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Synthesis of difunctional borasiloxanes and their behavior in metathesis reactions

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Abstract

New divinyl- and diallyl-borasiloxanes have been synthesized in good yield from corresponding boronic acids. They have been characterized by ^{1}H-, ^{13}C-, ^{29}Si- and ^{11}B-NMR, as well as by MS. Their behavior in metathesis reactions initiated by two different catalysts ([RhCl(COD)]$_2$ for vinylsiloxanes and [Mo] Schrock's catalyst for allylsiloxanes) has been studied. This has led to new cycloborasiloxanes that have been characterized. © 1998 Elsevier Science S.A. All rights reserved.

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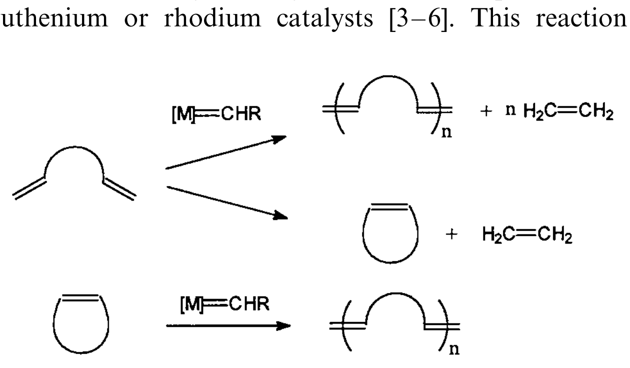
1. Introduction

Metathesis reactions of alkenes and dienes (Scheme 1) have been limited for a long time to organic compounds without any functional groups. However, recent developments have shown that catalysts can be found to accommodate such groups [1,2]. For example, Marciniec and collaborators reported the possibility of metathesis of vinyl or allyl silanes in the presence of ruthenium or rhodium catalysts [3–6]. This reaction usually leads to a mixture of different products. Recently, Wagener and collaborators showed that polycarbosiloxanes could be synthesized through acyclic diene metathesis (ADMET) polymerization using Schrock's catalyst [7].



Scheme 1. Metathesis reactions of alkenes and dienes.

In our research towards new organometallic polymers, we investigated whether polyborasiloxanes could be obtained following the same method. Indeed, it has been shown that these polymers could not be synthesized through ring-opening polymerization, since this reaction leads to a mixture of polysiloxanes and cycloboroxins [8] and never to the expected polymer.

We report here the results obtained in metathesis reactions of unsaturated borasiloxanes, which did not give polymers as we hoped, but instead well-defined cyclocarboborasiloxanes.

2. Results and discussion

2.1. Synthesis of borasiloxanes **1–4**

Several dialkenylborasiloxanes **1–4** were synthesized following the method described by Wannagat et al. for

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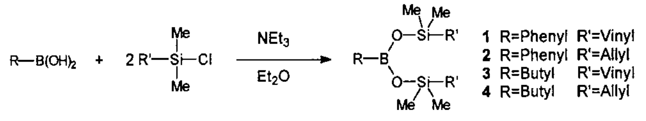


Scheme 2. Reactions between aryl/alkylboronic acid and a chlorosilane.

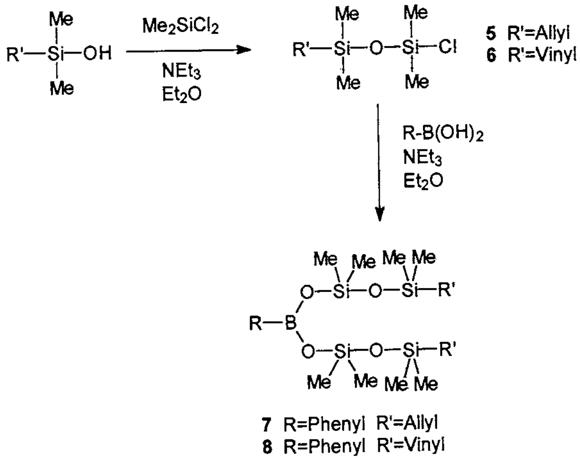
the synthesis of cycloborasiloxanes [9]. They were obtained from a simple reaction between aryl- or alkylboronic acid and a chlorosilane (Scheme 2). All experimental conditions and the corresponding results are reported in Table 1. NMR data (Table 2) and MS spectra (Fig. 1) are consistent with the structure.

