



A new catalytic method for the synthesis of boroxanes

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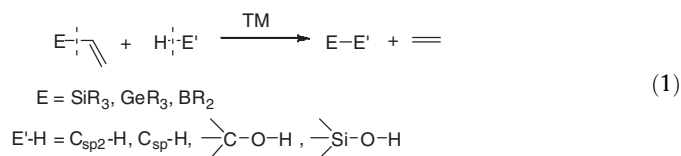
Ruthenium coupling reactions

ABSTRACT

A new Ru–H complex catalyzed *O*-borylation of boronic acids with vinylboronates leading to boroxane bond formation with evolution of ethylene is described. Under the optimum conditions, when [Ru(CO)Cl(H)(PPh₃)₃] and excess vinylboronate are used, the reaction gives exclusively the corresponding boroxane in high yield. The proposed mechanism of catalysis is supported by the results of the equimolar reaction of Ru–B complex with 1,3,2-dioxaborinan-2-ol.

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We have previously developed a new type of transition metal (TM) catalyzed reaction of vinyl substituted organosilicon compounds with a variety of olefins, a process known as silylative coupling (SC), which occurs in the presence of complexes containing or generating M–H and M–Si (silicometallic) bonds.^{1,2} This mode of catalytic reactivity has been recently found to be general and was also exhibited by vinyl derivatives of other p-block elements (e.g., boron³ and germanium⁴). It has also been extended to catalytic activation of C_{sp}–H,⁵ C_{aryl}–H,⁶ as well as by the O–H bond, of silanols⁷ and alcohols⁸ indicating a new general role of vinyl metalloids compounds as metallation agents and hydrogen acceptors. Such reactions proceed according to the following general equation (Eq. 1).¹



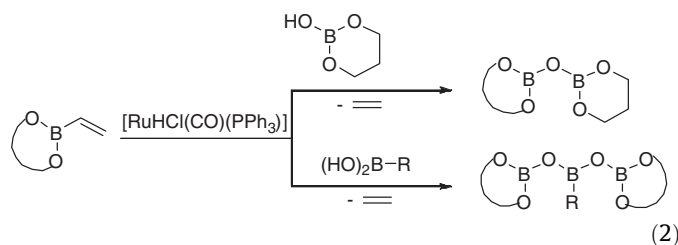
All these reactions lead to the synthesis of a variety of linear and cyclic organometallic (Si, B, Ge) compounds as potential reagents in organic synthesis⁹ and as precursors of optoelectronic and ceramic materials.¹⁰

In view of our very recent reports on the new role of vinylboronates as hydrogen acceptors for the *O*-borylation of silanols^{7a} and alcohols,^{8a} the aim of this work was to make use of this general feature in the *O*-borylation of boronic acids. These processes can be used as a versatile method for blocking the hydrogen atom in boronic acids as well as in borylations of inorganic and organometallic materials.

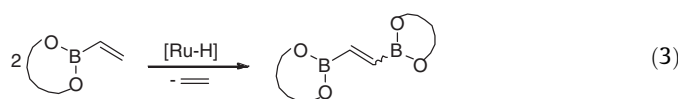
Compounds with covalently linked B–O–B bonds can be used as precursors for self-assembly linear polymers. This type of self-repairing polymer is typically synthesized via condensation reactions of boronic acids with polyols.¹¹

Boroxane chemistry is used to initiate the formation of linkages in polymeric materials or anion acceptors for battery applications. This strategy is also used for the synthesis of porous thermally stable boronate networks with high surface area.^{12,13} The presence of boron atoms in the molecular structures of compounds also has a strong influence on the mechanical and thermal resistance of new materials, for example, ceramics.^{10–13}

To check the efficiency of the *O*-borylation process a number of boronic acids were tested. The reaction with vinylboronate was catalyzed by ruthenium hydride complexes and proceeded via activation of the H–O bond and elimination of ethylene (Eq. 2).



This process can be accompanied by vinylboronate homocoupling, also catalyzed by the same complexes, as previously reported (Eq. 3).³



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When $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ (**I**), the most active catalyst for metallative coupling of olefins,^{1–5} alkynes,⁶ and silanols⁷ with vinylmetaloids was used as the catalyst, the homocoupling of vinylboronates giving bis(boryl)ethenes was also observed (see Table 1).

Higher chemoselectivity was achieved with the ruthenium catalyst with coordinated triphenylphosphine as the ligand $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ (**II**), the most efficient catalyst for *O*-borylation of alcohols and silanols.^{7a,8} A two-fold excess of vinylboronate for each hydroxy group in the boronic acid was necessary to obtain the desired products. It is worth noting that under such conditions, when the concentration of vinylboronate was much higher than that of the boronic acid, homocoupling of the vinylboronate was not observed, even in trace amounts (see Tables 2 and 3).

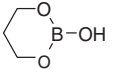
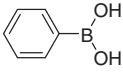
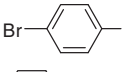
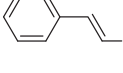
The reactions proceed in very high, almost quantitative conversions. All products were isolated and the structures were determined by ¹H, ¹³C and ¹¹B NMR spectroscopy.¹⁴ The ¹¹B NMR spectra of the products showed two signals assigned to the boron atom bonded to three oxygen atoms (~30 ppm) and the boron atom with one B–C and two B–O bonds (~37–42 ppm).

