



## A facile approach for the synthesis of novel silsesquioxanes with mixed functional groups

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*In this paper, an efficient method for the preparation of new silsesquioxanes with mixed functional groups of general formula  $(RSiMe_2O)_n(ViSiMe_2O)_{8-n}Si_8O_{12}$  is described. Proposed protocols are based on hydrosilylation of octakis(dimethylvinylsiloxy)octasilsesquioxane  $((ViSiMe_2O)_8Si_8O_{12})$  with unsymmetrical disiloxanes. As an example of possible modification of  $(RSiMe_2O)_n(ViSiMe_2O)_{8-n}Si_8O_{12}$  derivatives, a thiol addition was distinguished. A series of silsesquioxane compounds with a variety of functional groups (silylamine, epoxy, chlorine) were obtained and characterized. The obtained compounds can be considered as novel multi-substituted materials which significantly increase the possibility of synthesis and design of new functional materials*

### Introduction

Polyhedral oligomeric silsesquioxanes described by the general formula  $(RSiO_{3/2})_n$  are inorganic-organic hybrids possessing a SiO-based cubic core surrounded by eight organic groups located at its vertices<sup>[1]</sup>. These nanostructures exhibit diameters in the range 1–3 nm and, hence, they may be considered as the smallest silica particles<sup>[2]</sup>. The presence of the SiO-based cage is responsible for their high thermal, mechanical and chemical stabilities<sup>[3]</sup>. On the other hand, the inorganic silsesquioxane core can be substituted with several reactive species such as SiOH, SiVi, and SiH, which opens the possibilities of functionalization by means of a series of chemical transformations<sup>[4]</sup>. The above-described facts make this group of compounds excellent starting buildings block for designing and synthesizing new materials, as confirmed by thousands of papers describing the syntheses, characterization, and application of silsesquioxane derivatives in many fields of science and industry<sup>[1, 5]</sup>. Moreover, in recent years we have observed a growing interest in the silsesquioxane synthesis bearing mixed functional groups. The presence of different organic/organometallic moieties in their structure opens the possibilities for the synthesis of a new generation of this group of compounds with simultaneous control of their properties, resulting from the type and number of functional groups. However, literature reports regarding the

synthesis of multifunctional silsesquioxane derivatives are still very scant<sup>[6]</sup>. Takeuchi et al. have published a procedure allowing the preparation of polyhedral oligomeric silsesquioxane (POSS) with hydroxyl groups and methyl, vinyl or methacryloxy units. Unfortunately, the information about the distribution of products and the formation of disordered architectures has not been provided.<sup>[6v]</sup> Hydrolytic condensation has also been applied by Asuncion and co-workers. They developed a multistep synthetic route leading to the synthesis of silsesquioxane bearing phenyl and vinyl groups.<sup>[6f, 7]</sup> However, the typical condensation method also led to the formation of many by-products such as ladder-like structures and disordered resins. On the other hand, the use of silsesquioxane substrates with well-defined structure as starting materials in hydrometallation reactions excludes the formation of unwanted, crosslinked, disordered products. For example, Wang et al. proposed the synthetic pathway for the synthesis of new silsesquioxane derivatives *via* hydrothiolation (thiol-ene addition) of partially hydroxylated octakis(dimethylvinylsiloxy)octasilsesquioxane<sup>[6n, 6r]</sup> with organofunctional thiols<sup>[6y, 6z]</sup>. This methodology led to the formation of products with statistical distributions of functional groups around the silsesquioxane core. However, in view of the published data, the hydrosilylation reaction is still the most convenient process for obtaining new organosilicon compounds. Thanks to its high selectivity and tolerance for a variety of functional groups, hydrosilylation was also applied as an efficient synthetic tool for synthesizing silsesquioxane derivatives with different functionalities. It has been shown that the cages bearing mixed functional groups have potential applications as monomers, components of coatings or hydrophobic materials<sup>[8]</sup>. It should be strongly emphasized that most of multifunctional silsesquioxane derivatives synthesized

