## **Ruthenium(II) Complex Catalyzed O-Borylation of Alcohols with Vinylboronates**

Bogdan Marciniec,\* Jędrzej Walkowiak

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland Fax +48(61)8291508; E-mail: marcinb@amu.edu.pl

Received 28 May 2009

**Abstract:** A new, highly effective method for the selective synthesis of boryl ethers via O-borylation of alcohols with vinylboronates catalyzed by the Ru-H complexes  $[Ru(CO)ClH(PPh_3)_3]$  and  $[Ru(CO)ClH(PCy_3)_2]$  is described. The mechanism of catalysis of this new de-ethenative borylation is supported by equimolar reaction of Ru–B complex with alcohol.

**Key words:** homogeneous catalysis, vinylboronates, ruthenium, coupling reactions, boryl ethers

The silylative coupling of olefins with vinyl-silicon compounds, which we have developed over the last two decades, generally takes place in the presence of complexes (Ru, Rh, Ir) containing or generating M–H and M–Si (silicometallics) bonds, and has become a very valuable synthetic tool for the preparation of vinyl-substituted organosilicon reagents and polymers.<sup>1</sup> However, we have recently found that this mode of reactivity is general and also exhibited by vinyl derivatives of other p-block elements, for example boron<sup>2</sup> and germanium.<sup>3</sup> It has also been extended to catalytic activation by such vinylmetalloids (mainly vinylsilicon) as  $\equiv C_{sp}$ -H,<sup>4</sup> =  $C_{Ar}$ -H<sup>5</sup> and even the O–H bond of alcohols<sup>6</sup> and silanols,<sup>7</sup> indicating a new general role of vinylmetalloids as metalloid agents and hydrogen acceptors.<sup>1a</sup>

O-Borylation of silanols with vinylboronates proceeding in the presence of a ruthenium complex, leads to the formation of boryl silyl ethers (borasiloxanes) with evolution of ethylene (Equation 1).<sup>8</sup>





The aim of this work was to make use of the new role of vinyl-boronates as hydrogen acceptors in the O-borylation of alcohols, which can be useful in borylation strategies because the boryl group is suitable for the protection

SYNLETT 2009, No. 15, pp 2433–2436 Advanced online publication: 27.08.2009 DOI: 10.1055/s-0029-1217732; Art ID: G18409ST © Georg Thieme Verlag Stuttgart · New York of alcohols owing to its thermal stability.<sup>9</sup> On the other hand, boronic esters have been attractive intermediates in the synthesis of organic derivatives containing B–C bonds, which are of great importance in Suzuki transformations.<sup>10</sup> Alkoxyboranes are also used in the synthesis of nanocomposites and nanotubes.<sup>11</sup>

For this reason, a variety of O-borylation methods have been developed for preparing boryl ethers via esterification.<sup>12</sup> Those processes are, however, restricted by the necessity to remove water, and by the instability of the substrates in when contact with moisture. Common methods used for preparing boryl ethers involve reactions of chloroboranes as well as boranes or sodium tetraborohydrides with alcohols, however, under these conditions, corrosive HCl or explosive H<sub>2</sub> are evolved respectively.<sup>13</sup>

Herein, we present a new catalytic reaction that involves activation of the O–H bond of alcohols by vinylboronates. The reaction occurs in the presence of ruthenium-hydride complexes, yielding boryl ethers with elimination of ethylene (Equation 2).

Equation 2

The borylation reactions were first examined in the presence of  $[Ru(CO)ClH(PCy_3)_2]$  (I), which is known to be the most active catalyst for metallative coupling of olefins and alkynes by vinylsilanes,<sup>1,4</sup> vinylgermanes<sup>3,4b,c</sup> and vinylboronates<sup>2</sup> in both open and closed (sealed ampoules) systems in toluene (60–80 °C, under argon).

A two or three-fold excess of vinylboronate was used to achieve either quantitative or very high yields of the boryl ethers. Under such conditions, a competitive homo-coupling of the vinylboronates was observed to give bis(boryl)ethenes as by-products (Equation 3 and Table 1). The latter could be effectively separated by column chromatography.

In order to eliminate formation of the side-product, another catalyst  $[Ru(CO)ClH(PPh_3)_3]$  (**II**) was used, which has been recently recognized to be inactive in the homo-coupling of vinylboronates.<sup>2a</sup> Under such conditions, the above process leads to the exclusive formation of boryl ethers, without any vinylboronate homo-coupling products (Table 2).



