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Additional Information

## Synthesis of Borasiloxanes by Oxidative Hydrolysis of Silanes and Pinacolborane using $\text{Cu}_3(\text{BTC})_2$ as Solid Catalyst

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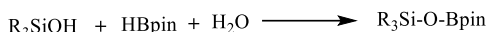
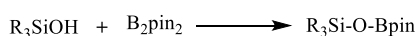
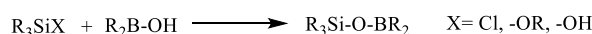
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**A convenient method for the synthesis of borasiloxanes from silanes and pinacolboranes using  $\text{Cu}_3(\text{BTC})_2$  as heterogeneous catalyst in acetonitrile at 70 °C is reported. The procedure is more convenient than others based on the use of Ru and Pd homogeneous catalysts, since in addition to avoiding noble metals the starting materials are easy to handle and the catalyst can be recovered from the reaction mixture and reused.**

Borasiloxanes are attracting increasing attention due to the unique properties of derived polymers, including heat resistance and notable chemical stability.<sup>1-3</sup> In addition, borasiloxanes are also intermediates in organic synthesis and they have application as electrolytes and in material chemistry.<sup>4</sup> This type of compounds can be prepared by reaction of boranols with chloro,<sup>5-8</sup> alkoxy silanes<sup>9</sup> or silanols<sup>10, 11</sup> (Scheme 1). Alternatively, borasiloxanes can also be prepared by reaction between silanols with borane derivatives<sup>12-16</sup> (Scheme 1). However, the above mentioned conventional methods suffer from some drawbacks, such as the use of moisture-sensitive starting materials, high reaction temperature, low to moderate selectivity to the wanted products and formation of undesired byproducts such as HCl, water and disiloxanes. Hence, there is still room for the development of clean and selective syntheses of borasiloxanes using readily available starting materials. In this regard, a more convenient approach is the catalytic three component reaction of silanes, boranes and water, whereby hydrogen is, in principle, the only by-product formed and the substrates are stable under ambient conditions in the absence of catalyst.

Marciniec and co-workers have reported the versatility of Ru complexes to produce borasiloxanes by the reaction between silanols with vinylboronates in high yields,<sup>17</sup> but in this

case silanols can form easily disiloxanes and the vinyl moiety of the boronated reagent is not incorporated in the final product. In another method, the synthesis of  $\text{Me}_3\text{SiOBpin}$  by the reaction of  $\text{Me}_3\text{SiOH}$  and  $\text{B}_2\text{pin}_2$  in the presence of  $[\text{Ir}(\text{OMe})(\text{cod})]_2$  (cod = 1,5-cyclooctadiene) as catalyst was reported.<sup>18</sup> Alternatively, preparation of borasiloxanes was also carried out by using palladium acetate as catalyst for the dehydrogenative O-borylation of a variety of silanols with easily available diborons.<sup>19</sup> Later, preparation of poly(borasiloxane) was promoted by polycondensation of  $\text{Ph}_2\text{Si}(\text{OH})_2$  with  $\text{ArBH}_2$  (Ar = mesityl) in the presence of rhodium or palladium catalysts at room temperature,<sup>3</sup> but again silanediols are highly reactive and prone to undergo self-condensation to polysiloxanes. On the other hand, the reaction of hydrosilanes with bisboryloxide/boroxine led to the selective formation of borasiloxanes in the presence of Mo, W and Fe complexes.<sup>20</sup> More related to the present study, it has been recently reported an alternative protocol for the synthesis of borasiloxanes using Ru-catalysed reaction of hydroboranes (or boronic acids) with silanes and water at 125 °C in toluene.<sup>21</sup>



Scheme 1. Methods for the synthesis of borasiloxanes.

For the sake of sustainability and affordability, it would be important to develop other catalysts for this process, based on abundant metals and also to develop heterogeneous catalyst that can simplify the work-up of the reaction mixture and eventually even allow them to be reused. In this context, metal organic frameworks (MOFs) have shown a wide range of applicability as solid catalysts in liquid phase reactions under conditions compatible with their structure.<sup>22, 23</sup> Among the various advantages of MOFs as solid catalysts, those that have been shown to be more important are their large surface area, accessibility to the active sites and their versatility in the synthesis and design of these materials, allowing the selection of these components that are suitable as active sites.

