



## New catalytic route to silylene–vinylene–boronate systems

Jędrzej Walkowiak, Bogdan Marciniak\*, Magdalena Jankowska–Wajda

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland

### ARTICLE INFO

#### Article history:

Received 19 January 2010

Accepted 17 February 2010

Available online 21 February 2010

#### Keywords:

Cross-coupling

Silyldiene

Vinylborane

Ruthenium complex

### ABSTRACT

Cross-coupling of divinylorganosilicon compounds with vinylboranes in the presence of complexes containing Ru–H bonds (preferably  $[\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2]$ ) leads to formation of borylfunctionalized dienes, which can be potentially used as monomers for polymerization reactions or reagents in Pd-catalyzed coupling. The influence of the catalyst, temperature, time and molar ratio of substrates and Ru-complex on the yields and selectivities of the obtained products were tested.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

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 (SC) or trans-silylation, which takes place in the presence of complexes containing or generating the M–H and M–Si (silicometallics) where  $M = \text{Ru}, \text{Rh}, \text{Ir}$  (for a recent review see [1,2]). This model of vinyl-silicon reactivity has been recently found to be general and also exhibited by vinyl derivatives of other p-block elements (e.g. vinylboronates [3] and vinylgermanes [4] and perhaps, vinyl derivatives of other p-block elements). The general scheme of this reaction occurring in the presence of the Ru–H complex is as follows [1–4]. (Fig. 1).

While silylative coupling of various olefins catalyzed by Ru–H complexes leads predominantly to *trans*-product accompanied by 1,1-*geminal* derivatives, trans-borylation of olefins gives exclusively a mixture of *E* + *Z* products [3,5]. Catalytic and mechanistic studies on heterocoupling of vinylsilanes with vinylboronates in the presence of ruthenium hydride catalyst show that the reaction occurs according to the silylative coupling mode i.e. vinylsilane was used as a silylative agent [5]. (Fig. 2).

However, under optimum conditions the reaction offers a selective route to 1-silyl-1-boryl(ethenes) which can be attractive intermediates in organic synthesis and precursors of advanced materials [5].

Borylsilyl substituted alkenes, dienes and alkynes play an important role in organic synthesis [6–10] because silyl and boryl moieties can be easily converted into other functional groups

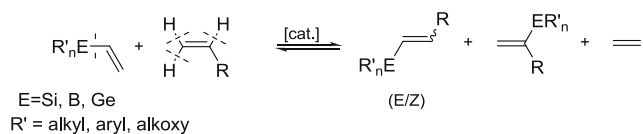
(halogen, aryl, alkenyl, hydroxyl) via demetallation processes, with a special inclusion of palladium catalyzed coupling reactions based on the formation of the new C–C bonds (Suzuki, Hiyama couplings). This unsymmetrical functionalization opens the possibility for selective replacement of one of the metalloids groups with retention of the other and the use of the latter for further functionalization in a different process. The compounds obtained having two boryl groups in terminal positions can be used as monomers in many types of polymerization, for example polycondensation with polyols or via Suzuki coupling with organodiodides giving products of different kinds. Organometallic compounds, which contain silicon and boron atom are used as precursors for special materials and ceramics, because the presence of these atoms has a significant influence on mechanical, thermal and chemical resistance of these new materials. Such polymers depending on the structure have different applications (for example as photosensitisers) [11].

In this paper we report catalytic transformations of vinylboranes (2-vinyl-1,3,2-dioxaborinane and 2-vinyl-1,3,2-dioxaborolane) with divinylsubstituted organosilicon compounds occurring especially in the presence of ruthenium complex containing the Ru–H bond  $[\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2]$ .

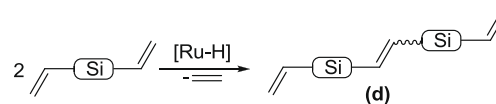
### 2. Results and discussion

The coupling reactions of vinylboranes with divinylsubstituted silicon compounds were examined particularly in the presence of  $[\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2]$  (2 mol%) which is well-known as the most effective catalyst in the silylative coupling reactions of vinylboranes with vinylsilanes [5] and trans-borylation process [3]. A range of catalytic tests of the silylative coupling reaction of divinylsilicon compounds with vinylboranes were carried out using

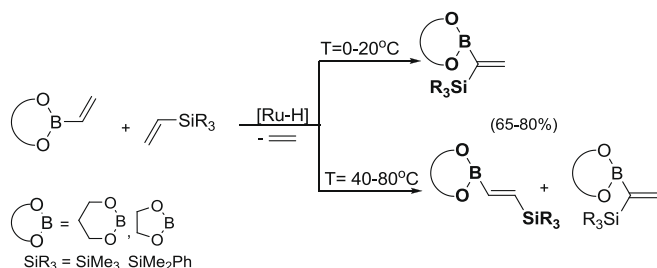
\* Corresponding author. Tel.: +48 61 8291 366; fax: +48 61 8291 508.  
E-mail address: [bogdan.marciniak@amu.edu.pl](mailto:bogdan.marciniak@amu.edu.pl) (B. Marciniak).



**Fig. 1.** General scheme of trans-metallation reaction of vinylmetalloids with olefins.



**Fig. 4.** Homocoupling of divinyl substituted organosilicon compounds – the side reaction.



**Fig. 2.** Silylative coupling of vinylboranes with vinylsilanes.

ruthenium(II) complexes: [Ru(CO)ClH(PCy<sub>3</sub>)<sub>2</sub>] and [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>] as catalysts. The model substrates were methylphenyl-divinylsilane and tetramethyldivinylsiloxane for which the optimizations of the process were performed. (Fig. 3).

The side reaction of homocoupling of divinylsilicon compounds was also detected in some processes (product (d)), but only if high concentration of Ru catalyst was used (see Fig. 4). However, we did not observe polymerization of divinylsilicon compounds via silylative coupling reaction under the conditions studied.

The effects of the kind of catalyst and its amount, temperature, time and molar ratio of reagents were examined.