## **Equation 3**

**Table 1**O-Borylation of Alcohols with 2-Vinyl-1,3-dioxaborinane,Catalyzed by  $[Ru(CO)ClH(PCy_3)_2]$ 

Entry	Alcohol <sup>a</sup>	Conversion of alcohol (%) <sup>b</sup>	Selectivity A/B (%) <sup>b</sup>
1	ОН	100	83:17
2	С	82	76:24
3	С	85	82:18
4	OH OH	56	88:12

<sup>a</sup> Reaction conditions: [Ru]:[ROH]:[B] =  $2 \times 10^{-2}$ :1:3, toluene (0.5M), 24 h, 80 °C; [Ru] = [Ru(CO)ClH(PCy\_3)\_2].

<sup>b</sup> Determined by GC and GC-MS.

In some cases, O-borylation of alcohols by vinylboronates proceeded quantitatively and many of the boryl ethers were isolated and characterized spectroscopically (<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>11</sup>B NMR, GC-MS); unisolated compounds were identified by GC-MS spectroscopy.<sup>14</sup> It is interesting to note that, in the reaction of vinylboronate with pent-4-en-1-ol (entry 7), the product of O-borylation was obtained exclusively and no trace of the *trans*-alkene borylation product was observed.

The same reaction with allyl alcohol (entry 8) did not proceed at all, presumably because the strong simultaneous  $\pi$ -allyl and O–H interaction of the substrate with the ruthenium center blocks the subsequent possible reactions of *trans*- vs. O-borylation.

On the basis of the results obtained here and on our previous reports on Ru-H catalyzed metallation of alkenes, alkynes and silanols by vinylsilanes, vinylgermanes and vinylboronates, the insertion-elimination mechanism of catalysis is also proposed for this new process. While the insertion of vinylboronates into ruthenium-hydride bond has already been reported,<sup>2a</sup> in order to provide evidence for the second-half of the catalytic cycle, a stoichiometric reaction of alcohol with the ruthenium-boryl complex was examined. Thus, the reaction of equimolar amounts complex of the ruthenium-boryl  $[Ru(BO_2C_6H_4)(CO)Cl(PCy_3)_2]$  (III) (prepared according) to the previously reported procedure<sup>2,15</sup>) and cyclohexanol, was carried out at 60 °C and the progress of the reaction was monitored by <sup>1</sup>H NMR and GC-MS.<sup>16</sup>

 Table 2
 O-Borylation of Alcohols with 2-Vinyl-1,3-dioxaborinane

 Catalyzed by [Ru(CO)ClH(PPh\_3)\_3]

Entry	ROH	Molar ratio [ROH]:[B] <sup>a</sup>	Conversion of alcohol (%) <sup>c</sup>	Isolated yield (%)
1	ОН	1:3	100	
2		1:2	100	78
3		1:2 <sup>b</sup>	96	
4		1:1.5	93	
5	ОН	1:3	100	71
6	он	1:3	98	75
7	OH	1:3	84	-
8	ОН	1:3	0	-
9	—ОН	1:3	100	67
10	—	1:2	99	
11		1:2 <sup>b</sup>	98	_
12		1:1.5	87	-
13	ОН	1:5	82	58
14		1:3	70	-
15		1:3 <sup>b</sup>	53	
16	С	1:5	88	61
17		1:3	76	-
18		1:3 <sup>b</sup>	72	
19	ОН	1:5	54	
20	0	1:3	48	
21	NCOH	1:3	100	73

<sup>a</sup> Reaction conditions: [Ru-H]:[ROH] =  $2 \times 10^{-2}$ :1, toluene (0.5 M), 80 °C; [Ru-H] = [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>].

<sup>b</sup> Reaction conducted at 60 °C.

<sup>c</sup> Determined by GC and GC-MS.



Figure 1 <sup>1</sup>H NMR spectrum of the stoichiometric reaction of complex (III) with cyclohexan-1-ol: a) after 2 h; b) after 24 h.

After 24 hours, the <sup>1</sup>H NMR spectra confirmed the formation of the Ru-H complex (triplet signal  $\delta = -24.3$  ppm,  $J_{\text{H-P}} = 20.3$  Hz) of high intensity and a still weak triplet at  $\delta = -5.09$  ppm (Figure 1b).

While the former signal provides evidence for recovery of the Ru-H complex (I), the latter can be attributed to the Ru(IV)-H bond of the intermediate formed by the oxidative addition of the alcohol to Ru–B bond [with formation of (RO)Ru(IV)–H bond].

