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## COMMUNICATION

### Ruthenium-catalysed multicomponent synthesis of borasiloxanes

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We present the selective atom economical synthesis of borasiloxanes using a multi-component approach directly from the one-pot ruthenium catalysed reaction of boranes, silanes and water.

Boron and silicon compounds have found extensive applications in synthetic, medicinal and material chemistry.<sup>1</sup> Borasiloxanes are used in functional inorganic material synthesis as they possess inherent molecular properties such as high stability providing resistance to heat and chemical reactions.<sup>2</sup> Borasiloxanes form cages, act as bifunctional molecules and used as polymeric sensor for amines.<sup>3</sup> The conventional synthetic methods comprise the reaction of hydroxyborane with silane derivatives or the reaction of silanol with borane derivatives leading to the formation of borasiloxanes.<sup>4</sup> Such conventional synthesis of silane and borane derivatives<sup>5</sup> requires stoichiometric reagents, tedious experimental conditions and work up, which make the ultimate synthesis of borasiloxanes multi-step.

To alleviate these problems, two catalytic methods were developed in recent times for the synthesis of borasiloxanes.<sup>6,7</sup> Marciniec reported the pioneering coupling of vinylboronates with silanol (Scheme 1a).<sup>6</sup> Nakazawa and coworkers have disclosed a remarkable metal carbonyl complex catalysed photolytic synthesis of borasiloxanes (Scheme 1b).<sup>7</sup> However, synthesis of borasiloxanes from borane, silane and water in a direct multicomponent pathway is desirable, highly atom economical, and remains a challenge (Scheme 1c). Recently, we have reported the ruthenium-catalysed chemoselective hydrosilylation<sup>8</sup> of aldehydes, and hydroboration<sup>9</sup> of carbonyl compounds, nitriles, imines and pyridines. Herein, we report the ruthenium-catalysed selective synthesis of borasiloxanes directly from boranes, silanes and water. This efficient catalytic process proceeds with the liberation of molecular hydrogen and water and generates no waste.

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a) Coupling of VinvIborate with Silane (Marciniec [Ru-H] R₂SiOH toluene 60-130 °C, 3-24 h n = 0.1b) Coupling of Bisboryloxide with Silane (Nakazawa Mo(CO), pinB-O-SiR<sub>2</sub> O(Bpin)<sub>2</sub> + R<sub>3</sub>SiH hv, H<sub>2</sub>O, toluene c) This Work: catalyst + R<sub>3</sub>SiH + 2H<sub>2</sub>O pinB-O-SiR<sub>2</sub> toluene. Δ catalyst RB(OH)<sub>2</sub> + R<sup>1</sup><sub>3</sub>SiH + nH<sub>2</sub>O  $RB(-OSiR_{3})_{2} + nH_{2}O + nH_{2}$ toluene. Δ R = alkyl, aryl, OH R = alkyl, aryl, OSiR1

Scheme 1 Recent advances in the synthesis of borasiloxanes.

Catalyst screening embarked on [(Ru(p-cymene)Cl<sub>2</sub>)<sub>2</sub>] 1. Thus, reaction mixture of 1 (0.5 mol%), pinacolborane (1 mmol), triethylsilane (1 mmol) and water (3 mmol) in toluene (2 ml) were stirred at room temperature for 2 h and then heated to 100 °C for 24 h, which provided borasiloxanes in 57% isolated yield (entry 1, Table 1); similar reaction at 125 °C provided the product in 63% yield (entry 2). This result indicated that the elegant catalytic coupling of boranes, silanes and water to borasiloxanes is indeed feasible. Next, the monohydride bridged dinuclear complex [{( $\eta^6$ -p-cymene)RuCl}<sub>2</sub>( $\mu$ -H- $\mu$ -Cl)] **2**, was used as a catalyst leading to the formation of the borasiloxanes in 80% yield (entry 3). To develop more efficient catalyst, mononuclear ruthenium complexes 3-7 were explored.  $^{9\mathrm{b}}$  While PPh3 ligated ruthenium catalyst **3** (0.2 mol%) provided 50% yield (entry 4), electron-rich PCy<sub>3</sub> coordinated catalyst 4 provided borasiloxanes in 10% yield (entry 5), perhaps due to strongly bound phosphine ligands encumber further reaction at the metal centre. Thus, upon using labile pyridine ligated complex 5 as a catalyst in toluene at 100 °C and 125 °C, borasiloxane was obtained in 88% and 96% yields, respectively (entries 10-11). Further, catalysts 6 and 7 provided 29% and 80% yields, respectively (entries 12-13). When RuCl<sub>3</sub> is used as a catalyst, the product was isolated in 47% yield (entry 14). Control experiment provided unreacted

