DOI: 10.1002/chem.200800518

A New Catalytic Route to Boryl- and Borylsilyl-Substituted Buta-1,3-dienes

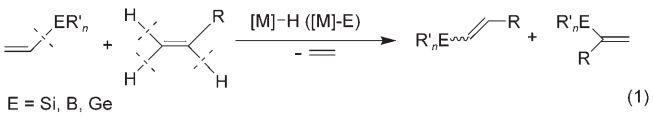
Jędrzej Walkowiak, Magdalena Jankowska-Wajda, and Bogdan Marciniec*[a]

Abstract: Vinyl-substituted boronates in the presence of complexes containing Ru–H bonds (preferably $[Ru(CO)ClH(PCy_3)_2]$, Cy: cyclohexyl) react regioselectively with terminal ethynes (involving silylethynes), albeit with the exception of phenylacetylene, to produce boryl- and borylsilyl-substituted buta-1,3-dienes with a preference for *E*,*E*-diene. The reaction opens a new catalytic route for the preparation of dienylboronates, and particularly dienylsilylboronates, that are functionalised building blocks in the synthesis of organic and natural products. The mechanism of this new reaction was proved to involve an insertion of alkyne into Ru–H bonds followed by an insertion of coordinated vinyl boronate into the Ru–C= bond and β-hydrogen transfer to the metal to eliminate boryldiene or borylsilyldiene.

Keywords: alkynes · butadiene · homogeneous catalysis · silylacetylene · vinylboronates

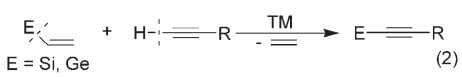
Introduction

The well-known transition-metal (TM)-catalysed reactions (developed by our group) of vinyl-substituted metalloid (E = Si, Ge, B) compounds with olefins, called silylative coupling (*trans*-silylation), *trans*-germylation and *trans*-borylation, respectively, are based on the activation of the =C–E bond and =C–H bonds of olefins in the presence of M–H and M–E catalysts [M = metal; see Eq. (1)].[1–3]



(1)

This process was recently extended to the activation of sp-hybridised C–H bonds in reaction with vinyl-silicon and -germanium compounds [Eq. (2)].[4–5]



(2)

[a] J. Walkowiak, Dr. M. Jankowska-Wajda, Prof. B. Marciniec
Department of Organometallic Chemistry
Faculty of Chemistry
Adam Mickiewicz University
Grunwaldzka 6, 60-780 Poznan (Poland)
Fax: (+48) 61-829-1508
E-mail: marcinb@amu.edu.pl

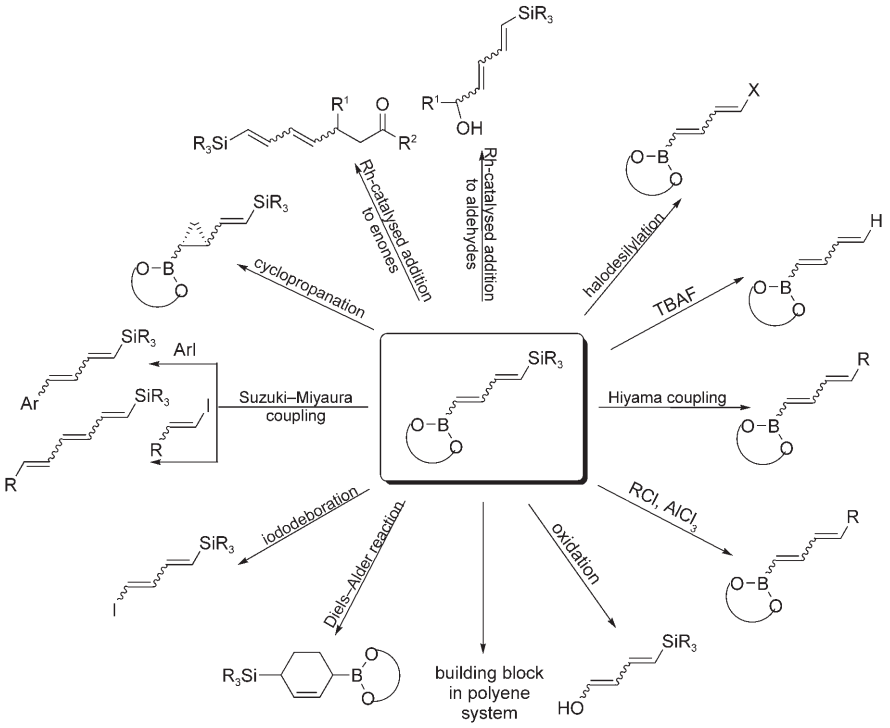
The reactions are widely recognised as efficient catalytic activations of =C–H, ≡C–H and =C–E bonds of a vinylmetalloid with evolution of ethylene. The mechanisms of these reactions involve the insertion of vinyl–E into the TM–H bond and β-hydrogen transfer to the metal with elimination of ethylene and generation of the TM–E bond. This is followed by the insertion of alkene or alkyne into the TM–E bond and β-hydrogen transfer to the metal to eliminate silyl-, germyl- or borylethene, or the substituted silyl- or germylethyne, respectively. The latter step is directly responsible for metallative coupling of olefins and acetylenes.[1b]

In recent years, several applications of alkynyl, alkenyl and dienyl boron derivatives have been developed as functionalised building blocks in the synthesis of organic and natural products.[6,7] This fact has made this topic a growing and steadily more appealing field of research.

Therefore, analogously to organosilicon and germanium derivatives, we used vinylboronates in reaction with terminal acetylenes catalysed by [Ru]–H complexes, but, unexpectedly, instead of boryl-substituted ethynes, boryl-functionalised buta-1,3-dienes were obtained in very good yields with high regioselectivity.

Dienylboronates and particularly dienylsilylboronates constitute a class of functionalised building blocks commonly used in the synthesis of organic and natural products, as the boronate moiety (as well as the silyl group) can be easily converted into other functional groups (see Scheme 1).[8,9]

Simultaneous unsymmetrical functionalisation of buta-1,3-dienes with boryl and silyl groups opens the possibility for



Scheme 1. Potential applications of borylsilyl-substituted buta-1,3-dienes.

selective replacement of one of these groups with retention of the other and the use of the latter in the further functionalisation in a different process.

π–π conjugated C=C bonds occur often in natural polyenic compounds, which exhibit significant biological activity. Indeed, a number of them have found clinical utility as drugs and antibacterial and antifungal compounds.[6–7]

Boryl-substituted 1,3-dienes can be prepared by classic stoichiometric routes using organometallic reagents[10,11] or by more recently applied catalytic methods, such as hydroboration of enynes,[12] cross-coupling of 1,1-diborylated alkenes with alkenyl halides,[13] Heck coupling of vinylboronate with vinylarylic iodides,[8e,14] as well as cross-metathesis of vinylboronates with 1,3-dienes.[15] Additionally, silylboryl-substituted dienes can be synthesised by means of nickel-catalysed silaborative dimerisation of alkynes.[16]

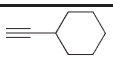
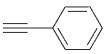
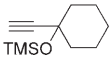
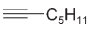
Herein we report a new catalytic transformation of vinyl-substituted boronates with selected terminal ethynes (also silylethynes) occurring in the presence of ruthenium complexes containing the Ru–H bond.

