New catalytic route to borasiloxanes†

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A new, highly selective method for effective synthesis of boryl silyl ethers (borasiloxanes) *via* O-borylation of silanols with vinylboronates catalyzed by the Ru–H complexes [RuHCl(CO)(PCy$_3$)$_2$] and [RuHCl(CO)(PPh$_3$)$_3$] is described.

In the last two decades we have developed a new type of TM catalyzed reaction of vinyl-substituted organosilicon compounds with a variety of olefins called the silylative coupling or *trans*-silylation, occurring in the presence of complexes containing initially or generating an M–H and M–Si bond (for a recent review see ref. 1). This reaction has become a very valuable synthetic tool in the preparation of vinyl-functionalized molecular and macromolecular organosilicon compounds. However, this mode of reactivity seems to be general and is also exhibited by vinylboronates (*trans*-borylation)[2a] and vinylgermanes (*trans*-germylation).[2b] The general scheme is as follows (eqn (1)).

$$(1)$$
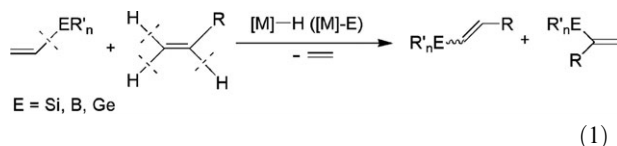
The mechanistic aspects of β-boryl and β-silyl elimination occuring in these processes based on DFT calculations have been recently reported.[3a,b]

The reaction, well-recognized as a new catalytic route for activation of =C–H bond of olefins and =C–E bond of vinylmetalloid derivatives (where E = Si, B, Ge and others) with ethylene evolution has been recently extended to the activation of ≡C–H[4,5] (for E = Si, Ge), =C$_{aryl}$–H (E = Si)[6] as well as –OH bonds of alcohols[7] and silanols,[8] particularly by vinylsilanes (for review see ref. 9). Those recent experiments emphasize that vinylsilicon compounds function as silylative agents and hydrogen acceptors.[9] O-Silylation of silanols with vinylsilanes, proceeding in the presence of ruthenium complex leads to formation of unsymmetric siloxanes *via* elimination of ethylene[8] (eqn (2)).

$$(2)$$
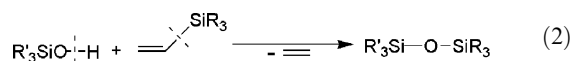
The aim of this work was to check the possibility of extending the role of vinylborane by its use as a hydrogen acceptor in

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O-borylation of silanols, which can be useful in the synthesis of boryl silyl ethers (borasiloxanes) as well as in borylation strategy of inorganic and organometallic materials. Molecular borasiloxanes have been the most useful precursors of borosilicate materials used in many areas.[10] Conventional approaches to compounds containing B–O–Si linkages involve condensation of boronic acids with chlorosilanes and chlorosiloxanes[11] (catalyzed by tertiary amines), alkoxysilanes[12] and silanols.[13] In these processes, borasiloxanes are prepared by azeotropic removal of water from the reaction mixture. Also condensation of chloroborates[14] and alkoxyborates[15] with silanols can lead to desired products. Some of these processes are restricted by the necessity of removal of corrosive HCl and H$_2$O or by instability of the substrates towards moisture.

Here, we present a new catalytic reaction that involves activation of the O–H bond in silanols by vinylboronates proceeding in the presence of ruthenium hydrogen catalysts yielding silyl boryl ethers with elimination of ethylene (eqn (3)).

$$(3)$$
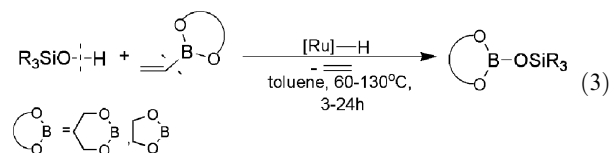
The borylation reaction was first examined in the presence of [RuHCl(CO)(PCy$_3$)$_2$] (**I**) (1–2 mol%), which is well-known as the most effective catalyst in metallative coupling of olefins and acetylenes[9] in an open and closed (sealed ampoules) system in toluene, under argon, 60–130 °C (See Tables 1 and 2).

Since a two- or threefold excess of vinylboronate was necessary to achieve quantitative or very high conversion of silanols, under such conditions, a competitive homo-coupling of vinylboronates occurs (see eqn (4)) to give bis(boryl)ethenes as by-products. However, this by-product can be separated by column chromatography.

$$(4)$$
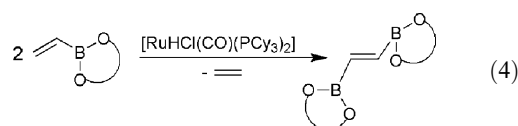
All of the reactions catalysed by [RuHCl(CO)(PCy$_3$)$_2$] (**I**), except those with triphenylsilanol as a reagent, proceeded in very good yields and selectivity. In order to eliminate the side reaction, another ruthenium complex [RuHCl(CO)(PPh$_3$)$_3$] (**II**) was used, which is well-known as an inactive catalyst in the homo-coupling of vinylboron compounds and allowed us

Table 1 Borylation of silanols ($HOSiR_3$) by vinylboronates catalyzed by [RuHCl(CO)(PCy$_3$)$_2$] (**I**)