2.2. Synthesis of borasiloxanes **7** and **8**

For the longer borasiloxanes, **7** and **8**, the appropriate chlorosiloxanes **5** and **6** were first synthesized (Scheme 3). This was realized by reacting an excess of dimethyldichlorosilane with the appropriate silanol obtained by the hydrolysis of the corresponding chlorosilane [10]. The chlorosiloxanes were obtained from the silanol in good yields. The reaction with an arylboronic acid then leads to the borasiloxanes. Unfortunately, the crude products displayed a slow decomposition upon heating during the purification process. This led to mixtures of borasiloxanes, boroxins and siloxanes. Therefore, the metathesis reaction of these borasiloxanes could not be studied.

2.3. Metathesis reactions of borasiloxanes **1**–**4**

The behavior of borasiloxanes **1**–**4** in metathesis reactions was studied under two different conditions: (1) with [Mo] Schrock's catalyst **9**, (2) and $[RhCl(COD)]_2$ (Scheme 4). This latter system is particularly effective in divinylsiloxane ADMET reactions [5], whereas with diallylsiloxanes, it mainly gives rise to the isomerization of an allyl into a propenyl group. In order to explain the metathesis activity, Marciniec and collaborators proposed the formation of a carbenic intermediate by reaction of the catalyst with the vinyl group [4]. They showed that this [Rh] system generally leads to 1,1- as well as 1,2-disubstituted alkenyl bridges [5].



Scheme 3. Borasiloxanes **7** and **8**.

With catalyst **9**, Schrock and collaborators have shown that vinylsiloxanes are unsuitable reactants since they lead to the formation of a stable metallacyclobutane [11]. However, diallylsilanes react via an usual ADMET reaction with Schrock's catalyst to give a disilane having a 1,2-disubstituted bridge. Therefore, in this work, Schrock's catalyst has only been tested on diallylborasiloxanes, whereas $[RhCl(COD)]_2$ has been used on divinylborasiloxanes.

The experimental conditions and the corresponding results are reported in Table 3; NMR characteristics of the products (**10**–**12**) synthesized are presented in Table 4. It is noteworthy that compounds **10** and **11** are the only isomers obtained from the metathesis reactions of **1** and **3** (Scheme 5), since there is no evidence of a 1,2-dialkenyl bridge formation from NMR and MS spectra (Fig. 1). This is contrary to what Marciniec et al. [5] reported for ADMET reactions of vinylsilanes. Our result is likely to be due to a favorable conformation (i.e. a favorable position of the double bonds), either in the starting product or in the corresponding carbenic intermediate, leading mostly to the six-membered ring.

The reaction of Schrock's catalyst **9** with **2** gives a mixture of *cis* and *trans* isomers of cycloborasiloxanes **12**/**12'** (Table 4), for which the ^1H- and ^{13}C-NMR data are consistent with those reported by Wagener for siloxane **13**. Their formation by ring-closing metathesis

Table 1
Experimental conditions for the synthesis of linear borasiloxanes **1**–**4**

Compound	Et_2O (ml)	$R-B(OH)_2$ g (mmol)	Chlorosilane g (mmol)	NEt_3 g (mmol)	Product g (mmol)	Yield[a] (%)
1	90	4.1 (34)	8.2 (68)	8.6 (85)	8.3 (29)	84
2	40	2.1 (17)	4.6 (34)	4.3 (43)	3.9 (12)	71
3	100	1.95 (19)	4.6 (38)	4.4 (44)	4.5 (17)	88
4	50	2.05 (20)	5.4 (40)	5.1 (50)	5.1 (17)	82

[a] Yield of purified product.

