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Catalytic Approach to Germanium-Functionalized Silsesquioxanes and Germasilsesquioxanes

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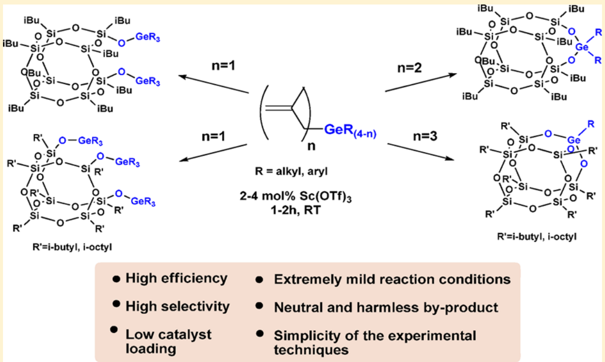
Supporting Information

ABSTRACT: Silsesquioxanes have attracted considerable attention in recent years due to their unique hybrid structure and versatile properties. Herein, we report the first catalytic approach to the synthesis of completely and partially condensed germanium-functionalized silsesquioxanes as well as germasilsesquioxanes, mediated by scandium(III) triflate. We provide a solution for introducing germyl functionalities into various types of silsesquioxanes under mild conditions with excellent yields. This methodology turns out to be a highly efficient and selective synthesis route to obtaining novel germanium-containing silsesquioxanes. These new multielement POSS derivatives may have great potential for further applications as valuable multifunctional building blocks in material chemistry.



INTRODUCTION

Silsesquioxanes represent a class of organosilicon compounds of well-defined nanosized structure and versatile hybrid properties.[1−4] Due to their unique features, completely condensed as well as partially condensed functionalized silsesquioxanes are of considerable interest and high relevance in various fields of material chemistry and optoelectronics.[5−9] They are widely used as elastomers, optic and electronic materials, hybrid adhesives, engineering materials, and precursors of nanocomposites.[5−9] Moreover, a particularly attractive group of POSS derivatives known as heterosilsesquioxanes has attracted much attention owing to the presence of heteroatoms (e.g., Ge, Sn, Al, B, P, transition metals, and others) in addition to silicon and oxygen atoms in the POSS skeleton.[10−13] For instance, the first germasilsesquioxane has been synthesized by Feher and co-workers.[14] Germasilsesquioxanes may serve as multielement precursors of hybrid inorganic−organic materials. Furthermore, the presence of germanium atoms in the POSS skeleton affects the dimensions and parameters of the POSS framework. Germasilsesquioxanes have been the subject of the experimental and computational studies which have shown that the differences in the POSS structure have a significant influence on the kinetics of trapping and detrapping of atoms incorporated into the POSS cage.[15] Furthermore, the germanium-functionalized POSS compounds containing Ge−O−Si bond in their structure may combine the excellent physical, optical, and electrical properties of silsesquioxanes and the enhanced features of germasiloxanes (e.g., higher refractive index, low dielectric constant, and biocompatible properties).[16,17] It is also worth noting that organogermanium compounds have recently aroused much interest in various fields (e.g., as semiconductors in electronic industry, nanocomposite materials, pharmaceuticals and others).[18,19] It has been reported that germanium-functionalized materials containing the Ge−O−Si moiety may show improved mechanical properties and thermal stability.[20,21] Therefore, the germanium-containing POSS derivatives seem to be particularly attractive for further applications and their properties are still being investigated. Despite their great potential, the number of reports regarding germanium-functionalized silsesquioxanes and the methods for their synthesis is still limited.[22−25] There are even fewer protocols on the functionalization of incompletely condensed silsesquioxanes with organogermanium groups.[26]

Conventional methods for the synthesis of Ge−O−Si bond are based on the condensation reaction of silanols/chlorosilanes/alkoxysilanes with chloro-/alkoxygermananes or the cohydrolysis of chlorosilanes with chlorogermananes.[10,27] Unfortunately, these reactions are restricted by the formation of highly reactive and volatile byproducts (e.g., HCl). This synthesis route involves the necessity of using moisture-sensitive reagents and removal of corrosive byproducts. Furthermore, it suffers from the lack of chemoselectivity and low functional group tolerance. These significant drawbacks limit the utility of the conventional methods. However, the reports on the catalytic methods leading to the Ge−O−Si bond formation are few. They are mainly based on $B(C_6F_5)_3$-catalyzed dealkylative coupling of hydrosilanes with alkoxygermananes or hydrogermananes with alkoxysilanes,[28] the coupling reaction of silanols with vinylgermananes catalyzed by ruthenium(0) complexes[29] or $CpFe(CO)_2Me$-catalyzed reac-

