

Synthesis and Hydrosilylation of Vinyl-Substituted Open-Cage Silsesquioxanes with Phenylsilanes: Regioselective Synthesis of Trifunctional Silsesquioxanes

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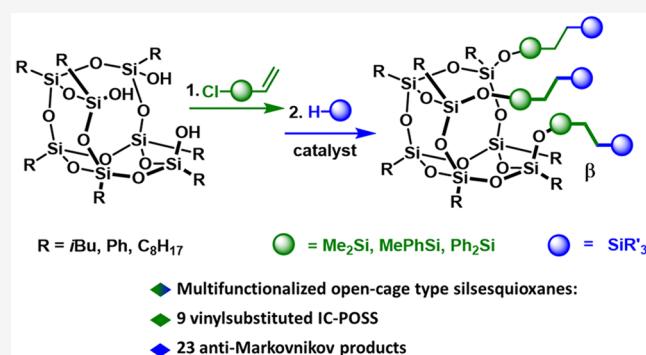
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ABSTRACT: Herein, we report an efficient synthesis and functionalization of trifunctional open-cage-type silsesquioxanes. The method proposed has been successfully applied for the synthesis of a library of incompletely condensed silsesquioxanes with vinylorganosilyl functional groups, which allows further modification. Detailed studies of hydrosilylation of sterically different open-cage vinylsilsesquioxanes with a wide spectrum of phenylsilanes catalyzed by platinum and rhodium compounds are also reported. The influence of the reaction parameters, types of reagents, and catalysts employed on the efficiency of the process was examined. Optimization of the process based on the above results permitted the design of a very attractive method for the synthesis of multifunctionalized silsesquioxanes with excellent yields and regioselectivity. Moreover, the results allowed the choice of the most efficient catalyst whose application led to the selective formation of substituted open-cage silsesquioxanes. These new compounds have been fully characterized and studied in terms of their thermal properties.



INTRODUCTION

Silsesquioxanes make up a group of organosilicon macromolecular cage compounds differing in the number and manner of combination of T units [the basic building blocks consist of one silicon atom covalently linked to three oxygen atoms (Figure 1)]. The research area focused on silsesquioxanes is one

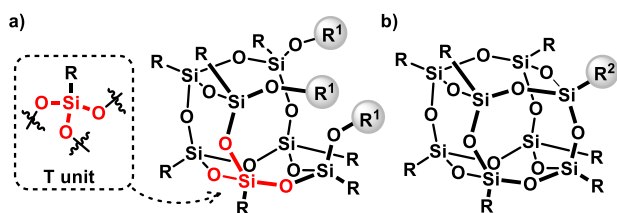


Figure 1. Structural differences between exemplary (a) open-cage-type and (b) completely condensed silsesquioxanes.

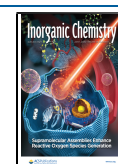
of the most dynamically developing in the chemistry of silicon compounds. Polyhedral oligomeric silsesquioxanes (POSSs) are characterized by structural diversity and the possibility of attachment of a variety of functional groups that significantly change their reactivity and solubility.^{1–4} These properties can be easily modified by the introduction of various substituents by using a wide spectrum of catalytic and noncatalytic chemical reactions (e.g., Heck coupling,^{5–9} metathesis,^{10–16} silylative

coupling,^{13–18} and many others^{1,2}). Among all of the above-mentioned methods, hydrosilylation of olefins (the addition of Si–H bonds to unsaturated systems, e.g., C=C bonds, resulting in the formation of a C–Si bond) is one of the fundamental processes used in industry and laboratory. This transformation is most often catalyzed by platinum compounds, although rhodium, nickel, and other transition-metal complexes are also used.^{19,20}

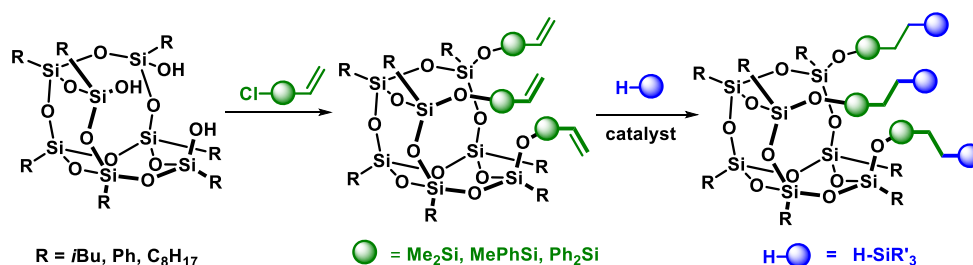
In scientific literature, the most widely described group is that of completely condensed silsesquioxanes, but an interesting alternative to cubic POSS cages may be incompletely condensed open-cage silsesquioxanes (IC-POSSs; Figure 1), which, thanks to their unique structure, may exhibit different physicochemical properties and different reactivity.^{21,22} Most literature reports about incompletely condensed silsesquioxanes focus on the use of POSS trisilanols as precursors for the synthesis of completely condensed derivatives^{1–3,23} and metallasilsesquioxanes complexes as molecular models for silica-grafted catalytic centers.^{21,22,24} Liu et al. investigated the hydrogen-bonded

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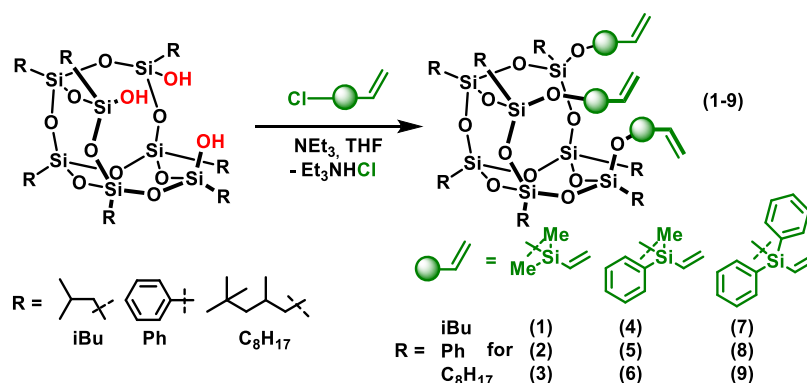
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Scheme 1. Scope of Work