Table 2
NMR chemical shifts of linear borasiloxanes in $CDCl_3$ at 20°C (ppm)

Compound	^1H	^{13}C	^{29}Si	^{11}B
1	0.33 (s, 12H, SiMe); 5.75–6.4 (m, system ABM ^2J (*gem*) $= 4.3$ Hz ^3J (*trans*) $= 19.8$ Hz, ^3J (*cis*) $= 14.8$ Hz, 6H, CH=CH$_2$); 7.39 (m, 3H, *m*, *p* BPh); 7.8 (dd ^3J (*o*, *m*) $= 7.8$ Hz, ^4J (*o*, *p*) $= 1.8$ Hz, 2H, *o* BPh)	0.8 (SiMe); 128.2 (*o* BPh); 131.3 (*p* BPh); 133.2 (=CH$_2$); 135.9 (*m* BPh); 139.1 (CH=)	−1.23 (SiMe)	25.3 (BPh)
2	0.26 (s, 12H, SiMe); 1.74 (d, $J = 8$ Hz, 4H, CH$_2$–=); 4.8–5.0 (2dd, ^3J (*trans*) $= 17.9$ Hz, ^2J (*gem*) $= 1.1$ Hz, ^3J (*cis*) $= 10$ Hz, 4H, =CH$_2$); 5.7–5.95 (m, ^3J (*trans*) $= 17.9$ Hz, ^3J (*cis*) $= 10$ Hz, ^3J (vinyl, CH$_2$Si) $= 8$ Hz, 2H, CH=); 7.41 (m, 3H, *m*, *p* BPh); 7.76 (dd, ^3J (*o*, *m*) $= 6.6$ Hz, ^4J (*o*, *p*) $= 1.8$ Hz, 2H, *o* BPh)	0.3 (SiMe); 26.5 (CH$_2$–=); 114.7 (=CH$_2$); 128.2 (*o* BPh); 131.3 (*p* Bph); 134.5 (=CH); 135.7 (*m* BPh)	7.48 (SiMe)	0
3	0.2 (s, 12H, SiMe); 0.67 (t, $J = 7.2$ Hz, 2H, –CH$_2$–B); 0.86 (t, $J = 6.8$ Hz, 3H, CH$_3$–); 1.2–1.44 (m, 4H, –CH$_2$–); 5.66–6.27 (m, system ABM, ^2J (*gem*) $= 4.7$ Hz, ^3J (*trans*) $= 20$ Hz, ^3J (*cis*) $= 15.5$ Hz, 3H, CH=CH$_2$)	0.38 (SiMe); 14.7 (CH$_3$–); 26.1 (–CH$_2$–); 27.6 (–CH$_2$–B–); 132.7 (=CH$_2$); 139.2 (=CH)	−0.63 (SiMe)	29.4 (B–CH$_2$–)
4	0.14 (s, 12H, SiMe); 0.65 (t, $J = 7.2$ Hz, 2H, –CH$_2$–B–); 0.86 (t, $J = 6.8$ Hz, 3H, CH3–); 1.14–1.44 (m, 4H, –CH$_2$–); 1.62 (d, $J = 8$ Hz, 4H, –CH$_2$–); 4.83–4.9 (2 dd, ^3J (*trans*) $= 16.4$ Hz, ^2J (*gem*) $= 1.2$ Hz, ^3J (*cis*) $= 10$ Hz, 4H, =CH$_2$); 5.65–5.92 (m, ^3J (*trans*) $= 16.4$ Hz, ^3J (*cis*) $= 10$ Hz; ^3J (vinyl, CH$_2$–Si) $= 8$ Hz, 2H, =CH)	−0.06 (SiMe); 14.7 (CH3–); 26.3 (CH2–); 27.6 (–CH$_2$–B–); 114.3 (=CH$_2$); 134.7 (=CH)	8.03 (SiMe)	29.5 (B–CH$_2$–)

