New catalytic route to functionalized vinylboronates†

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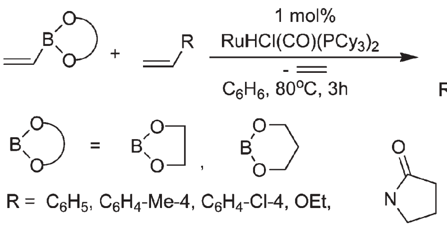
Vinylsubstituted boronates *i.e.* vinyldioxaborolane and vinyldioxaborinane react regioselectively with olefins in the presence of RuHCl(CO)(PCy$_3$)$_2$ with the formation of functionalized vinylboron derivatives. The reaction opens a new catalytic route for preparation of organoboranes.

Functionalized vinylboronates make a class of organoboron compounds commonly used in organic synthesis since the boronate moiety can be converted into other functional groups (aldehyde, halide, amine, alkyl *etc.*).[1,2] Methodologies including classical stoichiometric routes as well as hydroboration of alkynes are usually employed to prepare vinylboron reagents.[3,4] Recently new catalytic methods for their synthesis, namely Heck-type borylation,[5] cross-coupling borylation,[6] dehydrogenative borylation[7] and cross-metathesis[8] of alkenes with vinylboronates, have been reported.

In the last two decades we developed two universal methods for the synthesis of well-defined molecular compounds with vinylsilicon functionality. Both methods *i.e.* silylative coupling (also called *trans*-silylation or silyl group transfer) and cross-metathesis, are based on catalytic transformations of vinyl-silicon compounds with olefins and lead to synthesis of respective functionalized vinylsilicon reagents.[9] While the cross-metathesis (CM) is catalyzed by well-defined Ru and Mo carbene complexes, the silylative coupling (SC) takes place in the presence of complexes initiating or generating M–H and M–Si bonds (where M = Ru, Rh, Ir). The mechanism of SC proved by Wakatsuki[10] and by us[11] proceeds *via* insertion of vinylsilanes into the M–H bond and β-Si transfer to the metal with elimination of ethylene to generate a M–Si species, followed by insertion of an alkene into the M–Si bond and β-H transfer to the metal with elimination of substituted vinylsilane.

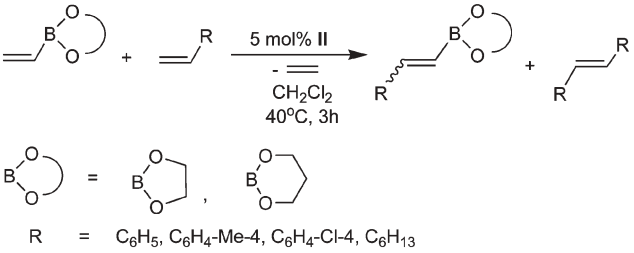
We have found that this mode of reactivity, well known for vinylsilanes, seems to be more general and is exhibited also by vinylboronates. In this communication we report a new catalytic transformation of vinylboranes with alkenes which occurs in the presence of a catalytic amount of RuHCl(CO)(PCy$_3$)$_2$ (**I**) according to the non-metallacarbene mechanism, and leads to the effective formation of vinylboron derivatives[12] [eqn. (1)].



(1)

Fivefold excess of olefin was used in order to avoid the homocoupling of vinylboronate. For styrenes *trans*-borylation proceeds stereo- and regioselectively giving *E*-styryl boronates. When 1-alkenes were used as the reacting partner, the formation of significant amounts of vinylboronate homo-coupling products could not be avoided, even at a fivefold excess of an olefin. In addition, in the presence of ruthenium hydride complexes, the reaction is accompanied by olefin isomerization, so in this case a mixture of alkenylboronates (with a high predominance of *E*-1,2-alkenylboronates) is formed. The obtained results are compiled in Table 1.

