

## Research paper

# O-Metalation of silanols and POSS silanols over Amberlyst-15 catalyst: A facile route to unsymmetrical siloxanes, borasiloxanes and gemasiloxanes



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## ABSTRACT

A simple and highly practical Amberlyst-catalyzed direct *O*-metalation of silanols, POSS silanols and alkoxysilanes under mild conditions is proposed. This protocol can be applied to the synthesis of a wide range of important organosilicon derivatives such as siloxanes, gemasiloxanes, borasiloxanes and functionalized silsesquioxanes. It is worth noting that Amberlyst-15 can be reused for further experiments and its catalytic activity in this process is well-preserved for several recycling steps.

## 1. Introduction

In broad terms, organosilicon compounds play a vital role in inorganic, organic and material chemistry [1]. Some of the most important derivatives are those containing Si-O-E moiety (where E = Si, Ge and B) [2]. Therefore, investigation of this moiety formation has attracted great attention of the chemical community (especially when E = Si) (see Fig. 1). The stoichiometric reactions reported to date often suffer from the formation of large amounts of wastes and poor selectivity [3]. On the other hand, several catalytic approaches have recently been developed [4–6]. Unfortunately, many of them require expensive catalysts and harsh conditions. In the course of our recent studies on the formation of Si-O-E moieties, we noticed that silanols can be mildly transformed via *O*-metalation pathway using 2-methylallyl reagents in the presence of catalytic amounts of metal triflate [7]. In continuation of our interest in the synthesis of siloxyl bonds, we have recently focused on the use of heterogeneous systems. We have already shown that the use of Nafion resin allows obtaining a library of organosilicon derivatives [8]. The aim of this work was to check the possibility of replacing Nafion, by a more accessible and inexpensive heterogeneous catalyst.

In this paper, we present a highly chemoselective and efficient method for the *O*-metalation of silanols and POSS silanols mediated by Amberlyst-15. As a result, numerous compounds such as di-, tri- and tetrasiloxanes, gemasiloxanes, borasiloxanes and functionalized silsesquioxanes (SQs) have been efficiently synthesized in good yields. What is more, this method is also applicable to more stable alkoxysilanes, which undergo one-pot hydrolysis, followed by *O*-silylation of

in-situ formed silanols. All of the above-mentioned processes can be considered as an important extension of earlier reports on the effectiveness of allylsilanes in the silylation reaction [7–9].

## 2. Materials and methods

Reagents used for experiments were purchased from Sigma-Aldrich Co. 2-Methylallyl reagents were synthesized in accordance to known procedures based on the reactions with Grignard reagents [10]. Silanols, as well as POSS monosilanol used for the preparation of compounds 7 and 9–19 were obtained via known procedures [11]. AMBERLYST-15DRY was purchased from Sigma-Aldrich Co (in accordance with specification, the concentration of acid sites is more than 5.0 eq/kg). All reactions were carried out under air atmosphere. The structure of products was determined by NMR spectroscopy. The <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (101 MHz), <sup>29</sup>Si NMR (79 MHz) spectra were recorded on a Bruker Avance III HD NanoBay spectrometer, using CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> as solvents. Mass spectra of most products were determined by GC-MS analysis on a Varian Saturn 2100 T, equipped with a BD-5 capillary column (30 m) and Finnigan Mat 800 ion trap detector.

## 2.1. General procedure for the synthesis of compounds 1–15

To a 25 mL one-necked flask equipped with a stirring bar, Amberlyst-15, silanol (germanol), disilanol or silanediol, 2-methylallyl reagent and 0.5 mL of acetonitrile (or dichloromethane in case of product 4) were added under air atmosphere. Molar ratio of appropriate substrates as well as the amount of the catalyst were different in several