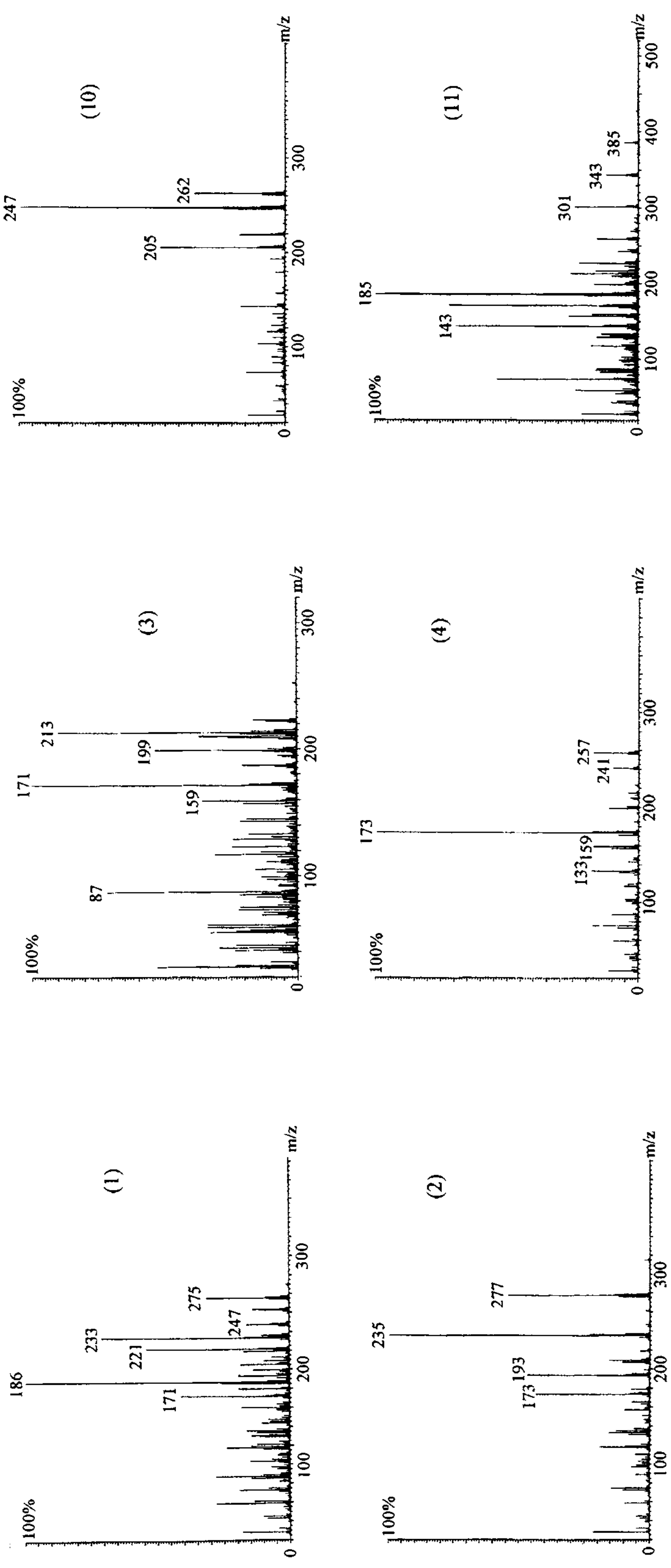
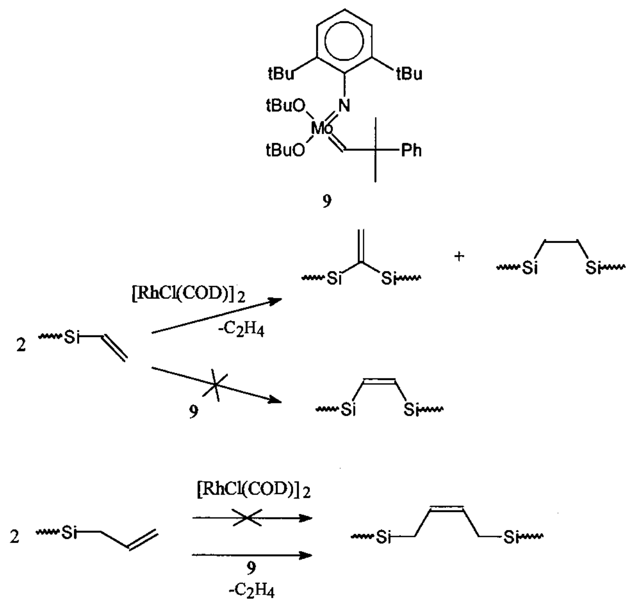


