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Highly selective synthesis of 1-(silyl)-1-(boryl)ethenes via a ruthenium-catalyzed silylative coupling reaction

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Abstract—An efficient silylative coupling of trisubstituted vinylsilanes with dialkoxy(vinyl)boranes is described. Under optimum conditions the reaction offers a selective route to 1-(silyl)-1-(boryl)ethenes, which are potentially attractive intermediates in organic synthesis

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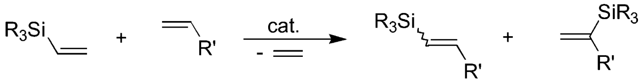
Methods for the synthesis of organodimetallic compounds have attracted a great deal of attention, as they can serve as versatile intermediates in organic synthesis.[1,2] In view of the growing interest in *gem*-organodimetallics, novel selective synthetic methods should be of great significance. Olefins bearing both silyl and boryl groups are useful starting materials in organic synthesis and combine the synthetic potential of both functionalities.[3–6] 1-(Silyl)-1-(boryl)alkenes are usually prepared via hydroboration of silylalkynes, for which a number of selective systems have been described.[7,8] However, the synthesis of 1-(silyl)-1-(boryl)ethenes is not possible by this method.[9] Recently, the selective synthesis of 1-(silyl)-1-(boryl)ethenes via geminal dimetallation of alkylidene type carbenoids with silylboranes was reported.[10,11] Although the reaction leads to moderate to high yields of products, the procedure involves the use of highly volatile and harmful vinyl derivatives and reactive organolithium compounds in stoichiometric amounts.

In the last 15 years we have developed two new catalytic reactions, which occur between the same parent substances that is silylative coupling (also called *trans*-silylation or silyl group transfer) and cross-metathesis of alkenes with vinylsilanes, which have provided a universal route for the synthesis of well defined molecular and macromolecular compounds possessing a vinylsilicon functionality. While the cross-metathesis is catalyzed by Ru and Mo carbene complexes, the silylative coupling is catalyzed by complexes containing or generating M–H or M–Si bonds (where M = Ru, Rh, Ir).[12] Our examination of the silylative coupling of vinylsilanes with styrenes and other vinyl derivatives, including those containing heteroatoms, has led to selective syntheses of a variety of vinylsilanes containing various functional groups[12] (Eq. 1).



R = alkyl, aryl, alkoxyl, siloxyl
R' = alkyl, aryl, amide, amine, OR"

(1)

Our recent examples of the new synthetic route, based on the silylative coupling reaction, included functionalization of cyclosiloxanes, cyclosilazanes and silsesquioxanes.[13–15]

We now report a new convenient method for the selective synthesis of 1-(silyl)-1-(boryl)ethenes via a one-step catalytic process. When trisubstituted vinylsilanes bearing methyl- and/or phenyl-substituents are treated with 2 equiv of vinylboranes in the presence of ruthenium

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Keywords: Silylative coupling; Vinylsilanes; Vinylboranes; Ruthenium complexes.

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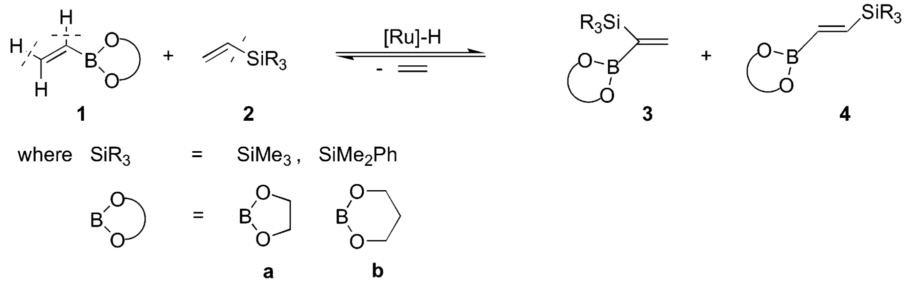
hydride complexes (1 mol%), high conversion of the silane and formation of *E*-1-(silyl)-2-(boryl)alkenes, 1-(silyl)-1-(boryl)ethenes and ethylene is observed (Eq. 2).