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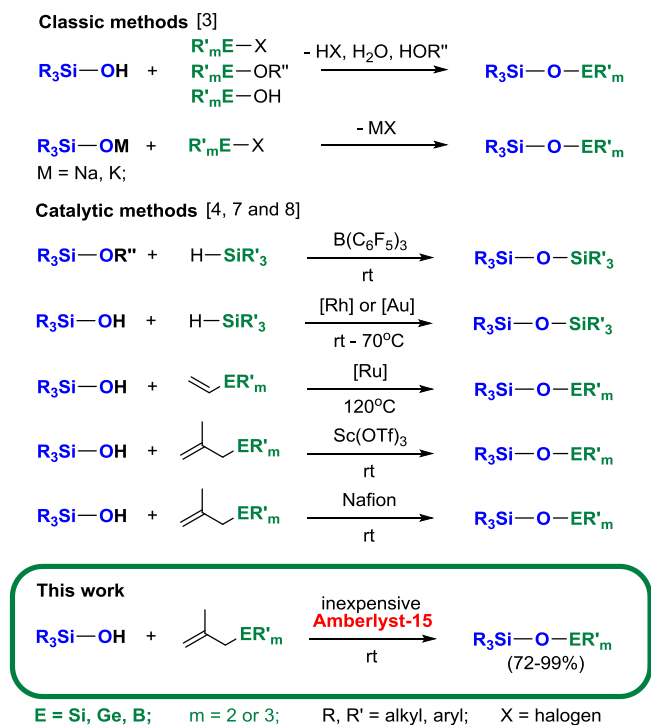


Fig. 1. The formation of Si-O-E moieties.

samples and are specified in Table 2. Subsequently, the reaction mixture was stirred at rt for a definite time (Table 2). After this time, the product was separated from the catalyst by simple filtration using Pasteur pipette equipped with cotton wool and then the solvent and all volatiles were evaporated under reduced pressure to give the corresponding compounds 1–15. To our knowledge, all compounds are known in literature, except for compounds 8 and 9.

## 2.2. General procedure for the synthesis of functionalized silsesquioxanes 16–19

To a 25 mL one-necked flask equipped with a stirring bar, 0.015 g of Amberlyst, POSS silanol (1 equiv., 0.06 mmol), 2-methylallyl reagent (3.0 equiv., 0.018 mmol) and 1 mL of toluene were added under air atmosphere. Subsequently, the reaction mixture was stirred at rt for 20 h. After this time, the product was separated from the catalyst by simple filtration using Pasteur pipette equipped with cotton wool and then the solvent and all volatiles were evaporated under reduced pressure. After that, the product was separated from the remaining substrate by adding acetonitrile to dissolve the excess of the 2-

methylallyl reagent (silsesquioxanes are not soluble in acetonitrile), which was followed by final evaporation under reduced pressure to give the corresponding compounds 16–19. All compounds are known in literature [8].

## 2.3. General procedure for the synthesis of compounds 20–21

To a 25 mL one-necked flask equipped with a stirring bar, 0.015 g of Amberlyst, alkoxy silane (2.0 equiv., 0.036 mmol), 2-methylallyl reagent (1.0 equiv., 0.018 mmol), H<sub>2</sub>O (1.0 equiv., 0.018 mmol) and 0.5 mL of acetonitrile were added under air atmosphere. Subsequently, the reaction mixture was stirred at rt for 1 h. After this time, the product was separated from the catalyst by simple filtration using Pasteur pipette equipped with cotton wool and then the solvent and all volatiles were evaporated under reduced pressure to give the corresponding compounds 20–21.

## 2.4. Gram-scale synthesis of 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane

To a 100 mL one-neck round-bottom flask diphenylsilanediol (2.0 g, 9.2 mmol, 1.0 equiv), 2-methylallyltrimethylsilane (3.54 g, 27.6 mmol, 3.0 equiv), Amberlyst-15 (0.76 g), and acetonitrile (30 mL) were added under an air atmosphere, and the flask was closed with a stopper. Subsequently, the reaction mixture was stirred at rt for 0.5 h. After this time, the product was separated from the catalyst by simple filtration using glass column equipped with cotton wool and then the solvent and all volatiles were evaporated under reduced pressure to give 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane (11) in 91% (3.03 g).

## 3. Results and discussion

Encouraged by our previous works, we decided to examine the commercially available and stable Amberlyst-15 catalyst (A-cat). This inexpensive ion exchange resin based on polystyrene has strongly acidic sulfonic groups. Because of this, A-cat plays an important role as a reusable catalyst in organic chemistry [12]. To explore the generality and scope of this catalytic system, we initially performed the O-silylation of trimethylsilanol with 2-methylallyltrimethylsilane in different organic solvents and in the presence of various amounts of the catalyst (see Table 1). When the reaction was carried out in the absence of solvent, the corresponding unsymmetrical disiloxane was obtained in 35% yield after 1 h (Table 1, entry 1). The best results were observed in acetonitrile (ACN) and dichloromethane (Table 1, entries 3 and 5). Because of that both solvents were used in further experiments (CH<sub>2</sub>Cl<sub>2</sub> was used in the synthesis of product 3, which is very volatile; see Table 2).