Scheme 2. Synthesis of Open-Cage Silsesquioxanes with Three Vinyldiorganosilyl Groups



interaction in POSS silanols and the possibility of their usage as anion receptors to form host–guest complexes.²⁵ The scientific reports about trifunctional IC-POSSs are scarce. There are only a few examples of the synthesis and use of its vinylfunctional derivatives, which, because of the presence of several functional groups protruding from the cage, can be as multifunctional precursors and nanofillers of many materials used, e.g., in electronics and hybrid materials. Lorenz et al. have provided the first example of complete functionalization of the POSS trisilanol (with cyclohexyl groups in the corners) with chlorodimethylvinylsilane, leading to the formation of a product with three functional groups.²⁶ In 2010, Miyasaka et al. demonstrated that this compound can be functionalized by hydrosilylation, and it is used for the synthesis of branched polysiloxanes.²⁷ We have recently focused on open-cage POSSs, but in this work, the substrate scope was limited only to chlorodimethylvinylsilane and chlorodimethylvinylgermane with various kinds of commercially available POSS silanols.²⁸ Our recent work has been aimed at the synthesis of a library of IC-POSSs with three types of vinyldiorganosilyl groups and their further catalytic functionalization. Recently, Hreczycho's group has reported the $\text{Sc}(\text{OTf})_3$,²⁹ $\text{Bi}(\text{OTf})_3$,³⁰ and also Nafion³¹-catalyzed formation of Si–O–Si bonds, which has been successfully used in the functionalization of POSS silanols, and methods were expanded to the introduction of boron³² and germanium³³ functionalities to silsesquioxanes. Laine's group has presented another approach to the functionalization of such structures by blocking hydroxyl groups in trisilanolphenyl POSS, followed by modification of inert phenyl groups, resulting in the synthesis of stilbene–silsesquioxanes.³⁴ Other examples of using trivinyl-substituted open-cage silsesquioxanes are based on the substitution of one functional group with POSS or silane, followed by the formation of cyclic compounds and polymers.^{35,36} There are also reports on the application of trifunctional silsesquioxanes with Si–H groups in film-forming materials,³⁷ amphiphilic molecules,³⁸ hyperbranched poly-

mers,³⁹ carbazole-functionalized structures,⁴⁰ and composite films of poly(methyl methacrylate) matrixes with IC-POSS fillers.^{41,42}

It should be emphasized that the above-mentioned studies concerning hydrosilylation of trivinyl-substituted open-cage silsesquioxanes have not been devoted to optimization of the hydrosilylation process. Some of the above-mentioned literature reports only concerned the preparation of functional silsesquioxanes without their further modification. Therefore, this study was undertaken to comprehensively investigate hydrosilylation of trivinylsilyl-substituted open-cage silsesquioxanes with phenylsilanes (Scheme 1). The influence of the types of IC-POSSs and silane structures as well as the nature of the catalyst and reaction conditions on the effectiveness and selectivity of the hydrosilylation process was examined. The reactions were monitored with ^1H , ^{13}C , and ^{29}Si NMR and *in situ* Fourier transform infrared (FT-IR) spectroscopies. As follows from the perusal of relevant literature, it seems that no detailed comparison of the activity of various silanes and open-cage vinylsilsesquioxanes in the hydrosilylation reaction has been performed until now. To date, no one has ever compared a spectrum of catalysts in the hydrosilylation of trivinyl functional open-cage silsesquioxanes. Moreover, in our study for the first time, real-time FT-IR spectroscopy was applied to the monitoring of hydrosilylation of trifunctional IC-POSSs, which provided detailed data about the kinetics of hydrosilylation of these compounds and the influence of substrate structures on the course of the reaction. Additionally, the structure-dependent thermal properties of a series of IC-POSSs and their selected derivatives are presented.

RESULTS AND DISCUSSION

Synthesis of Incompletely Condensed Silsesquioxanes. The first and fundamental part of the study was the preparation of incompletely condensed silsesquioxanes with different steric hindrances protruding from the POSS core's

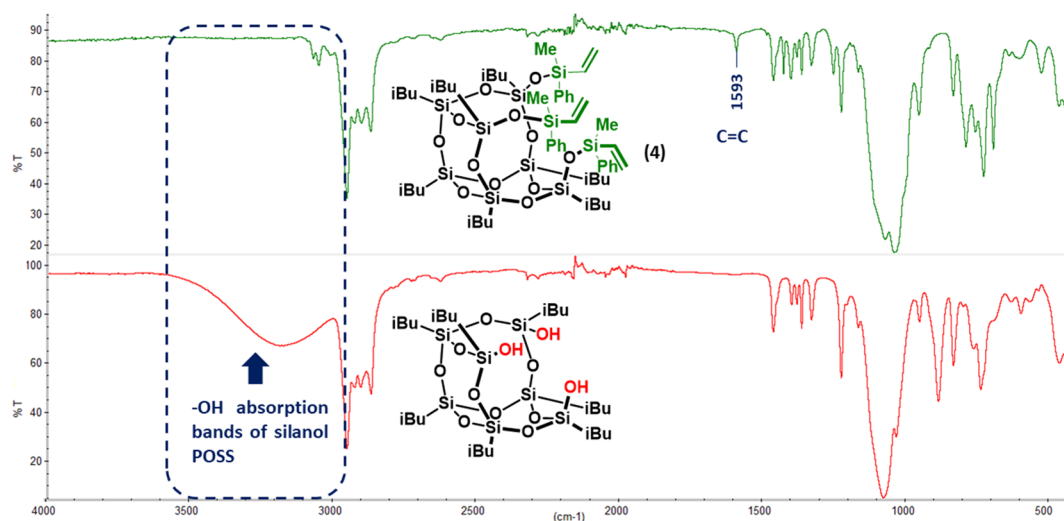


Figure 2. Examples of the FT-IR spectrum of the reaction mixture of 4 synthesis compared with that of trisilanolisobutyl POSS.