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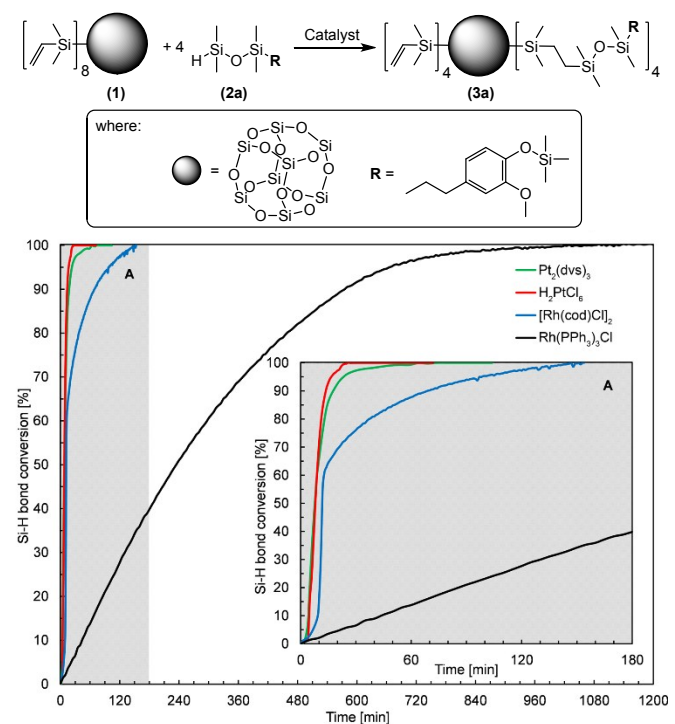
via hydrosilylation protocol have been obtained using SiH-containing precursors.<sup>[6a, 6k, 6m, 6p, 6r, 9]</sup>

In this work, we would like to present the inverse approach leading to novel multifunctional spherosilicates employing octakis(dimethylvinylsiloxy)octasilsesquioxane ((ViSiMe<sub>2</sub>O)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>, **1**) as a substrate instead of octakis(dimethylsiloxy)octasilsesquioxane (HSiMe<sub>2</sub>O)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>, commonly used as starting material for the synthesis of organofunctional silsesquioxane derivatives based on catalytic hydrometallation transformations.<sup>[10]</sup> One of the main reasons why this approach has never been applied for the synthesis of the discussed group of compounds so far was the lack of appropriate organofunctional silicon derivatives bearing the reactive SiH bond. Recently published research on the development of a selective and efficient method for the synthesis of asymmetrically substituted disiloxanes and silanes, containing in their structure both attractive organic functional groups as well as SiH bonds, have significantly contributed to formulation of the proposed protocol and enabled its development.<sup>[11]</sup> The proposed strategy employs the unique reactivity of SiVi group not only in hydrosilylation reaction but also subsequently in different catalytic or stoichiometric transformations e.g. silylative coupling, hydrothiolation, epoxidation, etc. This approach can lead to novel multi-substituted materials and significantly extend the possibilities in the field of synthesis and design of new functional materials.

## Results and discussion

Hydrosilylation is a simple, practical and one of the best-studied methods for the functionalization of organosilicon compounds.<sup>[12]</sup> This reaction can be catalyzed by platinum<sup>[13]</sup>, rhodium<sup>[11c]</sup>, cobalt<sup>[14]</sup>, iron<sup>[15]</sup>, iridium<sup>[16]</sup> and ruthenium<sup>[17]</sup> based complexes which, depending on the needs, allows the selective addition of a SiH to an unsaturated compounds, such as alkene (or alkyne). Thus, during the first step of our research, hydrosilylation of silsesquioxane **1** with **2a** in the presence of the most commonly used hydrosilylation catalyst was performed (Table 1). We decided to compare the activity of Karstedt's catalyst (Pt<sub>2</sub>(dvs)<sub>3</sub>) with those of Speier's catalyst (H<sub>2</sub>PtCl<sub>6</sub>), rhodium(I) chloride dimer ([Rh(cod)Cl]<sub>2</sub>), and that of Wilkinson's catalyst (Rh(PPh<sub>3</sub>)<sub>3</sub>Cl) by measuring the time required for quantitative SiH consumption in pilot reactions monitored by *in situ* FT-IR spectroscopy (Figure 1). Such investigation is possible because the stretching vibrations of the SiH bond ( $\bar{\nu}$ =900 cm<sup>-1</sup>) are distinct from the signals assigned to disiloxane organic unit, therefore, both the reaction time and the catalyst activity can be reliably established. In the performed experiment **2** (0.32 mmol) with silsesquioxane **1** (0.08 mmol) were reacted in the presence of the proposed complexes ([**1**]:[M] = 1:10<sup>-4</sup>, M=Pt or Rh) in order to identify the most appropriate catalytic system. The process was conducted in toluene as a solvent

(m<sub>1</sub>/V<sub>tol.</sub>=50 mg/mL), at 90°C and the reaction time was determined by *in situ* FT-IR (Figure 1).