Results and Discussion

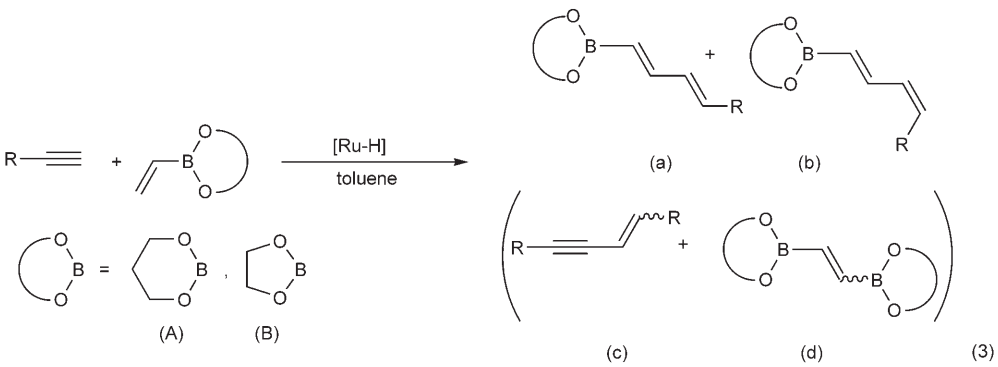
The reaction, catalysed by $[Ru(CO)ClH(PCy_3)_2]$ (**I**; Cy: cyclohexyl), $[Ru(CO)ClH(PiPr_3)_2]$ (**II**) or cationic $[Ru(CO)ClH(MeCN_2)(PCy_3)_2][BF_4]$ (**III**), is a convenient new method for selective synthesis of 1-boryl- and 1-silyl-4-boryl-substituted buta-1,3-dienes [(a)+(b)], sometimes accompanied by traces of ethyne dimerisation (c) and/or vinylboronate homocoupling (d) [see Eq. (3) and Table 1].

Most of the reactions examined here proceed with high conversion of acetylene (quantitatively under optimal conditions) and in very good yields to give predominantly *E*,*E*-1,3-diene (a) accompanied by one *E*,*Z* isomer (b). Although vinylborane has to be used in excess, its homocoupling[3] has been practically insignificant in this reaction. On the other hand, dimerisation of acetylene has been observed, but in the presence of most catalysts used, only as a side reaction affording traces of byproducts (c). A threefold excess of vinylborane over acetylene was tested as the optimum amount for the co-dimerisation process to reduce acetylene

Table 1. Co-dimerisation of terminal acetylenes with 2-vinyl-1,3-dioxaborinane (A).

Entry	≡R	Cat.[d]	Conversion [%][e]	Selectivity a/b/c/d [%][f]	Isolated yield of (a) [%]	Product no.[g]
1		**I**[a]	100	83/15/traces/2	74	**1**
2		**I**[b]	77	86/14/0/0		
3		**II**	93	81/19/traces/traces		
4		**III**[c]	49	77/23/0/0		
5		**IV**	67	11/0/89/0		
6		**V**[c]	20	0/0/100/0		
7		**I**, **IV**	0	0/0/0/0		
8		**V**[c]	46	0/0/100/0		
9		**I**	85	84/16/0/0	66	**2**
10		**I**	97	81/19/0/0	70	**3**
11		**I**	99	60/40/0/0/		**4**

[a] Reaction conditions unless otherwise stated: [Ru]/[acetylene]/[borane] = 2×10^{-2}:1:3; open system, toluene (0.5 M), t = 18 h, T = 80 °C. [b] [Ru]/[acetylene]/[borane] = 10^{-2}:1:3. [c] Dichloroethane (0.5 M) as a solvent. [d] Catalyst: $[Ru(CO)ClH(PCy_3)_2]$ (**I**), $[Ru(CO)ClH(PiPr_3)_2]$ (**II**), $[Ru(CO)H(MeCN_2)(PCy_3)_2][BF_4]$ (**III**), $[Ru(CO)ClH(PPh_3)_3]$ (**IV**), $[RuCl(PCy_3)(p\text{-cymene})]OTf$ (**V**). [e] Substituted acetylene conversion; determined by GC analysis. [f] Determined by GC analysis and ^1H NMR spectroscopy. [g] See the Experimental Section.



dimerisation, as well as homocoupling of vinylboronate. However, when six-coordinated $[RuCO(Cl)H(PPh_3)_3]$ (**IV**) is used as the initial catalyst, then dimerisation of acetylene is a major reaction.

In our research we observed that the co-dimerisation reaction with vinylboronates occurred not only for terminal organic acetylenes, but also for alkynylsilanes (see Table 2). Triethylgermylacetylene was also tested in the reaction with 2-vinyl-1,3-dioxaborinane, but its homocoupling played, in this case, a significant role (see Table 2).

Optimisation of the synthesis parameters was carried out for the reaction of triethylsilylacetylene with 2-vinyl-1,3-dioxaborinane. The best results (the highest yield and selectivity) were observed for the reaction carried out at 80 °C for 18 h and at a threefold excess of borane compound (see Table 2). A fivefold excess of boronate over acetylene increased the contribution of the side reaction of vinylboronate homocoupling.

Similarly to the previously described *trans*-metalation reactions of vinylmetalloid with olefins and acetylenes[2–5] (for a review see ref. [1]), $[Ru(CO)ClH(PCy_3)_2]$ (**IV**) was the most effective and selective catalyst for this process.

Application of 2-vinyl-1,3-dioxaborolane as a reagent in the reactions with terminal silyl and organic acetylenes with the optimal process parameters gives boryl- and borylsilyl-substituted dienes also with good yields and selectivity comparable to the reactions with 2-vinyl-1,3-dioxaborinane (see Table 3).

Our separate study of the reaction of equimolar amounts of the ruthenium–boryl complex $[Ru(BO_2C_6H_4)(CO)Cl(PCy_3)_2]$ (**VI**) and silylacetylene monitored by ^1H NMR spectroscopy and GC–MS reveals that the insertion of acetylene into the Ru–B bond occurs to a very low degree (silylboryl-substituted ethyne is not observed in the GC–MS spectrum and only traces of regenerated Ru–H bond (triplet at $\delta = -24.3$ ppm) were detected by ^1H NMR spectroscopy). This is the reason why contrary to vinylsilane[4] and vinylgermane,[5] the metalation of acetylene with vinylboronate was not observed during the catalytic process. Instead, the co-dimerisation of vinylboronate with most terminal acetylenes (except phenylacetylene) was noted.

It is well recognised that ruthenium–hydride complexes react with terminal acetylenes very smoothly at room temperature (with phenylacetylene reaction occurred immediately even at −20 °C) to form the vinylphenylruthenium complex[4,17,18] according to Equation (4).