Table 1. Condensation of POSS Silanols with Chlorosilanes

Product	Trisilanol POSS	●	Reaction time [h] ^a	Isolated yield [%]	²⁹ Si NMR resonance lines in CDCl ₃ [ppm]	
1	<i>i</i> Bu	●	2.5	92	● -2.68 ● -67.29, -67.81, -68.04	
2	Ph		3.5	90	● -0.16 ● -77.40, -77.79, -78.15	
3	C ₈ H ₁₇	●	3	91	● -2.75, -2.84, -2.95 ● -67.51, -67.86, -67.98, -68.02, -68.06, -68.24, -68.32, -68.36, -68.52.	
4	<i>i</i> Bu	●	3	92	● -12.59 ● -67.23, -67.40, -67.51	
5	Ph	●	8	87	● -10.43 ● -77.33, -77.37, -77.80	
6	C ₈ H ₁₇	●	6	90	● -12.67 ● -67.45, -67.63, -67.85	
7	<i>i</i> Bu	●	6	93	● -22.63 ● -66.94, -67.26, -67.45	
8	Ph	●	12	89	● -20.66 ● -77.08, -77.43, -77.50	
9	C ₈ H ₁₇	●	9	87	● -21.99, -22.35, -22.40 ● -66.72, -66.82, -67.20, -67.28, -67.44, -68.21, -68.55, -68.61, -68.65	

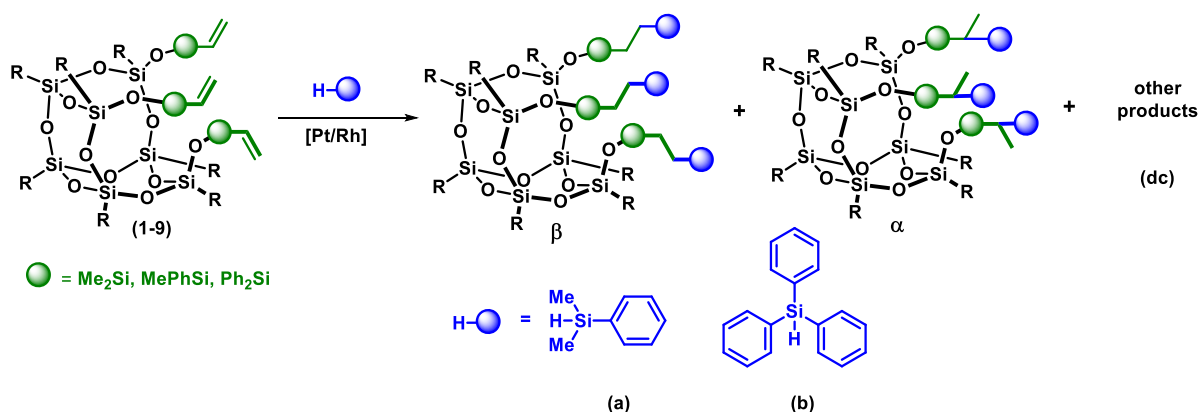
^aReaction conditions: [POSS silanol]:[chlorosilane]:[Et₃N] = 1:3.1:6; THF; 0–25 °C. The progress of the reaction was followed by FT-IR spectroscopy.

moieties. For this purpose, the IC-POSS architectures (1–9) were synthesized by the hydrolytic condensation of commercially available POSS trisilanols with chlorodimethylvinyl-, chloromethylphenylvinyl-, and chlorodiphenylvinylsilanes, according to Scheme 2.

In the process of reaction optimization, the effects of the amount of silane, triethylamine, and solvent used in condensation were determined. Because the efficiency and time of condensation reaction also strongly depend on the concentration of the reagents, we decided to use tetrahydrofuran (THF) as a reaction medium because silsesquioxane silanols are highly soluble in it. To avoid side-reactions, it was necessary to

cool the reaction mixture in an ice bath during the addition of chlorosilane. A small excess of chlorosilane was used to fully convert POSS silanol (molar ratio [POSS trisilanol]:[chlorosilane] = 1:3.1). Then, the cooling bath was left to warm to room temperature. The progress of the condensation reactions was monitored by FT-IR spectroscopy as the disappearance of the signals assigned to the stretching vibrations of the –OH groups present in the silanol substrates and the simultaneous appearance of characteristic absorption bands at 1593 cm⁻¹ attributed to C=C bonds from vinyl groups in the formed product (Figure 2).

Scheme 3. Hydrosilylation of Incompletely Condensed Trivinyl-Substituted Silesquioxanes with Phenylsilanes in the Presence of Platinum and Rhodium Catalysts

Table 2. Hydrosilylation of Selected IC-POSSs with Dimethylphenylsilane in the Presence of Platinum and Rhodium Catalysts^d

Entry	IC-POSS	Catalyst	Conversion of POSS [%]	Selectivity $\beta/\alpha/\text{dc}$ [%]	Main product
1	1	C1 ^{b,c}	100	100/0/0	<p>1a</p>
2		C2 ^{b,c}	100	100/0/0	
3		C3 ^{b,c}	100	100/0/0	
4		C4	99 ^b 99 ^c	99/0/1	
5		C5 ^{a,b}	100	100/0/0	
6	4	C1 ^{b,c}	99	100/0/0	<p>4a</p>
7		C2 ^{b,c}	99	100/0/0	
8		C3 ^{b,c}	99	100/0/0	
9		C4 ^{b,c}	98	99/0/1	
10		C5 ^{a,b}	100	100/0/0	
11	7	C1	99 ^b 98 ^c	100/0/0	<p>7a</p>
12		C2	98 ^b	100/0/0	
13		C3	97 ^c	100/0/0	
14		C4 ^{b,c}	99	96/1/3	
15		C5 ^{a,b}	100	100/0/0	

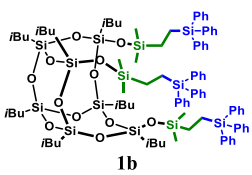
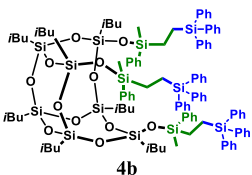
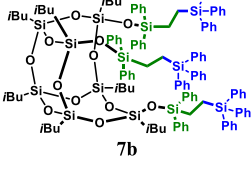
^dC1 = PtO_2 , C2 = PtCl_2 , C3 = H_2PtCl_6 , C4 = $[\text{Rh}(\text{COD})\text{Cl}]_2$, and C5 = $\text{Pt}_2(\text{dvs})_3$. Reaction conditions: $[\text{IC-POSS}]:[\text{silane a}]:[\text{platinum or rhodium}] = 1:3:(3 \times 10^{-4})^a/(3 \times 10^{-3})^b/(3 \times 10^{-2})^c$; $T = 95^\circ\text{C}$; toluene; $m_{\text{POSS}}/V_{\text{tol}} = 100 \text{ mg/mL}$; reaction time 48 h (C1 and C2) and 24 h (C3–C5).

