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Synthesis of *B*-trisubstituted borazines via the rhodium-catalyzed hydroboration of alkenes with *N*,*N*′,*N*″-trimethyl or *N*,*N*′,*N*″-triethylborazine

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Abstract

Hydroboration of terminal and internal alkenes with *N*,*N*′,*N*″-trimethyl- and *N*,*N*′,*N*″-triethylborazine was carried out at 50 °C in the presence of a rhodium(I) catalyst. Addition of dppb or DPEphos (1 equiv.) to $RhH(CO)(PPh_3)_3$ gave the best catalyst for hydroboration of ethylene at 50 °C, resulting in a quantitative yield of *B*,*B*′,*B*″-triethyl-*N*,*N*′,*N*″-trimethylborazine. On the other hand, a complex prepared from $(t\text{-Bu})_3P$ (4 equiv.) and $[Rh(coe)_2Cl]_2$ gave the best yield for hydroboration of terminal or internal alkenes.

Keywords: Borazine catalytic hydroboration of alkene

1. Introduction

The recent design and synthesis of a range of new borazines, which serve as precursors of borazine-based polymers and BN ceramics [1] or as core skeletons of electroluminescent devices [2], has sparked new interest in the chemistry and properties of these ring compounds. However, chemical studies, as well as practical applications, of borazines compounds have been held back by the absence of efficient and economical synthetic methods. The introduction of organic groups at both the boron and nitrogen atoms of borazine has been reported. *N*-Substituted borazines are accessible by thermolysis of primary amine–borane complexes $RNH_2 \cdot BH_3$ [3], usually obtained by the reaction of metal borohydride with primary amine salts [4]. A catalytic method using metal complexes has recently developed by Manners [5]. The presence of rhodium(0) colloid in situ generated from $[RhCl(cod)]_2$ allowed such a dehydrocoupling of amine–borane adducts at 45 °C. Nitriles are often used in place of primary amines to synthesize *N*-alkylborazines [6]. There are various methods for preparing *B*-substituted borazines [7]. *B*,*B*′,*B*″-Trihaloborazines react with Grignard reagents [8] or alkyllithiums [9] to give *B*,*B*′,*B*″-trialkylborazines, though similar reactions of *N*,*N*′,*N*″-trialkylborazines are less selective, resulting in a mixture of mono-, di-, and tri-*B*-alkylborazines [10]. A practical method applicable to various *B*-alkyl and *B*-alkenyl derivatives has recently been developed by Sneddon [11] *via* metal-catalyzed hydroboration of alkenes or alkynes with borazine $B_3N_3H_6$ [12]. The protocol provided the most convenient method for selective synthesis of *B*,*B*′,*B*″-trialkyl, *B*,*B*′-dialkyl or *B*-monoalkylborazines and for isolation of these moisture-sensitive materials without workup with water.

In this paper, we report the first preparation of hexaalkylborazines via catalyzed hydroboration. The preparation of *N*,*N*′,*N*″-trialkylborazines (**3**) from amine–borane

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adducts (**1**) was followed by catalyzed hydroboration with ethylene and terminal or internal alkenes for the synthesis of *B*- and *N*-substituted borazines (**4**–**6**) (Scheme 1). The catalysts effective for these alkenes were reoptimized because of the ineffectiveness of $RhH(CO)(PPh_3)_3$ previously recommended for borazine $B_3N_3H_6$ [11].

2. Results and discussion

2.1. Synthesis of *N*,*N*′,*N*″-trialkylborazines

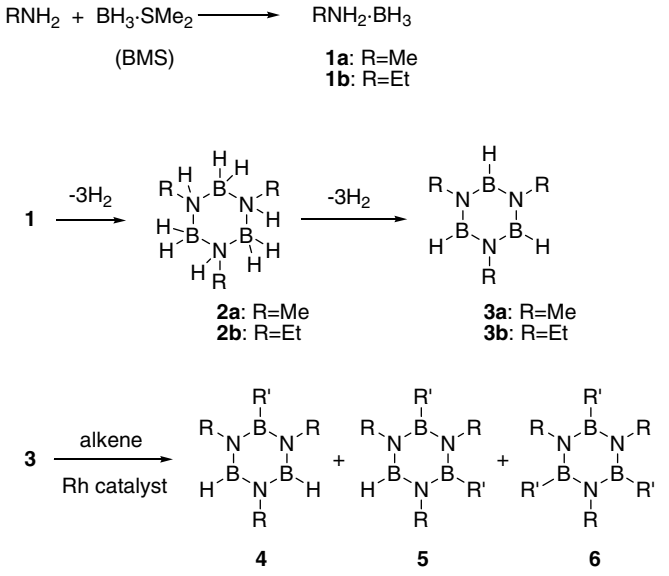
Borane–amine complexes (**1**) are accessible by a reaction between lithium borohydride and primary amine salts or diborane and primary amines [4]. Thermolysis of these primary amine–borane complexes (**1**) thus obtained provides *N*,*N*′,*N*″-trialkylborazines (**3**). We adopted a modified method of Vaultier [3] that involves preparation of **1** from primary amines and $BH_3 \cdot SMe$ (BMS) at −78 °C, evaporation of the solvent and dimethyl sulfide in *vacuo*, and finally thermolysis of **1** at room temperature to 200 °C without using any solvent. This method was most convenient and reliable for preparation of pure *N*,*N*′,*N*″-trialkylborazines in excellent yields (Table 1). Among the preparations of representative *N*,*N*′,*N*″-trialkylborazines, the synthesis of **3a** suffered from a low yield of impure material (entry 1). The difficulty was mainly due to the low boiling point of the borazine product (**3a**, 133 °C) and sublimation of **2a** during heating at 200 °C. Alternatively, the thermolysis of **1a** in tetraglyme, which was previously adopted for the thermolysis of $BH_3 \cdot NH_3$, gave pure **3a** in high yield (entry 2).