The decision about using such a simple silanol stemmed from the

Table 1

Comparison of a catalytic activity of Amberlyst-15 in O-silylation under different conditions.<sup>a</sup>

Entry	Solvent	Catalyst amount [g]	Time [h]	Conversion [%] <sup>b</sup>
1	–	0.015	1	35
2	Acetonitrile	0.030	0.5	99
3	Acetonitrile	0.015	1	99
4	Acetonitrile	0.0075	1	45
5	Dichloromethane	0.015	1	99
6	Toluene	0.015	1	40
7	Tetrahydrofuran	0.015	1	10
8	Hexane	0.015	1	70

<sup>a</sup> rt, air atmosphere, 0.5 mL of solvent, 0.025 g (0.278 mmol) of trimethylsilanol, 0.065 g (0.187 mmol) of 2-methylallyltrimethylsilane.

<sup>b</sup> Determined by GC chromatography.

**Table 2**  
Substrate scope of the O-metalation of silanols and germanols.<sup>a</sup>

$[E^1]-OH + \text{CH}_2=C(\text{CH}_3)\text{CH}_2-[E^2] \xrightarrow[\text{rt, air}]{\text{Amberlyst}} [E^1]-O-\text{CH}_2-C(\text{CH}_3)=\text{CH}-[E^2]$

$E^1 = \text{Si, Ge};$   
 $E^2 = \text{Si, Ge, B};$

Entry	Molar ratio <sup>b</sup>	Time (h)	Product <sup>c</sup>
1	1.5:1.0	1	<b>1</b> (93%)
2	1.5:1.0	0.5	<b>2</b> (83%)
3 <sup>d</sup>	1.0:1.2	0.5	<b>3</b> (95%)
4	2.1:1.0	0.5	<b>4</b> (92%)
5	1.0:1.2	0.25	<b>5</b> (93%)
6	1.0:1.2	0.25	<b>6</b> (84%)
7	1.0:1.5	0.5	<b>7</b> (90%)
8	1.0:1.5	1	<b>8</b> (72%)
9	1.0:1.2	0.5	<b>9</b> (91%)
10	1.0:1.2	0.5	<b>10</b> (83%)
11	1.0:3.0	0.5	<b>11</b> (89%)
12	1.0:2.4	0.5	<b>12</b> (87%)
13	1.0:3.0	0.5	<b>13</b> (87%)
14	1.0:3.0	1.5	<b>14</b> (88%)
15	1.0:3.0	1.5	<b>15</b> (85%)

<sup>a</sup> rt, air atmosphere, 0.5 mL of acetonitrile, 0.015 g of A-cat (entries 1–10) or 0.030 g of A-cat (entries 11–15).

<sup>b</sup> [Silanol]:[2-Methylallyl reagent].

<sup>c</sup> Isolated yields.

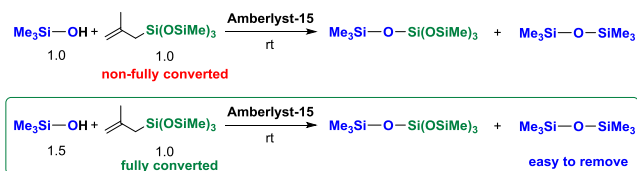
<sup>d</sup> 0.5 mL of dichloromethane.

fact that non-sterically hindered molecules can undergo homocondensation in the presence of an acid. We wanted to check the chemoselectivity of this process. We expected to observe the symmetrical hexamethyldisiloxane and it came true. Equimolar amounts of both reagents (trimethylsilanol:2-methylallyltris(trimethylsiloxy)silane – 1:1) led to a mixture of two products – symmetrical and unsymmetrical disiloxanes (in ratio 1:8). Because of that, we decided to use an excess of trimethylsilanol (1.5 eq.) to achieve full conversion of 2-methylallyl reagent. Fortunately, the formation of hexamethyldisiloxane is

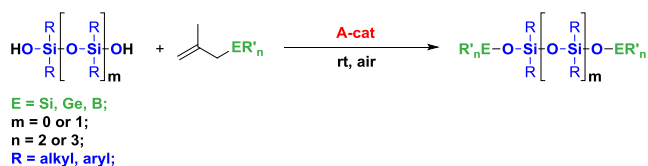
completely unrestricted aspect due to the fact that the formed symmetrical disiloxane is highly volatile and can be easily removed from the system (Fig. 2).

With the optimized conditions in hand (0.015 g of A-cat per 0.18 mmol of the substrate, acetonitrile as the solvent), the reactivity of a large number of silanols and 2-methylallyl reagents was explored (Table 2).