**Figure 1.** Kinetic plots for hydrosilylation reaction of **1** with disiloxane **2a** determined by *in situ* FT-IR spectroscopy. Reaction conditions: [**1**]:[**2**]:[M] = 1:4:10<sup>-4</sup>, 90°C, toluene, m<sub>1</sub>:V<sub>tol.</sub> = 50 mg mL<sup>-1</sup>.

The *in situ* FT-IR measurements demonstrate that the rate of the reaction catalyzed by platinum complexes was higher than the rhodium-catalyzed one. Moreover, the time required for the full conversion of the reagents was similar for both platinum-based complexes and the progression of kinetic plots similar to them. The addition of a catalyst to the reaction mixture starts the reaction after a short initiation time. Then, rapid consumption of SiH is observed up to 90-95% of the starting amount. The time required for the reaction of the remaining 5-10% of SiH was much longer – 10-600 min (Figure 1).

On the basis of our preliminary study and earlier experience<sup>[4a]</sup>, we decided to use Karstedt's catalyst for the synthesis of compounds **3a-f**. The reactions were performed in the previously established conditions i.e. [Pt<sub>2</sub>(dvs)<sub>3</sub>], [**1**]:[**2**]:[Pt] = 1:4:10<sup>-4</sup>, toluene (m<sub>1</sub>/V<sub>tol.</sub> = 50 mg mL<sup>-1</sup>), at 90°C. After the SiH conversion reached 100, the reaction mixture was concentrated and after solvents evaporation, it was washed with methanol and dried under vacuum. Then products were fully characterized by NMR which confirmed the selective formation of targeted silsesquioxanes. The compounds, described by the general formula (RSiMe<sub>2</sub>O)<sub>n</sub>(ViSiMe<sub>2</sub>O)<sub>8-n</sub>Si<sub>8</sub>O<sub>12</sub>, were obtained with 89-97% yield. For all synthesized compounds, the exclusive formation of hydrosilylation products was observed. No reaction products competitive to the hydrosilylation were found (such as dehydrogenative silylation or isomerization), some minor amounts (less than 2%) of  $\alpha$ -hydrosilylation isomer formation was observed, as confirmed by <sup>29</sup>Si NMR analysis. These results were

similar to those recently described for  $(\text{ViSiMe}_2\text{O})(i\text{Bu})_7\text{Si}_8\text{O}_{12}$  hydrosilylation.<sup>[4a, 18]</sup> To get more detailed information about the reactivity of particular disiloxanes **2a-f** in the hydrosilylation process, the reactions with wider groups of SiH modifiers were monitored by *in situ* FT-IR. It was observed that the reaction times required for quantitative SiH consumption were significantly different and varied considerably depending on the type of disiloxane. The shortest time needed to reach full SiH conversion was observed for **3b** and **3e**, which can be explained by strong polarizing effect due to the presence of the oxirane group and fluorine atoms at the end of the disiloxane molecule. According to the mechanism of hydrosilylation<sup>[12a]</sup>, the electron-withdrawing groups attached to the disiloxane core increase the reactivity of SiH in the reaction (Table 1). It should be mentioned that the arrangement of the functional groups in the spherosilicates **3a-f** skeleton is statistical. Obtaining bifunctional moieties with an average stoichiometry very similar to 4/4 of each functional group type will always give statistical numbers of additions as it was disclosed by authors in earlier studies<sup>[9]</sup>. Distribution of products depends on the many factors including stoichiometry, alkene steric and electronic properties, however, the exact position of each substituent cannot be specified by NMR. The specification of particular groups would be determined if X-ray analysis were possible. Unfortunately, silsesquioxanes derivatives were obtained as a viscous liquids. In order to define the ratio between the content of particular functional groups in the obtained molecules of the general formula  $(\text{RSiMe}_2\text{O})_n(\text{ViSiMe}_2\text{O})_{8-n}\text{Si}_8\text{O}_{12}$ , the MALDI TOF MS and GPC analyses were performed. A combination of these two methods was necessary to estimate the structure of the obtained products in a qualitative and quantitative manner. Molecular weights measured by MS confirmed the formation of the desired products and appropriate molecular weights were found at recorded spectra. On the other hand GPC analysis revealed single peaks with low polydispersity indexes (1.1-1.2) which made it impossible to distinguish individual structures. However, Mn values for all compounds increased when compared to **1** and confirmed total consumption of starting silsesquioxane **1**. In view of the published data, employment of synthetic methods based on the addition reactions, such as hydrosilylation or hydrothiolation, always leads to the products with statistical distribution of functional groups around the silsesquioxane cage. Moreover, the NMR experiments confirmed the formation of mixture desired products, since the ratio of the integral for remaining vinyl groups (6.16-5.72 ppm) to those for new signals derived from the appropriate functional groups (see ESI) clearly indicated that the obtained products contained statistically four unmodified vinylsilyl groups. That observation is consistent with the earlier published results on the syntheses of silsesquioxanes bearing mixed functional groups<sup>6a, 6ab</sup>. Compounds with general formula  $(\text{RSiMe}_2\text{O})_n(\text{ViSiMe}_2\text{O})_{8-n}\text{Si}_8\text{O}_{12}$ , where  $n = 2, 3, 4, 5, 6$ , were found (see ESI). The main fraction can be assigned to the designed 4/4 addition product by matching of the observed mass to the calculated one. On the other hand, tetra-functionalized silsesquioxanes can occur with different structural isomers and

