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Highly Efficient Catalytic Route for the Synthesis of Functionalized Silsesquioxanes

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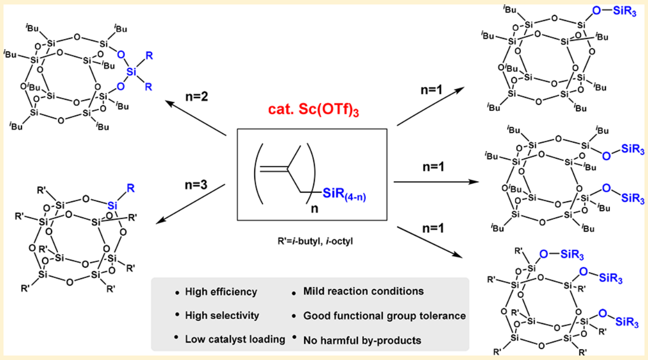
Supporting Information

ABSTRACT: Silsesquioxanes (POSS) have recently become the subject of growing interest in many branches of materials chemistry. Despite this great interest, no direct metal-catalyzed method to cap the corner of the POSS molecules has yet been proposed. In this report, we present a highly efficient method for the synthesis of functionalized silsesquioxanes mediated by scandium(III) triflate, which opens up the possibility of introducing a wide variety of functional groups into this class of organosilicon compounds under mild conditions with excellent yields. We also investigated the differences in the activity of the Lewis acid ($Sc(OTf)_3$) and the hidden Brønsted acid (TfOH) generated in situ from triflates as catalysts in the functionalization of silsesquioxanes. What is more, this solution provides an efficient corner-capping reaction and other functionalizations to obtain silsesquioxane derivatives which are often not possible to synthesize with good yields, efficiency, and chemoselectivity using conventional methods.



■ INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) as well as partially condensed silsesquioxanes have attracted much attention recently due to their versatile applications.[1] They possess unique features, e.g., well-defined nanosized structure,[1,2] hybrid properties,[3,4] high thermo- and photostability,[2] and excellent physical, electrical and optical properties.[1,5,6] Therefore, they might be used in different fields of materials chemistry: e.g., as engineering materials, elastomers, hybrid adhesives, coatings, optic materials, etc.[1,7−13] Last but not least, POSS molecules may have a great potential in the biomedical field owing to their inert nature, low cellular toxicity, biocompatibility, and biological stability.[6,14−17]

Conventional methods for the synthesis of silsesquioxanes and their functionalization are mainly based on the hydrolytic condensation of organotrichlorosilanes or organotrialkoxysilanes.[1,18,19] Unfortunately, these processes proceed with the evolution of highly reactive and volatile byproducts HX (HCl, HBr) and suffer from low functional group tolerance. Additionally, the use of moisture-sensitive halosilanes does not allow introduction of a wide variety of substituents with good chemoselectivity (e.g., hydroxy groups) because of the risk of self-condensation. Incompletely condensed silsesquioxanes with silanol groups (Si−OH) are a particularly interesting class of compounds. The synthesis of these compounds involves the kinetically controlled hydrolytic condensation of organotrichlorosilanes,[20] whereas POSS trisilanols can also be synthesized by removal of one silicon atom from the corner of a fully condensed cage in the presence of strong acid or base.[21]

Incompletely condensed silsesquioxanes are useful and easily accessible precursors of other derivatives. Therefore, in the course of studies on the functionalization of POSS, many chemists have focused their attention on this group of silsesquioxanes.[1] It is also worth mentioning here that silsesquioxanes containing, for example, Si−H or unsaturated bonds can further undergo catalytic transformations such as the hydrosilylation reaction,[1,22] arylation,[23] and a silylative coupling as well as cross-metathesis to obtain valuable derivatives.[24−30]

However, the use of organotrihalosilanes in the modification of incompletely condensed silsesquioxanes involves the necessity of removing corrosive byproducts. Furthermore, the lack of selectivity and low functional group tolerance limit the utility of this method. To the best of our knowledge, there is only one catalytic method for the modification of incompletely condensed silsesquioxanes that eliminates the formation of corrosive stoichiometric byproducts. The Shimada group has reported a pioneering work on the selective synthesis of hydro-substituted silsesquioxane by Au-catalyzed dehydrogenative cross-coupling reaction of a phenylsilane with a POSS containing silanol groups.[31] Nevertheless, this method is limited to just one example because the number of commercially available di- and trihydrosilanes is very small and it seems that this method does not allow "the corner capping reaction" of POSS trisilanol.