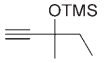
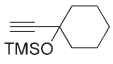
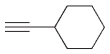
These complexes are therefore well known as catalysts of acetylene dimerisation occurring by means of insertion of

Table 2. Co-dimerisation of terminal silylacetylenes and triethylgermylacetylene with 2-vinyl-1,3-dioxaborinane (A).[a]

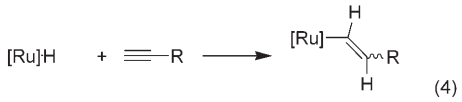
Entry	≡–R	Cat.[f]	T [°C]	Conversion [%][g]	Selectivity a/b/c/d [%][h]	Isolated yield of (a) [%]	Product no.[i]
1	≡–$SiEt_3$	**I**[b]	80	88	80/13/7/traces		
2		**I**	80	98	84/16/traces/traces	78	**5**
3		**I**[c]		83	82/18/traces/traces		
4		**I**[d]	80	99	78/14/0/8		
5		**I**	40	10	89/11/traces/traces		
6		**I**	60	35	88/12/traces/traces		
7		**I**	100	100	70/15/15/0		
8		**II**	80	91	80/20/0/traces		
9		**III**[e]	80	54	72/28/0/0		
10		**IV**	80	73	12/7/81/0		
11		**V**[e]	80	35	0/0/100/0		
12	≡–$Si(iPr)_3$	**I**		100	83/17/traces/traces	79	**6**
13	≡–$Si(Me_2)tBu$	**I**		100	84/16/0/0	81	**7**
14	≡–$Si(Me_2)Ph$	**I**		94	90/10/0/traces	79	**8**
15	≡–$SiMe_3$	**I**		43	40/5/55/0		**9**
16	≡–$GeEt_3$	**I**		88	44/14/21/23		**10**

[a] Reaction conditions unless otherwise stated: [Ru]/[acetylene]/[borane] = 2×10^{-2}:1:3; open system, toluene (0.5 M), t = 18 h. [b] [Ru]/[acetylene]/[borane] = 2×10^{-2}:1:2. [c] [Ru]/[acetylene]/[borane] = 10^{-2}:1:3. [d] [Ru]/[acetylene]/[borane] = 2×10^{-2}:1:5. [e] Dichloroethane (0.5 M) as a solvent. [f] Catalyst: $[Ru(CO)ClH(PCy_3)_2]$ (**I**), $[Ru(CO)ClH(PiPr_3)_2]$ (**II**), $[Ru(CO)H(MeCN_2)(PCy_3)_2][BF_4]$ (**III**), $[Ru(CO)ClH(PPh_3)_3]$ (**IV**), $[RuCl(PCy_3)(p\text{-cymene})]OTf$ (**V**). [g] Substituted acetylene conversion; determined by GC analysis. [h] Determined by GC analysis and ^1H NMR spectroscopy. [i] See the Experimental Section.

Table 3. Co-dimerisation of terminal acetylenes with 2-vinyl-1,3-dioxaborolane (B).

Entry	≡–R	Conversion [%][b]	Selectivity a/b/c/d [%][c]	Isolated yield of (a) [%]	Product no. [d]
1	≡–$SiEt_3$	95[a]	83/14/3/0	71	**11**
2	≡–$Si(iPr)_3$	92	86/14/0/0		**12**
3	≡–$Si(Me_2)tBu$	84	83/17/traces/0	74	**13**
4	≡–$Si(Me_2)Ph$	88	75/25/0/0	63	**14**
5		78	70/30/traces/0		**15**
6		73	89/11/0/0		**16**
7		96	82/18/0/0		**17**

[a] Reaction conditions unless otherwise stated: $[Ru(CO)ClH(PCy_3)_2]$/[acetylene]/[borane] = 2×10^{-2}:1:3; open system, toluene (0.5 M), $t = 18$ h, $T = 80$ °C. [b] Substituted acetylene conversion; determined by GC analysis. [c] Determined by GC analysis and ^{1}H NMR spectroscopy. [d] See the Experimental Section.



(4)

the second molecule of acetylene into the Ru–vinyl complex and were also observed in an experiment with $[Ru(CO)ClH(PPh_3)_3]$ (**IV**) used as the initial catalyst.

To check why the reaction of vinylboronates with terminal acetylenes occurs differently from those with vinylsilanes and vinylgermanes, as well as to identify the mechanism of the co-dimerisation process, we carried out stoichiometric reactions of ruthenium hydride complex $[Ru(CO)ClH(PCy_3)_2]$ (**I**) with silylacetylene and vinylboronate.

The first step leads to the synthesis of a vinylene ruthenium complex (two doublets at $\delta = 5.62$–5.66 and 8.80–8.85 ppm) [see Eq. (5) and Figure 1a].

The reaction was carried out for 24 h. After the total disappearance of the Ru–H bond (triplet at $\delta = -24.3$ ppm), the equimolar amount of vinylboronate was added to the reaction mixture. The [Ru]–H complex was monitored after 24 h (by ^{1}H NMR spectroscopy), whereas borylsilyl-substituted dienes (yield 47%) were monitored by GC–MS analyses. Reduction of the resonance line characteristic of vinylene–ruthenium complexes and the appearance of new lines typical of olefinic protons also proved the co-dimerisation route (Figure 1b).

During stoichiometric processes we also observed evolution of ethylene (singlet at $\delta = 5.25$ ppm) in the ^{1}H NMR spectrum. We can explain this fact by formation of the Ru–B complex followed by insertion of the vinylboronate used in excess to the regenerated (after elimination of borylsilyl-substituted buta-1,3-diene) Ru–H complex [see Eq. (6)]. Bis(boryl)ethene as a product of vinylboronate homocou-