The activity of ruthenium complex with tricyclohexylphosphine was much higher than for the [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>] complex, which was in agreement with the previously presented results of the silylative coupling of vinylsilanes with vinylboranes [5]. The molar ratios of substrates and catalyst also had great influence on the conversion of silane and the selectivity of these processes. 2 mol% of the catalyst was found as the optimal amount for effective trans-silylation. These conditions ensure high conversion of substrates and the lack of side-products of homocoupling of silicon compounds. Lower concentration of the catalyst did not provide the high reagents conversion. On the other hand, in the presence of 5 molar% of ruthenium complex more side-products (d) of the divinylsilicon coupling were obtained, up to 15% of all products.

The regioselectivity of the silylative coupling of vinylboranes with divinylsilicon compounds depends on temperature. The effect of high temperature of the process on the formation of 1-boryl-1-silyl or 1-boryl-2-silyl substituted ethenes was previously reported [5]. If the reaction is carried out at room temperature, the formation of 1,1-isomer increases. At elevated temperatures the yields are higher, whereas the selectivity is lower (higher amount of

1,2-isomer). When tetraethoxydivinylsiloxane and tetramethyldivinylsilazane were used as reagents in the silylative coupling reaction, only isomers with *trans* configuration of all double bonds were obtained as products.

The presence of geminal isomers in the reaction mixture proves that the reaction proceeds via silylative coupling reaction, with activation of the Si–C bond in vinylsilane and the C–H bond in vinylborane. We have previously reported that in the borylative coupling only 1,2-disubstituted ethenes were formed [3].

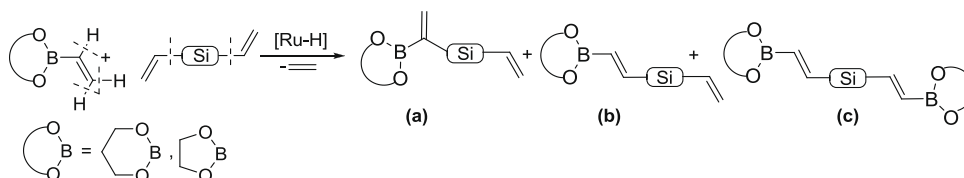
We also observed that the conversions and selectivities of the reactions were lower when 2-vinyl-1,3-dioxaborolane was used instead of 2-vinyl-1,3-dioxaborinane, which can be explained by the fact, that the reactions with five-member ring were conducted in closed system. Ethylene was not removed from the reaction environment and the equilibrium was shifted to the substrates.

Some of the borylsilyl dienes were isolated and characterized spectroscopically (<sup>1</sup>H, <sup>13</sup>C, NMR and GC–MS). Unisolated compounds were identified by GC–MS spectroscopy.

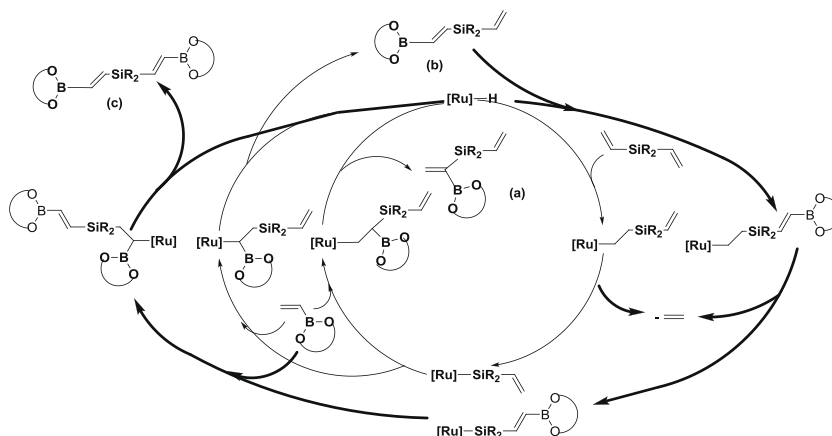
The cross-coupling of divinylsilicon compound with vinylborane involves insertion of vinylsilane into the Ru–H bond followed by β-Si elimination of ethylene and migratory insertion of vinylborane into the Ru–Si bond. The last step of the mechanism is the β-H elimination of silylboryldiene and regeneration of the Ru–H bond. The product obtained, which contains the second unsubstituted vinyl group, undergoes insertion into the regenerated Ru–H bond. The mechanism was previously proved for Ru–H and Ru–Si catalyzed reaction of vinyltrisubstituted silanes with 2-vinyl-1,3,2-dioxaborinane [5].

The plane drawn cycle shows two routes of monoborylsubstituted silyldienes formation, where boryl and silyl atoms are linked to the same or to different carbon atoms. The formation of *geminal* or *trans* isomer is highly dependent on the temperature of the process. Room temperature favors the synthesis of *geminal* isomer. Elevated temperatures shifted the selectivity of the process to compound with *trans* configuration. High temperatures have also positive influence for the synthesis of diborylsubstituted silyldienes (the bolded cycle in the mechanism). In this case monoborylsubstituted silyldiene obtained in the first catalytic cycle is inserted into the Ru–H bond of the regenerated complex and then subsequent steps of the cycle are repeated giving bisborylsubstituted silyldiene as the final product (Scheme 1).

In conclusion, in the paper we report the catalytic activity of vinylboranes in silylative coupling reactions with divinylsilicon compounds catalyzed by Ru–H complexes. The products obtained can be potentially used as monomers for polymerization to obtain organic–inorganic hybrid polymers and precursors of new materials, especially ceramic or reagents in palladium catalyzed cross-coupling reactions.



**Fig. 3.** Silylative coupling of vinylboranes with divinyl substituted organosilicon compounds.



Scheme 1. Mechanism of the catalytic silylation of vinylborane with divinylsilicon compounds.