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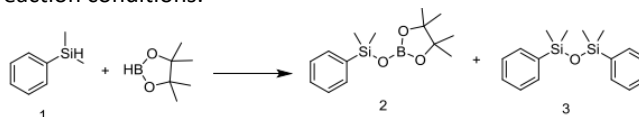
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Among the MOFs that have shown high catalytic activity in a large variety of reactions, one that has been frequently studied for a wide range of reactions is  $\text{Cu}_3(\text{BTC})_2$  (BTC: 1,3,5-benzenetricarboxylate).<sup>24–28</sup> This MOF is constituted by dimeric  $\text{Cu}_2$  units with paddle wheel shape forming the nodes coordinated to the carboxylic groups of BTC. The structure of  $\text{Cu}_3(\text{BTC})_2$  defines large cages of 11, 16 and 6 Å diameter.<sup>29</sup> One of the positions of each octahedrally coordinated Cu atom is not compromised with the crystal structure and it is typically occupied by water or solvent molecules that can be exchanged with reagents and substrates under reaction conditions. Recently, we have reported that  $\text{Cu}_3(\text{BTC})_2$  can promote the dehydrogenative coupling of silane with alcohols<sup>30</sup> and later, the hydrogenation of acetophenone to 1-phenylethanol by silanes as reducing agents.<sup>31</sup> Continuing with this research and considering the current interest of borasiloxanes previously commented, it was of interest to test the activity of  $\text{Cu}_3(\text{BTC})_2$  to promote the hydrolytic coupling of silanes and pinacolborane (HBpin). In the present manuscript, it would be presented that  $\text{Cu}_3(\text{BTC})_2$  is also a suitable catalyst for the selective formation of borasiloxanes by oxidative hydrolysis of silanes followed by coupling with boranes exhibiting wide scope. It was observed that the material becomes partly deactivated during the course of this coupling, probably due to the partial reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  by HBpin.

In the first stage of our work, dimethylphenyl silane (**1**) and HBpin were selected to determine their hydrolytic coupling to the corresponding borasiloxane (**2**). A blank control experiment between **1** and HBpin in the absence of any catalyst in acetonitrile at 70 °C showed no product at all (entry 1, Table 1). In contrast,  $\text{Cu}_3(\text{BTC})_2$  was able to promote the oxidative coupling in different conversion and selectivity depending on the material and reaction conditions. The observed results are summarized in Table 1. As it can be seen in this Table 1,  $\text{Cu}_3(\text{BTC})_2$  promotes the formation of **2** over 10 % conversion at room temperature after 4 h (entry 2, Table 1). It was observed that heating at 70 °C, either in toluene or particularly in acetonitrile, increased the conversion of **1** (entries 3 and 4, Table 1). Conversion of **1** was 70 % under ambient air atmosphere, probably due to the unwanted influence ambient moisture. It will be commented below that the reaction rate is negatively influenced by water. A very low conversion of **1** (12 %) was noticed when the reaction is performed with diborane  $\text{B}_2\text{pin}_2$  and enhanced selectivity towards unwanted disiloxane **3** is observed after 4 h under identical conditions (entry 5, Table 2). A complete conversion of **1** was achieved with 97% selectivity of **2** using  $\text{Cu}_3(\text{BTC})_2$  as catalyst in acetonitrile under nitrogen atmosphere at 70 °C after 4 h (entry 6, Table 1). The other product that could be detected under these optimal conditions was disiloxane **3** formed by the oxidative coupling of **1**.