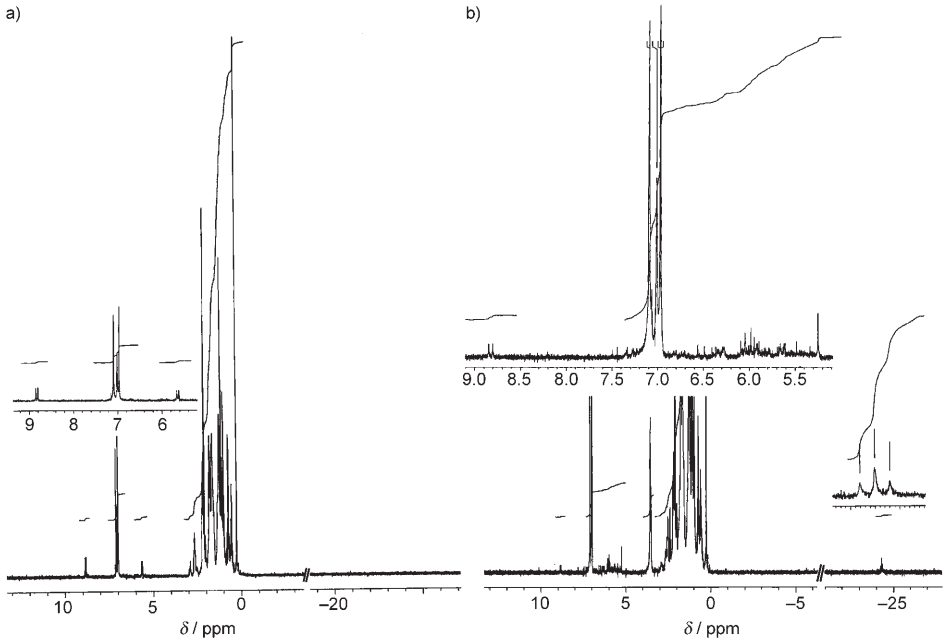
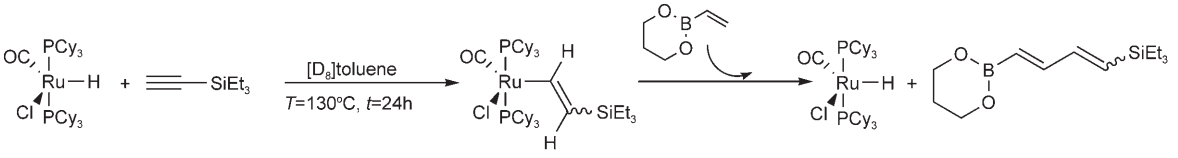
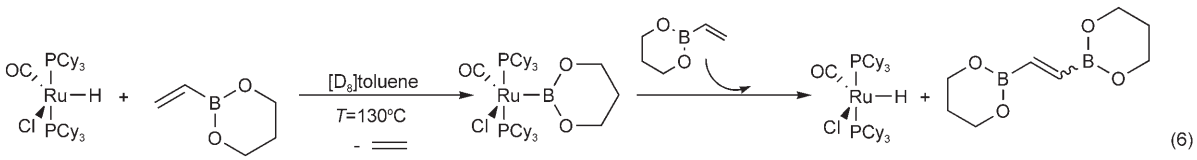


Figure 1. a) ^{1}H NMR spectrum of silylvinylene ruthenium complex generated in situ; b) ^{1}H NMR spectrum of the stoichiometric reaction of silylvinylene ruthenium complex with 2-vinyl-1,3-dioxaborolane, monitored after 24 h.



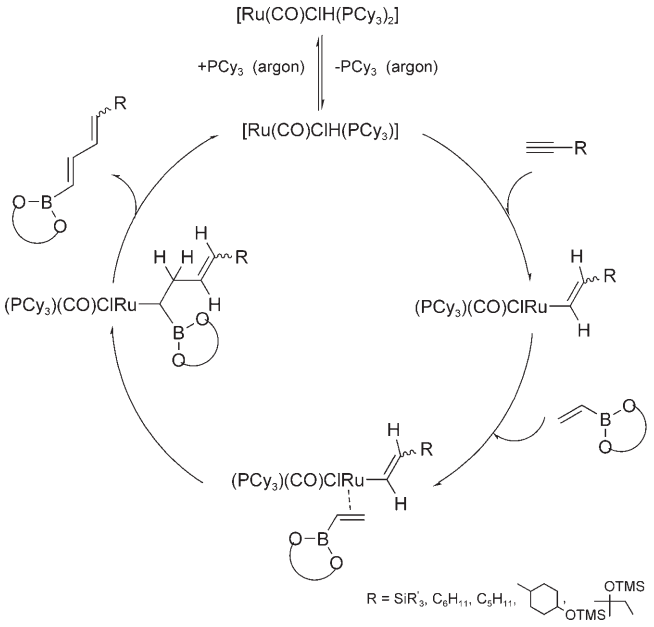
Molar ratio [Ru-H]/[silylacetylene]/[borane] = 1 : 1.5 : 1.6

(5)



pling is also observed in the GC–MS spectrum (for detailed experiments of vinylborane homocoupling see ref. [3]).

The above-described experiment provides convincing evidence for the mechanism of the new catalytic reaction occurring in the presence of $[Ru(CO)ClH(PCy_3)_2]$ (**I**) (see Scheme 2).



Scheme 2. Mechanism of co-dimerisation of terminal acetylene (silylacetylene) with vinylboronates.

The crucial point of this mechanism (contrary to that established in vinylsilane and vinylgermane) is the fact that reaction of Ru–H with vinylboronate does not compete with that with acetylene. The latter is preferred in this case to yield the Ru–vinylene complex (instead of Ru–silyl and Ru–germyl complexes, which are preferred in the previous systems[4,5]) directly responsible for the final step yielding co-dimerisation products.

The co-dimerisation process of inactivated olefins with terminal acetylenes, such as phenyl and cyclohexyl, was previously reported to be catalysed by the cationic ruthenium complex $[RuCp(PPh_3)_2Py]$ (generated in situ; Cp: cyclopentadienyl) to yield a mixture of *E*,*E*- and *E*,*gem*-dienes (100 °C, 10 h, $NaPF_6$, pyridine), but neither boryl nor silyl compounds were studied. Our experiments on the reaction of vinylboronate with phenyl-, cyclohexyl- and triethylsilylacetylene carried out in the presence of cationic complex $[RuCl(p\text{-cymene})(PCy_3)][OTf]$ (**V**; OTf: trifluoromethanesulfonate) show the exclusive presence of the products of acetylene dimerisation (see Tables 1 and 2). The mechanism of the reaction was proposed to involve the ruthenium vinylidene complex as an active intermediate responsible for this catalytic process.[19]

Conclusion

We have developed a new catalytic route for the efficient coupling of vinylboronates with terminal alkynes involving silylacetylenes (except phenylacetylenes) catalysed by ruthenium complexes containing a Ru–H bond. This leads to boryl- and borylsilyl-substituted buta-1,3-dienes in high yield with a preference for the *E*,*E*-diene. It is worth noting that we have established the optimal reaction parameters to obtain the target compound without any byproducts.

Experimental Section

General methods: ^1H (300 MHz), ^{13}C (75 MHz), ^{29}Si (79 MHz) and ^{11}B NMR (96 MHz) spectra were recorded by using a Varian XL 300 MHz spectrometer with samples in a solution of $CDCl_3$ or $[D_8]$toluene ($C_6D_5CD_3$). Chemical shifts are reported in ppm with reference to the residue portion solvent (CH_3Cl) peak for ^1H and ^{13}C, to TMS for ^{29}Si and to BF_3–Et_2O for ^{11}B. Analytical GC analyses were performed by using a Varian Star 400CX with a DB-5 fused-silica capillary column (30 m × 0.15 mm) and thermal-conductivity detector (TCD). Mass spectra of the substrates and products were obtained by GC–MS analysis (VarianSaturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion-trap detector). Elemental analyses were carried out by using a Vario EL III system and high-resolution (HR) MS analyses were performed by using an AMD-402 instrument. Thin-layer chromatography (TLC) was carried out by using plates coated with 250 μm-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; $CDCl_3$ and $C_6D_5CD_3$ from Dr. Glaser, A.G. Basel. The substituted acetylene was bought from Aldrich. 2-Vinyl-1,3-dioxaborolane and 2-vinyl-1,3-dioxaborinane were synthesised according to the literature with some modifications.[20,21] The ruthenium complexes **I**–**VI** were prepared according to the literature.[3,22–25]

Representative experimental procedure for synthesis of boryl- and borylsilyl-substituted buta-1,3-diene: In a typical test, the ruthenium catalyst **I** (2 mol %) was dissolved in toluene and placed in a glass ampoule under an argon atmosphere. The reagents and dodecane as internal standard (all components 5% by volume), acetylene and vinylborane (usually used in the molar ratio [Ru]/[acetylene]/[vinylborane] 2×10^{-2}:1:3) were added. Subsequently, the ampoule was heated to 80–90 °C and maintained at that temperature for 24 h. The progress of the reaction was monitored by GC and GC–MS analyses. The conversion and chemoselectivity of the reactions and yields were calculated by using the internal

standard method. The final products were separated from the residues of the catalyst and reactants by purification using a silica gel column with hexane/ethyl acetate (1:1) as eluent. All products of catalytic transformation of terminal alkynes with vinylboronates were pale yellow oily liquids.