The reaction produced a mixture of *N*,*N*′,*N*″-trialkylcycloborazane (**2**) [13], typically white solids, and *N*,*N*′,*N*″-trialkylborazine (**3**) at 90–120 °C with evolution of hydrogen at a rate depending on the bulkiness of *N*-substituents. They were then converted into *N*,*N*′,*N*″-trialkylborazines (**3**) with evolution of additional hydrogen when the temperature was raised from 120 to 200 °C over a period of 1 h. The reaction rates estimated by the amount of hydrogen evolved during the thermolysis of two borane–amine complexes (1 mmol, neat) are shown in Figs. 1 and 2. Thermolysis of borane/methylamine complex (**1a**) at room temperature to 120 °C resulted in the evolution of 70% of the theoretical amount of hydrogen required for its conversion to *N*,*N*′,*N*″-trimethylborazine (**3a**), thus suggesting the formation of a mixture of borazane (**2a**) and borazine (**3a**) at 120 °C. In contrast, thermolysis of borane/*n*-butylamine complex showed a typical pattern for stepwise conversion to borazane and then borazine. The reaction at room temperature to 120 °C resulted in the evolution of 50% hydrogen selectively giving borazane (**2**, R = *n*-Bu) and an additional 50% hydrogen at 120–200 °C to yield borazine (**3**).

Table 1
Synthesis of *N*,*N*′,*N*″-trialkylborazines (**3**)[a]

Entry	**1**, R=	Bp (°C/mmHg)[b]	Yield (%)[c]
1	Me (**1a**)	133	40
2[d]	Me (**1a**)	133	82
3	Et (**1b**)	75/2.8	73
4	*n*-Pr	85/3.4	84
5	*i*-Pr	59/1.3	75
6	*n*-Bu	122/2.2	82
7	*s*-Bu	92/1.6	79
8	*t*-Bu	75/2.8	76
9	$CH_2C(CH_3)_3$	140/2.0	85

[a] The preparation of **1** (0.1 mol) from amine and BMS was followed by thermolysis to give **3** at 120–200 °C.
[b] Boiling points of **3**.
[c] The isolated yields of **3** by distillation.
[d] The reaction was conducted in tetraglyme (10 ml).



Scheme 1. Synthesis of all alkylborazines via catalyzed hydroboration.

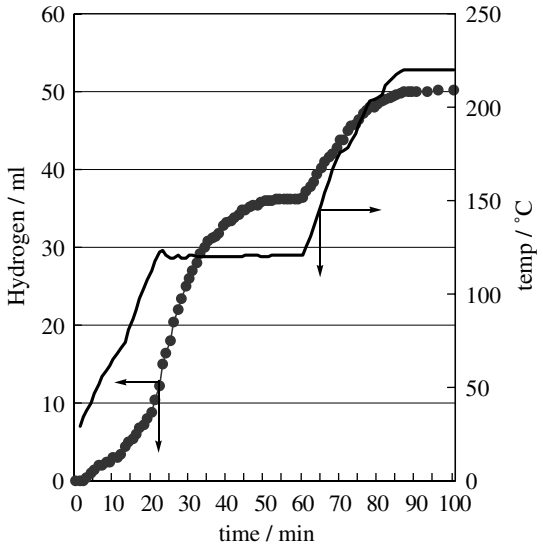


Fig. 1. Thermolysis of $MeNH_2 \cdot BH_3$ (1 mmol).

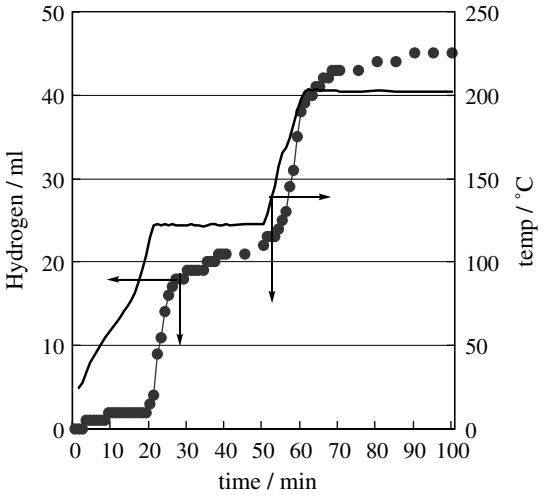
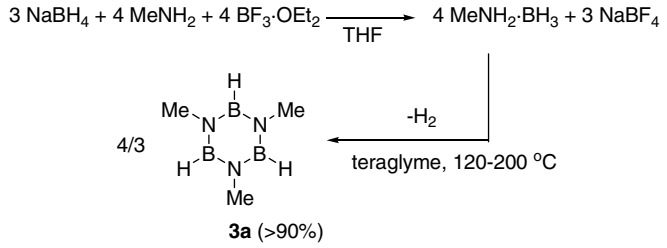


Fig. 2. Thermolysis of n-$BuNH_2 \cdot BH_3$ (1 mmol).