Finally, the crude product was isolated from the reaction mixture and purified. After the reactions, the mixtures were filtered off by a glass filter type G4 with silica gel and Celite, and then the column was flushed by ethyl acetate to rewash all products. HCl formed during the reaction was bound to triethylamine, and the side product Et_3NHCl (hardly soluble in the reaction mixture) was retained on the column. The excess of the solvent was evaporated, and the product was dried under vacuum. In the cases of 3, 6, and 9 (silesquioxanes with C_8H_{17} inert groups in the framework), the solution after filtration was evaporated, the product was extracted with dichloromethane/water, then the organic phase was dried over anhydrous magnesium sulfate for 24 h and filtered off, and the solvent

was evaporated. All products 1–9 were obtained with good yields of 87–93%.

During the course of the reactions, it was noted that the time needed for complete conversion of POSS trisilanol increases with increasing steric hindrance of the chlorosilane used, in the order from chlorodimethylvinyl- to chlorophenylmethylvinyl- to chlorodiphenylvinylsilane. The same effect was also observed for the derivatives containing Ph and C_8H_{17} inert groups. The reaction times were 2.5–8 h for 1–6 and 6–12 h for 7–9 (data are compiled in Table 1). It should be added that the *i*Bu and C_8H_{17} silanols react faster than the Ph silanol in the presented reaction. The reason for the longer times of condensation of POSS silanols with chlorodiphenylvinylsilane might be a greater

Table 3. Hydrosilylation of Selected IC-POSS with Triphenylsilane in the Presence of Platinum and Rhodium Catalysts^d

Entry	IC-POSS	Catalyst	Conversion of POSS [%]	Selectivity $\beta/\alpha/dc$ [%]	Main product
1	1	C1	97	98/1/1 ^b 97/1/2 ^c	 1b
2		C2 ^{b,c}	98	99/0/1	
3		C3 ^{b,c}	97	98/2/0	
4		C4 ^{b,c}	97	98/0/2	
5		C5 ^{a,b}	99	99/0/1	
6	4	C1 ^{b,c}	97	98/0/2	 4b
7		C2 ^{b,c}	98	98/0/2	
8		C3	97	98/0/2 ^b 99/0/1 ^c	
9		C4	98	98/0/2 ^b 93/0/7 ^c	
10		C5 ^{a,b}	98	98/1/1	
11	7	C1 ^{b,c}	97	97/1/2	 7b
12		C2 ^{b,c}	96	97/0/3	
13		C3 ^{b,c}	98	97/1/2	
14		C4 ^{b,c}	99	98/2/0	
15		C5 ^{a,b}	98	98/1/1	

^dC1 = PtO₂, C2 = PtCl₂, C3 = H₂PtCl₆, C4 = [Rh(COD)Cl]₂, and C5 = Pt₂(dvs)₃. Reaction conditions: [IC-POSS]:[silane b]:[platinum or rhodium] = 1:3:(3 × 10⁻⁴)^a/(3 × 10⁻³)^b/(3 × 10⁻²)^c; T = 95 °C; toluene; m_{POSS}/V_{tol} = 100 mg/mL; reaction time 48 h (C1 and C2) and 24 h (C3–C5).

steric hindrance caused by the phenyl groups in chlorosilane and changes in the electronic effects of the inert groups attached to the silsesquioxane core.

The differences in the properties and structures of the obtained open-cage silsesquioxanes are also manifested in the ²⁹Si NMR spectra as changes in the resonance lines assigned to silicon atoms. For derivatives 3 and 9, containing in their structures inert 2,4,4-trimethylpentyl (C₈H₁₇) groups, we observed the multiplicity of the signals in the Si NMR spectra probably caused by the interaction and rotation of these compounds. For all compounds, the chemical shifts of the three silicon atoms from the functional groups Si–CH=CH₂ were changed because of the differences in the electronic effects of the substituents at silicon atoms. The resonance lines were shifted toward lower chemical shift values from alkyl to aryl substituents and with the increasing number of phenyl substituents. On the other hand, chemical shifts of the silicon atoms derived from the Si–O–Si core were just slightly changed. A similar effect has been reported for tetrakis(methylsilylated) double-decker octaphenylsilsesquioxane and tris(methylsilylated) heptaphenylsilsesquioxane.⁴³

Synthesis of Functionalized Open-Cage Silsesquioxanes. Having these sterically and electronically different vinyl IC-POSSs, we decided to functionalize them via the hydrosilylation reaction. Moreover, the employment of real-time FT-IR spectroscopy allowed us to examine the influence of the structural diversity of POSS compounds as well as applied hydrosilanes on the reactivity of the investigated derivatives in the trifunctional POSS derivatives functionalization. We chose

the hydrosilylation reaction to selectively bond chromophores (in the form of phenylsilanes) to derivatives 1–9, which have three vinyl functional groups protruding from the silsesquioxane cage, thus enabling their further modification and making them molecular scaffolds for the bonding of chromophores.

Screening of Catalysts. At the beginning of this study, three IC-POSS derivatives with the same inert *i*Bu group and three different types of open moieties (dimethylvinylsilyl, 1; phenylmethylvinylsilyl, 4; diphenylvinylsilyl, 7) and two silanes, namely, dimethylphenylsilane (a) and triphenylsilane (b), with significantly different steric properties were selected as our model systems for catalyst screening (Scheme 3). Optimization of the reaction conditions was carried out using different loadings of selected catalysts [PtO₂, PtCl₂, H₂PtCl₆, [Rh(COD)Cl]₂, and Karstedt's catalyst Pt₂(dvs)₃] known for high catalytic activity in the hydrosilylation of olefins.^{19,20} The conversion of all reagents and the formation of products were determined by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The results of the experiments are presented in Tables 2 and 3.