### 3. Experimental

#### 3.1. General methods

$^1\text{H}$  (300 MHz),  $^{13}\text{C}$  (75 MHz) spectra were recorded by using a Varian XL 300 MHz spectrometer with samples in a solution of  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$ ; chemical shifts are reported in ppm with reference to the residue portion solvent ( $\text{CH}_2\text{Cl}$ ) peak for  $^1\text{H}$  and  $^{13}\text{C}$ . Analytical GC analyses were performed by using a Varian Star 400CX with a DB-5 fused-silica capillary column (30 ml, 0.15 mm) and thermal-conductivity detector (TCD). Mass spectra of the substrates and products were obtained by GC–MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion-trap detector). Elemental analyses were carried out by using a VarioEL III system. Thin-layer chromatography (TLC) was carried out by using plates coated with 250 mm-thick silica gel (Aldrich and Merck), and the column chromatography was performed by using silica gel 60 (70–230 mesh; Fluka). Toluene was dried by distillation using sodium and hexane from sodium hydride. Liquid substrates were also dried and degassed by using bulb-to-bulb distillation. All of the reactions were carried out under a dry argon atmosphere. The chemicals were obtained from the following sources: toluene, dodecane and hexane were purchased from Fluka; ethyl acetate from POCH;  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  from Dr. Glaser, A.G. Basel. The organosilicon compounds were purchased from ABCR or Aldrich. The ruthenium complexes  $[\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2]$  and  $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$  were prepared according to literature [12]. Dichlorovinylborane was synthesized from trichloroborane and tributylvinyltin. 2-vinyl-1,3,2-dioxaborinane and 2-vinyl-1,3,2-dioxaborolane were synthesized according to literature procedures with some modifications [13,14].

#### 3.2. Representative procedure for synthesis by silylative coupling reactions

In a typical test, the ruthenium catalyst  $[\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2]$  or  $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$  (2 mol%) was dissolved in toluene and placed in a glass ampoule under argon. The reagents and dodecane as internal standard (5% by volume all components) used in appropriate molar ratios (see Tables 1 and 2) were added. The reaction was conducted in an opened or closed system (when 2-vinyl-1,3,2-dioxaborolane was used as substrate). Subsequently, the ampoule was heated at 25–80 °C and maintained at this temperature for 24 h. The progress of the reaction was monitored by GC and GC–MS. The conversion of reagents, chemoselectivity of the reactions and yields of products were calculated by using the internal standard method. After the reaction, the crude product was purified by

silica gel column chromatography with hexane ethyl acetate as eluent.

##### 3.2.1. 1-Methylphenylvinylsilyl-1-(1',3',2'-dioxaborinan-2'-yl)ethene (**1a**)

Complex  $\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2$  (25 mg, 0.034 mmol), toluene (3.4 mL), 2-vinyl-1,3,2-dioxaborinane (0.76 g, 6.8 mmol) and methylphenyldivinylsilane (0.29 g, 1.7 mmol) were placed in a glass ampoule under argon atmosphere at 25 °C for 24 h. The conversion of silane was 63% (GC). The crude product was isolated using silica gel column (hexane/ethyl acetate = 4/1 as eluent). 0.160 g (0.620 mmol) of the product (**1a**) were obtained with 37% isolated yield.


$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.68 (s, 3H,  $\text{SiCH}_3$ ), 1.11 (t, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.46 (q, 4H,  $\text{OCH}_2\text{CH}_2$ ), 5.9 (dd, 1H,  $J$  (H,H) = 3.8, 19.7 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.15 (dd, 1H,  $J$  (H,H) = 3.9, 14.7 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.45 (d, 1H,  $J$  (H,H) = 5.8 Hz,  $\text{HHC}=\text{CB}(\text{Si})$ ), 6.78 (dd, 1H,  $J$  (H,H) = 14.5, 20.1 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 7.07 (d, 1H,  $J$  (H,H) = 5.8 Hz,  $\text{HHC}=\text{CB}(\text{Si})$ ), 7.73 (t, 2H,  $\text{C}_6\text{H}_6$ ), 7.27 (m, 3H,  $\text{C}_6\text{H}_6$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): -3.5 ( $\text{SiCH}_3$ ) 27.4 ( $\text{OCH}_2\text{CH}_2$ ), 61.7 ( $\text{OCH}_2\text{CH}_2$ ), 128.4 ( $\text{C}_6\text{H}_5$ ), 128.9 ( $\text{C}_6\text{H}_5$ ), 131.0 ( $\text{C}_6\text{H}_5$ ) 133.4 ( $\text{C}_6\text{H}_5$ ), 135.2 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 137.9 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 145.8 ( $\text{CH}_2=\text{CB}(\text{Si})$ ) ppm; MS (EI) [ $m/z$  (%): 258( $\text{M}^+$ , 2), 243(100), 215(26), 201(18), 181(21), 163(51), 147(27), 121(70), 105(50), 87(30), 53(45), Elemental Anal. Calc. for  $\text{C}_{14}\text{H}_{19}\text{BO}_2\text{Si}$ : C, 65.12; H, 7.42. Found: C, 64.88; H 7.63%.

##### 3.2.2. (1E)-1-(methylphenylvinylsilyl)-2-(1',3',2'-dioxaborinan-2'-yl)ethene (**1b**)

Complex  $\text{Ru}(\text{CO})\text{ClH}(\text{PCy}_3)_2$  (25 mg, 0.034 mmol), toluene (3.0 mL), 2-vinyl-1,3,2-dioxaborinane (0.19 g, 1.7 mmol) and methylphenyldivinylsilane (0.29 g, 1.7 mmol) were placed in a glass ampoule under argon atmosphere at 80 °C for 48 h. The conversion of silane was 100% (GC). The crude product was isolated using silica gel column (hexane/ethyl acetate = 4/1 as eluent). 0.105 g (0.408 mmol) of the product (**1b**) were obtained with 24% isolated yield.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.61 (s, 3H,  $\text{SiCH}_3$ ), 1.15 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.42 (t, 4H,  $\text{OCH}_2\text{CH}_2$ ), 5.84 (dd, 1H,  $J$  (H,H) = 3.8, 19.7 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.11 (dd, 1H,  $J$  (H,H) = 3.8, 14.5 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.18 (d, 1H,  $J$  (H,H) = 19.5 Hz,  $\text{SiHC}=\text{CHB}$ ), 6.66 (dd, 1H,  $J$  (H,H) = 14.5, 20.1 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 7.11 (d, 1H,  $J$  (H,H) = 19.5 Hz,  $\text{SiHC}=\text{CB}$ ), 7.21 (m, 3H,  $\text{C}_6\text{H}_6$ ), 7.63 (m, 2H,  $\text{C}_6\text{H}_6$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): -3.4 ( $\text{SiCH}_3$ ) 27.5 ( $\text{OCH}_2\text{CH}_2$ ), 61.3 ( $\text{OCH}_2\text{CH}_2$ ), 128.5 ( $\text{C}_6\text{H}_5$ ), 130.2 ( $\text{C}_6\text{H}_5$ ), 131.3 ( $\text{C}_6\text{H}_5$ ) 133.8 ( $\text{C}_6\text{H}_5$ ), 135.2 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 138.4 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 143.3 ( $\text{SiCH}=\text{CHB}$ ) ppm; MS (EI) [ $m/z$  (%): 258( $\text{M}^+$ , 2), 243(100), 215(26), 201(18), 181(21), 163(51), 147(27),