To elucidate the role of  $\text{Cu}_3(\text{BTC})_2$  as catalyst in this reaction, a control experiment was performed by adding pyridine to  $\text{Cu}_3(\text{BTC})_2$  prior to check its activity. It was observed that pyridine quenched almost the catalytic activity of  $\text{Cu}_3(\text{BTC})_2$ , suggesting that Lewis acidity of  $\text{Cu}^{2+}$  ions plays a key role in this reaction (entry 7, Table 1). The catalytic activity of  $\text{Cu}_3(\text{BTC})_2$  sharply contrasts with the lack of activity of other MOFs such as commercially available Fe(BTC), MIL-53(Al) and MIL-101(Cr) in spite that it is known that some of these MOFs exhibit catalytic activity in many different reaction types requiring Lewis acidity (entries 11–13, Table 1).

Table 1. Hydrolytic coupling of **1** with HBpin under various reaction conditions.<sup>a</sup>



Run	Catalyst	Time (h)	Conversion <b>1</b> (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>	
				<b>2</b>	<b>3</b>
1	-	4	-	-	-
2	$\text{Cu}_3(\text{BTC})_2^c$	4	10	100	-
3	$\text{Cu}_3(\text{BTC})_2^d$	4	40	100	-
4	$\text{Cu}_3(\text{BTC})_2^e$	4	70	100	-
5	$\text{Cu}_3(\text{BTC})_2^{e,f}$	4	12	90	10
6	$\text{Cu}_3(\text{BTC})_2$	4	100	97	3
7	$\text{Cu}_3(\text{BTC})_2^g$	4	10	100	-
8	$\text{Cu}_3(\text{BTC})_2^h$	1	100	33	67
9	$\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	4	85	96	4
10	$\text{Cu}_2\text{O}$	4	43	100	-
11	MIL-101(Cr)	6	-	-	-
12	MIL-53(Al)	6	-	-	-
13	Fe(BTC)	6	-	-	-
14	Cu/G	4	6	100	-
15	$\text{Cu}_2\text{O}/\text{G}$	4	14	100	-

<sup>a</sup>Reaction conditions: **1** (0.5 mmol), HBpin (0.5 mmol), catalyst (30 mg),  $\text{CH}_3\text{CN}$  (2 mL), 70 °C, nitrogen atmosphere; <sup>b</sup>Determined by GC; <sup>c</sup>At room temperature; <sup>d</sup>Toluene as solvent; <sup>e</sup>Moist ambient atmosphere; <sup>f</sup>With 0.5 mmol of  $\text{B}_2\text{pin}_2$ ; <sup>g</sup>With 0.1 mL of pyridine; <sup>h</sup>Reaction with 0.5 mmol of dimethylphenylsilanol.

In contrast to the lack of activity of MOFs not containing Cu, a soluble Cu salt, namely,  $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  exhibits a remarkable activity in promoting the hydrolytic three components coupling, although conversion of **1** was not complete and a small amount of **3** was also detected under the optimized conditions after 4 h (entry 9, Table 1). On the other hand,  $\text{Cu}_2\text{O}$  displayed much lower activity for borasiloxane formation compared to  $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ , probably due to the lack of porosity, lower surface area or the absence of  $\text{Cu}^{2+}$  (entry 10, Table 1). Furthermore,  $\text{Cu}_3(\text{BTC})_2$  was more efficient than Cu metal or  $\text{Cu}_2\text{O}$  supported on graphene (entries 14–15, Table 1). These data indicate that  $\text{Cu}_3(\text{BTC})_2$  is the most active catalyst among the various Cu-containing catalysts studied here in promoting the oxidative hydrolytic coupling of **1** and HBpin to form borasiloxane.

In agreement with the presumed reaction mechanism for this hydrolytic coupling involving as the first step hydrolysis of silane to silanol, dimethylphenylsilanol also gives rise to the formation of **2** in the presence of  $\text{Cu}_3(\text{BTC})_2$ , although with much less selectivity due to the formation of **3** by condensation as the predominant product in 67% selectivity after 1 h (entry 8, Table 1). On the other hand, the evolved gas from the reaction mixture arising by the hydrolytic coupling of **1** with HBpin under the optimized reaction conditions was collected by a micro syringe and analyzed by gas chromatography. This analysis confirmed the formation of hydrogen, being consistent with the formation of silanol as an intermediate from silane. It seems that the presence of large amount of silanol at the initial reaction time does not favour achieving high selectivity of **2**, due to the tendency of silanols to undergo condensation.