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silane and hydroxyborane implying the catalyst is essential for successful formation of products (entry 15). To test weather chloride ion play any role in catalysis, TBACI (1 mol%) was employed in which no reaction was observed (entry 16). Thus, pyridine ligated complex **5** is preferred as the most suitable catalyst for the synthesis of borasiloxanes.

Table 1 Screening of catalysts and reaction conditions for the selective synthesis of borasiloxanes^{a}



entry	catalyst	Solvent	temp.	pinBOSiEt₃
	(mol %)		(°C)	(% yield) <sup>b</sup>
1	<b>1</b> (0.5 )	toluene	100	57
2	<b>1</b> (0.5 )	toluene	125	63
3	<b>2</b> (0.2)	toluene	125	80
4	<b>3</b> (0.2)	toluene	100	50
5	4 (0.2)	toluene	125	10
6	<b>5</b> (0.2)	toluene	80	80
7	<b>5</b> (0.2)	toluene	rt	-
8	<b>5</b> (0.2)	CH₃CN	80	-
9	<b>5</b> (0.2)	THF	80	15
10	<b>5</b> (0.2)	toluene	100	88
11	5 (0.2)	toluene	125	96
12	<b>6</b> (0.2)	toluene	100	29
13	<b>7</b> (0.2)	toluene	100	80
14	RuCl₃ (0.2)	toluene	125	47
15 <sup>°</sup>	-	toluene	125	-
16 <sup>d</sup>	TBACI (1)	toluene	125	-

<sup>a</sup>Catalyst, pinacolborane (1 mmol), silane (1 mmol), degassed water (3 mmol) and solvent (2 ml) were stirred at room temperature for 2 h and then heated at indicated temperature for 24 h. <sup>b</sup>Yield of isolated product. <sup>c</sup>Control experiment without catalyst.<sup>d</sup>Tetrabutylammonium chloride is used as catalyst.

The formation of silanol was highly efficient with catalyst **5** and the evolution of dihydrogen at room temperature was observed during the reaction progress.<sup>10</sup> Upon reaction with H<sub>2</sub>O, pinacolborane produced hydroxyborane quantitatively with concomitant liberation of dihydrogen, which also occurred at room temperature. The condensation reaction of silanol and hydroxyboranes was realized upon heating the reaction mixture at 125 °C to accomplish the formation of borasiloxanes selectively, overcoming the self-condensation due to the formation of stronger B–O–Si bond.<sup>3,11</sup> Thus, applying the optimized condition, the substrate scope (alkyl, alkoxy and aryl silanes) was investigated and found that the complex **5** is highly effective in synthesis of a wide-range of borasiloxanes from boranes, silanes and water (Scheme 2).



Scheme 2 Synthesis of borasiloxanes. Silane (1 mmol), borane (1 mmol), catalyst 5 (0.2 mol%), degassed water (3 mmol) and toluene (2 ml) were stirred at room temperature for 2 h and then heated to 125 °C for 24 h. Yield corresponds to isolated pure products.