During the stoichiometric reaction, the color of the reaction mixture changed from pale-yellow [the rutheniumboryl complex (**III**)], through blue [Ru(IV)-H complex, after 2 h], to yellow-greenish [Ru(II)-H (**I**), after 24 h].

According to the spectroscopic literature data on hydride complexes of ruthenium, including also alkoxy and aryloxy ligands,<sup>17</sup> higher oxidation states of ruthenium in such hydride complexes lead to an increase in the value of <sup>1</sup>H NMR chemical shifts of the corresponding proton. Electron-accepting alkoxy substituents in Ru(IV)-H complexes are also responsible for downfield-shifting the Ru-H <sup>1</sup>H NMR signal.

Therefore, the stoichiometric reaction provides convincing evidence for the proposed mechanism of oxidative addition of the alcohol to ruthenium–boron bonds, followed by reductive elimination of the boryl ether and regeneration of the Ru-H complex (Scheme 1).

In conclusion, we have developed a new catalytic route for O-borylation of alcohols with vinylboronates in which vinylboronate acts as both borylating agent and hydrogen acceptor, to form boryl ether with evolution of ethylene. Further applications of this protocol to the borylation (metallation) of other heteroatom–hydrogen bonds are under investigation.



Scheme 1 Proposed mechanism for the O-borylation reaction of alcohols with vinylbronates

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

## Acknowledgment

Financial support from the Ministry of Science and Higher Education (Poland); Grant PBZ KBN 118/T09/17 is gratefully acknowledged. J. W. wishes to acknowledge a grant from the Operational Programme for Human Resources, Action 8.2., co-financed by the EU European Social Fund and the Polish State.

## **References and Notes**

 For recent reviews, see: (a) Marciniec, B. Acc. Chem. Res. 2007, 40, 943. (b) Marciniec, B. Coord. Chem. Rev. 2005, 249, 2374.

- (2) (a) Marciniec, B.; Jankowska, M.; Pietraszuk, C. *Chem. Commun.* 2005, 663. (b) Jankowska, M.; Pietraszuk, C.; Marciniec, B.; Zaidlewicz, M. *Synlett* 2006, 1695.
- (3) (a) Marciniec, B.; Ławicka, H.; Majchrzak, M.; Kubicki, M.;
   Kownacki, I. *Chem. Eur. J.* **2006**, *12*, 244. (b) Marciniec,
   B.; Ławicka, H. *Appl. Organomet. Chem.* **2008**, *22*, 510.
- (4) (a) Marciniec, B.; Dudziec, B.; Kownacki, I. Angew. Chem. Int. Ed. 2006, 45, 8180. (b) Marciniec, B.; Ławicka, H.; Dudziec, B. Organometallics 2007, 26, 5188.
  (c) Marciniec, B.; Ławicka, H.; Dudziec, B. J. Organomet. Chem. 2008, 693, 235. (d) Dudziec, B.; Marciniec, B. Organometallics 2008, 27, 5598.
- (5) Kakiuchi, F.; Matsumoto, M.; Sonoda, M.; Fukuyama, T.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Chem. Lett.* 2000, 750.
- (6) (a) Park, J.-W.; Chang, H.-J.; Jun, Ch.-H. *Synlett* **2006**, 771.
  (b) Park, J.-W.; Jun, Ch.-H. *Org. Lett.* **2007**, *9*, 4073.
- (7) Marciniec, B.; Pawluć, P.; Hreczycho, G.; Macina, A.; Madalska, M. *Tetrahedron Lett.* **2008**, *49*, 1310.
- (8) Marciniec, B.; Walkowiak, J. Chem. Commun. 2008, 2695.
- (9) (a) Bell, N. J.; Cox, A. J.; Cameron, N. R.; Evans, J. S. O.; Marder, T. B.; Duin, M. A.; Elsevier, C. J.; Baucherel, X.; Tulloch, A. A. D.; Tooze, R. P. *Chem. Commun.* 2004, 1854. (b) Hoffmann, R. W.; Schafer, F.; Haeberlin, E.; Rhode, T.; Korber, K. *Synthesis* 2000, 2060. (c) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; John Wiley & Sons, Inc.: New York, 1999, 196.
- (10) (a) Baron, O.; Knochel, P. Angew. Chem. Int. Ed. 2005, 44, 3133. (b) Billingsley, K. L.; Buchwald, S. L. Angew. Chem. Int. Ed. 2008, 47, 4695. (c) Chan, K. L.; Watkins, S. E.; Mak, Ch. S. K.; McKiernan, M. J.; Towns, C. R.; Pascua, S. I.; Holmes, A. B. Chem. Commun. 2005, 5766.
  (d) Dudek, S. P.; Pouderoijen, M.; Abbel, R.; Schenning, A. P. H. J.; Meijer, E. W. J. Am. Chem. Soc. 2005, 127, 11763.
- (11) Oki, A.; Adams, L.; Luo, Z. Inorg. Chem. Commun. 2008, 11, 275.
- (12) Malkowsky, I. M.; Fröhlich, R.; Griesbach, U.; Pütter, H.; Waldvogel, S. R. Eur. J. Inorg. Chem. 2006, 1690.
- (13) (a) Alaviuhkola, T.; Bobacka, J.; Nissinen, M.; Rissanen, K.; Ivaska, A.; Pursiainen, J. *Chem. Eur. J.* 2005, *11*, 2071.
  (b) Pineschi, M.; Bertolini, F.; Crotti, P.; Macchia, F. *Org. Lett.* 2006, *8*, 2627.
- (14) O-Borylation of alcohols by vinylboronates; general procedure: The ruthenium catalyst [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>]
  (II) (2 mol%) was dissolved in toluene and placed in a glass ampoule. The reagents and dodecane as internal standard (5% by volume all components), alcohol (0.5 mmol) and