For this new *O*-borylation of boronic acids with vinylboronates, on the basis of the obtained results and the previously reported mechanisms of the *O*-borylation of alcohols⁸ and silanols^{7a} with vinylboronates, an analogous insertion-elimination mechanism is proposed. The insertion of vinylborane into the ruthenium–hydride bond and the generation of a ruthenium–boron bond with simultaneous elimination of ethylene was previously reported.³ This experiment, monitored by ¹H NMR and GC–MS, confirmed clearly the first-half of the catalytic cycle. For the *O*-borylation reaction of boronic acids the process analogous to that for the coupling of vinylboranes with silanols and alcohols occurred. Deuterated DMSO and THF were used as reaction solvents, because the boronic acids were insoluble in deuterated toluene or benzene, the solvents typically used in such experiments.

Initially, the catalytic reaction of vinylborane and 1,3,2-dioxaborinan-2-ol catalyzed by $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ (**II**) was monitored by ¹H NMR spectroscopy. After a few hours the evolution of ethylene was apparent from the appearance of a singlet at 5.25 ppm, which provided evidence of the formation of a ruthenium–boryl complex.

The stoichiometric reaction of the ruthenium–boryl complex $[\text{Ru}(\text{BO}_2\text{C}_6\text{H}_4)(\text{CO})\text{Cl}(\text{PCy}_3)_2]$ (**III**) with 1,3,2-dioxaborinan-2-ol was carried out at 60 °C in THF-*d*₈ and the progress of the reaction was monitored by ¹H NMR spectroscopy.¹⁵ Regeneration of the

Table 1
The *O*-borylation of boronic acids with 2-vinyl-1,3,2-dioxaborinane catalyzed by $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PCy}_3)_2]$ (**I**)^a

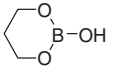
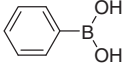
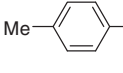
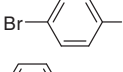
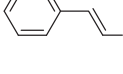
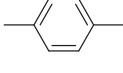
B–OH reagent	Conversion of B–OH (%) ^b	Selectivity (%) ^{b, c}
	100	90/10
	100	86/14
	100	89/11
	95	83/17

^a Reaction conditions: $[\text{Ru}]:[\text{B–OH}]:[\text{vinylboronate}] = 2 \times 10^{-2}:1:2$; 1,4-dioxane (0.5 M), *T* = 80 °C, *t* = 24 h.

^b Determined by GC analysis.

^c Selectivity: [*O*-borylation/homocoupling].

Table 2
The *O*-borylation of boronic acids with 2-vinyl-1,3,2-dioxaborinane catalyzed by $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ (**II**)^a

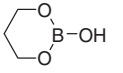
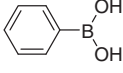
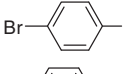
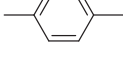
B–OH reagent	Conversion of B–OH (%) ^b	Yield (%) ^c
	92	71
	100	77
	100	74
	100	71
	89	74
	92	72

^a Reaction conditions: $[\text{Ru}]:[\text{B–OH}]:[\text{vinylboronate}] = 2 \times 10^{-2}:1:2$; 1,4-dioxane (0.5 M), *T* = 80 °C, *t* = 24 h.

^b Determined by GC analysis.

^c Yield of isolated product.

Table 3
The *O*-borylation of boronic acids with 2-vinyl-4,4,5,5-tetramethyl-1,3,2-dioxaborinane catalyzed by $[\text{Ru}(\text{CO})\text{Cl}(\text{H})(\text{PPh}_3)_3]$ (**II**)^a

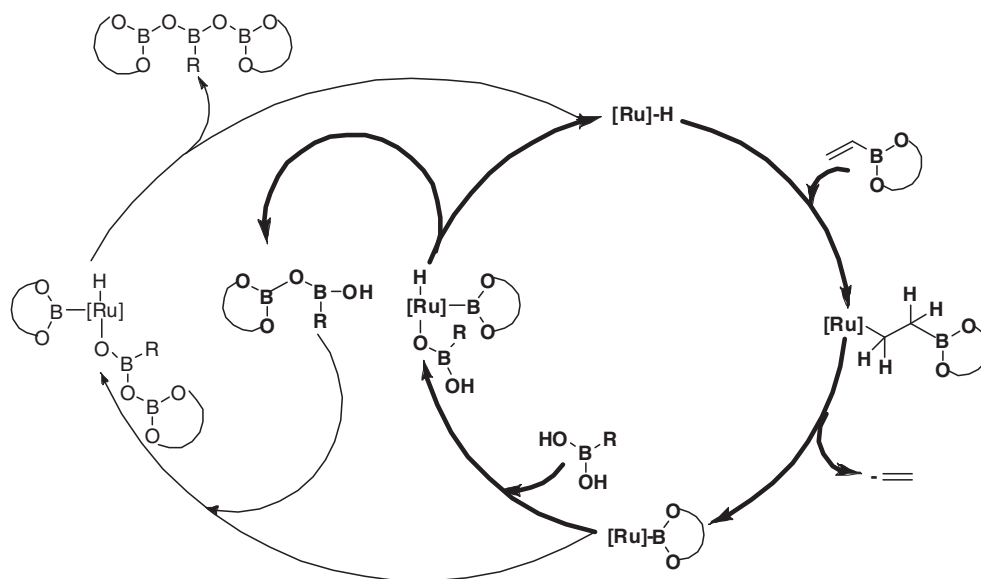
B–OH reagent	Conversion of B–OH (%) ^b	Yield (%) ^c
	90	73
	96	65
	96	60
	87	59