In order to compare the applicability of *trans*-borylation and cross-metathesis for the synthesis of vinylboron derivatives, the same parent substances were also tested in cross-metathesis in the presence of Grubbs 1st generation catalysts Cl$_2$(PCy$_3$)$_2$Ru(=CHPh) (**II**) [eqn. (2)].



(2)

A fivefold excess of olefin was used in order to eliminate the formation of vinylboronate homo-metathesis products. However, in these conditions some amounts of olefin homo-metathesis products cannot be avoided. CM and *trans*-borylation were found to give the same boron derivatives [see eqns. (1) and (2)]. In contrast to unsuccessful *trans*-borylation, relatively high yield of cross-metathesis products was obtained for the reaction with 1-alkenes, which is in good agreement with earlier results.[8] The results obtained are given in Table 1. Non-isolated products were identified on the basis of mass spectra.

To distinguish between the metallacarbene mechanism of metathesis and the non-metallacarbene mechanism of *trans*-borylation, the reactions of styrene-d$_8$ with vinyldioxaborolane catalyzed by **I** or **II** have been studied.[13] In the case of a non-metallacarbene mechanism the formation of borylstyrene-d$_7$ and ethylene-d$_1$ is to be expected (Scheme 1). In contrast, the metallacarbene mechanism should afford borylstyrene-d$_6$ and ethylene-d$_2$.

Analysis of the reaction mixture after 0.5 h, *i.e.* in the initial stage of reaction when the conversion did not exceed 10%, revealed only the formation of borylstyrene-d$_7$ while d$_6$ olefin was not detected. Therefore, the metallacarbene mechanism in the conditions of *trans*-borylation reactions[12] can be excluded. In contrast, a similar experiment clearly proved the metallacarbene mechanism

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† Electronic supplementary information (ESI) available: synthesis and spectroscopic data for **III** and styrylboronates. See http://www.rsc.org/suppdata/cc/b4/b414644a/

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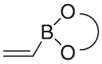
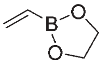
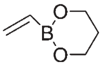
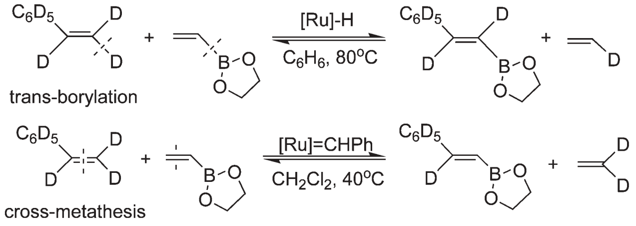
Table 1 *Trans*-borylation (TB) and cross-metathesis (CM) of vinylboronates with selected olefins

		*Trans*-borylation	Cross-metathesis	Homo-metathesis by-products
	R =	Yield (*E*/*Z*) [%]	Yield (*E*/*Z*) [%]	Yield [%]
	C_6H_5	91[a](*E*)	59[a]	11[b]
	$BO_2C_2H_4$	55 (6/1)	—	80[c]
	C_6H_5	80[a] (*E*)	85[a] (*E*)	5[b]
	C_6H_4–Me–4	90 (*E*)	85 (*E*)	0
	C_6H_4–Cl–4	95 (*E*)	90 (*E*)	0
	C_6H_{13}	38[d]	75 (25/1)	15[b],8[c]
	pyrrolid–2–one	10 (*E*)	0	0
	OEt	60 (*E*)	0	0
	OPr	80 (*E*)	0	0
	$BO_2C_3H_6$	80 (8/1)	—	60[c]

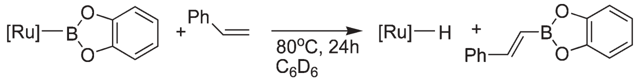
[a] Isolated yield. [b] Homo-metathesis of olefin. [c] Homo-metathesis of vinyl boronate. [d] 5 isomers formed, reaction accompanied by vinyldioxaborinane homo-coupling. Reaction conditions: *trans*-borylation: benzene, 80 °C, 3 h, [vinylboronate]:[olefin] = 1:5. Cross-metathesis: CH_2Cl_2, 40 °C, 3 h, [vinylboronate]:[olefin] = 1:1



Scheme 1 *Trans*-borylation and cross-metathesis of styrene-d_8 with vinyldioxborolane.