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tion of diphenylgermanane with silanes in DMF.[16] Nevertheless, none of these reactions seems to be useful for functionalization of commercially available POSS silanols. This particularly interesting class of silsesquioxanes containing silanol groups (Si−OH) plays an important role as easily accessible precursors of other POSS derivatives.

To the best of our knowledge, the direct formation of Ge−O−Si bond in all reported literature examples of Ge-functionalized POSS derivatives and germasilsesquioxanes has been achieved using conventional stoichiometric methods.[22−26] Moreover, there has been only one report regarding incompletely condensed silsesquioxanes with organogermanium functionalities.[26] Marciniec and co-workers have recently reported the synthesis of Ge-substituted incompletely condensed silsesquioxanes, however, their procedure does not eliminate the formation of corrosive and reactive byproducts.

Our research group has recently found a new method for the formation of E−O−Si bond (E = Si, Ge and B)[30−35] included the *O*-metalation of silanols with 2-methylallylsilanes or 2-methylallylgermananes in the presence of scandium(III) trifluoromethanesulfonate.[30−33] Just recently, we have reported the successful use of scandium(III) triflate in the *O*-silylation of POSS silanols by 2-methylallylsilanes.[36] Encouraged by these results, we decided to extend this methodology for the synthesis of germanium-functionalized silsesquioxanes as well as POSS derivatives containing germanium atoms incorporated into the POSS skeleton.

■ RESULTS

Herein, we report a successful extension of *O*-silylation of POSS silanols to the synthesis of Ge-containing silsesquioxanes. We present an efficient, selective and useful technique for the formation of Ge−O−Si bond within POSS molecules. The aim of this work was to examine the use of 2-methylallylgermananes as germylating reagents in $Sc(OTf)_3$-catalyzed *O*-germylation of commercially available POSS silanols (Scheme 1).

First, we discovered that POSS monosilanol containing the silanol group (Si−OH) successfully undergoes selective *O*-germylation with 2-methylallylgermananes in the presence of 2 mol % of $Sc(OTf)_3$ in toluene at room temperature with the evolution of isobutylene as neutral and harmless byproduct (Table 1). These optimal conditions were applied to various 2-methylallylgermananes providing the desired products in high isolated yields (Table 1, entries 1−4).

Scheme 1. Synthesis of Mono-, Di-, Trifunctional Ge-Substituted POSS Derivatives and Germasilsesquioxanes

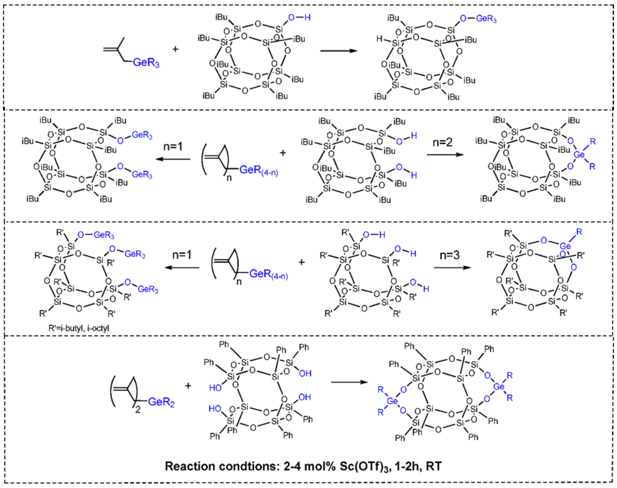
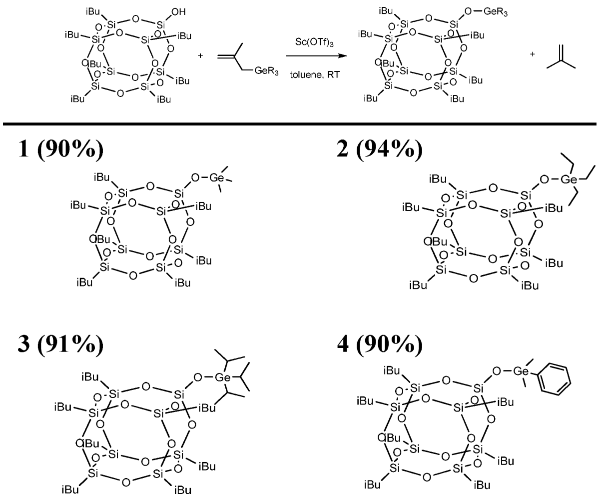