Sodium borohydride is an economical borane source that has been utilized for the preparation of BH_3–THF or other borane-base adducts by treatment of $BF_3 \cdot OEt_2$ [14]. The reaction took place smoothly in the presence of a slight excess of methylamine (1.4 equiv.) at 0–25 °C. This procedure provided a borane-methylamine complex in quantitative yield in a volatile easily removed solvent (Scheme 2). Filtration of $NaBF_4$ through a Celite pad and evaporation of THF in vacuo was directly followed by thermolysis of the borane–amine residue in tetraglyme at 200 °C to afford **3a** in 94% yield. The preparation of a borane-methylamine complex by this method suffered from contamination of a fluoroborane complex. This byproduct was completely eliminated when $NaBH_4$ was used in excess of the required stoichiometry for $BF_4 \cdot OEt_2$ [15].

2.2. Hydroboration of ethylene with *N,N′,N″*-trimethylborazine

The effects of catalysts and temperatures on conversions and their selectivities (**4a**, **5a**, **6a**) in the hydroboration of ethylene (8 kg/cm^2) with *N,N′,N″*-trimethylborazine (**3a**) are shown in Table 2. $RhH(CO)(PPh_3)_3$, previously recommended for hydroboration of ethylene and other alkenes with borazine $B_3N_3H_6$ [11], failed in full conversion of three B–H bonds (Table 2, entries 2 and 3). Ethylene is known to be a good ligand for slowly deactivating the catalyst in hydrogenation of alkenes with rhodium complexes



Scheme 2. Synthesis of *N,N′,N″*-trimethylborazine from $NaBH_4$.

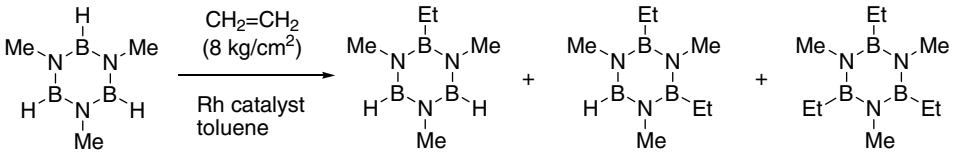
[16], but the catalyst activity can be restored by stabilizing the catalyst with a good chelating ligand such as bisphosphines. The reaction was retarded by addition of Ph_3P (2 equiv.) to $RhH(CO)(PPh_3)_3$ (entry 4), but dppp (entries 8–12), dppb (entries 13 and 14) and DPEphos (entries 15–17) possessing a relatively large bite angle exhibited high catalyst efficiency (entries 5, 6, and 8). Among these representative bisphosphine ligands, dppb and DPEphos resulted in a high turnover number of the catalyst exceeding 10 000 for the B–H bond (entries 13–17). To reduce the catalyst loading to 0.02 mol%, the use of a minimum amount of solvent was also effective to restore the catalyst activity (entries 14 and 17). However, the conversions were significantly deceased when no solvent was used or when using an amount larger than 0.3 ml for 10 mmol of **3a** (entries 12, 13 and 15, 16). The effect of solvents was not systematically studied, but the reaction resulted in a mixture of **4a** and **5a** with a low conversion when $RhH(CO)(PPh_3)_3$ was used in CH_2Cl_2, presumably by reacting with the catalyst to yield $RhCl_3$ species.

2.3. Hydroboration of typical alkenes with *N*-trimethylborazine

Hydroboration of 1-hexene with **2a** needed reoptimization of catalysts since those for ethylene such as $RhH(CO)(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$/DPEphos (entries 1 and 2) were not effective for 1-hexene and other aliphatic alkenes (Table 3). Alternatively, rhodium(I) chloride/phosphine complexes *in situ* generated from $[RhCl(coe)_2]_2$ and triphenyl- or trialkylphosphines (3.3 mol%) were found to catalyze the reaction with yields being increased by increasing the bulkiness and donating ability of the phosphine ligands (entries 5–11). The reaction required a large excess of 1-hexene (2–5 equiv.) and 3 mol% catalyst loading in toluene, but a complete conversion of **3a** to *N,N′,N″*-trihexylborazine (**6 b**) was easily achieved at 50 °C when tri-*t*-butylphosphine (1 or 2 equiv. to Rh) was used as a ligand for the catalyst (entries 10 and 11). The role of *t*-Bu_3P is not well known, but it has been used in platinum-catalyzed hydroboration of allenes with pinacolborane [17] and in hydrosilylation of alkynes to achieve high regioselectivity and high catalyst efficiency [18].