**Table 1**  
Silylative coupling of 2-vinyl-1,3,2-dioxaborinane with divinylsubstituted organosilicon compounds.

(Si)	[cat]:(Si):[B]	T (°C)	Conversion of (Si) (%) <sup>a</sup>	Selectivity (a)/(b)/(c) (%) <sup>b</sup>	Isolated yield (%)
Me	$2 \times 10^{-2}$ :1:3 <sup>c</sup>	80	89	20/28/52	
Si	$2 \times 10^{-2}$ :1:4	100	100	2/21/77	
Ph	$10^{-2}$ :1:4	80	67	15/31/54	
	$2 \times 10^{-2}$ :1:4	80 <sup>d</sup>	100	4/25/71	24(1b) <sup>g</sup>
	$2 \times 10^{-2}$ :1:4 <sup>e</sup>	80	57	9/15/76	
	$5 \times 10^{-2}$ :1:4	80	100	2/12/74/12 <sup>f</sup>	
	$2 \times 10^{-2}$ :1:8	80	100	5/17/78	70(1c)
	$2 \times 10^{-2}$ :1:4	60	83	23/27/50	
	$2 \times 10^{-2}$ :1:4	25	63	67/24/9	37(1a)
Me	$2 \times 10^{-2}$ :1:4	80	100	4/33/63	55(2c)
Si					
Me					
		60	84	20/36/44	
Ph	$2 \times 10^{-2}$ :1:4	80	0	–	
Si					
Ph					
	$2 \times 10^{-2}$ :1:4	100	83	7/15/78	
Me Me	$2 \times 10^{-2}$ :1:4	100	86	2/28/70	
Si-O-Si					
Me Me					
	$2 \times 10^{-2}$ :1:3	80	63	14/27/59	
	$10^{-2}$ :1:4	80	53	10/35/55	
	$2 \times 10^{-2}$ :1:4	80	78	2/31/67	
	$2 \times 10^{-2}$ :1:4	80 <sup>d</sup>	86	4/27/69	49(4c)
	$2 \times 10^{-2}$ :1:4 <sup>e</sup>	80	44	5/32/63	
	$5 \times 10^{-2}$ :1:4	80	100	1/16/70/13 <sup>f</sup>	
	$2 \times 10^{-2}$ :1:4	60	57	17/28/55	
	$2 \times 10^{-2}$ :1:4	25	43	38/28/36	
OEt OEt	$2 \times 10^{-2}$ :1:4	80	71	0/30/70	45(5c)
Si-O-Si					
OEt OEt					
Me H Me	$2 \times 10^{-2}$ :1:4	80	90	0/92/8	
Si-N-Si					
Me Me					

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

<sup>b</sup> Determined by GC and <sup>1</sup>H NMR.

<sup>c</sup> t = 24 h, [Ru(CO)ClH(PCy<sub>3</sub>)<sub>2</sub>] unless otherwise stated.

<sup>d</sup> t = 48 h.

<sup>e</sup> [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>].

<sup>f</sup> Selectivity of a/b/c/d (%).

<sup>g</sup> The numeration of the isolated products described in Section 3 is given in brackets.

**Table 2**  
Silylative coupling of 2-vinyl-1,3,2-dioxaborolane with divinylsilicon compounds.

(Si)	T <sup>a</sup> (°C)	Conversion of (Si) (%) <sup>b</sup>	Selectivity <sup>c</sup> (a)/(b)/(c) (%)	Isolated yield (%)
Me	80	77	8/27/65	47 (7c) <sup>d</sup>
Si				
Ph	25	61	74/26/0	41 (7a)
	80	87	0/41/59	50 (8c)
Me				
Si	60	59	14/38/48	
Me				
Si-O-Si	80	93	3/29/68	59 (9c)
Me Me				
	25	36	37/39/24	
Me H Me	80	84	0/94/6	
Si-N-Si				
Me Me				

<sup>a</sup> Reaction conditions: [Ru]: [(Si)]:[B] =  $2 \times 10^{-2}$ :1:4; t = 24 h, [Ru] = [Ru(CO)ClH(PCy<sub>3</sub>)<sub>2</sub>], toluene (0.5 M), argon, closed system.

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

<sup>c</sup> Determined by GC and <sup>1</sup>H NMR.

<sup>d</sup> The numeration of isolated compounds described in Section 3 is given in brackets.

121(70), 105(50), 87(30), 53(45); Elemental Anal. Calc. for  $C_{14}H_{19}B_2O_2Si$ : C, 65.12; H, 7.42. Found: C, 65.75; H 7.78%.

### 3.2.3. Bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-yl]methylphenylsilane (**1c**)

Complex  $Ru(CO)ClH(PCy_3)_2$  (6.2 mg, 0.0085 mmol), toluene (1.0 mL), 2-vinyl-1,3,2-dioxaborinane (0.3 g, 3.4 mmol) and methylphenyldivinylsilane (0.075 g, 0.425 mmol) were placed in a glass ampoule under argon atmosphere at 80 °C for 24 h. The conversion of silane was 100% (GC). The crude product was isolated using silica gel column (hexane/ethyl acetate = 4/1 as eluent). 0.10 g (0.3 mmol) of the product (**1c**) were obtained with 70% isolated yield.