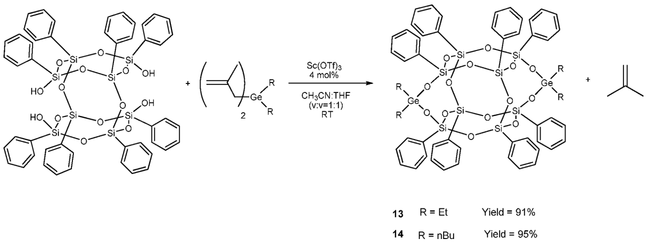
Table 1. Synthesis of Monofunctional Derivatives in the Reaction of POSS Monosilanol with 2-Methylallylgermananes Catalyzed by $Sc(OTf)_3$[a]



[a]Reaction conditions: toluene, rt, 1 h, $Sc(OTf)_3$, catalyst loading 2 mol %, molar ratio of POSS/germanane = 1:4.

Thereafter, we decided to extend this methodology to the functionalization of incompletely condensed silsesquioxanes: POSS disilanol, trisilanol and double decker silsesquioxane (DDSQ) with four Si−OH groups (Scheme 1 and 2). All reactions were performed at room temperature, using toluene as a solvent or a mixture of solvents CH_3CN/THF (v/v = 1:1) when using double-decker derivatives due to their poor solubility in toluene. The catalyst loading required for the *O*-germylation of incompletely condensed silsesquioxanes containing two, three or four Si−OH groups was 4 mol % of $Sc(OTf)_3$ to obtain desired products (Tables 2 and 3).

Scheme 2. Synthesis of Digermasilsesquioxanes in the Reaction of POSS Tetrasilanol (Double Decker Silsesquioxane) with Bis(2-methylallyl)germananes Catalyzed by $Sc(OTf)_3$



The purity of obtained compounds was determined by NMR spectroscopy and elemental analysis. The conversion of reagents was determined by NMR spectroscopy, in particular by ^{29}Si NMR spectroscopy (79 MHz, C_6D_6). In the ^{29}Si spectra of the obtained products, we did not observe the peaks from silicon atoms of silanol groups which proves the full conversion. The ^{29}Si spectra of the products as well as the reagents used for the synthesis; POSS silanols are presented in the Supporting Information.

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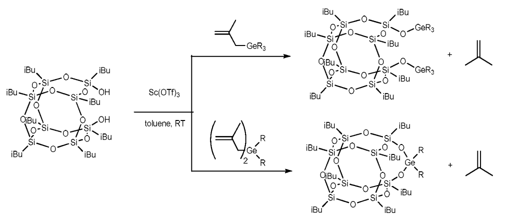
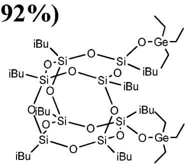
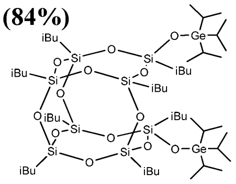
Table 2. Reactions of POSS Disilanol with 2-Methylallylgermananes and Bis(2-methylallyl)germananes Catalyzed by $Sc(OTf)_3$[a,b]



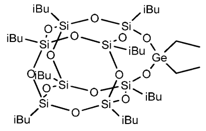
5[a] (92%)



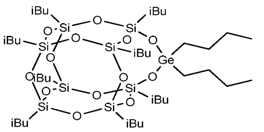
6[a] (84%)



7[b] (89%)

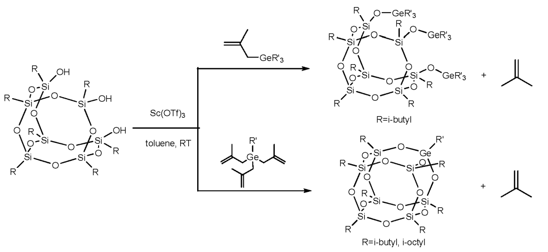


8[b] (97%)

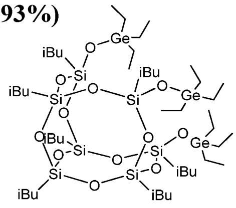


[a]Reaction conditions: toluene, rt, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, molar ratio of POSS/germanane = 1:4. [b]Reaction conditions: toluene, rt, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, molar ratio of POSS/germanane = 1:1.