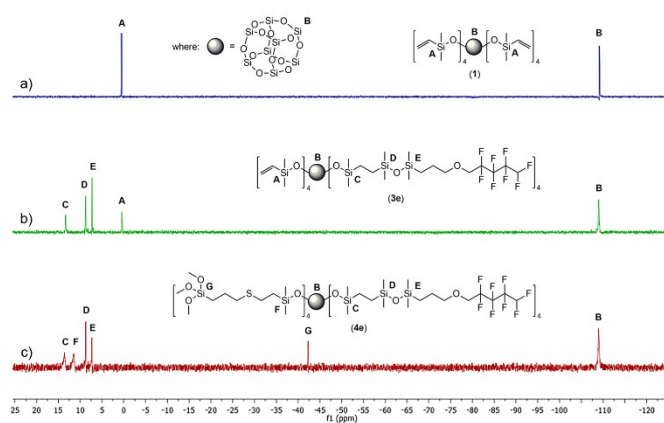
stereoisomers. The main signal is accomplished by two others, assigned to products tri- and pentafunctionalized (where  $n = 3$  and 5 respectively). Two others low intensity signals were observed and identified as di- and hexa-substituted products. Signals from utmost silsesquioxanes (1 and octa-substituted), as well as those with  $n = 1$  and 7, have not been identified. Partially functionalized spherosilicates (**3a-f**) seem to be very interesting starting materials for further modifications. The above-presented new POSS compounds still contain statistically distributed reactive SiVi groups located around the cage. In view of the published data describing the vinylsilyl groups as capable of other catalytic and stoichiometric transformations (such as silylative coupling<sup>[19]</sup>, hydrophosphorylation<sup>[20]</sup>, thiol addition<sup>[21]</sup>, N-silylation<sup>[22]</sup>, additive crosslinking<sup>[23]</sup>, epoxidation<sup>[24]</sup> etc.), which can lead to new derivatives bearing specific functional groups and can significantly extend the synthetic possibilities in the design of new specific architectures, (as well as the range of functional groups which can be linked to the silsesquioxane cage) we decided to experimentally verify our hypothesis. We selected derivative **3e** as an exemplary substrate for its subsequent functionalization based on thiol-ene addition and verification of the reactivity of external vinyl groups still present in the silsesquioxane **3e** structure.

**Table 1.** Synthesis of  $(\text{RSiMe}_2\text{O})_n(\text{ViSiMe}_2\text{O})_{8-n}\text{Si}_8\text{O}_{12}$  derivatives by hydrosilylation of silsesquioxane **1** with disiloxanes **2a-f** in the presence of  $\text{Pt}_2(\text{dvs})_3$ .