$^1H$  NMR (300 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 0.64 (s, 3H,  $SiCH_3$ ), 1.13 (m, 4H,  $OCH_2CH_2$ ), 3.46 (t, 8H,  $OCH_2CH_2$ ), 6.07 (d, 1H,  $J$  (H,H) = 19.5 Hz,  $SiHC=CHB$ ), 6.72 (d, 1H,  $J$  (H,H) = 19.6 Hz  $SiHC=CB$ ), 7.24 (m, 3H,  $C_6H_6$ ), 7.59 (m, 2H,  $C_6H_6$ ) ppm;  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ,  $\delta$ , ppm): -3.4 ( $Si(CH_3)_2$ ) 27.8 ( $OCH_2CH_2$ ), 61.0 ( $OCH_2CH_2$ ), 128.7 ( $C_6H_5$ ), 131.2 ( $C_6H_5$ ), 132.0 ( $C_6H_5$ ) 133.8 ( $C_6H_5$ ), 135.3 ( $Ph(Me)SiCH=CH$ ), 144.3 ( $SiCH=CHB$ ) ppm; MS (EI) [ $m/z$  (%): 258( $M^+$ , 2), 243(100), 215(26), 201(18), 181(21), 163(51), 147(27), 121(70), 105(50), 87(30), 53(45); Elemental Anal. Calc. for  $C_{17}H_{24}B_2O_4Si$ : C, 59.69; H, 7.07. Found: C 59.37; H 7.00%.

### 3.2.4. 1-Dimethylvinylsilyl-1-(1',3',2'-dioxaborinan-2'-yl)ethene (**2a**) and (E)-1-dimethylvinylsilyl-2-(1',3',2'-dioxaborinan-2'-yl)ethene (**2b**)

Complex  $Ru(CO)ClH(PCy_3)_2$  (25 mg, 0.034 mmol), toluene (3.4 mL), 2-vinyl-1,3,2-dioxaborinane (0.76 g, 6.8 mmol) and dimethyldivinylsilane (0.19 g, 1.7 mmol) were placed in a glass ampoule under argon atmosphere at 60 °C for 24 h. The conversion of dimethyldivinylsilane was 84% (GC).

(**2a**) MS (EI) [ $m/z$  (%): 196(49), 168(50) 138(62), 129(100), 119(32), 110(18) 89(32), 66 (50), 53(48).

(**2b**) MS (EI) [ $m/z$  (%): 181( $M^+$ -15, 100), 153(76), 139(62), 101(85) 85(38), 155(35) 59(56).

### 3.2.5. Bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-yl]dimethylsilane (**2c**)

Complex  $Ru(CO)ClH(PCy_3)_2$  (25 mg, 0.034 mmol), toluene (3.4 mL), 2-vinyl-1,3,2-dioxaborinane (0.76 g, 6.8 mmol) and dimethyldivinylsilane (0.19 g, 1.7 mmol) were placed in a glass ampoule under an argon atmosphere at 80 °C for 24 h. The conversion of dimethyldivinylsilane was 100% (GC). The crude product was isolated using silica gel column (hexane/ethyl acetate = 4/1 as eluent). 0.26 g (0.94 mmol) of the product (**2c**) were obtained with 55% isolated yield.

$^1H$  NMR (300 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 0.64 (s, 3H,  $SiCH_3$ ), 1.13 (m, 4H,  $OCH_2CH_2$ ), 3.46 (t, 8H,  $OCH_2CH_2$ ), 6.07 (d, 1H,  $J$  (H,H) = 19.5 Hz,  $SiHC=CHB$ ), 6.72 (d, 1H,  $J$  (H,H) = 19.6 Hz  $SiHC=CB$ ), 7.24 (m, 3H,  $C_6H_6$ ), 7.59 (m, 2H,  $C_6H_6$ ) ppm;  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ,  $\delta$ , ppm): -3.4 ( $Si(CH_3)_2$ ) 27.5 ( $OCH_2CH_2$ ), 61.3 ( $OCH_2CH_2$ ), 128.5 ( $C_6H_5$ ), 130.2 ( $C_6H_5$ ), 131.3 ( $C_6H_5$ ) 133.8 ( $C_6H_5$ ), 135.2 ( $Ph(Me)SiCH=CH_2$ ), 138.4 ( $Ph(Me)SiCH=CH_2$ ), 143.3 ( $SiCH=CHB$ ) ppm; MS (EI) [ $m/z$  (%): 342( $M^+$ , 10), 291(28), 267(8), 241(12), 207(32), 179(31), 147(63), 121(89), 105(29), 91(100), 77(12), 67(33)

Elemental Anal. Calc. for  $C_{12}H_{22}B_2O_4Si$ : C, 57.41; H, 7.92. Found: C, 57.57; H 7.90%.

### 3.2.6. 1,4-Bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-yl]dimethylsilyl benzene (**3c**)

Complex  $Ru(CO)ClH(PCy_3)_2$  (10 mg, 0.014 mmol), toluene (3.4 mL), 2-vinyl-1,3,2-dioxaborinane (0.31 g, 2.8 mmol) and bis(1,4-dimethylvinylsilyl)benzene (0.29 g, 0.69 mmol) were placed in a glass ampoule under argon atmosphere at 100 °C for

24 h. The conversion of 1,4-bis(dimethylvinylsilyl)benzene was 83% (GC).

MS (EI) [ $m/z$  (%): 399( $M^+$ -15, 100), 341(18), 281(15), 245(15), 207(20), 169(75), 141(35).

### 3.2.7. [(E)-2-(1',3',2'-Dioxaborinan-2'-yl)ethen-1-yl]tetramethylvinylidisiloxane (**4b**) and bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-yl]tetramethylidisiloxane (**4c**)

Compound (**4c**) was prepared from the appropriate starting materials according to the above procedure for **2c**. The conversion of the tetramethyldivinylidisiloxane was 86%. The reaction afforded (**4c**) (0.3 g, 0.83 mmol, isolated yield 49%).