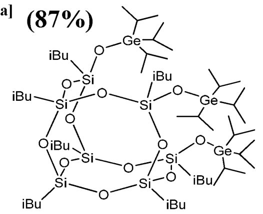
Table 3. Reactions of POSS Trisilanol with 2-Methylallylgermananes and Tris(2-methylallyl)germananes Catalyzed by $Sc(OTf)_3$[a,b]



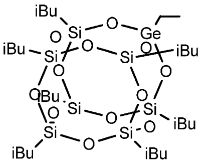
9[a] (93%)



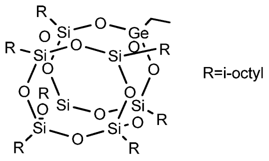
10[a] (87%)



11[b] (94%)



12[b] (89%)



[a]Reaction conditions: toluene, rt, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, molar ratio of POSS/germanane = 1:6. [b]Reaction conditions: toluene, rt, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, molar ratio of POSS/germanane = 1:1.

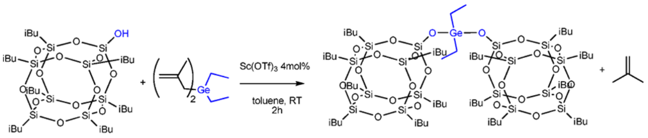
The important features of this procedure are high efficiency and selectivity, low catalyst loading required (2−4 mol %), mild reaction conditions, short time of reactions (1−2 h), and the simplicity of experimental techniques. The coupling reaction of POSS silanols and 2-methylallylgermananes proceeds with the evolution of no corrosive or reactive byproducts. The only byproduct formed in this reaction is a neutral and harmless olefin-isobutylene.

It is worth noting that another advantage of this procedure is the simplicity of separating the product from the catalyst as well as the excess of germylating reagent by adding acetonitrile after the reaction is completed. This particular solvent dissolves both the catalyst and the excess of 2-methylallylgermanane but does not dissolve POSS derivatives. The difference between the solubility of $Sc(OTf)_3$ and the silsesquioxanes in acetonitrile allows obtaining the product as a precipitate.

Herein, we also report the first and efficient catalytic method for capping the corner within incompletely condensed POSS molecules with a germanium atom. We performed the corner-capping reaction of POSS trisilanols with tris(2-methylallyl)-germananes (Table 3, entries 11 and 12), POSS disilanol with bis(2-methylallyl)germananes (Table 2, entries 7 and 8) and double-decker silsesquioxane with bis(2-methylallyl)-germananes (Scheme 2, entries 13 and 14). As a result, we successfully synthesized various fully condensed germasilsesquioxanes and digermasilsesquioxanes (Scheme 2). This approach to germanium-capped POSS derivatives seems to be an unprecedented catalytic method for the corner-capping reaction and introducing germanium atoms into the POSS skeleton.

Moreover, we performed the reaction of POSS monolsilanol with bis(2-methylallyl)germanane (Scheme 3). We successfully obtained Ge-functionalized bridged POSS compound consisting of two POSS molecules of nanometer size linked together by a organogermanium functionality (entry 15). The structure was confirmed by NMR spectroscopy, elemental analysis, and MS spectrometry.