The hydroboration of representative alkenes with **3a** in the presence of the $[RhCl(coe)_2]_2$/4*t*-Bu_3P catalyst is shown in Table 4. The reactions of terminal and internal alkenes smoothly took place under the optimized conditions shown in Table 3 to selectively provide *B*-(*n*-alkyl)borazines (**6b–e**) in high yields (entries 1–10). However, the synthesis failed to yield *B*-(*sec*-alkyl)borazines because hydroboration of (*E*)- and (*Z*)-4-octene resulted in the formation of *n*-alkyl derivatives via complete isomerization to the terminal carbon (entries 4–7). The corresponding reaction of (*E*)- and (*Z*)-2-butene also resulted in isomerization to the terminal carbon (entries 9 and 10). It has been reported that such isomerization is slow in hydroboration with catecholborane using a neutral or cationic rhodium(I) catalyst and

Table 2
Catalyzed hydroboration of ethylene with *N*,*N*′,*N*″-trimethylborazine (**2a**)[a]



Entry	Catalyst (mol%)	Additive (mol%)	Temp. (C)	Toluene (ml)	Conversion (%)[b]	4	5	6
1	$RhCl(PPh_3)_3$ (2)	None	rt	3	100	9	69	22
2	$RhH(CO)(PPh_3)_3$ (2)	None	rt	3	100	0	36	64
3	$RhH(CO)(PPh_3)_3$ (2)	None	100	3	100	14	60	26
4	$RhH(CO)(PPh_3)_3$ (1)	PPh_3 (2)	rt	3	100	16	45	39
5	$RhH(CO)(PPh_3)_3$ (1)	dppm (1)	rt	3	100	27	63	10
6	$RhH(CO)(PPh_3)_3$ (1)	dppe (1)	rt	3	100	1	42	57
7	$RhH(CO)(PPh_3)_3$ (1)	dppe (1)	50	3	100	0.5	0.5	99
8	$RhH(CO)(PPh_3)_3$ (1)	dppp (1)	rt	3	100	0	0	100
9	$RhH(CO)(PPh_3)_3$ (0.1)	dppp (0.1)	rt	3	Trace	–	–	–
10	$RhH(CO)(PPh_3)_3$ (0.1)	dppp (0.1)	rt	0.3	100	2	42	56
11	$RhH(CO)(PPh_3)_3$ (0.1)	dppp (0.1)	50	0.3	100	0	2	98
12	$RhH(CO)(PPh_3)_3$ (0.01)	dppp (0.01)	50	0.3	63	79	19	2
13	$RhH(CO)(PPh_3)_3$ (0.01)	dppb (0.01)	50	0.3	87	55	38	7
14[c]	$RhH(CO)(PPh_3)_3$ (0.02)	dppb (0.02)	50	0.06	100	0	4	96
15	$RhH(CO)(PPh_3)_3$ (0.01)	DPEphos (0.01)	50	0.3	97	33	53	14
16	$RhH(CO)(PPh_3)_3$ (0.01)	DPEphos (0.01)	50	0.03	100	2	59	39
17[c]	$RhH(CO)(PPh_3)_3$ (0.02)	DPEphos (0.02)	50	0.06	100	0	5	95
18	$RhH(CO)(PPh_3)_3$ (0.01)	Xantphos (0.01)	50	0.3	96	35	51	14
19	$RhH(PPh_3)_4$ (0.1)	dppp (0.1)	50	0.3	6	100	0	0
20	$RhF(CO)(PPh_3)_2$ (0.1)	dppp (0.1)	50	0.3	82	69	29	2
21	$[RhCl(CO)_2]_2$ (0.05)	dppp (0.1)/PPh_3 (0.1)	50	0.3	100	0	33	67
22	$Rh_4(CO)_{12}$ (0.025)	dppp (0.1)/PPh_3 (0.1)	50	0.3	100	0	11	89

[a] A mixture of **3a** (10 mmol) in toluene was stirred for 16 h in the presence of a rhodium catalyst and additive (if used) under an atmosphere of ethylene (8 kg/cm^2).
[b] The conversion of **3a** and the area ratio of products were analyzed by GC.
[c] The mixture was stirred for 72 h in toluene (0.06 ml).

that the use of a much bulkier pinacolborane is more prone to afford isomerized 1-alkylboronates [19]. 1,1-Disubstituted ethenes were more strongly resistant than were those of terminal and internal alkenes (entries 11–16). The reaction further proceeded to some extent when the reaction mixture was treated with a fresh catalyst, but all attempts at selective preparation of *B*,*B*′-dialkyl- (**5**) or *B*,*B*′,*B*″-trialkylborazines (**6**) failed (entries 11–15). Hydroboration of 4-*t*-butyl-methylenecyclohexane and cyclohexene was very slow (entries 17 and 19), but under forced conditions in which a fresh catalyst was added after 24 h, *B*,*B*′-bis((4-*tert*-butylcyclohexyl)methyl)-*N*,*N*′,*N*″-trimethylborazine (**5h**) and *B*,*B*′-dicyclohexyl-*N*,*N*′,*N*″-trimethylborazine (**5i**) were exceptionally given in 58 and 70% yields as the sole products (entries 18 and 20). Two (4-*tert*-butylcyclohexyl)methyl or cyclohexane rings perpendicular to the borazine ring may be effective for stopping the reaction before the trialkylborazine stage, thus allowing selective synthesis of *B*,*B*′-dialkylborazine and subsequent transformation to mixed *B*,*B*′,*B*″-trialkylborazines.