In all experiments, the conversion of substrates was very high and amounted to over 96%. Moreover, hydrosilylation of 1, 4, and 7 with dimethylphenylsilane a resulted in the exclusive formation of β -isomeric products (1a, 4a, and 7a) with a selectivity of over 99% in the presence of platinum catalysts. Some test reactions with the bis(1,5-cyclooctadiene)dirhodium(I) dichloride complex led to the formation of α and β (main) products and dehydrogenative coupling products (entry 14 in Table 2 and entry 9 in Table 3). However, hydrosilylation of selected silsesquioxanes with triphenylsilane b brought about

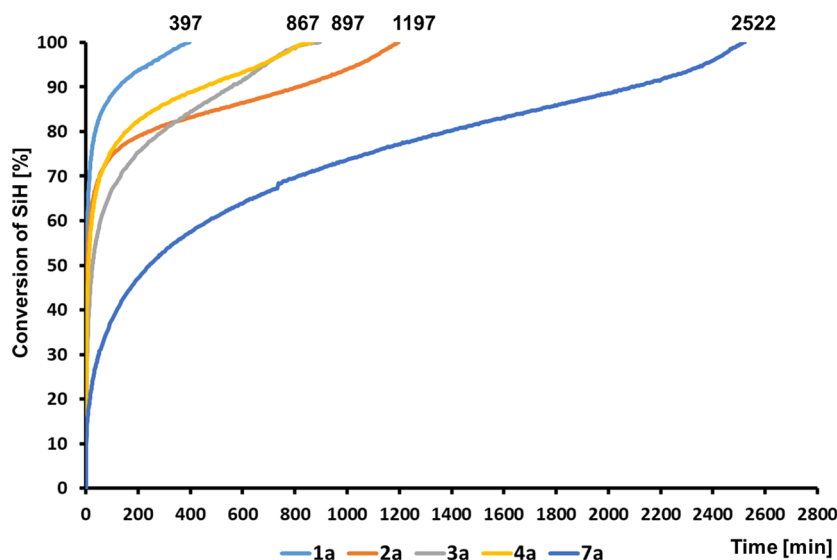


Figure 3. Kinetic plots for hydrosilylation of silsesquioxanes 1–4, and 7 with dimethylphenylsilane (a), in the presence of Karstedt's catalyst, measured by *in situ* FT-IR (the formation of products 1a–4a and 7a). Reaction conditions: toluene; 95 °C; $m_{\text{POSS}}/V_{\text{tol}} = 100 \text{ mg/mL}$; $\text{Pt}_2(\text{dvs})_3$ catalyst; $[\text{POSS}]:[\text{silane}]:[\text{platinum}] = 1:3:(3 \times 10^{-4})$.

the predominant formation of β products (1b, 4b, and 7b over 94%) and a greater number of dehydrogenative coupling products and α products. The conducted experiments showed that the rhodium catalyst was the least selective in hydrosilylation of IC-POSS with phenylsilanes. All catalysts showed less selectivity in the reactions with the more sterically crowded silane b. Although in the initial tests with 10^{-2} mol of C1–C4 and 10^{-3} mol of C5 of metal loading per 1 mol of Si–H group we obtained products with similar conversion of the reagents and selectivity, we decided to reduce the catalyst loadings. It turned out that C5 proved to be in all cases the most selective catalyst with the lowest metal loading (10^{-4} mol of platinum per Si–H group). On the basis of the preliminary results, we decided to use Karstedt's catalyst, as the most efficient hydrosilylation promoter, in our further study.

In Situ FT-IR Experiments. On the basis of earlier results, we decided to perform several additional experiments using *in situ* FT-IR spectroscopy to more precisely explore the effect of the silsesquioxane structure on the reaction time. The applied methodology allowed precise monitoring of the experiments by measurement of the reaction trends and profiles in real time, providing highly specific information, e.g., about the kinetics, reaction initiation, and conversion of the reagents in the course of the reaction. For this purpose, we chose simple dimethylphenylsilane (a) and two groups of silsesquioxanes: the first of 1–3 with the same dimethylvinylsilyl opening moiety and different inert groups in the POSS cage and the second of 1, 4, and 7 with the same inert group and different types of vinylorganosilyl moieties. In these experiments, 1 equiv of silsesquioxane (1–4 or 7), 3 equiv of dimethylphenylsilane, and 1 mL of toluene were added to a glass reactor equipped with an *in situ* FT-IR probe and placed in an oil bath at 95 °C, and then 10^{-4} mol of platinum (per each Si–H group) of Karstedt's catalyst was added. The progress of hydrosilylation of selected silsesquioxanes with PhSiMe_2H in the presence of Karstedt's complex was possible to control by monitoring of the high absorption bands assigned to Si–H units ($\nu = 822 \text{ cm}^{-1}$), which decreased over time. All results are shown in Figure 3.

The rate of hydrosilylation of the C=C bond was found to strongly depend on the silsesquioxane structure. The time

required for total hydrosilylation of C=C bonds in the reactions between phenyldimethylsilane and POSS derivatives (1–3) reached 397, 1197, and 897 min, respectively. So, for the POSSs with alkyl inert groups, the reaction was faster than that for the aromatic (phenyl) group, although, at the beginning of the process, the reaction of 2 was faster than that of 3. However, eventually more time was needed to complete the addition of Si–H to C=C bonds. Additionally, the smaller the alkyl substituent, the shorter the reaction ($\text{time}_{i\text{Bu}} < \text{time}_{\text{octyl}}$). The reason for such a reactivity could be the different electronic effects and steric hindrances of the alkyl and aryl groups. In the case of IC-POSSs with the same *i*Bu inert cage groups and different moieties protruding from the cage dimethylvinylsilyl (1), phenylmethylvinylsilyl (4), and diphenylvinylsilyl (7), the reaction time increased with increasing steric hindrance of the functional groups. The reaction time was 397 min for 1, 867 min for 4, and 2522 min for 7, and differences in the reactivity and reaction times were quite significant.