Experimental procedure for stoichiometric reaction: Complex **I** (0.01 g, 0.012 mmol), triethylsilylacetylene (0.01 g, 0.018 mmol) and [D_8]toluene (0.6 mL) were placed in an NMR tube under an argon atmosphere. The reaction was carried out at 100 °C and after disappearance of Ru−H and appearance of Ru−CH=CH−$SiEt_3$ bonds (monitored by ^{1}H NMR spectra), 2-vinyl-[1,3,2]dioxaborinane (0.019 mmol) was added and the course of the reaction was monitored by using ^{1}H NMR spectroscopy.

Syntheses

(1*E*,3*E*)-1-(1′,3′-Dioxaborinan-2′-yl)-4-cyclohexylbuta-1,3-diene (1): Complex **I** (0.015 g, 0.02 mmol), toluene (1 mL), 1-ethynylcyclohexane (0.11 g, 1 mmol) and 2-vinyl-1,3-dioxaborinane (0.34 g, 3 mmol) were placed in a glass ampoule and heated under an argon atmosphere at 80 °C for 18 h. Then the excess of borane and solvent were removed under vacuum and the crude product was separated from the residues of the catalyst and reactants using a column of silica gel (hexane/ethyl acetate 1:1) to afford **1** as a pale yellow liquid (0.163 g, 0.740 mmol, 74 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.85 (t, 4H; C_6H_{11}), 1.25 (br, 2H; C_6H_{11}), 1.69 (br, 4H; C_6H_{11}), 0.83–1.65 (br m, 10H; C_6H_{11}), 1.30 (s, 3H; CCH_3), 1.96 (quintet, J(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.03 (t, J-(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.33 (d, J(H,H) = 17.6 Hz, 1H; B−C*H*=CH), 5.78 (d, J(H,H) = 15.4 Hz, 1H; −CH=C*H*−C), 6.07 (dd, J(H,H) = 9.9, 15.4 Hz, 1H; −C*H*=CH−C), 6.89 ppm (dd, J(H,H) = 10.2, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 25.91 (3,5-C_6H_5), 26.1 (4-C_6H_5), 27.4 ($BOCH_2CH_2$), 32.5 (2,6-C_6H_5), 40.7 (1-C_6H_5), 62.7 ($BOCH_2CH_2$), 129.8 (*C*H=CH−C), 144.2 (CH=*C*HC), 148.1 ppm (B−CH=*C*H); C_α to boron atom is not observed; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3–Et_2O): δ = 27.6 ppm; MS (EI): *m/z*: 220 (49) [M^+], 205 (11), 177 (32), 164 (61), 151 (7), 138 (17), 121 (69), 110 (28), 105 (43), 91 (54), 79 (100), 67 (54); HRMS: *m/z* calcd for $C_{13}H_{21}BO_2$ [M^+]: 220.16347; found: 220.16193.

(1*E*,3*E*)-1-(1′,3′-Dioxaborinan-2′-yl)-5-methyl-5-trimethylsiloxyhepta-1,3-diene (2): Compound **2** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **2** as a colourless liquid (0.186 g, 0.659 mmol, 66 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.09 (s, 9H; OSi−(CH_3)$_3$), 0.81 (t, 3H; CCH_2CH_3), 1.30 (s, 3H; CCH_3), 1.51 (quartet, 2H; CCH_3), 1.97 (quintet, J(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.43 (d, J(H,H) = 17.3 Hz, 1H; B−C*H*=CH), 5.83 (d, J(H,H) = 15.4 Hz, 1H; −CH=C*H*−C), 6.17 (dd, J(H,H) = 10.4, 15.4 Hz, 1H; −C*H*=CH−C), 6.90 ppm (dd, J(H,H) = 10.4, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 2.48 (OSi−(CH_3)$_3$), 8.39 (CCH_2CH_3), 26.84 (CCH_3), 27.39 ($BOCH_2CH_2$), 36.35 (CCH_2CH_3), 61.75 ($BOCH_2CH_2$), 75.82 (CCH_2CH_3), 129.59 (C−CH=*C*H−), 144.22 (B−CH=*C*H−), 147.20 ppm (C−CH=*C*H−); C_α to boron atom is not observed in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$, 25 °C, BF_3–Et_2O): δ = 27.7 ppm; MS (EI): *m/z* (%): 282 (11) [M^+], 267 (11), 253 (97), 193 (16), 183 (19), 159 (58), 145 (6), 131 (26), 117 (29), 105 (16), 93 (35), 73 (100), 59 (7); HRMS: *m/z* calcd for $C_{15}H_{27}BO_3Si$ [M^+]: 282.18225; found: 282.18308.

(1*E*,3*E*)-1-(1′,3′-Dioxaborinan-2′-yl)-4-(1″-trimethylsiloxycyclohex-1″-yl)buta-1,3-diene (3): Compound **3** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **3** as a colourless liquid (0.216 g, 0.700 mmol, 70 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.07 (s, 9H; OSi−(CH_3)$_3$), 0.83–1.65 (br m, 10H; C_6H_{10}), 1.30 (s, 3H; CCH_3), 1.97 (quintet, J(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.44 (d, J(H,H) = 17.6 Hz), 1H; B−C*H*=CH), 5.90 (d, J(H,H) = 15.4 Hz, 1H; −CH=C*H*−C), 6.18 (dd, J(H,H) = 10.2, 15.7 Hz, 1H; −C*H*=CH−C), 6.89 ppm (dd, J(H,H) = 10.2, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 2.57 (OSi−(CH_3)$_3$), 22.28 (3,5-C_6H_{10}), 25.72 (4-C_6H_{10}), 27.39 ($BOCH_2CH_2$), 38.35 (2,6-C_6H_{10}), 61.76 ($BOCH_2CH_2$), 74.07 (1-C_6H_{10}), 130 (C−CH=*C*H), 144.18 (B−CH=*C*H−), 147.32 ppm (C−CH=*C*H−); C_α to boron atom is not observed in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3–Et_2O): δ = 27.5 ppm; MS (EI): *m/z* (%): 308 (7) [M^+], 293 (9), 279 (5), 265 (35), 251 (16), 238 (5), 209 (11), 193 (28), 167 (25), 159 (24), 134 (38), 119 (49), 105 (29), 91 (95), 73 (100), 59 (9); HRMS: *m/z* calcd for $C_{15}H_{21}BO_2Si$ [M^+]: 272.14038; found: 272.13880.