Scheme 3. Synthesis of Ge-Functionalized Bridged POSS Derivative 15

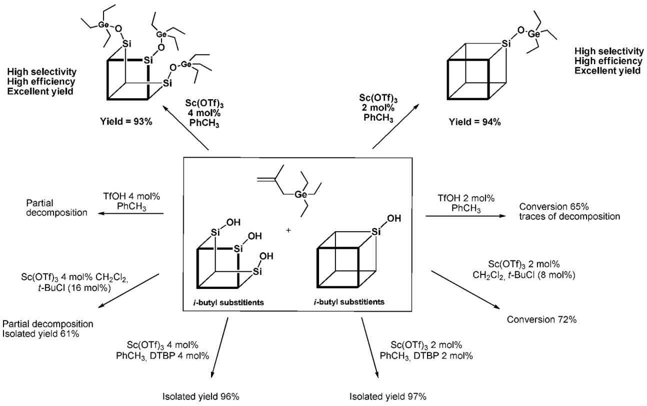


15 Yield = 96%

It has been reported that bridged silsesquioxanes can be applied as porous materials (e.g., gels with meso- and macropores) owing to their unique three-dimensional structure.[37] When using metal triflate as a catalyst, both the Lewis acid catalysis and the hidden Brønsted acid (TfOH) catalysis may be competitive because triflic acid can be generated *in situ* from triflates.[38−40] During the course of our study, we also examined the difference in activity of Lewis acid ($Sc(OTf)_3$) and Brønsted acid (TfOH) as catalysts in *O*-germylation of POSS silanols (Scheme 4). We decided to check which one is the active catalytic species in the coupling reactions between POSS silanols and 2-methylallylgermananes.

Our first experiment was to check the performance of the same loading of pure TfOH (2−4 mol %), instead of $Sc(OTf)_3$, as the catalyst in the *O*-gemylation of POSS monosilanol and partially condensed POSS trisilanol. Our experiments confirmed that TfOH can serve as the catalyst in this process but it leads to partial decomposition of incompletely condensed

Scheme 4. Difference in Activity of $Sc(OTf)_3$ and TfOH as Catalysts in *O*-Germylation of POSS Silanols



silsesquioxanes. Then, we examined the $Sc(OTf)_3$-catalyzed coupling reaction of POSS monosilanol and triethyl(2-methylallyl)germanane in CH_2Cl_2 with the addition of cocatalytic amounts of *tert*-butyl chloride (2 mol % $Sc(OTf)_3$ and 8 mol % *t*-BuCl) to generate the hidden Brønsted acid (TfOH) released from scandium(III) triflate in halogenated solvents. We discovered that the reaction of POSS trisilanol with 2-methylallylgermanane in CH_2Cl_2 in the presence of $Sc(OTf)_3$ and *t*-BuCl leads to partial decomposition of incompletely condensed silsesquioxanes. The decomposition of POSS compounds was observed in the NMR spectra which are presented in the Supplement Information. We also investigated this coupling reaction catalyzed by $Sc(OTf)_3$ with the Brønsted base 2,6-di-*tert*-butylpyridine (DTBP) (2 mol % $Sc(OTf)_3$ and 2 mol % DTBP in the case of POSS monosilanol and 4 mol % $Sc(OTf)_3$ and 4 mol % DTBP in the case of POSS trisilanol). DTBP was added in order to bind/coordinate the hidden Brønsted acid. In this experiment, we obtained products in similarly good yields which proves that the Lewis acid catalysis seems to be the favorable catalytic pathway. These experiments lead to the conclusion that our optimized reaction conditions (the use of $Sc(OTf)_3$ as a catalyst and toluene as a solvent) enable the highly selective and efficient *O*-germylation of POSS silanols, especially the incompletely condensed silsesquioxanes. Moreover, the main advantages of using $Sc(OTf)_3$ over pure TfOH are the simplicity of experimental techniques and the lack of POSS decomposition during the catalytic cycle.

As a result of our study, we obtained a series of completely and partially condensed POSS molecules substituted with organogermanium functional groups. We also synthesized the completely condensed germasilsesquioxanes containing germanium atoms in the POSS core. All newly obtained compounds were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis. These novel POSS derivatives can be of high relevance because multielement compounds turn out to be beneficial and useful in material science. Therefore, they may have significant potential for further applications.

In conclusion, we present the first catalytic method for the synthesis of germanium-functionalized silsesquioxanes. This convenient synthesis route allows us to obtain germasilsesquioxanes and Ge-containing completely and partially condensed POSS derivatives with excellent yields and high selectivity. Moreover, our procedure provides a highly effective method for capping the corner of incompletely condensed silsesquioxanes and introducing germanium atoms into the POSS skeleton. This methodology has many favorable features and advantages including mild reaction conditions, no corrosive byproducts, short reaction time, low catalyst loading, and high efficiency. We believe that it can be of great importance and practical use for the functionalization of silsesquioxanes. We also investigated the differences in the activity of the Lewis acid ($Sc(OTf)_3$) and the hidden Brønsted acid (TfOH) as catalysts in the *O*-germylation of silsesquioxanes. Our study proves that $Sc(OTf)_3$ is the active catalytic species in this reaction and does not cause the decomposition of POSS molecules. The novel multifunctional POSS derivatives reported in this paper can be suitable as valuable precursors of various functional materials with enhanced mechanical and thermal properties. They also have the great potential for the application in many areas of material chemistry, for instance as multielement building blocks in the synthesis of hybrid materials.