Figure 4 shows 2D and 3D illustrations of the disappearance of the characteristic Si–H signal in the course of an exemplary hydrosilylation reaction of 7 with dimethylphenylsilane, which leads to complete conversion of the substrates, selective functionalization of all functional groups, and formation of 7a.

Hydrosilylation of Open-Cage Silsesquioxanes with Phenylsilanes. The positive results achieved in the catalytic tests of hydrosilylation of selected IC-POSSs with silanes a and b prompted us to extend the range of POSSs and silanes. We decided to extend the described method to functionalization of all obtained IC-POSSs (1–9). Our choice of silanes was based on the tests with silanes with different steric hindrances (Tables 2 and 3). Therefore, we decided to perform the next experiments with silanes containing a dimethylsilylhydride moiety. In the earlier selected reaction conditions, new trisubstituted derivatives were obtained in the stoichiometric reaction of IC-POSSs (1–9) with phenylsilanes (Scheme 4). The molar ratio was as follows: $[\text{IC-POSS}]:[\text{silane a/b/c/d}]:[\text{platinum}] = 1:3:(3 \times 10^{-4})$. For 1–6, we conducted the reaction for 24 h, and for 7–9, the reaction was for 48 h. Using silane e in the stoichiometric reactions with silsesquioxanes, various types of cross-linked structures were obtained, which is related to the presence of two

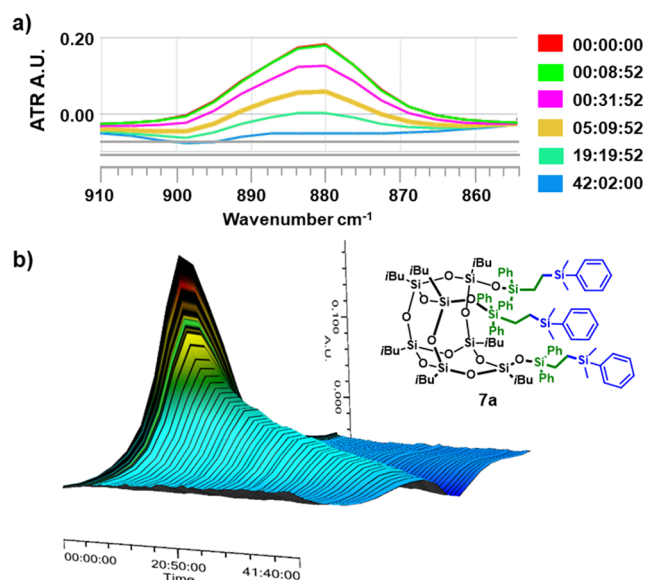


Figure 4. (a) 2D and (b) 3D illustrations of the Si–H bond disappearance recorded in real time during hydrosilylation of **7** with dimethylphenylsilane (the formation of **7a**) in the presence of Karstedt's catalyst.

reactive Si–H groups in the 1,4-bis(dimethylsilyl)benzene molecule. However, by changing the molar ratio and using a little excess of silane, we obtained compounds **1e** and **2e** at the molar ratio [IC-POSS]:[silane **e**]:[platinum] = 1:3.1:(3×10^{-4}) by selective functionalization of only one functional group in silane. We assume that, at the initial stage of reaction, monosubstitution of 1,4-bis(dimethylsilyl)benzene is observed. However, when conversion of the substrates is very high, the remaining vinyl groups may react with the dimethylsilyl units incorporated with the POSS molecules, which leads to the cross-linked structure. In order to avoid hydrosilylation of both dimethylsilyl groups in 1,4-bis(dimethylsilyl)benzene, the equilibrium of the reaction must be shifted toward the formation of monosubstituted products; therefore, for selective monofunctionalization, a slight excess of silane **e** was required. A similar effect was observed, e.g., for functionalization of 1,1,3,3-tetramethyldisiloxane with vinylsilanes;⁴⁴ however, for functionalization of POSS compounds with 1,4-bis(dimethylsilyl)benzene, a significantly lower excess of silane **e** had to be used

compared with the disiloxanes, which could be explained by the steric properties of the POSS molecules.

A definite advantage of **1d**, **2d**, **3d**, **1e**, and **2e** is the presence of three bromine atoms and three Si–H groups, which may allow further functionalization of these compounds and their application, for example, in hybrid materials^{45,46} and building blocks for organic optoelectronic materials.^{47–51}

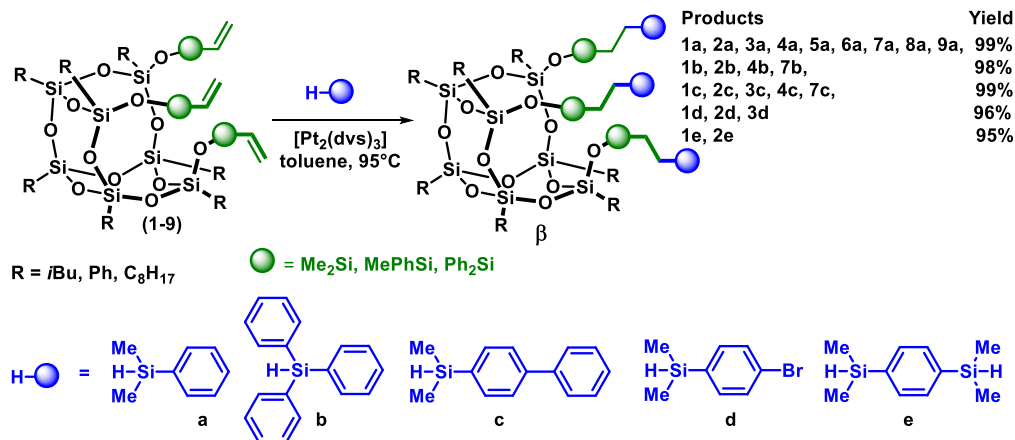
Figure 5 shows an exemplary starting mixture and the postreaction mixture of **1e** formation. Progress of the reaction was followed by attenuated-total-reflectance FT-IR. Because of overlap of the substrate signals at about 900 cm^{-1} , the progress of the reaction was monitored by observing decreasing signals assigned to Si–H groups at 2119 cm^{-1} , and additionally, as the reaction progresses, a band around 800 cm^{-1} started to appear. The reaction was completed after 24 h because changes in the conversion of Si–H were no longer observed. After the reactions, the mixtures were filtered off by a glass filter type G4 with silica gel and Celite. The solvent was evaporated, and the products were dried under vacuum.