(2)

The reaction did not occur when alkoxysubstituted vinylsilanes were used. Since vinylsilanes were found to be active in homo-coupling (disproportionation),[12] the vinylboranes were used in excess. Thus, it was possible to minimize the role of competitive vinylsilane homocoupling. Ruthenium hydride complexes $RuHCl(CO)(PPh_3)_3$ (**I**) and $RuHCl(CO)(PCy_3)_2$ (**II**), known to be active in silylative coupling of vinylsilanes with olefins were tested in this process. No conversion was observed in the presence of the Grubbs type ruthenium carbene complexes for all the vinylsilanes tested. The results are compiled in Table 1. Outstanding catalytic activity was observed for the catalytic system containing $RuHCl(CO)(PCy_3)_2$ and CuCl in the molar ratio [Ru]/[Cu] = 1/5 (**III**). Such a catalytic system, which was reported to be a selective and efficient catalyst for silylation of styrenes and some other olefins with vinylsilanes,[16] remained active when performing the reaction at ambient temperature (Table 1, entries 3 and 8) and even at 0 °C (entries 5 and 10). At lower temperatures a significant increase in the regioselectivity of the process was observed, so that at ambient temperature (for $SiR_3 = SiMe_3$) or at 0 °C (for $SiR_3 = SiMe_2Ph$) selective transformations were possible. Under optimal conditions the yield of 1-(silyl)-1-(boryl)ethenes was essentially equal to the conversion of the vinylsilane. No reaction was observed at ambient temperature in the presence of catalysts **I** or **II**.

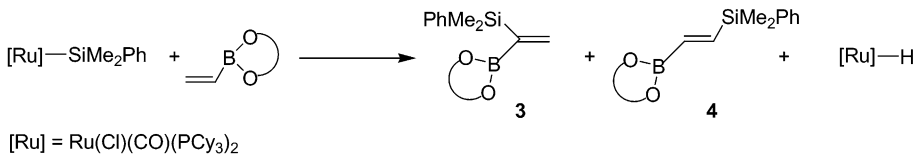
All products were isolated[18] and characterized spectroscopically.[19] DEPT analysis was used to confirm the formation of *gem*-disubstituted ethenes.

On the basis of the results obtained and our previous reports on the silylative coupling of vinylsilanes with olefins[12] an insertion–elimination mechanism is postulated for the process (Scheme 1).

The formation of the catalytically active Ru–H intermediate proceeds via decoordination of a PCy_3 group from the catalyst precursor. Phosphine decoordination is strongly accelerated by the addition of CuCl to the reaction mixture.[20] Insertion of the vinylsilane into the Ru–H bond, migration of the silyl group to the metal and elimination of ethylene lead to the formation of the ruthenium silyl complex. The reversible insertion of vinylsilane into the ruthenium–hydride bond as reported by Wakatsuki et al. for analogous systems[21] provides evidence for half of the catalytic cycle.

Insertion of vinylborane into the Ru–Si bond can be realized in two ways, leading to two different intermediate complexes **A** and **B**. The β-H migration to ruthenium in complexes **A** and **B** leads to the formation of *E*-1-(silyl)-2-(boryl)ethene and 1-(silyl)-1-(boryl)ethene, respectively. Under milder conditions, the reaction pathway proceeding via intermediate **B** starts to dominate and at ambient temperature (for $SiR_3 = SiMe_3$) or at 0 °C (for $SiR_3 = SiMe_2Ph$) the reaction proceeds with complete regioselectivity. In order to provide evidence for the stoichiometric insertion of vinylboranes into the Ru–Si bond, ruthenium dimethylphenylsilyl complex $Ru(SiMe_2Ph)(Cl)(CO)(PCy_3)_2$[22] was synthesized and tested in stoichiometric reactions with vinylboranes.[23,24]

Analysis of the reaction mixture by ^1H NMR spectroscopy and GC–MS revealed the formation of silylborylethenes (isomers **3** and **4**) (Eq. 3).



(3)

Analogous reactions performed in the presence of CuCl ([Ru]/[Cu] = 1/5) at 0 °C led to the exclusive formation of **3**. Although no ruthenium hydride complex was observed by ^1H NMR spectroscopy in this stoichiometric test, the experiment strongly supports the concept of vinylborane insertion (silyl group transfer) and consequently the insertion–elimination mechanism (Scheme 1).