Recently, our research group developed a new catalytic route for the formation of Si−O−Si bonds in the coupling reaction of

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silanols with 2-methylallylsilanes catalyzed by scandium(III) trifluoromethanesulfonate.[32−35] Herein, we report a successful extension of this procedure to the functionalization of silsesquioxanes. Of particular importance, we describe an unprecedented catalytic method for the corner-capping reaction.

■ EXPERIMENTAL SECTION

The reagents and $Sc(OTf)_3$ used for experiments were purchased from Sigma-Aldrich Co. and ABCR GmbH & Co. KG. Various 2-methylallylsilanes were synthesized from chlorosilanes via the Grignard reaction. POSS compounds were obtained from Hybrid Plastics. (Isobutyl monosilanol POSS was synthesized according to the literature procedure.[36]) The structures of the products were determined by NMR spectroscopy. The ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and ^{29}Si NMR spectra (79 MHz) were recorded on a Varian XL 300 spectrometer using C_6D_6 as the solvent. The EIMS analysis was performed using a Bruker 320 MS/450 GC.

All details concerning the general procedure for the synthesis of POSS derivatives are presented in the Supporting Information.

■ RESULTS AND DISCUSSION

The aim of this work was to check the possibility of using 2-methylallylsilanes as silylating agents in the O-metalation of silsesquioxane molecules containing silanol groups, in the presence of $Sc(OTf)_3$ (Scheme 1). This turns out to be a selective and highly effective catalytic approach to the synthesis of various silsesquioxane derivatives.

The coupling reaction of POSS silanols with 2-methylallylsilanes proceeds under mild conditions at room temperature with the formation of isobutylene as the only byproduct, which is neutral and harmless. This procedure is useful and effective for the modification of a variety of silsesquioxanes containing one, two, and three as well as four Si−OH groups which successfully undergo selective O-silylation with 2-methylallylsilanes in the presence of $Sc(OTf)_3$. We optimized the reaction conditions for the synthesis of monofunctionalized siloxy-substituted silsesquioxanes from POSS monosilanol using 2 mol % of scandium(III) triflate and toluene as a solvent (Table 1). The conversion of reagents was determined by NMR spectroscopy. In particular, valuable information was given by ^{29}Si NMR spectroscopy (79 MHz, C_6D_6). The ^{29}Si spectrum of the reagent POSS monosilanol is presented in the Supporting Information. The chemical shift of the silicon atom in a silanol group within POSS monosilanol molecules is −101.15 ppm. However, when a POSS molecule is substituted with a siloxyl group, the signal from the silicon atom from the corner of a POSS cage appears as a peak ranging from −109 to −111 ppm, depending on the substituent. We did not observe the peaks from silicon atoms of silanol groups in the ^{29}Si spectra, which proves the full conversion.

Thereafter, we decided to extend this method to the functionalization of incompletely condensed silsesquioxanes: POSS disilanol and trisilanol and double-decker silsesquioxane (DDSQ) with four Si−OH groups (Tables 2−4). In all cases, a higher catalyst loading was required (4 mol %) to obtain the desired products. The O-silylation of DDSQ was performed in a CH_3CN/THF solvent mixture (v/v 1/1) because of the poor solubility of DDSQ in toluene and acetonitrile. The important feature of our procedure is the simplicity of separating the product from the catalyst as well as the excess of silylating reagent by adding acetonitrile after the reaction is completed. This particular solvent dissolves both the catalyst and the excess of 2-methylallylsilane 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. The conversion of reagents was also determined by NMR spectroscopy. We did not observe the peaks from silicon atoms of silanol groups in the ^{29}Si spectra. The ^{29}Si spectra of POSS silanols used for the synthesis are also shown in the Supporting Information.