(**4c**)  $^1H$  NMR (300 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 0.17 (s, 12H,  $SiCH_3$ ), 1.10 (m, 4H,  $OCH_2CH_2$ ), 3.40 (t, 8H,  $OCH_2CH_2$ ), 6.21 (d, 1H,  $J$  (H,H) = 19.8 Hz,  $SiHC=CHB$ ), 6.93 (d, 1H,  $J$  (H,H) = 19.8 Hz  $SiHC=CB$ ) ppm;  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 0.2 ( $Si(CH_3)_2$ ) 26.3 ( $OCH_2CH_2$ ), 61.1 ( $OCH_2CH_2$ ), 149.7 ( $BCH=CHSi$ ) ppm; MS (EI) [ $m/z$  (%): 339( $M^+$ -15, 37), 281(51), 253(30), 243(100), 215(69), 185(8), 173(19), 143(17), 73(7), 59(4); Elemental Anal. Calc. for  $C_{14}H_{28}B_2O_5Si_2$ : C, 47.48; H, 7.97. Found: C, 47.11; H, 7.57%.

(**4b**) MS (EI) [ $m/z$  (%): 255( $M^+$ -15, 49), 230(18), 227(100), 169(28), 173(49), 85(37) 73(21).

### 3.2.8. Bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-y]tetraethoxydisiloxane (**5c**)

Compound (**5c**) was prepared from the appropriate starting materials according to the above procedure for (**2c**). The conversion of the tetraethoxydivinylidisiloxane was 71%. The crude product was isolated using silica gel column modified with HMDS (hexane/ethyl acetate = 4/1 as eluent). The reaction afforded (**5c**) (0.37 g, 0.77 mmol, isolated yield 45%).

$^1H$  NMR (300 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 1.10 (m, 4H,  $BOCH_2CH_2$ ), 1.22 (t, 12H,  $J$  (H,H) = 6.8 Hz,  $SiOCH_2CH_3$ ), 3.36 (t, 8H,  $BOCH_2CH_2$ ), 3.87 (q, 8H,  $J$  (H,H) = 6.8 Hz,  $SiOCH_2CH_3$ ) 6.11 (d, 1H,  $J$  (H,H) = 19.9 Hz,  $SiHC=CHB$ ), 6.78 (d, 1H,  $J$  (H,H) = 20.1 Hz,  $SiHC=CB$ ) ppm;  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ,  $\delta$ , ppm): 18.8 ( $SiOCH_2CH_3$ ) 26.5 ( $BOCH_2CH_2$ ), 57.8 ( $SiOCH_2CH_3$ ), 61.5 ( $BOCH_2CH_2$ ), 151.2 ( $BCH=CHSi$ ) ppm; MS (EI) [ $m/z$  (%): 474( $M^+$ , 4), 445 (16), 416 (11), 392(4), 308(100), 293 (92), 225(34), 159(7), 133(7), 85(36), 73(38), 59(45); Elemental Anal. Calc. for  $C_{18}H_{36}B_2O_9Si_2$ : C, 45.58; H, 7.65. Found: C, 45.41; H, 7.46%.

### 3.2.9. [(E)-2-(1',3',2'-Dioxaborinan-2'-yl)ethen-1-yl]tetramethylvinyl-disilazane (**6b**) and bis[(E)-2-(1',3',2'-dioxaborinan-2'-yl)ethen-1-yl]tetramethyldisilazane (**6c**)

The mixture of compound (**6b**) and (**6c**) (**6b/6c** = 98/2) was prepared from the appropriate starting materials according to the above procedure for (**2c**). The conversion of tetramethyldivinyl-disilazane was 90%.

(**6b**) MS (EI) [ $m/z$  (%): 254 ( $M^+$ -15, 100), 226(66), 184(72), 172(28), 154(37), 130(19) 100(18), 73(12), 59(21).

(**6c**) MS (EI) [ $m/z$  (%): 313( $M^+$ -30, 7), 298(11), 255(59), 227(100), 217(100), 189(68), 169(78), 149(23), 133(38), 99(13), 75(21), 59(45).

### 3.2.10. 1-(Methylphenylvinylsilyl)-1-(1',3',2'-dioxaborolan-2'-yl)ethene (**7a**)

Complex  $Ru(CO)ClH(PCy_3)_2$  (15 mg, 0.021 mmol), toluene (2.2 mL), 2-vinyl-1,3,2-dioxaborolane (0.43 g, 4.4 mmol) and methylphenyldivinylsilane (0.18 g, 1.1 mmol) were placed and sealed in a glass ampoule under argon atmosphere at 25 °C for 24 h. The conversion of methylphenyldivinylsilane was 61% (GC). The crude product was isolated using silica gel column (hexane/ethyl acetate = 4/1 as eluent). 0.11 g (0.45 mmol) of the product (**7a**) were obtained with 41% isolated yield.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.65 (s, 3H,  $\text{SiCH}_3$ ), 3.48 (s, 4H,  $\text{CH}_2$ ), 5.83 (dd, 1H,  $J$  (H,H) = 3.8, 20.2 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.12 (dd, 1H,  $J$  (H,H) = 3.8, 14.4 Hz,  $\text{Ph}(\text{Me})\text{SiCH}=\text{CHH}$ ), 6.23 (d, 1H,  $J$  (H,H) = 5.2 Hz  $\text{HHC}=\text{CB}(\text{Si})$ ), 6.59 (dd, 1H,  $J$  (H,H) = 14.7, 20.2 Hz  $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 6.9 (d, 1H,  $J$  (H,H) = 5.2 Hz  $\text{HHC}=\text{CB}(\text{Si})$ ). 7.32 (m, 3H,  $\text{C}_6\text{H}_6$ ), 7.63 (t, 2H,  $\text{C}_6\text{H}_6$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): -3.89 ( $\text{SiCH}_3$ ), 65.6 ( $\text{OCH}_2$ ), 128.9 ( $\text{C}_6\text{H}_5$ ), 129.4 ( $\text{C}_6\text{H}_5$ ), 131.0 ( $\text{C}_6\text{H}_5$ ), 134.0 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 135.1 ( $\text{C}_6\text{H}_5$ ), 137.7 ( $\text{Ph}(\text{Me})\text{SiCH}=\text{CH}_2$ ), 148.7 ( $\text{CH}_2=\text{B}(\text{Si})$ ) ppm; MS (EI) [ $m/z$  (%): 229( $\text{M}^+-15$ , 72), 201(42), 147(47), 121(100), 77(24), 53(40); Elemental Anal. Calc. for  $\text{C}_{13}\text{H}_{17}\text{BO}_2\text{Si}$ : C, 63.95; H, 7.02. Found: C, 64.08; H, 7.22%.