**Scheme 3** Synthesis of (diboryl)siloxanes and (disilyl)boroxanes. Substrates, catalyst (0.4 mol%), degassed water (10 mmol, 180 $\mu$ l) and solvent (2 ml) were stirred at room temperature for 5 h and then heated to 125 °C for 24 h. Yield corresponds to isolated pure compounds.

Scope of this direct coupling reaction was explored with disubstituted silanes. Diphenylsilane, diethylsilane, and methylphenylsilane exhibited efficient reactivity and provided the corresponding (diboryl)siloxanes in excellent yields (Scheme 3a). Further, we envisaged the reaction between boronic acids and silanes. Unexpectedly under the optimized condition, catalyst **5** provided the expected products in poor yields. However, upon using **2** as a catalyst, reactions occurred effectively and an assortment of aryl and alkyl boronic acids underwent facile reaction with various silanes to provide a

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range of (disilyl)boroxanes in good to excellent yields (Scheme 3b).

When boric acid was subjected to the **2** catalysed borasiloxane formation with different silanes (3 equiv.) and  $H_2O$  (10 equiv.), the corresponding tris(trialkylsilyl)borate products were isolated in good yields. Similarly, triphenylsilane also led to the formation of tris(triphenylsilyl) borate **8** in 70% yield (Scheme 4); unexpectedly, a minor amount (10%) of 1,1,1,3,3,3hexaphenyldisiloxane **9** also formed in this reaction. Further, the structure of tris(triphenylsilyl) borate (**8**) was unequivocally corroborated by single crystal X-ray analysis (Scheme 4).



Series of elementary reactions and labelling studies allowed us to understand the choice of catalysts (2 and 5) and the reaction mechanism (Scheme 5). When the independent reactions of triethylsilane, water with catalysts 2 and 5 (both 0.2 mol%) were monitored by <sup>1</sup>H NMR, quantitative triethylsilanol formation<sup>13</sup> was observed after 2 h and 6 h, respectively (Scheme 5a). <sup>1</sup>H NMR spectra of both reaction mixtures indicated that **2** ( $\delta$  -10.18 ppm) is the major catalytic species present in solution; however, a minor hydride signal was observed at  $\delta$  -11.54 ppm (1:10 for 2 and 1:8 for 5, major signal being **2**).<sup>13</sup> Monitoring the reaction of triethylsilane and  $D_2O$  catalysed by 2 (0.2 mol%), formation of HD (t,  ${}^2J_{HD}$  = 48.0 Hz) was observed in the <sup>1</sup>H NMR (Scheme 5b).<sup>14</sup> Control experiments revealed the necessity of catalyst in the silanol formation step (Scheme 5a and 5b). The tested silanol formation with RuCl<sub>3</sub> (0.2 mol%) and TBACI (1 mol%) also resulted in no reaction (Scheme 5a). Further, oxygen labelled water  $(H_2^{18}O)$  was used and the corresponding <sup>18</sup>O labelled borasiloxane was isolated in 90% yield. The presence of labelled oxygen in the product was identified by the mass spectroscopy  $[(m/z = 299.1521 (M+K)^{+}]$ , which confirmed water as the source of oxygen atom (Scheme 5c) in the products.14

Stoichiometric experiments were performed with complex 5 and triethylsilane or pinacolborane, which confirmed the formation of complex **2** (monitored by <sup>1</sup>H NMR,  $\delta_{\text{DP-P}}$  -10.18 ppm).<sup>8,9</sup> However, the generation of **2** from **5** in presence of triethylsilane was sluggish and reaction completed after 12 h, whereas the reaction was much faster in presence of pinacolborane and complete formation of 2 occurred within 30 min. On contrary, complex 5 didn't react with phenylboronic acid and no formation of complex 2 was observed (Scheme 5d). These observations confirm that 2 is the true catalyst involved in the reactions of pinacolborane as well (Scheme 2 and 3a). However, the relatively less reactivity of 2 (see Table 1) over catalyst 5 is not fully understood at this stage; perhaps the liberated pyridine from 5 (upon formation of 2) act as a weak base and influences the condensation reaction.  $^{\rm 15,16}\ {\rm As}$ the formation of complex 2 from 5 occurs on a diminished rate in silane, when boronic and boric acids (with them 5 do not react, see Scheme 5d) are used as boryl partners, catalyst 5 resulted in poor yields, whereas direct use of catalyst 2 provided good reactivity.