Scheme 1. $Sc(OTf)_3$-Catalyzed O-Silylation of POSS Silanols by 2-Methylallylsilanes

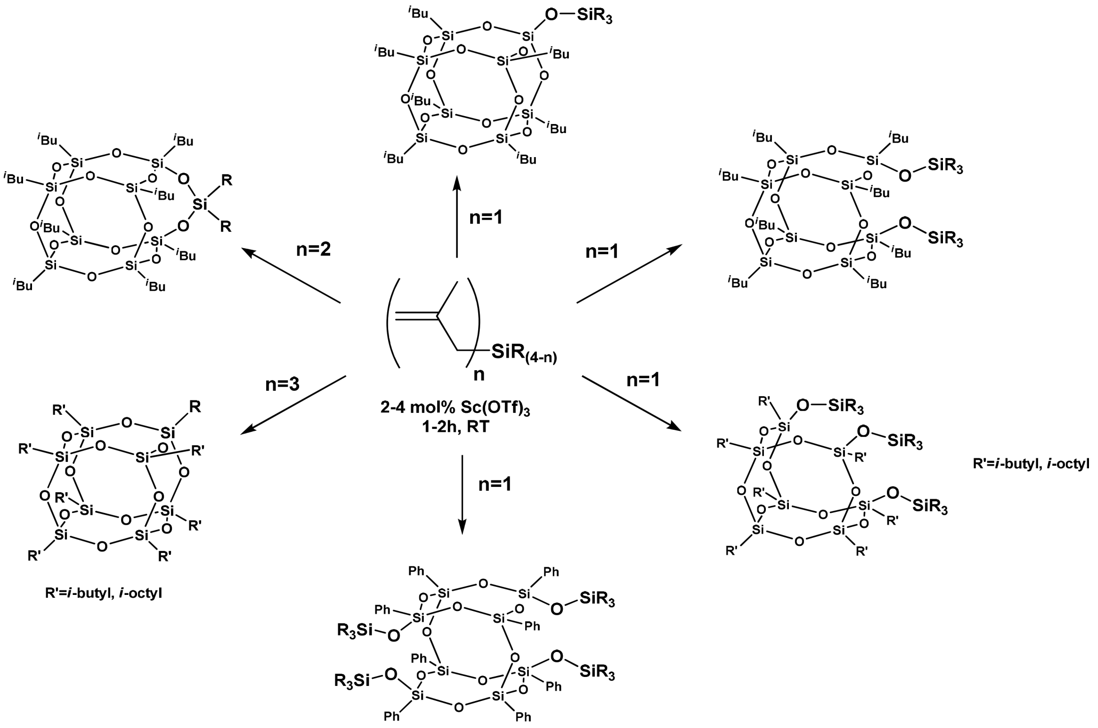
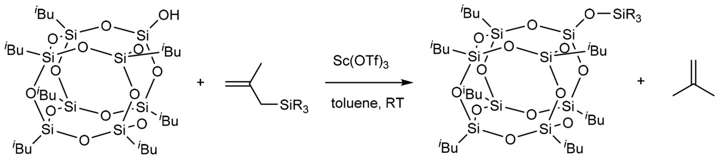


Table 1. Reactions of POSS Monosilanol with 2-Methylallylsilanes Catalyzed by $Sc(OTf)_3$[a]



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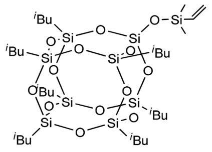

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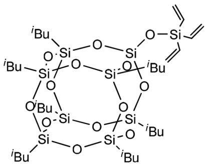

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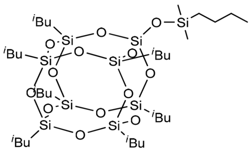