### 3.2.11. Bis[(*E*)-2-(1',3',2'-dioxaborolan-2'-yl)ethen-1-yl]phenylmethylsilane (**7c**)

$\text{Ru}(\text{CO})\text{ClI}(\text{PCy}_3)_2$  complex (15 mg, 0.021 mmol), toluene (2.2 mL), 2-vinyl-1,3,2-dioxaborolane (0.43 g, 4.4 mmol) and methylphenyldivinylsilane (0.18 g, 1.1 mmol) were placed and sealed in a glass ampoule under argon atmosphere at 80 °C for 24 h. The conversion of methylphenyldivinylsilane was 77% (GC). The crude product was isolated using silica gel column (hexane/ethyl = 4/1 as eluent). 0.16 g (0.52 mmol) of the product (**7c**) were obtained with 47% isolated yield.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.60 (s, 3H,  $\text{SiCH}_3$ ), 3.53 (s, 8H,  $\text{OCH}_2$ ), 6.12 (d, 2H,  $J$  (H,H) = 19.9 Hz,  $\text{SiHC}=\text{CHB}$ ), 6.65 (d, 2H,  $J$  (H,H) = 20.0 Hz,  $\text{SiHC}=\text{CHB}$ ), 7.29 (m, 3H,  $\text{C}_6\text{H}_6$ ), 7.61 (m, 2H,  $\text{C}_6\text{H}_6$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): -3.6 ( $\text{Si}(\text{CH}_3)_2$ ), 65.3 ( $\text{OCH}_2$ ), 128.7 (m  $\text{C}_6\text{H}_5$ ), 130.3 (p  $\text{C}_6\text{H}_5$ ), 131.2 ( $\text{C}_6\text{H}_5$ ), 133.8 (o  $\text{C}_6\text{H}_5$ ), 145.6 ( $\text{SiCH}=\text{CHB}$ ) ppm; Elemental Anal. Calc. for  $\text{C}_{15}\text{H}_{20}\text{B}_2\text{O}_4\text{Si}$ : C, 57.37; H, 6.42. Found: C, 57.00; H, 6.52%.

### 3.2.12. 1-Dimethylvinylsilyl-1-(1',3',2'-dioxaborolan-2'-yl)ethene (**8a**) and (*E*)-1-dimethylvinylsilyl-2-(1',3',2'-dioxaborolan-2'-yl)ethene (**8b**)

Complex  $\text{Ru}(\text{CO})\text{ClI}(\text{PCy}_3)_2$  (15 mg, 0.021 mmol), toluene (2.2 mL), 2-vinyl-1,3,2-dioxaborolane (0.43 g, 4.4 mmol) and dimethyldivinylsilane (0.12 g, 1.1 mmol) were placed and sealed in a glass ampoule under argon atmosphere at 60 °C for 24 h. The conversion of methylphenyldivinylsilane was 59% (GC).

(**8a**) MS (EI) [ $m/z$  (%): 167( $\text{M}^+-15$ , 12), 153(5), 138(100), 123(25), 114(63), 89(59), 66(82), 54(70), 45(80).

(**8b**) MS (EI) [ $m/z$  (%): ( $\text{M}^+-15$ , 16), 129(52), 142(45), 127(20), 114(23), 96(65), 84(64), 67(100), 53(76), 45(77).

### 3.2.13. Bis[(*E*)-2-(1',3',2'-dioxaborolan-2'-yl)ethen-1-yl]dimethylsilane (**8c**)

Compound (**8c**) was prepared from the appropriate starting materials according to the above procedure for (**7c**). The dimethyldivinylsilane conversion was 87%. The reaction afforded (**8c**) (0.21 g, 0.83 mmol, isolated yield 50%).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.13 (s, 6H,  $\text{SiCH}_3$ ), 3.52 (s, 4H,  $\text{OCH}_2$ ), 6.16 (d, 2H,  $J$  (H,H) = 19.5 Hz,  $\text{SiHC}=\text{CHB}$ ), 6.76 (d, 2H,  $J$  (H,H) = 19.5 Hz  $\text{SiHC}=\text{CB}$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.2 ( $\text{Si}(\text{CH}_3)_2$ ), 64.8 ( $\text{OCH}_2$ ), 148.8 ( $\text{BCH}=\text{CHSi}$ ) ppm; MS (EI) [ $m/z$  (%): 237( $\text{M}^+-15$ , 3), 222 (13) 207(3), 166(16), 142(45), 138(55), 129(69), 96(65), 89(55), 67(100), 55(31), 45(77); Elemental Anal. Calc. for  $\text{C}_{10}\text{H}_{18}\text{B}_2\text{O}_4\text{Si}$ : C, 47.67; H, 7.20. Found: C, 47.54; H, 7.08%.

### 3.2.14. [1-(1',3',2'-Dioxaborolan-2'-yl)ethen-1-yl]tetramethylvinylsiloxane (**9a**) and [(*E*)-2-(1',3',2'-dioxaborolan-2'-yl)ethen-1-yl]tetramethylvinylsiloxane (**9b**)

The mixture of compound (**9a**) and (**9b**) was prepared from the appropriate starting materials according to the above procedure for (**7a**). The conversion of the dimethyldivinylsilane was 36%.