Overall, the reaction afforded the corresponding siloxanes, germa-siloxanes and borasiloxanes (Table 2, entries 1–10) in good to excellent



**Fig. 2.** The reaction between trimethylsilanol and 2-methylallyltris(trimethylsiloxy)silane under different conditions.



**Scheme 1.** The *O*-metalation of disilanols or silanediols with various 2-methylallyl reagents.

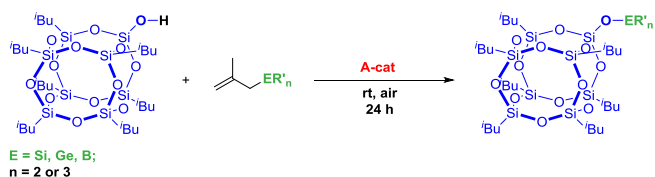
yields (up to 95%). In most cases, a slight excess of 2-methylallyl reagent was used to obtain unsymmetrical disiloxanes as a single product. The amount of A-cat was equal to 0.015 g per 0.18 mmol of the substrate. Increasing the steric hindrance of silanol molecule, with the exception of dimethylphenylsilanol, allowed delivering only the unsymmetrical siloxanes. Dimethylphenylsilanol is highly prone to undergo homocondensation under acidic conditions, and that is why the formation of both siloxanes (unsymmetrical and symmetrical) was observed (in ratio 30:70). At the next stage, silanediols and disilanols were also checked (Scheme 1).

To our delight, the series of tri- and tetrasiloxanes could also be achieved in the presence of 0.030 g of A-cat, which furnished the corresponding products in very good yields (Table 2, entries 11–15). Notably, the reactions between 1,1,3,3-tetraisopropyl-1,3-dihydroxydisiloxane with 2-methylallyl reagents (Table 2, entries 14 and 15) were slightly longer (1.5 h).

To further highlight the potential advantages of this methodology, the POSS silanol was also used in the *O*-metalation (Scheme 2). It is worth noting, that novel methods of POSS synthesis and functionalization, as well as their use in material chemistry are a key part of current studies in the field of organosilicon chemistry [13].

In general, the POSS monosilanol underwent the *O*-metalation with several 2-methylallyl reagents in the presence of Amberlyst-15 and afforded the functionalized silsesquioxanes (Table 3, all entries) in excellent yields (up to 99%). In contrast to the reaction of simple silanols, the POSS silanols required a longer reaction time (24 h) and higher amount of the catalyst (0.015 g of A-cat per 0.06 mmol of POSS molecule). The SQs are insoluble in acetonitrile, therefore toluene was used as solvent. The insolubility of SQs in acetonitrile is very useful, because it allows easy separation of the final product (the excess of 2-methylallyl reagent is soluble in ACN).

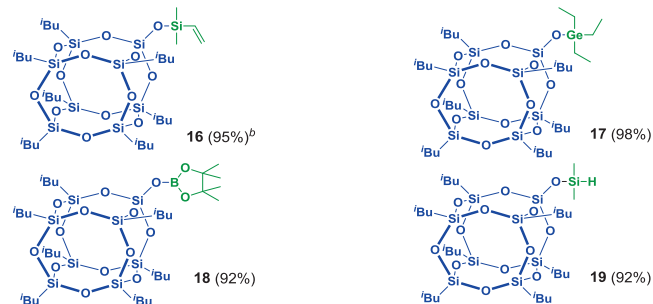
The synthetic merit of this protocol was illustrated by using stable alkoxy silanes instead of silanols. The silyl ethers can undergo one-pot hydrolysis, followed by *O*-silylation of in-situ formed silanols (Scheme 3). This methodology might be considered as a useful alternative to *O*-silylation of silanols, especially in the case of less stable reagents.



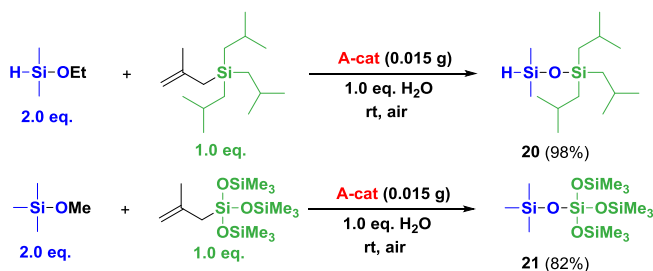
**Scheme 2.** The *O*-metalation of POSS-monosilanol with various 2-methylallyl reagents.

