrasiloxane catalyzed by a platinum Karstedt's complex. All compounds were characterized by NMR and FTIR spectroscopy, which show the substrates conversion and also prove the structure of resulted products obtained. In addition, the products were obtained with good yields (around 90%), demonstrating that both the condensation and the hydrosilylation reactions were appropriate and well developed.

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