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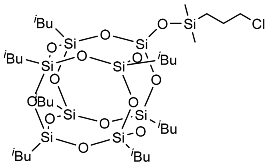

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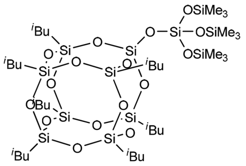

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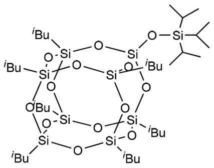

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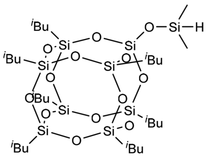

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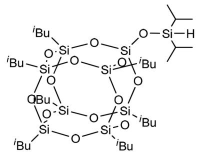

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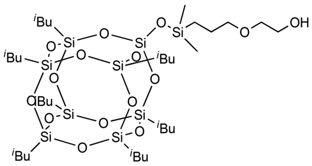
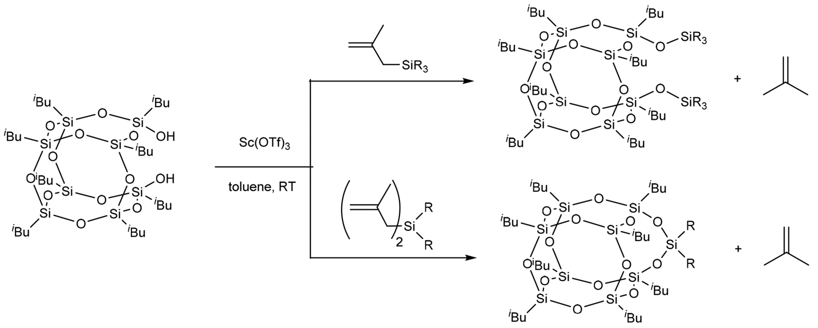


[a]Reaction conditions: toluene, room temperature, 1 h, $Sc(OTf)_3$, catalyst loading 2 mol %, POSS:silane molar ratio 1:4.

Table 2. Reactions of POSS Disilanol with 2-Methylallylsilanes and Bis(2-methylallyl)silanes Catalyzed by $Sc(OTf)_3$[a]



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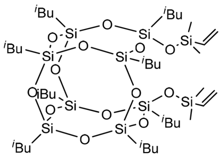

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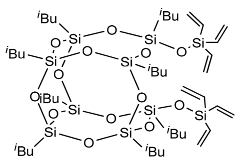

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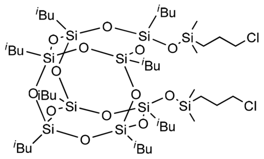

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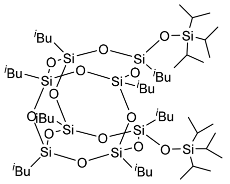
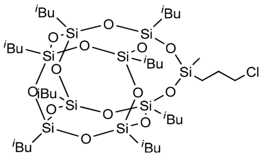


14[b] (87%)



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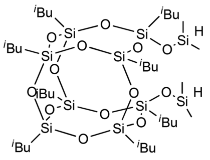
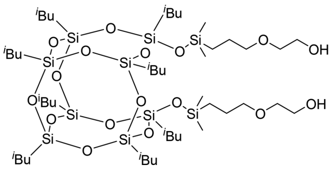
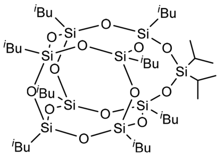


16 (78%)



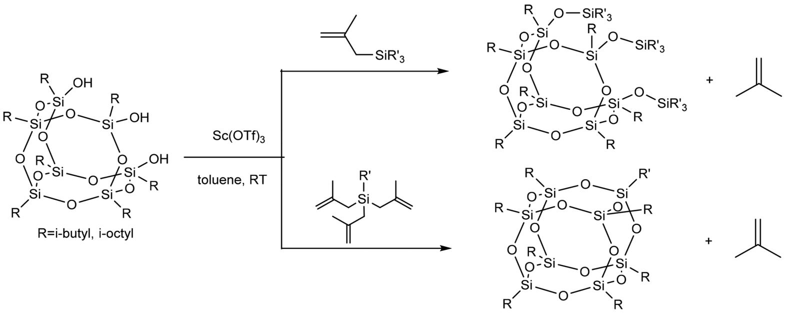
17[b] (92%)