2-[(1*E*,3*E*)-Nona-1,3-dienyl]-1,3-dioxaborinane (4): MS (EI): *m/z* (%): 208 (43) [M^+], 193 (11), 179 (23), 165 (47), 151 (27), 138 (27), 123 (13), 110 (30), 93 (57), 79 (100), 67 (54), 53 (13).

(1*E*,3*E*)-1-Triethylsilyl-4-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (5): Compound **5** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **5** as a pale yellow liquid (0.196 g, 0.77 mmol, 78 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.59 (quartet, J(H,H) = 7.9 Hz, 6H; Si−CH_2−CH_3), 0.92 (t, J(H,H) = 8.0 Hz, 9H; Si−CH_2−CH_3), 1.97 (quintet, J-(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.44 (d, J(H,H) = 17.3 Hz, 1H; B−C*H*=CH), 5.98 (d, J(H,H) = 18.4 Hz, 1H; −CH=C*H*−Si), 6.58 (dd, J(H,H) = 10.2, 18.4 Hz, 1H; −C*H*=CH−Si), 6.89 ppm (dd, J(H,H) = 10.2, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 3.35 (Si−CH_2CH_3), 7.32 (Si−CH_2CH_3), 27.39 ($BOCH_2CH_2$), 61.76 ($BOCH_2CH_2$), 134.47 (Si−*C*H=CH−), 147.07 (B−CH=*C*H−), 149.75 (Si−CH=*C*H−); C_α to boron atom is not observed in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3–Et_2O): δ = 27.6 ppm; ^{29}Si NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ = −0.83 ppm; MS (EI): *m/z* (%): 237 (1) [M^+−15], 223 (76), 209 (2), 195 (100), 181 (4), 167 (45), 153 (6), 139 (32), 109 (58), 81 (25), 59 (16); elemental analysis calcd (%) for $C_{13}H_{25}BO_2Si$: C 61.90, H 9.99; found: C 61.99, H 10.12.

(1*E*,3*E*)-1-Tri(isopropylsilyl)-4-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (6): Compound **6** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **6** as a pale yellow liquid (0.232 g, 0.788 mmol, 79 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.97–1.14 (m, 21H; Si−C*H*− (CH_3)$_2$), 1.97 (quintet, J(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.45 (d, J(H,H) = 17.6 Hz, 1H; B−C*H*=CH), 5.94 (d, J(H,H) = 18.4 Hz, 1H; −CH=C*H*−Si), 6.62 (dd, J(H,H) = 10.7, 18.4 Hz, 1H; −C*H*=CH−Si), 6.90 ppm (dd, J(H,H) = 9.9, 16.8 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 10.85 (Si−$CH(CH_3)_2$), 18.58 (Si−$CH(CH_3)_2$), 27.39 ($BOCH_2CH_2$), 61.78 ($BOCH_2CH_2$), 132.76 (Si−*C*H=CH−), 147.84 (B−CH=*C*H−), 150.02 ppm (Si−CH=*C*H−); C_α to boron atom is not observed in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3–Et_2O): δ = 27.8 ppm; ^{29}Si NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ = −0.45 ppm; MS (EI): *m/z* (%): 251 (78) [M^+−43], 223 (26), 209 (100), 193 (3), 181 (88), 165 (35), 153 (54), 139 (40), 123 (56), 111 (38), 95 (47), 81 (18), 59 (26); elemental analysis calcd (%) for $C_{16}H_{31}BO_2Si$: C 65.29, H 10.62; found: C 65.35, H 10.69.

(1*E*,3*E*)-1-(Dimethyl(*tert*-butyl)silyl)-4-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (7): Compound **7** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **7** as a pale yellow liquid (0.204 g, 0.809 mmol, 81 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.04 (s, 6H; Si(CH_3)$_2$), 0.86 (s, 9H; SiC-(CH_3)$_3$), 1.97 (quintet, J(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.46 (d, J(H,H) = 17.6 Hz, 1H; B−C*H*=CH), 6.01 (d, J(H,H) = 18.4 Hz, 1H; −CH=C*H*−Si), 6.55 (dd, J(H,H) = 10.2, 18.4 Hz, 1H; −C*H*=CH−Si), 6.76 ppm (dd, J(H,H) = 9.9, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = −6.25 (Si−(CH_3)$_2$), 16.65 (Si−$C(CH_3)_3$), 26.40 (Si−C(CH_3)$_3$) 27.38 ($BOCH_2CH_2$), 61.77 ($BOCH_2CH_2$), 135.24 (Si−*C*H=CH−), 147.02 (B−CH=*C*H−), 149.60 ppm (Si−CH=*C*H−); C_α to boron atom is not observed in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3–Et_2O): δ = 27.7 ppm; ^{29}Si NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.34 ppm; MS (EI): *m/z* (%): 237 (2) [M^+−15], 195 (100), 137 (81), 125 (19), 109 (7), 95 (34), 73 (11), 59 (11); elemental analysis calcd (%) for $C_{13}H_{25}BO_2Si$: C 61.90, H 9.99; found: C 61.95, H 10.05.

(1*E*,3*E*)-1-(Dimethylphenylsilyl)-4-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (8): Compound **8** was prepared from the appropriate starting materials according to the above procedure for **1**. The reaction afforded **8** as a pale yellow liquid (0.215 g, 0.789 mmol, 79 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.034 (s, 6H; Si−(CH_3)$_2$), 1.97 (quintet, J-

(H,H) = 5.5 Hz, 2H; $BOCH_2CH_2CH_2O$), 4.04 (t, J(H,H) = 5.5 Hz, 4H; $BOCH_2$), 5.49 (d, J(H,H) = 17.6 Hz, 1H; B−C*H*=CH), 6.12 (d, J(H,H) = 18.1 Hz, 1H; −CH=C*H*−Si), 6.63 (dd, J(H,H) = 10.2, 17.9 Hz, 1H; −C*H*=CH−Si), 6.91 (dd, J(H,H) = 10.1, 17.6 Hz, 1H; B−CH=C*H*−), 7.36 (m, 3H; *m*,*p*-C_6H_5), 7.46 ppm (m, 2H; *o*-C_6H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = −2.68 (Si−(CH_3)$_2$), 27.37 ($BOCH_2CH_2$), 61.77 ($BOCH_2CH_2$), 127.76 (C_6H_5), 128.99 (C_6H_5), 133.84 (C_6H_5), 135.09 (Si−*C*H=CH−), 147.37 (B−CH=*C*H−), 149.26 ppm (Si−CH=*C*H−); C_α to boron atom in ^{13}C NMR spectrum; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3-Et_2O): δ = 27.7 ppm; ^{29}Si NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ = −22 ppm; MS (EI): *m*/*z* (%): 271 (6) [M^+−1], 257 (36), 215 (19), 199 (33), 187 (26), 171 (41), 157 (65), 143 (65), 121 (36), 101 (100), 91 (38) 77 (50), 59 (15); HRMS: *m*/*z* calcd for $C_{15}H_{21}BO_2Si$ [M^+]: 272.14038; found: 272.13880.