According to the reaction shown in Scheme 1, the formation of **2** requires the presence of water as reagent. In the present case, it is believed that the amount of water for the reaction must come from the solvent, from the ambient or from the moisture adsorbed on the catalyst. It should be noted that the water content in acetonitrile (~1 wt%) and that of  $\text{Cu}_3(\text{BTC})_2$  (See TGA in Fig.S1) is more than enough than the water needed to meet the stoichiometry of the reaction under the present conditions.

To address the origin of water molecules, an additional experiment was carried out in where  $\text{Cu}_3(\text{BTC})_2$  was submitted to dehydration by evacuation at 150 °C under vacuum for 3 h. Then, the activated  $\text{Cu}_3(\text{BTC})_2$  was used as catalyst to promote the reaction under optimized conditions. It was observed that the evacuated  $\text{Cu}_3(\text{BTC})_2$  catalyst exhibited a clear induction period in the initial reaction time that can be interpreted as the time required to regain water on the active sites of  $\text{Cu}_3(\text{BTC})_2$  to promote the hydrolytic coupling. Figure 1 shows the temporal profile for the conversion of **1** under optimized reaction conditions catalyzed by  $\text{Cu}_3(\text{BTC})_2$  and the thermally evacuated  $\text{Cu}_3(\text{BTC})_2$  sample. Moreover, if an additional amount of water is added on purpose to the reaction mixture at initial reaction time, then, also an induction time in the conversion of **1** was observed, indicating again that too much water can have a negative effect, due to the blocking of active sites. This explanation is also in agreement with the observation that performing the reaction under nitrogen atmosphere results in faster conversion and higher selectivity of **2** than the reaction performed under ambient conditions, where moisture is present. Thus, an excess or defect of water appears to influence negatively the initial reaction rate, the ambient equilibrated  $\text{Cu}_3(\text{BTC})_2$  being the most efficient material to promote the hydrolytic coupling.

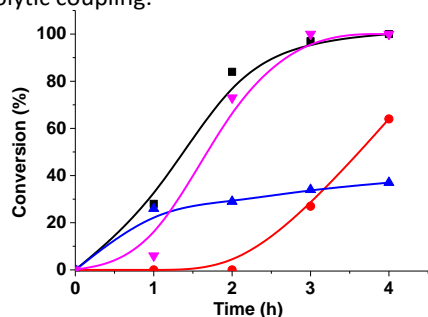


Figure 1. Time-conversion plot for the conversion of **1** under optimal reaction conditions (black square), with addition of 0.5 mmol of water (rose triangle), thermal activated  $\text{Cu}_3(\text{BTC})_2$  at 150 °C for 3 h under vacuum (red circle) and hot filtration of catalyst after 1 h (blue triangle).

To gain further information on the reaction mechanism, we performed a reaction starting with dimethylphenylsilanol and observing the formation of **2** and **3**, even at a faster reaction rate, thus indicating that silanol can be a possible reaction intermediate, its presence being mostly undetectable due to its faster reaction compared to silane. This was further supported by another experiment in which **1** was added first in the absence of HBpin and formation of silanol and **3** was observed, but conversion of **1** was low. In addition, it will be commented later that bulky triphenylsilane affords a mixture of the corresponding triphenylborasiloxane and triphenylsilanol. On the other hand, if HBpin is added first to the catalyst in the absence of **1**, a visually observable colour change of the

$\text{Cu}_3(\text{BTC})_2$  catalyst occurs. It is well known that boranes can be strong reducing agents and this colour change of  $\text{Cu}_3(\text{BTC})_2$  is compatible with the partial reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ . However, no boranol was detected under this experimental condition.

Accordingly, the most likely reaction mechanism of the oxidative coupling appears to involve the combined activity of Cu(II) as Lewis acid activating water and silanol with that of Cu(I) activating borane. Silanol will be an intermediate that will react promptly to form the desired product. This reaction illustrates the process that is compatible with the colour change observed in the catalyst during the reaction, indicating the presence of  $\text{Cu}^+$ , and the recovery of the characteristic  $\text{Cu}^{2+}$  visual appearance when the reaction completed.