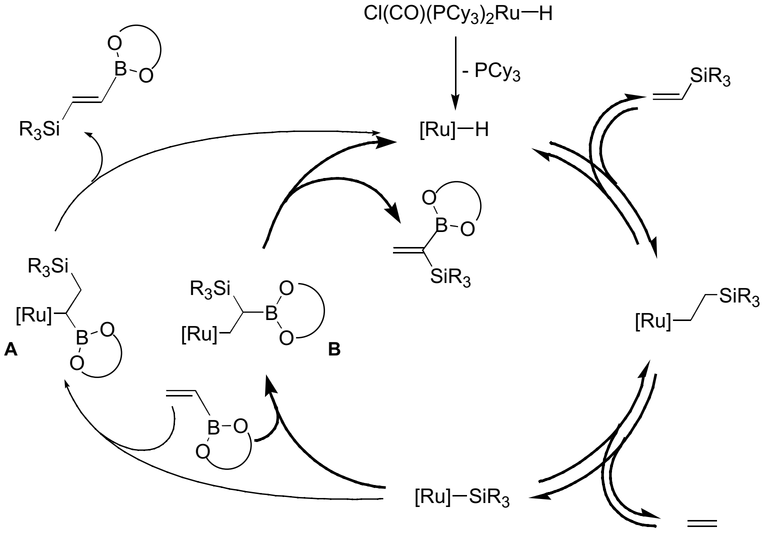
Table 1. Silylative coupling of vinylsilanes with 2-vinyl-[1,3,2]dioxaborolane **1a** and 2-vinyl-[1,3,2]dioxaborinane **1b**[17]

Entry	Vinylborane	Vinylsilane SiR_3	Cat.	Temp/time (°C)/(h)	Conv. of vinylsilane[a] (%)	Molar ratio[b] **3/4**	Isolated yield of **3**[18] (%)
1	**1a**	$SiMe_3$	**I**	80/24	20	50/50	
2	**1a**	$SiMe_3$	**II**	80/1	90	30/70	
3	**1a**	$SiMe_3$	**III**	20/5	80	100/0	65
4	**1a**	$SiMe_3$	**III**	80/1	100	30/70	
5	**1a**	$SiMe_2Ph$	**III**	0/1	100	100/0	80
6	**1a**	$SiMe_2Ph$	**III**	40/1	100	45/55	
7	**1a**	$SiMe_2Ph$	**III**	80/1	100	40/60	
8	**1b**	$SiMe_3$	**III**	20/5	90	100/0	75
9	**1b**	$SiMe_3$	**III**	80/1	100	50/50	
10	**1b**	$SiMe_2Ph$	**III**	0/1	100	100/0	85
11	**1b**	$SiMe_2Ph$	**III**	40/1	100	50/50	
12	**1b**	$SiMe_2Ph$	**III**	80/1	100	50/50	

Reaction conditions: [Ru]:[vinylsilane]:[vinylborane] = 10^{-2}:1:2, benzene, argon.

[a] Determined by GC.

[b] Determined by ^1H NMR spectroscopy.



Scheme 1.

In conclusion, a general and highly selective method for the synthesis of 1-(silyl)-1-(boryl)ethenes via cross-coupling of vinyl-substituted silanes with vinylboranes in the presence of the ruthenium-hydride catalyst $[RuH(Cl)(CO)(PCy_3)_2]$/CuCl is described. The reaction offers a new, interesting route to unsaturated organo(boro)silicon compounds, which are potentially attractive in organic synthesis.