2.4. Hydroboration of alkenes with N-triethylborazine

N,*N*′,*N*″-Triethylborazine (**3b**) was more resistant than was *N*,*N*′,*N*″-trimethylborazine (**3a**) due to its increased steric hindrance of *N*-substituents. Hydroboration of ethylene with **3b** failed to yield a single product under conditions optimized for *N*,*N*′,*N*″-trimethylborazine (Scheme 3). However, hydroboration of 1-hexene with **3b** gave *B*,*B*′,*B*″-trihexyl-*N*,*N*′,*N*″-triethylborazine in high yield (95%).

2.5. Synthesis of mixed B-alkylborazines

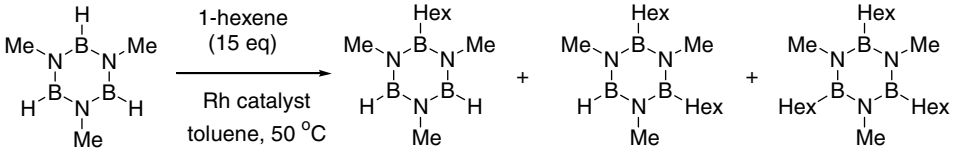
The selective formation of *B*,*B*′-dicyclohexyl-*N*,*N*′,*N*″-trimethylborazine (**5i**) via hydroboration of cyclohexene with **3a** allowed the synthesis of mixed *B*,*B*′,*B*″-trialkylborazines (Scheme 4). The hydroboration of terminal alkenes such as 1-hexene smoothly took place in the presence of $[RhCl(coe)_2]_2$/4*t*-Bu_3P (3 mol% for Rh) to give **7** in 80% yield.

3. Experimental

3.1. General

All reactions were performed under an atmosphere of nitrogen or argon. All solvents and reagents were dried over the appropriate drying agents such as Na and CaH_2, and distilled prior to use. $[RhCl(CO)_2]_2$ was purchased

Table 3
Catalyzed hydroboration of 1-hexene with *N*,*N*′,*N*″-trimethylborazine (**2a**)[a]



3a **4b** **5b** **6b**

Entry	Catalyst (mol%)	Additive (mol%)	Conversion (%)[b]	**4**	**5**	**6**
1	$RhH(CO)(PPh_3)_3$ (3)	None	6	100	0	0
2	$RhH(CO)(PPh_3)_3$ (3)	DPEphos (3.3)	54	24	76	0
3	$RhH(PPh_3)_4$ (3)	None	82	84	16	0
4	$[RhCl(cod)]_2$ (1.5)	PPh_3 (3.3)	36	100	0	0
5	$[RhCl(coe)_2]_2$ (1.5)	PPh_3 (3.3)	87	86	14	0
6	$[RhCl(coe)_2]_2$ (1.5)	PPh_3 (6.6)	0	0	0	0
7	$[RhCl(coe)_2]_2$ (1.5)	P^nPr_3 (3.3)	22	100	0	0
8	$[RhCl(coe)_2]_2$ (1.5)	P^iPr_3 (3.3)	100	4	64	32
9	$[RhCl(coe)_2]_2$ (1.5)	PCy_3 (3.3)	100	19	70	11
10	$[RhCl(coe)_2]_2$ (1.5)	P^tBu_3 (3.3)	100	0	0	100
11	$[RhCl(coe)_2]_2$ (1.5)	P^tBu_3 (6.6)	100	0	0	100

[a] A mixture of **3a** (1 mmol) and 1-hexene (15 mmol) in toluene (0.5 ml) was stirred for 24 h at 50 °C in the presence of a rhodium catalyst and additive (if used).
[b] The conversion of **3a** and the area ratio of products (**4**–**6**) were analyzed by GC.

from Strem Chemicals, $Rh_4(CO)_{12}$ were purchased from Aldrich. PPh_3, dppm, dppe, dppp, dppb, *n*-Pr_3P, *i*-Pr_3P, (*cyclo*-$C_6H_{11})_3P$ and *t*-Bu_3P were commercially available. All alkenes were commercially and purified by distillation if necessary. $RhCl(PPh_3)_3$ [20], $RhH(CO)(PPh_3)_3$ [21], $RhH(PPh)_4$ [22], $RhF(CO)(PPh_3)_2$ [22], $[Rh(cod)Cl]_2$ [23], $[Rh(coe)_2Cl]_2$ [24], DPEphos [25], and Xantphos [25] were synthesized by literature procedures.

3.2. Amine–borane complexes (1) from $BH_3 \cdot Me_2S$

A solution of 100 mmol of primary amine in 20 ml of THF was cooled to −78 °C. To this solution was dropwise added 100 mmol of $BH_3 \cdot Me_2S$ in 10 ml of THF. The reaction mixture was allowed to reach room temperature. THF and Me_2S were removed in vacuo and the resulting solid was dried under high vacuum.

$MeNH_2 \cdot BH_3$ (**1a**): ^{1}H NMR: $\delta = 1.51$ (q, $J = 94.7$ Hz, 3H), 2.57 (t, $J = 6.2$ Hz, 3H), 3.79 (s, broad, 2H). ^{13}C NMR: $\delta = 34.5$. ^{11}B NMR: $\delta = -18.5$.