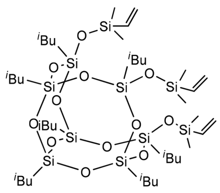
[a]Reaction conditions: toluene, room temperature, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, POSS:silane molar ratio 1:4. [b]The reaction proceeded with a equimolar ratio of POSS to silane (the POSS:silane molar ratio for compounds **14** and **17** is 1:1).

As a result, we synthesized a series of functionalized siloxy-substituted silsesquioxanes. The use of 2-methylallylsilane with a substituent containing an OH group enabled the synthesis of POSS derivatives containing a hydroxyl functionality in the side chain, which was a challenging matter (compounds **9** and **16**). It is not possible to achieve with good yields using chlorosilanes due to the self-condensation of substrates and the lack of selectivity. We also used our methodology to perform the first catalytic attempt to cap the corners of POSS disilanol (Table 2, compounds **14** and **17**)

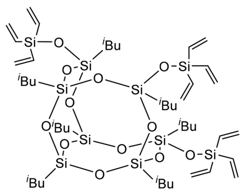
Table 3. Reactions of POSS Trisilanol with 2-Methylallylsilanes and Tris(2-methylallyl)silanes Catalyzed by $Sc(OTf)_3$[a]



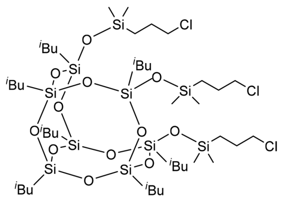
18 (94%)



19 (96%)



20 (82%)



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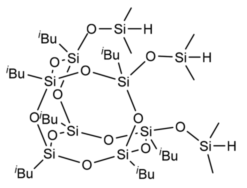
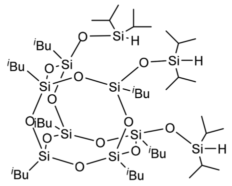
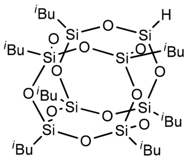


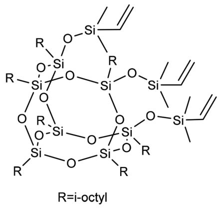
22 (91%)



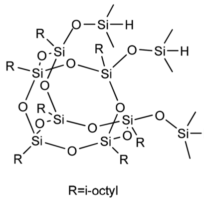
23[b] (93%)



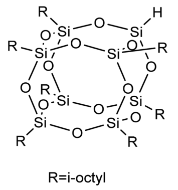
24 (94%)



25 (98%)

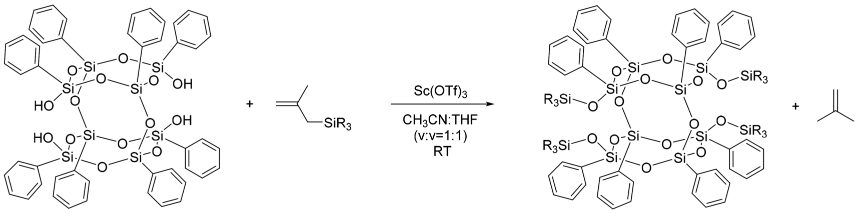


26[b] (91%)



[a] Reaction conditions: toluene, room temperature, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, POSS:silane molar ratio 1:6. [b] The reaction proceeded with an equimolar ratio of POSS to silane (the POSS:silane molar ratio for compounds **23** and **26** is 1:1).