Fig. 1. MS spectra of borasiloxanes **1–4** and **10–11**

is somewhat surprising, since nine-membered rings are usually not favored. Moreover, Wagener and collaborators have shown that ADMET reactions on siloxane **14** (without any boron atom) led to polymers [7]. In our case, it can be supposed that the small radius of the boron atom, as well as the sterically demanding phenyl group, enables a folded conformation leading preferably to cycles (which is confirmed by examining theoretical models of the molecules). In order to reduce the interactions between the phenyl group and the methyl substituents of the silicon atoms, the molecule has to adopt a folded conformation, thus leading to a smaller distance between the alkenes in **12** compared with the siloxane analog **14** described by Wagener [7].

Recently, some examples of ring-closing metathesis leading to medium-size cycles have been reported [12–16], but only with organic compounds. Moreover, in these examples, the reaction took place in favorable conditions, i.e. diluted solutions. What is surprising here is the fact that even in bulk, the dienes do not lead to ADMET polymerization, but to ring-closing metathesis.

Under the same conditions, borasiloxane **4** (with butyl on the boron atom) has an ambiguous behavior. Indeed, if some gas evolution was clearly observed upon its mixing with Schrock's catalyst, it stopped after a few minutes; this was still observed even after repeated purifications of **4**. So, apparently, only arylborasiloxanes exhibit efficient metathesis reactions initiated by Schrock's catalyst **9**. At this time, there is no explanation for this observation.



Scheme 4. The behavior of vinylsilanes **1**–**4** in metathesis reactions under different conditions.

3. Experimental

Dichlorosilanes and chlorosilanes (Roth-Sochiel) were stirred in the presence of magnesium for 18 h, and trap-to-trap distilled. Phenylboronic acid (Fluka), butylboronic acid (Aldrich), $[RhCl(COD)]_2$ and [Mo] Schrock's catalyst (Strem Chemicals) were used without further purification. Silanols were prepared according to a previously published procedure [10]. Triethylamine

Table 3
Ring-closing metathesis reactions of various borasiloxanes at 25°C in bulk conditions

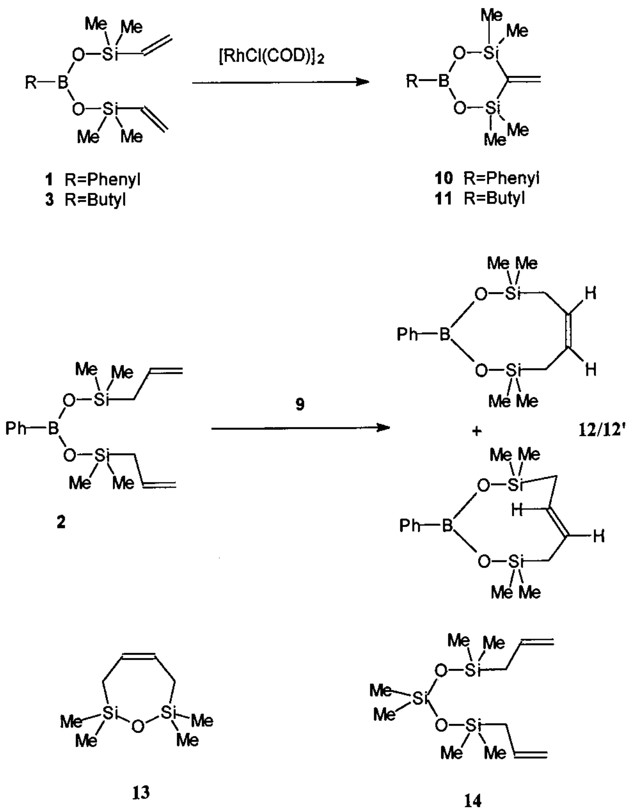
Compound	Reactant g (mmol)	Catalyst g (mmol)	Product g (mmol)	Yield (%)
10	**1** 6.9 (24)	$[RhCl(COD)]_2$ 0.17 (0.34)	5.0 (19)	80[a]
11	**3** 0.24 (0.9)	$[RhCl(COD)]_2$ 0.1 (0.2)	0.2	85[b]
12	**2** 0.5 (1.6)	**9** 0.1 (0.02)	Mixture **12**/**12'**/residual **2**	90[b]