$EtNH_2 \cdot BH_3$ (**1b**): ^{1}H NMR: $\delta = 1.26$ (dt, $J = 0.98$, 7.2 Hz, 3H), 1.08–1.76 (m, 3H), 2.81–2.89 (m, 2H), 3.95 (s, broad, 2H). ^{13}C NMR: $\delta = 14.3$, 43.4. ^{11}B NMR: $\delta = -20.0$.

n-$PrNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 0.97$ (t, $J = 7.4$ Hz, 3H), 1.11–1.86 (m, 3H), 1.66 (sextet, $J = 7.4$ Hz, 2H), 2.81 (quintet, $J = 7.1$ Hz, 2H), 3.63 (s, broad, 2H). ^{13}C NMR: $\delta = 10.9$, 22.4, 50.5. ^{11}B NMR: $\delta = -19.4$.

i-$PrNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 1.29$ (d, $J = 6.5$ Hz, 6H), 1.12–1.83 (m, 3H), 3.07 (septet, $J = 6.5$ Hz, 1H), 3.58 (s, broad, 2H). ^{13}C NMR: $\delta = 21.9$, 50.2. ^{11}B NMR: $\delta = -25.2$.

n-$BuNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 0.94$ (t, $J = 7.3$ Hz, 3H), 1.06–1.80 (m, 3H), 1.36 (sextet, $J = 6.2$ Hz, 2H), 1.61 (quintet, $J = 7.6$ Hz, 2H), 2.77–2.84 (m, 2H), 3.82 (s, broad, 2H). ^{13}C NMR: $\delta = 13.5$, 19.7, 31.1, 48.6. ^{11}B NMR: $\delta = -19.6$.

s-$BuNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 0.93$ (m, 3H), 0.97–1.77 (m, 3H), 1.24 (m, 3H), 1.49 (m, 1H), 1.71 (m, 1H), 2.82 (s, broad, 1H), 3.63 (d, broad, 2H). ^{13}C NMR: $\delta = 9.63$, 18.1, 28.6, 55.4. ^{11}B NMR: $\delta = -20.6$.

t-$BuNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 1.31$ (s, 9H), 1.08–1.78 (m, 3H), 3.55 (s, broad, 2H). ^{13}C NMR: $\delta = 28.0$, 53.2. ^{11}B NMR: $\delta = -23.0$.

neo-$PenNH_2 \cdot BH_3$: ^{1}H NMR: $\delta = 0.97$ (s, 9H), 1.02–1.91 (m, 3H), 2.61–2.65 (m, 2H), 3.45 (s, broad, 2H). ^{13}C NMR: $\delta = 26.9$, 30.8, 61.1. ^{11}B NMR: $\delta = -18.7$.

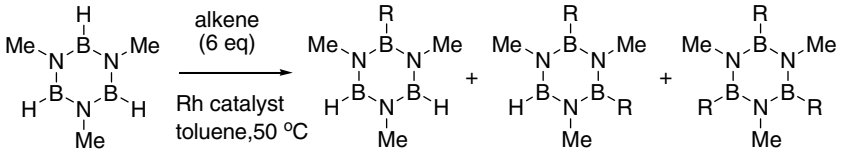
3.3. Synthesis of *N*,*N*′,*N*″-trialkylborazines (Table 1)

To a 100 ml flask, 100 mmol of $RNH_2 \cdot BH_3$ was introduced under nitrogen. The flask was heated in an oil bath by slowly raising the temperature to 120 °C during 30 min. This temperature was maintained for 1 h. The flask was then heated at 200 °C for another hour. Borazines were isolated by distillation in vacuo. For the preparation of *N*,*N*′,*N*″-trimethylborazine, the reaction of 100 mmol of $MeNH_2 \cdot BH_3$ was conducted in tetraglyme (10 ml).

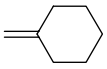
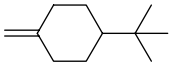
N,*N*′,*N*″-Trimethylborazine (MeN-BH)$_3$ (**3a**): IR: 2943 (m), 2484 (s), 1460 (s), 1064 (m). ^{1}H NMR: $\delta = 3.06$ (s, 9H), 4.46 (q, broad, 3H). ^{13}C NMR: $\delta = 38.0$. ^{11}B NMR: $\delta = 33.3$. MS (EI) *m*/*z* (%): 122 (M^+−H, 100). HRMS: calc for $C_3H_{12}N_3{}^{11}B_3$, $[M]^+ = 123.1310$; found: 123.1318.