**Table 3**

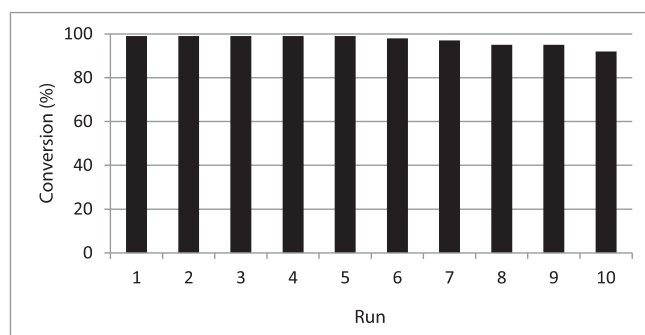
The *O*-metalation of POSS-monosilanol with various 2-methylallyl reagents.<sup>a</sup>



<sup>a</sup> rt, air atmosphere, 1 mL of toluene, 0.015 g of A-cat per 0.06 mmol of POSS molecule; Molar ratio [POSS]:[2-Methylallyl reagent] = 1.0:3.0. <sup>b</sup> Isolated yields.



**Scheme 3.** The *O*-silylation of alkoxy silanes.



**Fig. 3.** Recycling of Amberlyst-15 in *O*-silylation of diphenylsilanediol.

Last but not least, the reusability of Amberlyst-15 was also examined (Fig. 3). For the recycling tests, 0.030 g were used under the same reaction conditions (0.18 mmol, 0.039 g of diphenylsilanediol and 0.54 mmol, 0.069 g of (2-methylallyl)-trimethylsilane; in 0.5 mL of acetonitrile; rt and air atmosphere). The recovered A-cat was successfully reused without a significant loss of performance over 10 cycles (92–99%; conversion determined by GC chromatography; decane as an internal standard).

Finally, the reaction of diphenylsilanediol with 2-methylallyl-trimethylsilane also proceeds well on a gram scale, providing 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane in 91% yield (see the Material and Methods Section).

On the basis of our results and the known literature, a plausible mechanism was proposed (Fig. 4). *O*-silylation of silanols with various 2-methylallyl reagents can be explained as simple Brønsted acid catalysis. It assumes the activation of 2-methylallyl reagent in acidic conditions. This process is followed by the nucleophilic attack of silanol to form an intermediate, which undergoes a rapid conversion to the corresponding unsymmetrical siloxane and isobutene.

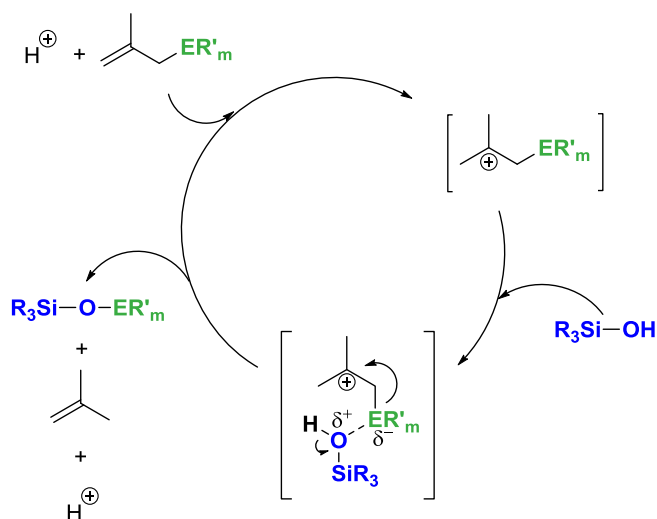


Fig. 4. The mechanism of O-silylation in the presence of Amberlyst-15 catalyst.

#### 4. Conclusions

In summary, an efficient approach to synthesize di-, tri- and tetrasiloxanes, germsiloxanes, borasiloxanes and functionalized silsesquioxanes has been proposed. We have shown that inexpensive and readily available Amberlyst-15 can be used as a highly active catalyst in the O-metalation of various silanols under metal-free conditions. What is more, our investigations revealed that alkoxy silanes can also be used as substrates, which undergo one-pot hydrolysis, followed by O-silylation of in-situ formed silanols. The favorable features of this solution are: mild conditions (rt, air atmosphere), inexpensive and reusable catalyst, very good isolated yields (72–99%), high chemoselectivity, satisfactory atom economy (isobutene as the only one by-product), and short reaction time, as well as the simplicity of the experimental techniques. Further extensions of the presented solution and related applications are currently under study.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jca.2019.03.025>.

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