2-vinyl-1,3,2-dioxaborinane (1–2.5 mmol) were added and the ampoule was heated at 60–80 °C for 24 h. Alcohol conversion was determined by GC and GC-MS. 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; hexane– EtOAc).

**2-Butoxy-1,3-dioxaborinane**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.10$  (t, J = 7.2 Hz, 3H,  $CH_3$ ), 1.78 (q, J = 7.0 Hz, 2H,  $CH_2CH_3$ ), 1.92 (quin, J = 5.5 Hz, 2H, BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.16 (brH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.85 [t, J = 4.6 Hz, 2H,  $CH_2(CH_2)_2CH_3$ ], 4.03 (t, J = 5.5 Hz, 4H, BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 15.8$  (CH<sub>3</sub>), 20.3 (CH<sub>2</sub>CH<sub>3</sub>), 27.2 (BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 33.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 62.7 (BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 64.7 [BOCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]. <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>):  $\delta = 28.7$ . MS (EI): m/z (%) = 143 (1) [M<sup>+</sup> - 15], 129 (2), 115 (100), 103 (29), 85 (22), 71 (11), 56 (14). Anal. Calcd for C<sub>7</sub>H<sub>15</sub>BO<sub>3</sub>: C, 53.21; H, 9.57. Found: C, 53.01; H, 9.44.

**3-**(**1**',**3**',**2**'-**Dioxaborinan-2**'-**yloxy**)**propanonitrile:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.99$  (quin, J = 5.5 Hz, 2H, BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.60 (t, J = 6.0 Hz, 2H, CH<sub>2</sub>C≡N), 3.89 (t, J = 6.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>C=N), 4.03 (t, J = 5.5 Hz, 4H, BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta =$ 26.3 (CH<sub>2</sub>C=N), 27.1 (BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 57.9 (BOCH<sub>2</sub>CH<sub>2</sub>C=N), 62.8 (BOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 117.6 (C=N). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>):  $\delta = 28.7$ . MS (EI): m/z (%) = 156 (6) [M<sup>+</sup> + 1], 140 (7), 125 (10), 115 (100), 98 (25), 85 (23), 71 (10), 54 (28). Anal. Calcd for C<sub>6</sub>H<sub>10</sub>BNO<sub>3</sub>: C, 58.74; H, 9.31; N, 9.04. Found: C, 58.88; H, 9.23; N, 9.18.

- (15) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. Organometallics **1997**, *16*, 5499.
- (16) Experimental procedure for the stoichiometric experiment: In an NMR tube, [Ru(BO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>] (III) (10 mg, 0.012 mmol) and cyclohexan-1-ol (1.6 mg, 0.016 mmol) and toluene-d<sub>8</sub> (0.6 mL) were placed under argon. The reaction was carried out at 80 °C and monitored by <sup>1</sup>H NMR.
- (17) (a) Ferrnando-Miguel, G.; Wu, P.; Huffman, J. C.; Caulton, K. G. *New. J. Chem.* 2005, *29*, 193. (b) Jazzar, R. F. R.; Bhatia, P. H.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* 2003, *22*, 670. (c) Churchill, M. R.; Keil, K. M.; Bright, F. V.; Pandey, S.; Baker, G. A.; Keister, J. B. *Inorg. Chem.* 2000, *39*, 5807. (d) Burling, S.; Kociok-Kohn, G.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* 2005, *24*, 5868.

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.