N,*N*′,*N*″-Triethylborazine (EtN-BH)$_3$ (**3b**): IR: 2968 (s), 2487 (s), 1441 (s), 1089 (m). ^{1}H NMR: $\delta = 1.14$ (t, $J = 7.2$ Hz, 9H), 3.32 (q, $J = 7.2$ Hz, 6H), 4.48 (d, broad,

Table 4
Catalyzed hydroboration of typical alkenes with *N*,*N*′,*N*″-trimethylborazine (**2a**)[a]

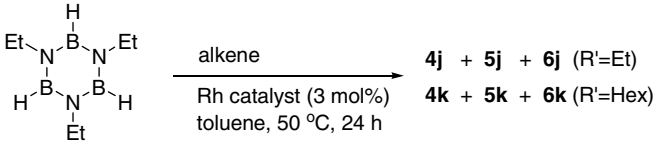


3a **4b-i** **5b-i** **6b-i**

Entry	Alkene	Product, R=	Yield (%)[b]	4	5	6
1[c]	1-Hexene	*n*-C_6H_{13}– (**b**)	84	0	0	100
2[c]	1-Octene	*n*-C_8H_{17}– (**c**)	79	0	17	83
3	1-Octene	*n*-C_8H_{17}– (**c**)	79	0	0	100
4[c,d]	(*E*)-4-Octene	*n*-C_8H_{17}– (**c**)	88	0	31	69
5[d]	(*E*)-4-Octene	*n*-C_8H_{17}– (**c**)	61	0	3	97
6[c,d]	(*Z*)-4-Octene	*n*-C_8H_{17}– (**c**)	75	0	20	80
7[d]	(*Z*)-4-Octene	*n*-C_8H_{17}– (**c**)	68	0	0	100
8[c]	3,3-Dimethyl-1-butene	$(CH_3)_3CCH_2$– (**d**)	85	0	0	100
9[e,f]	(*E*)-2-Butene	*n*-C_4H_9– (**e**)	71	0	2	98
10[e,f]	(*Z*)-2-Butene	*n*-C_4H_9– (**e**)	78	0	0	100
11[c]	2-Methyl-1-propene	$(CH_3)_2CHCH_2$– (**f**)	36	0	70	30
12[c,g]	2-Methyl-1-propene	$(CH_3)_2CHCH_2$– (**f**)	55	0	37	63
13[f]	2-Methyl-1-propene	$(CH_3)_2CHCH_2$– (**f**)	61	0	64	34
14[c]		Cyclohexylmethyl (**g**)	71	64	36	0
15[c,g]		Cyclohexylmethyl (**g**)	82	0	57	43
16[f]		Cyclohexylmethyl (**g**)	75	40	60	0
17[h]		(4-*t*-Butylcyclohexyl)methyl (**h**)	38	100	0	0
18[g]		(4-*t*-Butylcyclohexyl)methyl (**h**)	58	0	100	0
19[c]		*cyclo*-C_6H_{11}– (**i**)	93	30	70	0
20[g]		*cyclo*-C_6H_{11}– (**i**)	70	0	100	0

[a] A mixture of **3a** (0.5 mmol) and alkene (3 mmol) in toluene (0.5 ml) was stirred for 24 h at 50 °C in the presence of $[RhCl(coe)_2]_2$ (1.5 mol%) and P^{t}Bu$_3$ (6.6 mol%).
[b] Isolated yields of **6**.
[c] P^{t}Bu$_3$ (3.3 mol%) was used.
[d] B-(1-octyl) derivatives were selectively given.
[e] B-(1-butyl) derivatives were selectively given.
[f] Alkene (6 mmol) was used.
[g] After being reacted for 24 h, additional $[RhCl(coe)_2]_2$ (1.5 mol%) and P^{t}Bu$_3$ (3.3 mol%) were added.
[h] After being reacted for 24 h, Additional $[RhCl(coe)_2]_2$ (1.5 mol%) and P^{t}Bu$_3$ (6.6 mol%) were added.

3H). ^{13}C NMR: $\delta = 20.7$, 45.8. ^{11}B NMR: $\delta = 33.1$. MS (EI) *m*/*z* (%): 164 (M^+–H, 100), 150 (80). HRMS: calc for $C_6H_{18}N_3{}^{11}B_3$, $[M]^+ = 165.1780$; found: 165.1779.



3b

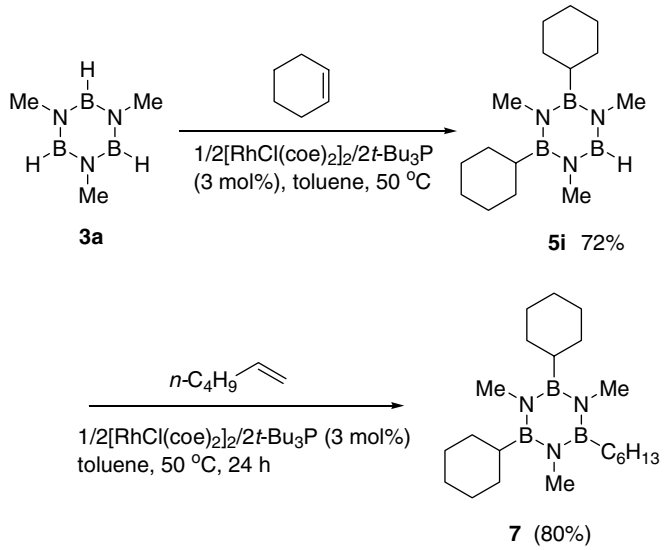
alkene	catalyst	yield/% (**4**/**5**/**6**)
CH_2=CH_2 (8 kg/cm^2)	$RhH(CO)(PPh_3)_3$/dppb	57 (0/86/14)
CH_2=CH_2 (8 Kg/cm^2)	$RhH(CO)(PPh_3)_3$/dppp	51 (0/23/77)
1-hexene (6 eq)	1/2$[RhCl(coe)_2]_2$/*t*-Bu_3P	91 (0/57/43)
1-hexene (12 eq)	1/2$[RhCl(coe)_2]_2$/2*t*-Bu_3P	95 (0/4/96)

Scheme 3. Hydroboration of alkenes with *N*,*N*′,*N*″-triethylborazine (**3b**).