Table 4. Reactions of POSS Tetrasilanol (Double-Decker Silsesquioxane) with 2-Methylallylsilanes Catalyzed by $Sc(OTf)_3$[a]



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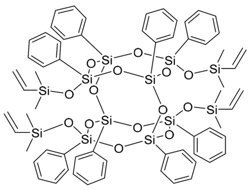

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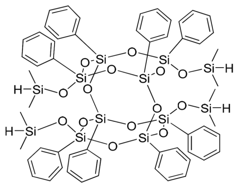
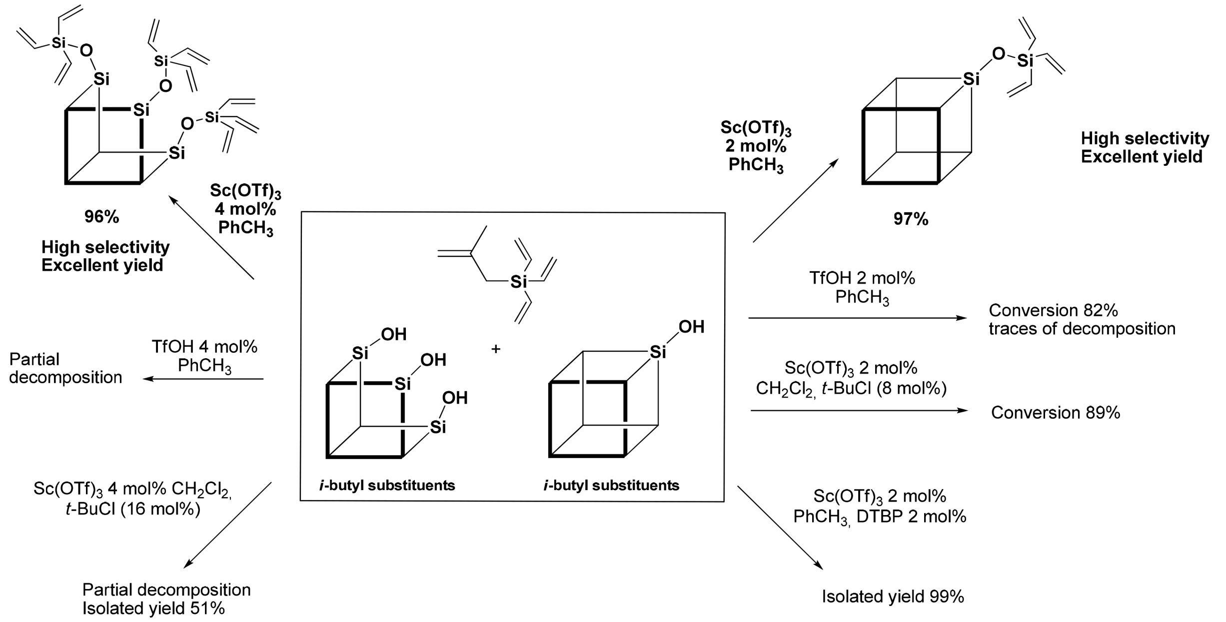


[a] Reaction conditions: CH_3CN/THF (v/v 1/1), room temperature, 2 h, $Sc(OTf)_3$, catalyst loading 4 mol %, POSS:silane molar ratio 1:6.

and trisilanol (Table 3, compounds **23** and **26**) in order to obtain fully condensed silsesquioxanes.

It is known that a metal triflate can serve as a source of triflic acid (TfOH), which may be generated in situ from triflates.[37,38] When using metal triflate as a catalyst, both the Lewis acid catalysis and the hidden Brønsted acid catalysis may be competitive. Therefore, we performed a series of experiments to check the difference in activity of a Lewis acid ($Sc(OTf)_3$) and a Brønsted acid (TfOH) in order to find out which one is the true active catalytic species in the coupling reactions between POSS silanols and 2-methylallylsilane (Scheme 2). We chose 2-methylallylsilanes containing vinyl groups as reagents, which are easily detected using NMR spectroscopy. First, we investigated the same loading of pure TfOH, instead of $Sc(OTf)_3$, as the catalyst in the O-silylation of POSS silanols. Our experiments confirmed that TfOH can serve as the catalyst in this process, but it is less effective than scandium(III) triflate, and we did not obtain the full conversion of POSS silanols. In the case of the O-silylation of a