In order to understand the role of  $\text{Cu}_3(\text{BTC})_2$  in this reaction, a series of FT-IR spectroscopic studies were performed in the presence of both **1** and HBpin as reactants from room temperature to 70 °C. In the pre-reacted sample a band at 3537  $\text{cm}^{-1}$  is observed, which could be associated to the hydroxy groups of  $(\text{Cu}^{2+}\text{-OH})$  species (Figure 2a). XPS and FT-IR spectra using NO as a probe molecule also agree with the existence of  $\text{Cu}^{2+}\text{-OH}$  species (Figs. S2 and S3). This  $\text{Cu}^{2+}\text{-OH}$  band clearly disappeared after the adsorption of **1** (Figure 2b). Besides these characteristic bands of **1**, two new bands appeared at 2044  $\text{cm}^{-1}$  and 3627  $\text{cm}^{-1}$ . The IR band at 2044  $\text{cm}^{-1}$  corresponds to Cu-H species,<sup>32</sup> while the band at 3627  $\text{cm}^{-1}$  is characteristic for silanol groups. Thus one can assume that the Si-H bond in **1** is converted to Si-OH, probably involving  $\text{Cu}^{2+}\text{-OH}$  species, resulting in the formation of Cu-H species. Hence, a control experiment was performed in where water and **1** were co-adsorbed on the same catalyst. After adsorption of **1**, heating to 70 °C led to the appearance of new IR bands at 1284, 1188, 1029, 818 and 797  $\text{cm}^{-1}$  attributable to the disilanoxy compound **3** (see also Figs. S4 and S5). When after adsorption of **1**, co-adsorption of HBpin was performed and then the solid heated, besides the bands precisely indicated corresponding to compound **3**, a new band at 976  $\text{cm}^{-1}$ , not observed before was recorded and attributed to Si-O-B bonds. In parallel to the new IR bands, the IR band at 2044  $\text{cm}^{-1}$  decreased in its intensity at increasing temperature which may be related to hydride recombination to give  $\text{H}_2$  formation.

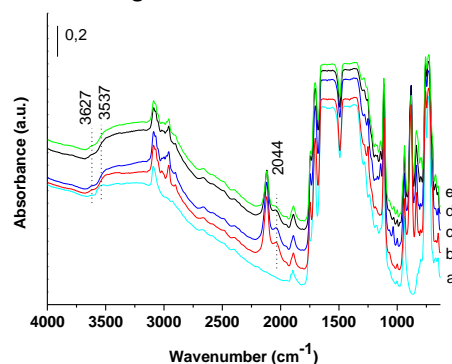


Figure 2. IR spectra of pre-reacted  $\text{Cu}_3(\text{BTC})_2$  sample (a), after 2.8 mbar **1** adsorbed at 25 °C (b), 2.6 mbar HBpin co-adsorbed at 25 °C (c), and followed by increasing temperature to 50 °C (d) and at 70 °C (e).

The heterogeneous nature of the process was confirmed by performing a hot filtration test (See SI for more details). In addition, ICP analysis showed that less than 2 ppm of copper leached to the solution. The catalyst stability was further assessed by reusing  $\text{Cu}_3(\text{BTC})_2$  in two consecutive reuses. It was observed that the conversion of **1** to be 100, 59 and 39% for fresh, first and second

reuses. This decrease in activity is associated to the appearance of new peaks at low angle in the powder XRD patterns of the two times used  $\text{Cu}_3(\text{BTC})_2$  catalyst (Figure 3). However, in spite of the appearance of new peaks, it seems that the crystallinity of  $\text{Cu}_3(\text{BTC})_2$  is retained during the reuse experiments.

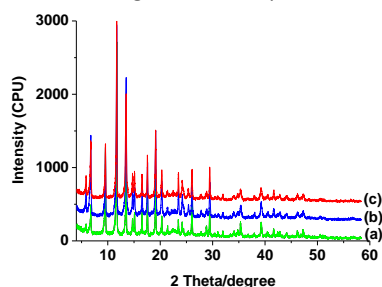


Figure 3. Powder XRD patterns of fresh (a), recovered (b) and two times reused  $\text{Cu}_3(\text{BTC})_2$  (c) catalysts.