(1*E*,3*E*)-1-Trimethylsilyl-4-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (9): MS (EI): *m*/*z* (%): 210 (3) [M^+], 195 (35) 167 (10), 153 (10), 137 (100), 125 (25), 109 (23), 95 (65), 59 (12).

(1*E*,3*E*)-1-Triethylgermyl-3-(1′,3′-dioxaborinan-2′-yl)buta-1,3-diene (10): MS (EI): *m*/*z* (%): 269 (100), 268 (78) [M^+−CH_2CH_3], 239 (39), 213 (22), 183 (25), 155 (15), 133 (4), 101 (26), 75 (8).

(1*E*,3*E*)-1-(Triethylsilyl)-4-(1′,3′-dioxaborolan-2′-yl)buta-1,3-diene (11): Complex **I** (0.015 g, 0.02 mmol), toluene (1 mL), triethylsilylacetylene (0.14 g, 1 mmol) and 2-vinyl-1,3-dioxaborolane (0.29 g, 3 mmol) were placed in a glass ampoule and heated under an argon atmosphere at 80 °C for 18 h. Then the excess of borane and solvent were removed under vacuum and the crude product was separated from the residues of the catalyst and reactants using a column of silica gel (hexane/ethyl acetate 1:1) to afford **11** as a pale yellow liquid (0.169 g, 0.709 mmol, 71 % isolated yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.61 (q, J(H,H) = 8.0 Hz, 6H; $SiCH_2CH_3$), 0.93 (t, J(H,H) = 8.0 Hz, 9H; $SiCH_2CH_3$), 4.24 (s, 4H; $BO_2(CH_2)$) 5.57 (d, J(H,H) = 17.6 Hz, 1H; B−C*H*=CH−), 6.04 (d, J(H,H) = 18.5 Hz, 1H; Si−C*H*=CH), 6.60 (dd, J(H,H) = 9.9, 18.5 Hz, 1H; −C*H*=CH−Si), 7.00 ppm (dd, J(H,H) = 10.0, 17.6 Hz, 1H; −B−CH=C*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 3.3 (Si(CH_2CH_3)$_3$), 7.31 (Si-(CH_2CH_3)$_3$), 65.6 ($BO_2C_2H_4$), 129.8 (*C*H=CH−C), 136.4 (CH=*C*HSi), 146.7 (B−CH=*C*H), 152.8 ppm (H*C*=CHSi); C_α to boron atom is not observed; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3−Et_2O): δ = 6.6 ppm; MS (EI): *m*/*z* (%): 209 (42) [M^+−29], 181 (100), 165 (6) 153 (38), 137 (18), 109 (31), 81 (20), 67 (2); elemental analysis calcd (%) for $C_{12}H_{23}BO_2Si$: C 60.51, H 9.73; found: C 60.59, H 9.81.

(1*E*,3*E*)-1-Tri(isopropylsilyl)-4-(1′,3′-dioxaborolan-2′-yl)buta-1,3-diene (12): MS (EI): *m*/*z* (%): 252 (14) [M^+−28], 237 (100), 209 (33), 195 (84), 181 (8) 167 (42), 151 (47), 137 (23), 123 (69), 109 (24), 95 (52), 81 (19), 67 (7), 59 (27).

(1*E*,3*E*)-1-(Dimethyl(*tert*-butyl)silyl)-4-(1′,3′-dioxaborolan-2′-yl)buta-1,3-diene (13): Compound **13** was prepared from the appropriate starting materials according to the above procedure for **11**. The reaction afforded **13** (0.176 g, 0.738 mmol, 74 % isolated yield) as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.05 (s, 6H; Si(CH_3)$_2$(C(CH_3)$_3$)), 0.87 (s, 9H; Si(CH_3)$_2$(C(CH_3)$_3$)), 4.25 (4H; s, $BO_2(CH_2)$) 5.58 (d, J-(H,H) = 17.6 Hz, 1H; B−C*H*=CH), 6.09 (d, J(H,H) = 18.4 Hz, 1H; −Si−C*H*=CH), 6.60 (dd, J(H,H) = 10.7, 18.1 Hz, 1H; −C*H*=CH−Si), 7.00 ppm (dd, J(H,H) = 10.0, 17.6 Hz, 1H; B−CH=C*H*−); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 16.65 (Si(CH_3)$_2$(*C*(CH_3)$_3$)), 26.4 (Si(CH_3)$_2$(C(*C*H$_3$)$_3$)), 65.6 ($BO_2C_2H_4$), 137.1 (CH=*C*HSi), 146.7 (B−CH=*C*H), 152.7 ppm (H*C*=CHSi); C_α to boron atom is not observed; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3−Et_2O): δ = 7.6 ppm; MS (EI): *m*/*z* (%): 181 (100) [M^+−57], 137 (100), 95 (87), 73 (12), 57 (6); elemental analysis calcd (%) for $C_{12}H_{23}BO_2Si$: C 60.51, H 9.73; found: C 60.63, H 9.85.

(1*E*,3*E*)-1-(Dimethylphenylsilyl)-4-(1′,3′-dioxaborolan-2′-yl)butadi-1,3-ene (14): Compound **14** was prepared from the appropriate starting materials according to the above procedure for **11**. The reaction afforded **14** (0.163 g, 0.631 mmol, 63 % isolated yield) as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.37 (s, 6H; Si(CH_3)$_2$), 4.25 (s, 4H; $BO_2(CH_2)$) 5.60 (d, J(H,H) = 17.9 Hz, 1H; B−C*H*=CH−), 6.18 (d, J-(H,H) = 18.1 Hz, 1H; −Si−C*H*=CH), 6.65 (dd, J(H,H) = 9.2, 18.1 Hz, 1H; −C*H*=CH−Si), 7.03 (dd, J(H,H) = 9.9, 17.9 Hz, 1H; B−CH=C*H*−), 7.38 (t, 1H; *p*-C_6H_5), 7.51 (t, 2H; *m*-C_6H_5), 7.60 ppm (d, 2H; *o*-C_6H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = −2.76 (Si(*C*H$_3$)$_2$(C_6H_5)), 65.6 ($BO_2C_2H_4$), 127.8 (C_6H_5), 129.1 (C_6H_5), 133.8 (C_6H_5), 137.0 (CH=*C*HSi), 146.9 (B−CH=*C*H), 152.3 ppm (H*C*=CHSi); C_α to boron atom is not observed; ^{11}B NMR (96 MHz, $CDCl_3$ 25 °C, BF_3−Et_2O): δ = 7.7 ppm; MS (EI): *m*/*z* (%): 257 (3) [M^+−1], 243 (35), 228 (3), 215 (58), 187 (100), 171 (64), 157 (87), 135 (30), 129 (93), 87 (56), 77 (46); elemental analysis calcd (%) for $C_{13}H_{21}BO_2Si$: C 65.12, H 7.42; found: C 65.00, H 7.51.