THERMAL PROPERTIES

Compounds **1–9** exhibit the so-called open-cage structure. Besides various substituents at the protruding groups (which affect steric hindrance), these structures have three types of inert groups surrounding the POSS core (*i*Bu, Ph, and C_8H_{17}). All presented types of structural modifications affected not only the syntheses of the compounds but also their physical properties such as the physical state, solubility, and thermal properties. Thermogravimetric analysis (TGA) revealed that both types of substituents (inert groups in the POSS framework and opening moieties) affected the thermal properties of the open-cage-type silsesquioxanes and their derivatives. The influence of the structural diversity on the thermal properties of the samples studied was evaluated for IC-POSSs **1–9** and their selected derivatives on the basis of the 5% ($T_d^{5\%}$) and 10% ($T_d^{10\%}$) mass loss temperatures and the amount of residue at $1000 \text{ }^\circ\text{C}$ (all results are shown in Table 4).

Considering the influence of the inert group, the highest thermal stability was found for the compounds with Ph groups (**2**, **5**, and **8**). Additionally, the presence of functional groups with greater steric hindrance increases the thermal stability of the derivatives ($1 < 4 < 7$), which is related to the generally greater stability of the phenyl compounds compared to the alkyl structures.^{52,53} However, for compounds with the alkyl inert

Scheme 4. Hydrosilylation of IC-POSSs (1–9) with Phenylsilanes (a–e) in the Presence of Karstedt's Catalyst



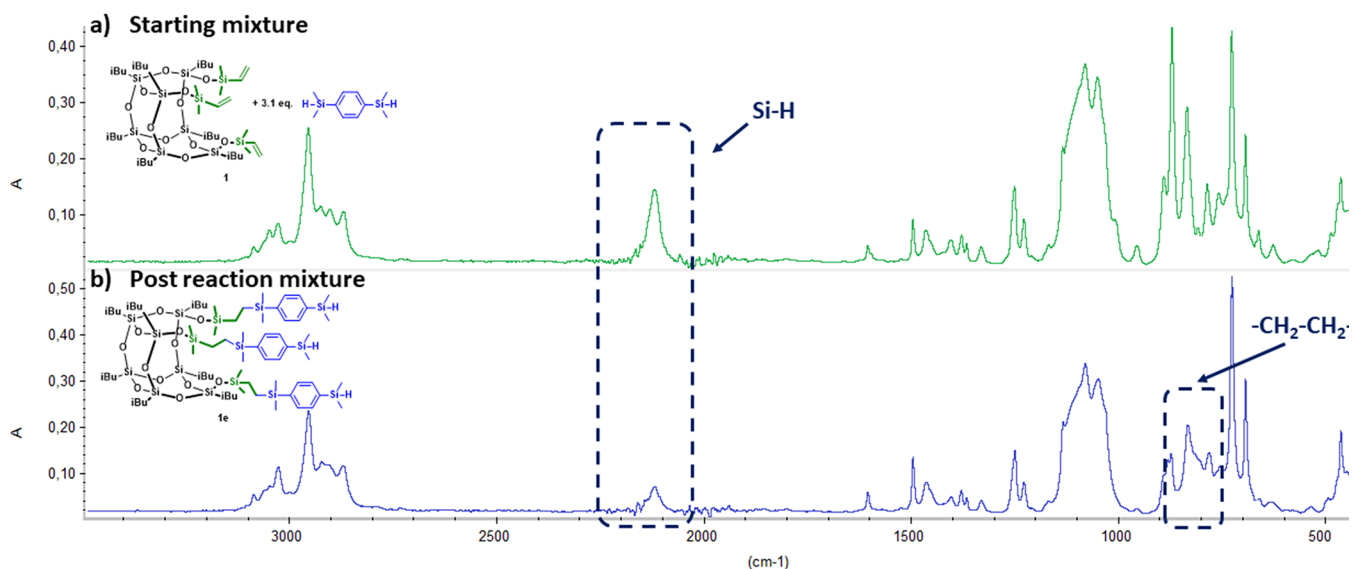


Figure 5. FT-IR spectra of (a) starting mixture **1** + 3.1 equiv of silane **e** and (b) postreaction mixture/formation of **1e**.

Table 4. Thermal Properties of IC-POSSs 1–9

entry	product	mass loss temperature [°C]		residue at 1000 °C [%]
		$T_d^{5\%}$	$T_d^{10\%}$	
1	1	269	340	33
2	2	440	499	42
3	3	335	359	32
4	4	372	434	32
5	5	427	488	39
6	6	364	385	26
7	7	388	427	32
8	8	464	520	39
9	9	269	320	28
10	1a	295	328	32
11	1b	295	339	21
12	1c	310	344	27
13	4a	334	387	30
14	7a	332	364	24

substituents *i*Bu and C_8H_{17} , only for the dimethylvinylsilyl group, compound **3** (C_8H_{17}) is more stable than **1** with the smaller *i*Bu inert group. When the functional groups are phenylmethylvinylsilyl (**4–6**) or diphenylvinylsilyl (**7–9**), the thermal stability increases in the order $6 < 4 < 5$ and $9 < 7 < 8$. The observed impact of the type of functional group on the thermal stability of silsesquioxanes may be caused by the changed distance between these groups and the wider opening of the silsesquioxane structure, making it more flexible. Furthermore, it should be strongly emphasized that the residue observed at 1000 °C was the highest for the trisilanolphenyl POSS-derived products, which is consistent with the literature data.⁵³

Figures 6 and 7 show the TGA curves obtained for selected functionalized structures. We compared the influence of the modifier (substituted silane) and different inert groups in the compounds with the same modifier on their thermal properties. Analysis of the obtained results showed that functionalization of IC-POSSs with phenylsilanes strongly influenced the thermal properties of the resulting products (**1a–1c**); the $T_d^{5\%}$ values significantly increased compared to those of the unmodified