2	R	Reaction time [min]	Product 3a-f Yield [%]
a		60	96
b		22	95
c		35	89
d		106	94
e		24	96
f		26	97

Reaction conditions: **[1]:[2]:[Pt]** = 1:4:10<sup>-4</sup>, 90°C, toluene, m1:Vtol = 50 mg mL<sup>-1</sup>. Full conversions of reagents were determined by <sup>1</sup>H NMR and confirmed formation of target compounds by FT-IR; the selectivity for all experiments was determined by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR.

Thiol addition was performed by using 3-mercaptopropyltrimethoxysilane as the model substrate. In the presence of benzophenone functionalization was accomplished by UV irradiation. The reaction was performed at room temperature in toluene and was monitored by  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopy. The reaction was carried out until the total disappearance of vinyl units was observed (6.25-5.75 ppm at  $^1\text{H}$  NMR and 0.43 ppm at  $^{29}\text{Si}$  NMR), which confirmed total conversion of mercaptosilane and its successful incorporation to the silsesquioxane structure. The  $^{29}\text{Si}$  NMR spectra, presented in Figure 2, clearly indicate that the conditions established for hydrosilylation of  $(\text{ViSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$  and its subsequent functionalization enabled total conversions of both applied reactants. During partial functionalization of **1** with unsymmetrical disiloxanes, a decrease in intensity of signal A and the appearance of a new signal C assigned to the  $\text{SiCH}_2$  moiety were observed. Moreover, the total conversion of disiloxanes was also confirmed by the disappearance of the signal derived from  $\text{HSiMe}_2\text{OR}$  group (-6.37 ppm at  $^{29}\text{Si}$  NMR for **2e**)<sup>[11a]</sup>, transformed into a new signal. The silicon NMR spectra of isolated **3e** showed two peaks D and E at 8.74 and 7.25 ppm respectively, which confirmed the presence of disiloxane moiety functionalized on both sides. The modification of the remaining vinyl-silicon groups with mercaptosilane resulted in total disappearance of peak A and the appearance of a new signal F ( $\text{SiCH}_2\text{CH}_2\text{S-R}$ ) at 11.46 ppm. Also a new peak at -42.28 was observed and assigned to the trimethoxysilyl group. On the other hand, it should be strongly underlined that all NMR spectra of isolated compounds showed signal B at 108-109 ppm assigned to the Q silicon atoms present in the silsesquioxane core. It confirmed the attractive properties of investigated compounds which can survive exposition to irradiation or treatment with chemicals containing different functional groups, which makes them very attractive compounds for special applications. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of all compounds, as well as detailed synthetic procedures, are available in ESI. The compound **4e** seems to be a very attractive starting material for preparation of chemically and thermally stable hydrophobic coatings, due to the presence of alkoxyethyl groups able to create a chemical bond with inorganic surface as well as fluoroalkyl units responsible for the superhydrophobic properties<sup>[25]</sup>. The synthesized compounds will be the subject of further studies and tested as surface modifiers, building blocks, and co-monomers.



**Figure 2.**  $^{29}\text{Si}$  NMR spectra of silsesquioxane **1** and products **3e** and **4e** – signals corresponding to the  $\text{CH}_2=\text{CHSiMe}_2\text{O}$ ,  $\text{RSiMe}_2\text{O}$ , and  $\text{R}'\text{SiMe}_2\text{O}$  groups

## Conclusions

The obtained compounds (**3a-f**) containing two types of modifiable groups i.e. SiVi, epoxy,  $\text{NR}_2$  or Cl, represent a very interesting group of silsesquioxane derivatives since they can be functionalized on both vinylsilane and organic sides. Derivative **3e** was successfully used in subsequent hydrothiolation reaction, as a representative example of one of the possible synthetic modifications. Our approach showed that partially functionalized compounds **3a-f** are capable of further functionalization based on one of the above-mentioned processes. The presented methodology based on two different reactions can be employed in the design and synthesis of new multifunctional silsesquioxane derivatives and can be significantly extended through the high reactivity of vinyl-silicon group. Despite the arrangement of the functional groups in the spherosilicates skeleton is statistical and their structure is not perfectly symmetric, they can be considered as nearly perfect Janus-type compounds as reported by Laine et al. for the group of compounds of similar structures.<sup>[6e]</sup> All new compounds were isolated and characterized by spectroscopic methods.

## Conflicts of interest

There are no conflicts to declare

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