(1*E*,3*E*)-1-(1′,3′-Dioxaborolan-2′-yl)-5-methyl-5-trimethylsiloxyhepta-1,3-diene (15): MS (EI): *m*/*z* (%): 268 (9) [M^+], 253 (7), 239 (90), 145 (18), 119 (12), 105 (8), 73 (100), 67 (5).

(1*E*,3*E*)-1-(1′,3′-Dioxaborolan-2′-yl)-4-(1″-trimethylsiloxycyclohex-1″-yl)buta-1,3-diene (16): MS (EI): *m*/*z* (%): 294 (3) [M^+], 279 (7), 265 (1), 251 (29), 237 (11), 183 (7), 167 (13), 145 (10), 134 (15), 119 (29), 105 (16), 91 (58), 73 (100), 67 (7).

(1*E*,3*E*)-1-(1′,3′-Dioxaborolan-2′-yl)-4-cyclohexylbuta-1,3-diene (17): MS (EI): *m*/*z* (%): 206 (37) [M^+], 191 (6), 177 (7), 163 (24), 150 (41), 121 (50), 105 (35), 93 (55), 79 (100), 67 (78), 53 (19).

Acknowledgements

This work was supported by the project of The Ministry of Science and High Education (PZB-KBN 118/T09/17).

[1] a) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374–2390; b) B. Marciniec, *Acc. Chem. Res.* **2007**, *40*, 943–952.
[2] B. Marciniec, H. Ławicka, M. Majchrzak, M. Kubicki, I. Kownacki, *Chem. Eur. J.* **2006**, *12*, 244–250.
[3] B. Marciniec, M. Jankowska, C. Pietraszuk, *Chem. Commun.* **2005**, *5*, 663–665.
[4] B. Marciniec, B. Dudziec, I. Kownacki, *Angew. Chem.* **2006**, *118*, 8360–8364; *Angew. Chem. Int. Ed.* **2006**, *45*, 8180–8184.
[5] B. Marciniec, H. Ławicka, B. Dudziec, *Organometallics* **2007**, *26*, 5188–5196.
[6] C. Thirsk, A. Whiting, *J. Chem. Soc. Perkin Trans. 1* **2002**, *8*, 999–1023.
[7] P. Knochel, H. Ila, T. J. Korn, O. Baron in *Handbook of Functionalized Organometallics, Applications in Synthesis, Vol. 1* (Ed.: P. Knochel), Wiley-VCH, Weinheim, **2005**, pp. 45–108.
[8] a) I. E. Marko, T. Kumamoto, T. Giard, *Adv. Synth. Catal.* **2002**, *344*, 1063–1067; b) T. Hayashi, K. Yamasaki, *Chem. Rev.* **2003**, *103*, 2829–2844; c) R. Morita, E. Shirakawa, T. Tsuchimoto, Y. Kawasaki, *Org. Biomol. Chem.* **2005**, *3*, 1263–1268; d) G. Hilt, P. Bolze, *Synthesis* **2005**, *13*, 2091–2115; e) G. N. Maw, C. Thirsk, J.-L. Toujas, M. Vaultier, A. Whiting, *Synlett* **2004**, *7*, 1183–1186; f) J. Uenishi, K. Matsui, A. Wada, *Tetrahedron Lett.* **2003**, *44*, 3093–3096; g) A. G. M. Barrett, A. J. Bennett, S. Menzer, M. L. Smith, A. J. P. White, D. J. Williams, *J. Org. Chem.* **1999**, *64*, 162–171; h) C. Prandi, A. Deagostino, P. Venturello, E. Occiato, *Org. Lett.* **2005**, *7*, 4345–4348; i) G. Desurmont, S. Dalton, D. Giolando M. Srebnik, *J. Org. Chem.* **1996**, *61*, 7943–7946.
[9] a) K. Itami, K. Mitsudo, T. Nokami, T. Kamei, T. Koine, T. Yoshida, *J. Organomet. Chem.* **2002**, *653*, 105–113; b) Z. Xi, Z. Song, G. Liu, T. Takahashi, *J. Org. Chem.* **2006**, *71*, 3154–3158; c) P. Pawlú, G. Greczycho, J. Walkowiak, B. Marciniec, *Synlett* **2007**, *13*, 2061–2064; d) W. Prukała, P. Pawluć, K. Posała, B. Marciniec, *Synlett* **2008**, *1*, 41–44; e) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192.
[10] B. Marciniec, C. Pietraszuk, I. Kownacki, M. Zaidlewicz, in *Comprehensive Organic Functional Group Transformation II, Vol. 1* (Eds.: A. R. Katryzky, R. J. K. Taylor), Elsevier, Amsterdam, **2005**, pp. 941–1024.
[11] P. B. Tivola, A. Deagostino, C. Prandi, P. Venturello, *Org. Lett.* **2002**, *4*, 1275–1277.
[12] a) J. N. Tene Ghomsi, O. Goureau, M. Treilhou, *Tetrahedron Lett.* **2005**, *46*, 1537–1539; b) S. A. Frank, W. R. Roush, *J. Org. Chem.* **2002**, *67*, 4316–4324.

[13] T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Schimizu, T. Hiyama, *Angew. Chem.* **2001**, *113*, 812–814; *Angew. Chem. Int. Ed.* **2001**, *40*, 790–792.
[14] A. P. Lightfoot, S. J. R. Twiddle, A. Whiting, *Org. Biomol. Chem.* **2005**, *3*, 3167–3172.
[15] T. W. Funk, J. Efskind, R. H. Grubbs, *Org. Lett.* **2005**, *7*, 187–190.
[16] M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **1998**, *17*, 5233–5236.
[17] M. R. Torres, A. Vegas, A. Santos, *J. Organomet. Chem.* **1986**, *309*, 169–177.
[18] S. M. Maddock, C. E. F. Rickard, W. P. Roper, L. J. Wright, *Organometallics* **1996**, *15*, 1793–1803.
[19] M. Murakami, M. Ubukata, Y. Ito, *Tetrahedron Lett.* **1998**, *39*, 7361–7364.
[20] F. E. Brinckman, F. G. A. Stone, *J. Am. Chem. Soc.* **1960**, *82*, 6218–6223.
[21] H. C. Brown, D. Basavalah, N. G. Bhat, *Organometallics* **1983**, *2*, 1309–1311.
[22] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* **1999**, *18*, 2043–2045.
[23] J. J. Levison, S. D. Robinson, *J. Chem. Soc. A* **1970**, 2947–2954.
[24] G. R. Clark, G. J. Irvine, W. R. Roper, L. J. Wright, *Organometallics* **1997**, *16*, 5499–6005.
[25] A. Furstner, M. Liebl, Ch. W. Lehmann, M. Picquet, R. Kunz, Ch. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847–1857.

Received: March 20, 2008
Published online: June 13, 2008