Borane	Silanol (HOSiR$_3$)	[Ru] : [Si] : [B]	T/°C	t/h	Silanol conversion[b] (%)	Selectivity A : B[b] (%)
	HOSi(i-Pr$_3$)	2×10^{-2} : 1 : 2.5	110	18	100	99 : 1
	HOSi(OSiMe$_3$)$_3$	2×10^{-2} : 1 : 2.5	130	18	95	100 : 0
	HOSiMe$_2$Ph	2×10^{-2} : 1 : 2.5	60	3	100	95 : 5
		10^{-2} : 1 : 2.5	100	6	100	97 : 3
	HO-SiPh$_3$	2×10^{-2} : 1 : 3	130	18	0	—
	HOSi(O-t-Bu)$_3$	2×10^{-2} : 1 : 3	130	18	100	100 : 0
	HOSiMe$_2$(t-Bu)	2×10^{-2} : 1 : 2	60	6	100	99 : 1
	HOSi(i-Pr$_3$)[a]	2×10^{-2} : 1 : 2.5	130	18	88	91 : 9
	HOSi(OSiMe$_3$)$_3$[a]	2×10^{-2} : 1 : 3	130	18	91	93 : 7
	HOSiMe$_2$Ph[a]	2×10^{-2} : 1 : 3	100	18	96	91 : 9
	HOSi(O-t-Bu)$_3$[a]	2×10^{-2} : 1 : 2.5	130	18	82	96 : 4
	HOSiMe$_2$(t-Bu)[a]	2×10^{-2} : 1 : 3	100	18	100	99 : 1

[a] Reaction carried out in a closed system. [b] Determined by GC; A : B = borasiloxane : bis(boryl)ethene.

Table 2 Quantitative borylation of silanols by vinylboronates catalyzed by [RuHCl(CO)(PPh$_3$)$_3$] (**II**)

| Borane	Silanol HOSiR$_3$	[Ru] : [Si] : [B]	T/°C	t/h	Silanol conversion[b] (isolated yield) (%)
	HOSi(i-Pr$_3$)	2×10^{-2} : 1 : 2	100	6	100 (78)
	HOSi(OSiMe$_3$)$_3$	2×10^{-2} : 1 : 2.5	100	18	100 (69)
	HOSiMe$_2$Ph	2×10^{-2} : 1 : 2.5	100	6	100 (67)
		2×10^{-2} : 1 : 2.5	60	6	88
	HOSi(O-t-Bu)$_3$	2×10^{-2} : 1 : 3	130	18	71
	HOSiMe$_2$(t-Bu)	2×10^{-2} : 1 : 2	60	6	100 (72)
	HOSiEt$_3$	2×10^{-2} : 1 : 2	60	6	100 (80)
	HOSi(i-Pr$_3$)[a]	2×10^{-2} : 1 : 2	100	6	100 (75)
	HOSi(OSiMe$_3$)$_3$[a]	2×10^{-2} : 1 : 3	130	18	68
	HOSiMe$_2$Ph	2×10^{-2} : 1 : 3	60	6	96
	HOSi(O-t-Bu)$_3$[a]	2×10^{-2} : 1 : 2.5	130	18	73
	HOSiMe$_2$(t-Bu)	2×10^{-2} : 1 : 2	60	6	100 (82)
	HOSiEt$_3$	2×10^{-2} : 1 : 2	60	6	100 (67)

[a] Reaction carried out in a closed system. [b] Determined by GC.

to obtain quantitative conversion of silanol into desired borasiloxane (Table 2).

Many of the borasiloxanes were isolated (see Table 2) and characterized spectroscopically (^{1}H, ^{13}C, ^{11}B, ^{29}Si NMR, GC-MS) and unisolated compounds were identified by GC-MS spectroscopy.

On the basis of the results obtained and our previous reports on silylation of silanols[8] and *trans*-borylation of alkenes with vinylboronates,[2a] the insertion–elimination mechanism of catalysis is proposed for this process. While the insertion of vinylboronate into a ruthenium–hydride bond was previously reported,[2a] in order to provide an evidence for the second-half of the catalytic cycle (Scheme 1) the stoichiometric reaction of silanol with Ru–B complexes was examined.

For this purpose [Ru(BO$_2$C$_6$H$_4$)Cl(CO)(PCy$_3$)$_2$] (**III**) was prepared[2a] and tested in equimolar reaction in the presence of 1.5-fold excess of *tert*-butyldimethylsilanol. The reaction yielded the respective borasiloxane and hydride complex (identified by NMR spectroscopy) according to eqn (5):
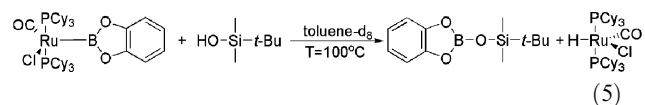
^{1}H NMR examination confirmed the formation of the Ru–H complex (triplet signal at −24.3 ppm) providing a convenient test for the oxidative addition of the silanol into the Ru–B bond and subsequent reductive elimination of borasiloxane. The postulated mechanism (omitting the competitive vinylboronate homo-coupling side reaction) is given in Scheme 1.

In conclusion, we have developed a new catalytic route for effective borylation of silanols with vinylboronates in the presence of ruthenium hydride catalysts, in which vinylboronate was used as a borylating agent and hydrogen acceptor to form a borasiloxane with evolution of ethylene.

(5)
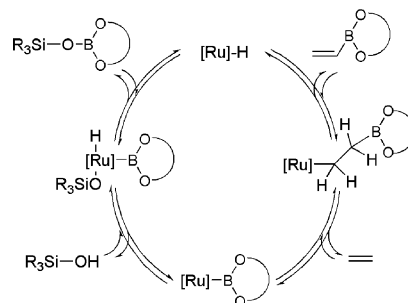
Scheme 1 Proposed mechanism for *O*-borylation of silanols with vinylboronates.

Notes and references

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