Acknowledgement

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17. *General procedure for the catalytic reactions*: An oven dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with benzene (3 mL), dodecane (internal standard), vinylsilane (2.10 mmol) and the respective vinylborane (4.50 mmol). The reaction mixture was heated (or cooled) to the required temperature, after which the ruthenium hydride complex RuH(Cl)(CO)(PCy$_3$)$_2$ (0.02 mmol) and CuCl (0.10 mmol) were added. The reaction progress was monitored by GC. Analyses were made before adding the catalyst and every hour thereafter for the duration of the reaction. The extent of conversion of the substrates was calculated using the internal standard method.
18. *Representative procedure for the synthesis of 1-(silyl)-1-(boryl)ethenes*: An oven dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with benzene (20 mL), dodecane, vinylsilane (0.022 mol) and vinylborane (0.045 mol). Then RuH(Cl)(CO)(PCy$_3$)$_2$ (0.22 mmol) and CuCl (1.1 mmol) were added (at ambient temp or at 0 °C) and the reaction was carried out for 2 h. The catalyst was removed via column chromatography and products were isolated by vacuum distillation (yields are included in Table 1).
19. *Spectroscopic data of selected new products*: *2-[1-(dimethylphenylsilyl)vinyl]-[1,3,2]dioxaborinane*. ^{1}H NMR (300 MHz, C_6D_6, ppm), 0.55 (s, 6H, SiMe); 1.07–1.11 (m, 2H, CH_2), 3.44 (t, $J = 5.5$ Hz, 4H, CH_2O), 6.33 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.06 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.23–7.31 (m, 3H, Ph), 7.67–7.70 (m, 2H, Ph); ^{13}C NMR (75 MHz, C_6D_6): −1.7 (SiMe), 27.4 (CH_2), 61.6 (CH_2O), 134.6, 128.9, 128.3 (Ph), 139.8 (C_i), 144.5 ($=CH_2$) 157.6 ($=C$); MS (EI) *m/z* (rel. int.): 246 (M^+, 3%), 232 (19), 231 (100), 230 (9), 203 (9), 169 (21), 161 (11), 151 (6), 143 (11), 135 (7); 121 (7), 105 (7), 53 (6).

    2-[1-(Dimethylphenylsilyl)vinyl]-[1,3,2]dioxaborolane. ^{1}H NMR (C_6D_6, ppm), 0.51 (s, 6H, SiMe), 3.49 (s, 4H, CH_2O), 6.35 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.05 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.16–7.26 (m, 3H, Ph), 7.60–7.68 (m, 2H, Ph); ^{13}C NMR (C_6D_6): −1.68 (SiMe), 66.0 (CH_2O), 134.9, 129.6, 128.8 (Ph), 139.3 (C_i), 147.9 ($=CH_2$), 156.8 ($=C$); MS (EI) *m/z* (rel. int.): 232 (M^+, 5%), 217 (100), 216 (28), 204 (32), 189 (48), 188 (15), 175 (14), 173 (27), 163 (16), 155 (20), 135 (34), 130 (16), 121 (24), 119 (10), 105 (17), 53 (11), 45 (9).

    2-[1-(Trimethylsilyl)vinyl]-[1,3,2]dioxaborinane. ^{1}H NMR (C_6D_6, ppm), 0.34 (s, 9H, SiMe), 1.13–1.24 (m, 2H, CH_2), 3.51 (t, $J = 5.4$ Hz, 4H, CH_2O), 6.38 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.02 (d, $J = 5.7$ Hz, 1H, $=CH$); ^{13}C NMR (C_6D_6): −0.7 (SiMe), 27.3 (CH_2), 61.5 (CH_2O), 142.6 ($=CH_2$), 158.1 ($=C$); MS (EI) *m/z* (rel. int.): 184 (M^+, 1%), 171 (8), 170 (16), 169 (100), 168 (19), 143 (6), 141 (33), 127 (17), 101 (12), 99 (28), 83 (10), 75 (8), 69 (9), 59(6), 45 (9).

    2-[1-(Trimethylsilyl)vinyl-[1,3,2]dioxaborolane. ^{1}H NMR (C_6D_6, ppm): 0.27 (s, 9H, SiMe), 3.65 (s, 4H, CH_2O), 6.37 (d, $J = 5.7$ Hz, 1H, $=CH$), 7.00 (d, $J = 5.7$ Hz, 1H, $=CH$); ^{13}C NMR (C_6D_6):−0.9 (SiMe), 65.5 (CH_2O), 145.6 ($=CH_2$), 158.5 ($=C$); MS (EI) *m/z* (rel. int.): 170 (M^+, 1%), 156 (14), 155 (100), 154 (32), 127 (20), 126 (7), 111 (26), 110 (7), 101 (6),73 (6), 59 (8), 45 (8).
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23. In an NMR tube 0.001 g (1.16×10^{-5} mol) of Ru(SiMe$_2$Ph)(Cl)(CO)(PCy$_3$)$_2$, dodecane (internal standard) and 0.5 mL of C_6D_6 were placed under argon. Next, 2.6 μL (2.32×10^{-5} mol) of vinyldioxaborinane was added and the reaction was monitored by ^{1}H NMR at room temp.
24. For analogous insertions of vinylsilane and styrene into Ru–Si bonds see: (a) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003–2004; (b) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320–4326.