■ EXPERIMENTAL SECTION

Materials and Methods. The reagents and $Sc(OTf)_3$ used for experiments were purchased from Sigma-Aldrich Co. and ABCR GmbH & Co. KG. Various 2-methylallylgermananes were synthesized from chlorogermananes via the Grignard reaction. POSS compounds were obtained from Hybrid Plastics. (Isobutyl monosilanol POSS was synthesized according to the literature procedure.[41,42] The procedure for the synthesis of POSS monosilanol is shown in Supporting Information. The structures of products were determined by mass spectrometry and NMR spectroscopy. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{29}Si NMR (79 MHz) spectra were recorded on a Varian XL 300 spectrometer using C_6D_6 as the solvent.

Synthetic Procedures. *General Procedure for the Synthesis of Completely Condensed Monofunctionalized POSS Derivatives* ***1*–*4***. A mixture of 1 mmol of POSS monosilanol, 4 mmol of 2-methylallylgermanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Next, 0.02 mmol (2 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 1 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile which dissolved both the catalyst and the excess of 2-methylallylgermanane. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give corresponding compounds **1**–**4**.

General Procedure for the Synthesis of Incompletely Condensed Difunctional Silsesquioxane Derivatives ***5*** *and* ***6***. A mixture of 1 mmol of POSS disilanol, 4 mmol of 2-methylallylgermanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Then, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile which dissolved both the catalyst and the excess of 2-methylallylgermanane. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give corresponding compounds **5** and **6**.

General Procedure for the Synthesis of Completely Condensed Germasilsesquioxanes ***7*** *and* ***8***. A mixture of 1 mmol of POSS disilanol, 1 mmol of bis(2-methylallyl)germanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Then, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give corresponding compounds **7** and **8**.

General Procedure for the Synthesis of Incompletely Condensed Trifunctional Silsesquioxane Derivatives ***9*** *and* ***10***. A mixture of 1 mmol of POSS trisilanol, 6 mmol of 2-methylallylgermanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Then, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile which dissolved both the catalyst and the excess of 2-methylallylgermanane. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give corresponding compounds **9** and **10**.

*General Procedure for the Synthesis of Completely Condensed Germasilsesquioxanes **11** and **12**.* A mixture of 1 mmol of POSS trisilanol, 1 mmol of tris(2-methylallyl)germanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Then, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile. The product was obtained as a precipitate which was then filtered off or as oil which was separated from acetonitrile to give corresponding compounds **11** and **12**.

*General Procedure for the Synthesis of Digermasilsesquioxanes **13** and **14**.* To a 50 mL one-necked round-bottomed flask were added 1 mmol of POSS tetrasilanol (DDSQ), 2 mmol of bis(2-methylallyl)-germanane, and 6 mL of the mixture of CH_3CN/THF (ratio v/v = 1:1). Then, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile. The product was obtained as a precipitate which was then filtered off to give products **13** and **14**.

*General Procedure for Obtaining the Bridged Ge-Functionalized POSS Derivative **15**.* A mixture of 2 mmol of POSS monosilanol, 1 mmol of bis(2-methylallyl)germanane, and anhydrous toluene (2 mL) was placed in a 50 mL one-necked round-bottomed flask equipped with a magnetic stirring bar. Next, 0.04 mmol (4 mol %) of $Sc(OTf)_3$ was added, and the reaction mixture was stirred at room temperature for 2 h. After this, the solvent was evaporated under vacuum, and the product was separated from the catalyst by adding acetonitrile which dissolved the catalyst. The product was obtained as a precipitate which was then filtered off to give compound **15**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00599.

Details concerning experimental techniques and NMR spectra of isolated products (PDF)

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Notes

The authors declare no competing financial interest.

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