[a] Yield of purified product; [b] yield of crude product.

Table 4
NMR chemical shifts of resulting products of ADMET cyclization in $CDCl_3$ at 20°C (ppm)

Compound	^1H	^{13}C	^{29}Si	^{11}B
10	0.31 (s, 12H, SiMe); 6.37 (s, 2H, $=CH_2$); 7.39 (m, 3H, *m*, *p* BPh); 7.89 (dd, ^3J (*o*, *m*) = 7.9 Hz, ^4J (*o*, *p*) = 1.7 Hz, 2H, *o* BPh)	0.17 (SiMe); 127.3 (*o* BPh); 130.7 (*p* BPh); 135.0 (*m* BPh); 140.4 ($=CH_2$); 153.5 (C=)	5.59 (SiMe)	26.7 (BPh)
11	0.23 (s, 12H, SiMe); 0.72 (t, *J* = 7.2 Hz, 2H, $-CH_2-B$); 0.87 (t, *J* = 6.8 Hz, 3H, CH_3-); 1.15–1.45 (m, 4H, $-CH_2-$); 6.3 (s, 2H, $=CH_2$)	0.87 (SiMe); 14.7 (CH_3-); 26.1 ($-CH_2-$); 27.4 ($-CH_2-B$); 140.8 ($=CH_2$); 154.0 (=C)	4.2 (SiMe)	0
12/**12'** [a]	0.23 (s, 12H, SiMe); 1.65 (m, 4H, $-CH_2-=$); 5.26–5.53 (m, 2H, CH=CH ratio *cis*/*trans* 1/4); 7.39 (m, 3H, *m*, *p* BPh); 7.75 (m, 2H, *o* BPh)	0.31 (SiMe); 24.7 (CH2–=); 124.9 (CH=CH); 128.1 (*o* BPh); 131.2 (*p* BPh); 135.6 (*m* BPh)		

[a] Crude product.



Scheme 5. Metathesis reactions of borasiloxanes **1**–**3**.

was stored under CaH_2 and trap-to-trap distilled before use. When useful, diethylether was distilled on CaH_2.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 200 at 200 and 50.32 MHz, respectively. ^{29}Si- and ^{11}B-NMR were carried out on a Bruker DPX200, respectively, at 39.8 and 64.21 MHz. MS spectra were realized on an AutospecEQ spectrometer (electron impact mode, 70 eV).

3.1. Synthesis of borasiloxanes 1–4

To a cooled solution (0°C) of aryl- or alkylboronic acid and triethylamine in diethylether, a solution of alkenyldimethylchlorosilane in 10 ml of diethylether was added dropwise. The solution was stirred over 4 h at ambient temperature. Filtration of triethylammonium chloride and evaporation of the solvent followed by trap-to-trap distillation under high vacuum afforded a colorless viscous oil.