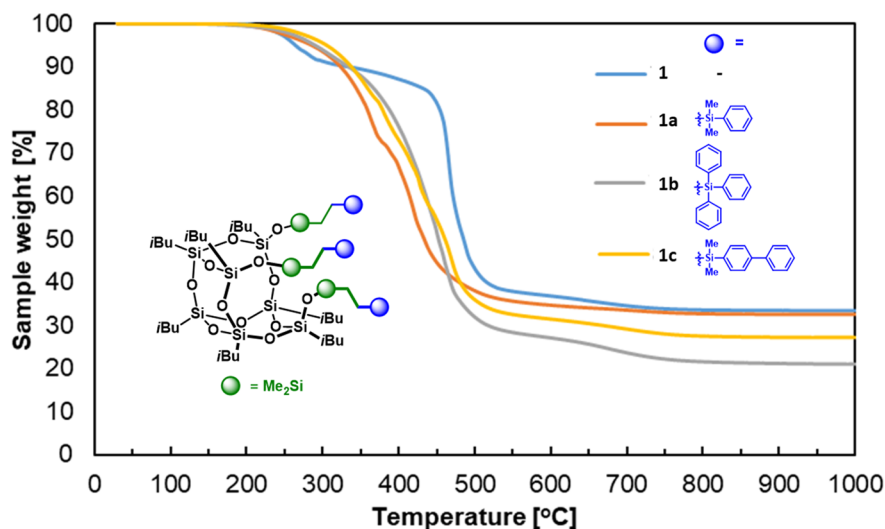


Figure 6. TGA curves obtained for selected compounds: **1** and **1a–1c** (influence of the modifier on the thermal properties).

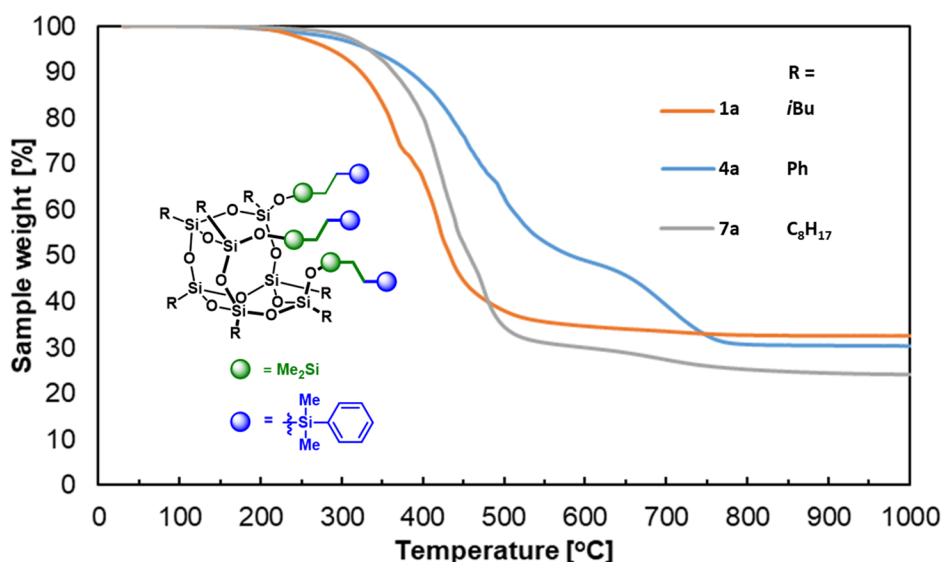


Figure 7. TGA curves obtained for selected compounds: **1a**, **4a**, and **7a** (influence of the inert group on the thermal properties).

silsesquioxanes. A similar effect of the thermal behavior of IC-POSSs after the incorporation of aryl groups into the silsesquioxane core was observed by the Naka group.⁴²

However, for **4a** and **7a**, the $T_d^{5\%}$ parameter was decreased for the modified structures probably because of differences in the steric hindrance of the silyl groups in the open corner of silsesquioxanes, which affected the arrangement of the aromatic units and interaction between them. For derivatives **1a**, **4a**, and **7a** modified with the same dimethylphenylsilane but containing different inert groups, we observed increasing thermal stability in the order from *i*Bu to C₈H₁₇ and Ph. On the other hand, after the initial degradation, the decomposition of **7a** progressed much faster compared with that of **4a**, which clearly indicates higher resistance of the phenyl derivative than the alkyl one to thermooxidative decomposition.

CONCLUSION

In summary, we synthesized a library of trifunctional open-cage silsesquioxanes differing in the structure of the inert groups and opening moiety. Having these sterically and electronically different vinyl IC-POSSs, we modified them with a series of silanes of different structures, functionalities, and steric hindrances in hydrosilylation reactions. Different homogeneous and heterogeneous catalytic systems were examined to determine their impact on the effectiveness and selectivity of hydrosilylation evaluated by monitoring of the processes with ¹H, ¹³C, and ²⁹Si NMR and *in situ* FT-IR spectroscopy.

The most interesting outcome of our study is the first example of a fully specified synthetic protocol allowing modification of trivinylsubstituted open-cage silsesquioxanes with silanes to be obtained via a hydrosilylation reaction. The applied methodology of synthesis does not require the use of complicated isolation of the final products. The hydrosilylation reactions catalyzed by Karstedt's catalyst proceeded in a highly regioselective manner to give exclusively anti-Markovnikov products.

Additionally, we studied the structure-dependent thermal properties of a series of IC-POSSs and their selected derivatives. Full characterization of the products enabled us to identify the relationship between the structures of the silsesquioxanes studied (e.g., the types of inert groups in the framework and

silicon substituents in the functional group) and phenylsilanes (e.g., their arrangement, structure, etc.) and their physicochemical properties allowing the design of macromolecules with desirable properties.

We believe that the compounds based on open-cage silsesquioxanes can undoubtedly become very useful reagents for the synthesis of building blocks and scaffolds for hybrid materials, which, because of the unique structure and greater flexibility of the core, can compete with completely condensed silsesquioxanes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00947>.

General procedures for the synthesis of IC-POSSs (**1–9**) and for hydrosilylation of IC-POSSs with phenylsilanes, NMR and MALDI-TOF data and spectra of compounds synthesized in this paper, and TGA curves obtained for selected compounds **1–9** (PDF)

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Notes

The authors declare no competing financial interest.

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