Table 2. Synthesis of various borasiloxanes catalysed by  $\text{Cu}_3(\text{BTC})_2$ .<sup>a</sup>

Run	Silane	Time (h)	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>
1	Dimethylphenylsilane	4	100	97
2	Triethylsilane	4	95	100
3	Methylphenylsilane	7	95	40(58) <sup>c</sup>
4	Di- <i>t</i> -butylsilane	4	21	100
5		8	50	68(32) <sup>d</sup>
6	Triisopropylsilane	5	17	100
7		21	62	100
8	<i>t</i> -Butyldimethylsilane	5	64	94
9	Triphenylsilane	4	34	68(32) <sup>e</sup>
10		24	90	75(25) <sup>e</sup>

<sup>a</sup>Reaction conditions: Silane (0.5 mmol), HBpin (0.5 mmol),  $\text{Cu}_3(\text{BTC})_2$  (30 mg),  $\text{CH}_3\text{CN}$  (2 mL), 70 °C, nitrogen atmosphere; <sup>b</sup>Determined by GC and the products were confirmed by GC-MS; <sup>c</sup>Selectivity of 2,4,6-trimethyl-2,4,6-triphenyl-1,3,5,2,4,6-trioxatrisilane; <sup>d</sup>Selectivity of bis addition of HBpin; <sup>e</sup>Selectivity of triphenylsilanol.

The scope of  $\text{Cu}_3(\text{BTC})_2$  to promote hydrolytic coupling of silanes and boranes was screened using HBpin as reagent for a variety of silanes having one or two Si-H bonds. The results are presented in Table 2. They can be summarized considering that conversion and selectivities are lower as the size of the silanes and the number of Si-H bonds increases. For instance, methylphenylsilane can be converted to the corresponding borasiloxane accompanied by the cyclic trioxasiloxane derivative (Scheme S1). Furthermore, di-*t*-butylsilane exhibits lower conversion due to the bulkiness of two *t*-butyl groups, undergoing mono and bis boronation by HBpin and increasing the selectivity of bis derivative as the reaction progresses. Also, triisopropylsilane requires long times to reach high conversion due to the bulkiness of this substrate. The reactivity patterns of triisopropylsilane, triphenylsilane and di-*t*-butylsilane is compatible with the reaction occurring on the external surface of the crystallites due to their large molecular dimensions, but at much slower rates than for less bulky substrates that can access both the external and internal surface.

In conclusion, in the present study, it has been shown that Cu-containing MOF is a suitable catalyst for the oxidative hydrolytic coupling of HBpin with silanes to the corresponding borasiloxanes. This reaction works under much milder reaction conditions than those reported with  $\text{Ru}^{2+}$  and  $\text{Pd}^{19}$  based homogeneous catalysts. The reaction seems to occur on the external and internal surface of the crystallites and to involve combined action of  $\text{Cu}^{2+}$  as Lewis acid sites

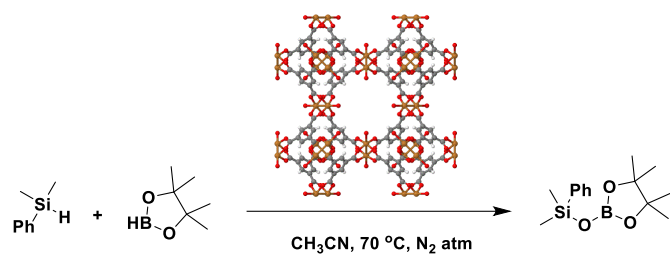
that can be blocked by pyridine and  $\text{Cu}^+$  generated by HBpin as reducing agent.

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## TOC



This work reports the synthesis of borasiloxanes from silanes and pinacolboranes using Cu<sub>3</sub>(BTC)<sub>2</sub> as heterogeneous catalyst in acetonitrile under milder conditions.