Scheme 2. Differences in the O-Silylation of Silsesquioxanes Catalyzed by a Lewis Acid ($Sc(OTf)_3$) and a Brønsted Acid (TfOH)



POSS trisilanol catalyzed by TfOH, we observed that a catalytic amount of triflic acid leads to partial decomposition of incompletely condensed silsesquioxanes. It has been reported that TfOH may catalyze the cleavage of siloxane bonds under cationic conditions, for instance in the process known as ring-opening polymerization.[39] Next, we performed the $Sc(OTf)_3$-catalyzed coupling reaction of a POSS monosilanol and trivinyl (2-methylallyl)silane in CH_2Cl_2 with the addition of cocatalytic amounts of *tert*-butyl chloride (2 mol % of $Sc(OTf)_3$ and 8 mol % of *t*-BuCl) to generate the hidden Brønsted acid (TfOH) released from scandium(III) triflate under these conditions in halogenated solvents.[40] As a result, we obtained a product with yield similar to that of the reaction carried out in toluene using the Lewis acid $Sc(OTf)_3$. However, we discovered that the reaction of POSS trisilanol with trivinyl(2-methylallyl)silane in CH_2Cl_2 in the presence of $Sc(OTf)_3$ and *t*-BuCl led to partial decomposition of incompletely condensed silsesquioxane. We also investigated this coupling reaction catalyzed by scandium(III) triflate with the addition of the Brønsted base 2,6-di-*tert*-butylpyridine (DTBP) (2 mol % of $Sc(OTf)_3$ and 2 mol % of DTBP), and in this experiment, we obtained the product in excellent yield (99%). The addition of a Brønsted base does not affect the efficiency of this reaction, which proves that Lewis acid catalysis seems to be the favorable catalytic pathway. This leads to the conclusion that a selective and efficient method for the modification especially of incompletely condensed silsesquioxanes in toluene in the presence of $Sc(OTf)_3$ is catalyzed by the Lewis acid. Moreover, the main advantages of using $Sc(OTf)_3$ over pure triflic acid is the simplicity of experimental techniques, as well as the lack of POSS decomposition during the catalytic cycle.

In conclusion, we present a new synthetic pathway for the synthesis and functionalization of polyhedral oligomeric silsesquioxanes via $Sc(OTf)_3$-catalyzed O-silylation of Si–OH groups in silsesquioxane molecules with 2-methylallylsilanes. From a synthetic point of view, this methodology has many favorable features and advantages over other methods (e.g., needs mild conditions, has a short reaction time (1–2 h), needs a relatively low catalyst loading (2–4 mol %), gives no corrosive byproducts, and has high efficiency, excellent yields, and good functional group tolerance) and can be of great importance and practical use. Other advantages include the simplicity of the experimental techniques and the ease of separating the product from the catalyst. It should be pointed out that our method is the first metal-catalyzed method for the corner-capping reaction. We also investigated the differences in the activity of a Lewis acid ($Sc(OTf)_3$) and a hidden Brønsted acid (TfOH) as catalysts in the O-silylation of silsesquioxanes. Our study proves that the use of scandium(III) triflate as a catalyst and toluene as a solvent are the optimized reaction conditions in which TfOH is not generated and does not cause the decomposition of POSS molecules. Under these conditions, the Lewis acid is the active catalytic species not affecting the POSS structure. Moreover, the synthesized silsesquioxanes containing reactive substituents (e.g., Si–H bonds or vinyl groups) are ideal substrates for further catalytic modifications and may undergo functionalization via hydrosilylation, silylative coupling, or cross-metathesis reactions. We believe that this procedure represents an important catalytic solution and a significant improvement of existing methods and that it will find extensive use in the synthesis of valuable precursors of versatile materials with desirable optical, thermal, and mechanical properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01504.

NMR data and spectra of compounds synthesized in this paper (PDF)

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Notes

The authors declare no competing financial interest.

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