Scheme 5 Mechanistic studies.

Silanol and hydroxyboranes were independently heated at 125 °C in toluene for 24 h and further <sup>29</sup>Si, <sup>11</sup>B and <sup>1</sup>H NMR analyses confirmed that there occur no self-condensations (Scheme 5e). The cross-condensation between silanol and hydroxyboranes proceeded with remarkable selectivity. The reaction of isolated triethylsilanol and hydroxyborane, provided the corresponding borasiloxane in 92% yield (Scheme 5f). The cross-condensation reaction was also performed with catalyst **2** (0.2 mol%), which provided 95% borasiloxane, indicating the insignificant effect of catalyst in cross-condensation reactions. Further, Reaction of isolated hydroxyboranes and triethylsilane was performed in the presence of catalyst **2**, which afforded the

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corresponding borasiloxane in only 9% yield and excluded the possibility of dehydrogenative coupling (Scheme 5g).

On the basis of above experiments, a plausible mechanism is proposed for the synthesis of borasiloxanes catalysed by 2 (Scheme 6). The complex 2 undergoes oxidative addition with water  $^{\rm 17}$  to form a Ru(IV) intermediate I, which reacts with silane to generate coordination complex II by liberating a molecule of hydrogen. Further oxidative addition of silane<sup>8,13</sup> provide Ru(IV) intermediate III from which silyl and hydroxyl ligands undergo reductive elimination to deliver silanol and Ru(II) intermediate IV, which reacts further with water to close a catalytic cycle. Hydroxyborane formed from the reaction of pinacolborane and water undergoes condensation reaction with catalytically generated silanol and results in borasiloxane and water (Scheme 6). The ESI-MS analysis of the reaction mixture of 2 with  $H_2O$  was performed in which I (m/z = 289 (M- $\mathrm{H})^{^{\!\!\!\!}})$  was observed, indicating the possible involvement of intermediate I in the catalytic cycles.<sup>1</sup>



Scheme 6 Proposed mechanism for the formation of borasiloxanes

In conclusion, an effective protocol for the selective synthesis of borasiloxanes catalysed by simple ruthenium catalysts is demonstrated. High atom-economy, selectivity, catalytic efficiency, abundant and cheap resources, benign by products (water and molecular hydrogen) makes this method highly attractive for synthesis of borosilaxane materials.

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- 12 As the reaction proceeded, <sup>1</sup>H NMR signal corresponds to Si–H ( $\delta$  = 3.67 ppm, multiplet) disappeared and a singlet signal  $\delta$  = 2.05 ppm, corresponds to Si-OH emerged.
- 13 This minor intermediate complex remains elusive to isolation and further characterization. However, the previously observed [Ru(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub>( $\eta^{6}$ -p-cymene)] complex ( $\delta$  -13.53 ppm) was not involved in this reaction. See Ref. 8.
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Ruthenium-catalysed multicomponent synthesis of borosiloxanes directly from silane, borane and water is reported.

HBpin + $R_3SiH$ + $2H_2O$ toluen	$p_{e}^{0}$ pinB-O-SiR <sub>3</sub> + H <sub>2</sub> O + 2H <sub>2</sub>
$RB(OH)_2 + R_{3}^{1}SiH + nH_2O = \frac{2(0.4-0.6)}{toluen}$ R = alkyl, aryl, OH n = 2,3	$ \begin{array}{c} \begin{array}{c} mol^{P_{0}} \end{array} \\ e \end{array} \qquad \qquad$