(**9a**) MS (EI) [ $m/z$  (%): 256( $\text{M}^+$ , 3), 241(100), 189(55), 153(64), 101(19), 85(25), 45(9).

(**9b**) MS (EI) [ $m/z$  (%): 241( $\text{M}^+-15$ , 100), 187(48), 155(75), 73(22), 45(20).

### 3.2.15. Bis[(*E*)-2-(1,3,2-dioxaborolan-2-yl)ethenyl]tetramethylsiloxane (**9c**)

Compound (**9c**) was prepared from the appropriate starting materials according to the above procedure for (**7c**). The conversion of the tetramethyldivinylsiloxane was 93%. The reaction afforded (**9c**) (0.33 g, 1 mmol, isolated yield 59%).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.15 (s, 12H,  $\text{SiCH}_3$ ), 3.60 (s, 8H,  $\text{CH}_2$ ), 6.15 (d, 2H,  $J$  (H,H) = 19.5 Hz,  $\text{SiHC}=\text{CHB}$ ), 6.86 (d, 2H,  $J$  (H,H) = 19.3 Hz  $\text{SiHC}=\text{CB}$ ) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm): 0.2 ( $\text{Si}(\text{CH}_3)_2$ ), 62.9 ( $\text{CH}_2$ ), 147.6 ( $\text{BCH}=\text{CHSi}$ ) ppm; MS (EI) [ $m/z$  (%): 311( $\text{M}^+-15$ , 50), 267(25), 229(100), 175(45), 143(40), 73(18), 45(10); Elemental Anal. Calc. for  $\text{C}_{12}\text{H}_{24}\text{B}_2\text{O}_5\text{Si}_2$ : C, 44.20; H, 7.42. Found C, 44.82; H, 7.70%.

### 3.2.16. [(*E*)-2-(1',3',2'-Dioxaborolan-2'-yl)ethen-1-yl]tetramethylvinylsilazne (**10b**) and bis[(*E*)-2-(1',3',2'-dioxaborolan-2'-yl)ethen-1-yl]tetramethylsilazane (**10c**)

The mixture of compounds (**10b**) and (**10c**) ((**10b**)/(**10c**) = 94/6) was prepared from the appropriate starting materials according to the above procedure for (**7c**).

(**10b**) MS (EI) [ $m/z$  (%): 240( $\text{M}^+-15$ , 27), 203(74), 187(26), 155(100), 131(30), 85(47), 59(45).

(**10c**) MS (EI) [ $m/z$  (%): 311( $\text{M}^++1$ , 46), 267(19), 229(100), 175(36), 143(35), 73(12), 45(14).

## Acknowledgement

This work was supported by the Ministry of Science and Higher Education (Poland) (N N204265538).

## References

- [1] B. Marciniec, Acc. Chem. Res. 40 (2007) 943–952.
- [2] B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374–2390.
- [3] B. Marciniec, M. Jankowska, C. Pietraszuk, Chem. Commun. (2005) 663–665.
- [4] (a) B. Marciniec, H. Ławicka, M. Majchrzak, M. Kubicki, I. Kownacki, Chem. Eur. J. 12 (2005) 244–250; (b) B. Marciniec, H. Ławicka, Appl. Organomet. Chem. 22 (2008) 510–515.
- [5] M. Jankowska, B. Marciniec, C. Pietraszuk, J. Cytańska, M. Zaidlewicz, Tetrahedron Lett. 45 (2004) 6615–6618.
- [6] L. Hevesi, in: A.R. Katritzky, O. Methcohn, C.W. Rees (Eds.), Comprehensive Organic Functional Group Transformations, vol. 2, Elsevier Science, Oxford, 1995, p. pp. 899 (Chapter 2.18).
- [7] (a) N. Miyaura, Bull. Chem. Soc. Jpn. 12 (2008) 1535–1553; (b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483; (c) A. Suzuki, in: F. Diederich, P.J. Stang (Eds.), w, Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH, Weinheim, 1998, pp. 49–98; (d) S.R. Chemler, D. Rauner, S.J. Danishefsky, Angew. Chem., Int. Ed. 40 (2001) 4544–4568; (e) N. Miyaura, Top. Curr. Chem. 11 (2002) 219.
- [8] (a) M. Sakai, M. Ueda, N. Miyaura, Angew. Chem., Int. Ed. 37 (1998) 3279–3281; (b) C.G. Frost, K.J. Wadsworth, Chem. Commun. (2001) 2316–2317.
- [9] (a) P.Y.S. Lam, S. Deudon, M.A. Kristin, R. Li, M. He, P. DeShong, C.G. Clark, J. Am. Chem. Soc. 22 (2000) 7600–7601; (b) H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, T. Kitagawa, J. Am. Chem. Soc. 122 (2000) 2124–2125; (c) D.A. Evans, J.L. Katz, T.R. West, Tetrahedron Lett. 39 (1998) 2937–2940; (d) P.Y.S. Lam, C.G. Clark, S. Saubern, J. Adams, K.M. Averill, D.M.T. Chan, A. Combs, Synlett. (2000) 674–676.
- [10] (a) T. Hiyama, J. Organomet. Chem. 653 (2002) 58–61; (b) T. Hiyama, E. Shirakawa, Top. Curr. Chem. 219 (2002) 61; (c) S.E. Denmark, J.D. Baird, Chem. Eur. J. 12 (2006) 4954–4963.
- [11] (a) W. Niu, M.D. Smith, J.J. Lavigne, J. Am. Chem. Soc. 128 (2006) 16466–16467; (b) B.M. Rambo, J.J. Lavigne, Chem. Mater. 19 (2007) 3732–3739; (c) N. Christinat, E. Croisier, R. Scopelliti, M. Cascella, U. Röthlisberger, K. Severin, Eur. J. Inorg. Chem. (2007) 5177–5181.
- [12] G.R. Clark, G.J. Irvine, W.R. Roper, L.J. Wright, Organometallics 16 (1997) 5499–6005.
- [13] F.E. Brinckman, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 6218–6233.
- [14] H.C. Brown, D. Basavaiah, N.G. Bhat, Organometallics 2 (1983) 1309–1311.