^a Reaction conditions: $[\text{Ru}]:[\text{B–OH}]:[\text{vinylboronate}] = 2 \times 10^{-2}:1:2$; 1,4-dioxane (0.5 M), *T* = 80 °C, *t* = 24 h.

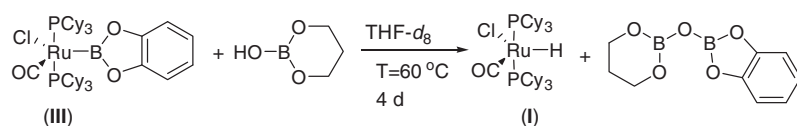
^b Determined by GC analysis.

^c Yield of isolated product.

ruthenium hydride bond was manifested as a low intensity triplet at –24.3 ppm [*J* (P–H) = 20.2 Hz], which appeared after 96 h. This was a clear evidence of the *O*-borylation process. When the reaction was carried out in DMSO-*d*₆ regeneration of the Ru–H bond was not observed in the ¹H NMR spectrum, even after a few days. This was probably due to the fact that DMSO shows a high propensity to coordinate with the metal center and reduces the activity of the ruthenium complex. A similar stoichiometric reaction occurred with phenylboronic acid as the reagent. The process was also monitored by ¹¹B NMR spectroscopy, which confirmed the generation of a product with the B–O–B moiety. After a few hours, a signal due to the boron connected to three oxygen atoms occurred (33.6 ppm), which was the evidence of product formation (Eq. 4).



Scheme 1. Mechanism of the O-borylation of boronic acids with vinylboronates.



(4)

On the basis of these experiments and the previously proposed mechanism for the O-borylation of silanols^{7a} and alcohols⁸ with vinylboronates, a catalytic mechanism for this new O-borylation reaction of boronic acids is proposed (Scheme 1) based on the activation of the B–C bond in the vinylborane and the H–O bond in the boronic acid.

The emboldened cycle shows the main mechanism for the O-borylation process. The product with one hydroxy group connected to the boron atom may undergo subsequent oxidative addition to the ruthenium–boryl complex and then reductive elimination giving a diboryloxy-substituted boronic acid derivative, which opens a new route to linear inorganic–organometallic polymers with boron atoms in the structure.

This coupling reaction allows the synthesis not only of symmetric, but also of non-symmetric boroxanes, which are difficult to obtain via typical synthetic processes. The much lower reactivity of vinylboronates compared to that of vinylsilanes and vinylgermanes is responsible for this high chemoselectivity, which is in agreement with previously published results.^{7,8a}

In conclusion, we have reported a new catalytic O-borylation of boronic acids with vinylboronates. This process extends the role of vinylboronates as hydrogen acceptors to form borylated products and indicates that such a strategy can also be used for the borylation of other heteroatom–hydrogen bonds. The boroxanes obtained may be used as monomers for the synthesis of polymers with boryl–oxygen–boryl bridges or substrates for new ceramic materials.

Acknowledgments

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Supplementary data

Supplementary data associated (spectroscopic data of new boroxane compounds and typical experimental procedures) with

this article can be found, in the online version, at [doi:10.1016/j.tetlet.2010.09.094](https://doi.org/10.1016/j.tetlet.2010.09.094).

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14. **Representative experimental procedure for the O-borylation of boronic acid by vinylboronates:** the ruthenium catalyst [Ru(CO)Cl(H)(PPh₃)₃] (**II**) (2 mol%) was dissolved in 1,4-dioxane and placed in a glass ampoule. Dodecane (used as internal standard, 5% by volume all components), boronic acid (0.5 mmol), and 2-vinyl-1,3,2-dioxaborinane (1–2 mmol) were added. The ampoule was heated at 80 °C for 24 h. The conversion of boronic acid was

determined by GC. After the reaction, the solvent and excess borane were removed under vacuum and the crude product was purified by column chromatography (silica gel modified with HMDS) with hexane/EtOAc as eluent.

15. **Experimental procedure for the stoichiometric experiment:** [Ru(BO₂C₆H₄)(CO)Cl(PCy₃)₂] (**III**) (0.012 mmol), 1,3,2-dioxaborinane-1-ol (0.016 mmol) and THF-*d*₈ (0.8 mL) were placed in an NMR tube under argon. The reaction was carried out at 80 °C and the reaction course was monitored by ¹H NMR spectroscopy.