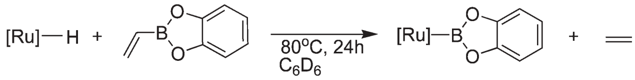
of the reaction carried out in the presence of the Grubbs catalyst (**II**). In these circumstances GC/MS analysis (performed after 15 min of the reaction progress) revealed the exclusive formation of borylstyrene-d_6.

In order to provide evidence for the insertion of olefin into Ru-B bond, stable $Ru(BO_2C_6H_4)Cl(CO)(PCy_3)_2$ (**III**) was prepared[14] and tested in reaction with a twofold excess of styrene. The reaction yielded styrylboronates (identified by NMR spectroscopy and GC-MS) and hydride complex $RuHCl(CO)(PCy_3)_2$ (identified by ^1H NMR spectroscopy) according to the proposed equation [eqn. (3)].†



(3)

In another experiment, a benzene solution of complex **I** was treated with a twofold excess of vinylcatecholborane. Analysis of the reaction mixture by ^1H NMR demonstrated formation of ethylene [eqn. (4)], however boryl complex was not isolated.



(4)

While insertion of an olefin into an M–B bond is a known process,[15] formation of Ru–B bond *via* migration of a boryl group from a position β- to the metal [as proposed in eqn. (4)] has not been, to the best of our knowledge, reported in the literature.

Presented results allow us to propose a reasonable mechanism for the reaction of vinylboronates with styrene (alkene) (Scheme 2).

A mechanistic scheme of this new type of vinylboronate conversion, studied for the reaction with styrene, involves the migratory insertion of styrene, a representative alkene (or vinylboronate in the case of homo-coupling) into a Ru–B bond followed by β-H elimination to give *E*-phenyl(boryl)ethene and insertion of vinylboronate into a Ru–H bond followed by β-B elimination of ethylene (Scheme 2). Dissociation of phosphine is postulated to generate the active catalyst.[16] The proposed mechanism is analogous to that proved for silylative coupling.[11b]

In conclusion, borylation of non-isomerising olefins with vinylsubstituted boronates, *i.e.* vinyldioxaborolane and vinyldioxaborinane, in the presence of catalysts containing an Ru–H bond opens a new, effective catalytic route to functionalized vinyl boronates.

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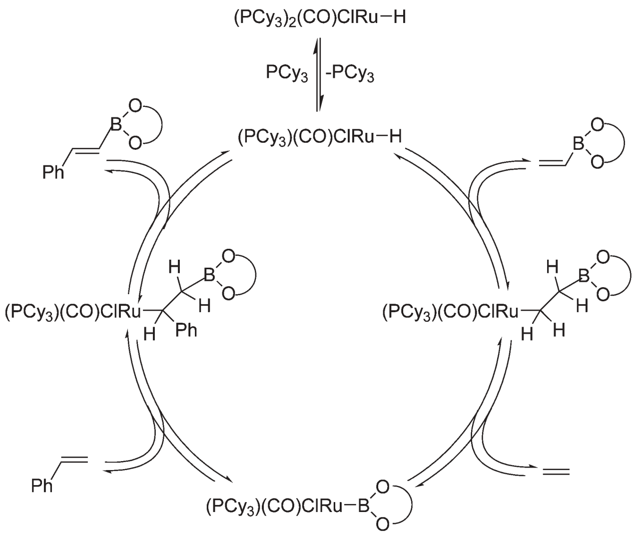

Scheme 2 Proposed mechanistic scheme for *trans*-borylation.

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13 For similar experiment see: ref. 7a.

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