3.2. Synthesis of allyltetramethylchlorodisiloxane 5

To a cooled (0°C) solution of dimethyldichlorosilane (18.3 g, 142 mmol) in diethylether (50 ml), a solution of allyldimethylsilanol (5.5 g, 47 mmol) and triethylamine (4.8 g, 47 mmol) in diethylether (50 ml) was added dropwise. The solution was stirred at ambient temperature for 4 h, then filtered and the solvent evaporated, together with the excess of dimethyldichlorosilane. The resulting product was trap-to-trap distilled under vacuum to yield 8.1 g of a colorless liquid (82%).

^{1}H-NMR ($CDCl_3$; δ ppm): 5.65–5.9 (m, 1H, CH=); 4.78–4.95 (2dd ^3J (*trans*) = 16.2 Hz, ^3J (*cis*) = 10.2 Hz, 2H, =CH_2); 1.62 (d, J = 8 Hz, 4H, CH_2–=); 0.43 (s, 6H, SiMeCl); 0.15 (s, 6H, SiMe).

3.3. Synthesis of vinyltetramethylchlorodisiloxane 6

Compound **6** was synthesized following the same procedure as for **5** (yield 51%).

^{1}H-NMR ($CDCl_3$; δ ppm): 5.65–6.28 (m ABM system ^2J (*gem*) = 4.8 Hz, ^3J (*trans*) = 19.4 Hz, ^3J (*cis*) = 14.9 Hz, 3H, CH=CH_2); 0.43 (s, 6H, SiMeCl); 0.21 (s, 6H, SiMe). ^{13}C-NMR ($CDCl_3$; δ ppm): 138.9 (CH=); 133.1 (=CH_2); 4.86 (SiMeCl); 0.71 (SiMe).

3.4. Synthesis of borasiloxanes 7 and 8

The procedure was the same as for **1**.

7: ^{1}H-NMR ($CDCl_3$; δ ppm): 7.88 (m, 2H, *o* BPh); 7.3–7.5 (m, 3H, *m* and *p* BPh); 5.69–5.95 (m, 2H, CH=); 4.8–5.0 (2dd ^3J (*trans*) = 18 Hz, ^2J (*gem*) = 0.8 Hz, ^3J (*cis*) = 9.5 Hz, 4H, =CH_2); 1.63 (d ^3J = 8 Hz, 4H, CH_2–=); 0.25 and 0.15 (2s, 24H, SiMe). ^{13}C-NMR ($CDCl_3$; δ ppm): 136.1 (*m* BPh); 134.8 (CH=); 131.4 (*p* BPh); 128.1 (*o* BPh); 114.2 (=CH_2); 26.9 (CH_2–=); 1.73 (OSiO); 0.40 (Si–allyl).

8: ^{1}H-NMR ($CDCl_3$; δ ppm): 7.84 (dd ^3J (*o*, *m*) = 7.9 Hz ^{4}J (*o*, *p*) = 1.7 Hz, 2H, *o* BPh); 7.3–7.5 (m, 3H, *m*, *p* BPh); 5.69–6.25 (m, ABM system, ^2J (*gem*) = 4.5 Hz, ^3J (*trans*) = 19.6 Hz, ^3J (*cis*) = 14.8 Hz, 6H, CH=CH_2); 0.21 and 0.18 (2s, 24H, SiMe). ^{13}C-NMR ($CDCl_3$; δ ppm): 139.7 (=CH); 136.2 (*m* BPh); 132.6 (=CH_2); 131.4 (*p* BPh); 128.1 (*o* BPh); 1.76 (OSiO); 0.93 (SiVi). ^{29}Si-NMR (δ ppm): -3.09 (SiVi); -18.9 (OSiO).

3.5. Metathesis reactions of borasiloxanes 1–4

A small quantity of the desired catalyst was added to the dialkenylborasiloxane under nitrogen. The mixture was stirred under vacuum for 18 h. Ethylene evolution immediately occurred and was continuously eliminated by pumping until no gas formation was observed. The crude product was vacuum trap-to-trap distilled under high vacuum.

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