N,*N*′,*N*″-Tripropylborazine (*n*-PrN-BH)$_3$: IR: 2961 (s), 2488 (s), 1437 (s), 1075 (m). IR: 2961 (m), 2488 (s), 1437 (s), 1074 (m). ^{1}H NMR: $\delta = 0.85$ (t, $J = 7.4$ Hz, 9H), 1.49 (sextet, $J = 7.3$ Hz, 6H), 3.23 (t, $J = 7.2$ Hz, 6H), 4.40 (d, broad, 3H). ^{13}C NMR: $\delta = 11.0$, 28.1, 53.0. ^{11}B NMR: $\delta = 33.2$. MS (EI) *m*/*z* (%): 206 (M^+–H, 68), 178 (100). HRMS: calc for $C_9H_{24}N_3{}^{11}B_3$, $[M]^+ = 207.2249$; found: 207.2248.

N,*N*′,*N*″-Triisopropylborazine (*i*-PrN-BH)$_3$: IR: 2969 (s), 2475 (m), 1440 (s). ^{1}H NMR: $\delta = 1.23$ (dd, $J = 0.85$, 6.7 Hz, 18H), 3.67 (septet, $J = 6.7$ Hz, 3H), 4.63 (d, broad, 3H). ^{13}C NMR: $\delta = 26.4$, 51.7. ^{11}B NMR: $\delta = 32.3$. MS (EI) *m*/*z* (%): 206 (M^+–H, 89), 192 (100), 123 (13). HRMS: calc for $C_9H_{24}N_3{}^{11}B_3$, $[M]^+ = 207.2249$; found: 207.2246.

N,*N*′,*N*″-Tri-*n*-buthylborazine (*n*-BuN-BH)$_3$: IR: 2957 (s), 2875 (s), 1444 (s), 1083 (m). ^{1}H NMR: $\delta = 0.90$ (t, $J = 7.3$ Hz, 9H), 1.28 (sextet, $J = 7.3$ Hz, 6H), 1.47 (quintet, $J = 7.7$ Hz, 6H), 3.26 (t, $J = 7.3$ Hz, 6H), 4.44



Scheme 4. Synthesis of mixed alkylborazine (**7**).

(s, broad, 3H). ^{13}C NMR: $\delta = 13.9$, 19.6, 37.5, 50.9. ^{11}B NMR: $\delta = 32.6$. MS (EI) *m*/*z* (%): 248 (M^+-H, 100), 206 (58), 163 (9). HRMS: calc for $C_{12}H_{30}N_3{}^{11}B_3$, $[M]^+ = 249.2719$; found: 249.2711.

N,*N*′,*N*″-Tri-*sec*-butylborazine (*sec*-BuN-BH)$_3$: IR: 2965 (s), 2477 (s), 1437 (s), 992 (m). ^{1}H NMR: $\delta = 0.79$ (t, $J = 7.4$ Hz, 9H), 1.23 (d, $J = 6.8$ Hz, 3H), 1.46–1.61 (m, 6H), 3.32 (sextet, $J = 6.9$ Hz, 3H), 4.49 (d, broad, 3H). ^{13}C NMR: $\delta = 11.3$, 24.5, 32.5, 57.7. ^{11}B NMR: $\delta = 32.4$. MS (EI) *m*/*z* (%): 248 (M^+-H, 13), 220 (100), 161 (12). HRMS: calc for $C_{12}H_{30}N_3{}^{11}B_3$,$[M]^+ = 249.2719$; found: 249.2726.

N,*N*′,*N*″-Tri-*tert*-buthylborazine (*t*-BuN-BH)$_3$: IR: 2972 (m), 2554 (w), 1418 (s), 1084 (w). ^{1}H NMR: $\delta = 1.36$ (s, 27H), 5.06 (d, broad, 3H). ^{13}C NMR: $\delta = 33.8$, 53.4 ^{11}B NMR: $\delta = 31.0$. MS (EI) *m*/*z* (%): 248 (M^+-H, 100), 234 (90), 194 (24), 151 (18), 137 (9). HRMS: calc for $C_{12}H_{30}N_3{}^{11}B_3$, $[M]^+ = 249.2719$; found: 249.2716.

N,*N*′,*N*″-Tri-*neo*-penthylborazine (*neo*-PenN-BH)$_3$: IR: 2953 (m), 2499 (m), 1428 (s), 1089 (s). ^{1}H NMR: $\delta = 0.82$ (s, 27H), 3.12 (s, 6H), 4.37 (d, broad, 3H). ^{13}C NMR: $\delta = 27.5$, 32.8, 62.9. ^{11}B NMR: $\delta = 33.8$. MS (EI) *m*/*z* (%): 291 (M^+, 3), 276 (9), 234 (100), 178 (8), 149 (10). HRMS: calc for $C_{15}H_{36}N_3{}^{11}B_3$, $[M]^+ = 291.3188$; found: 291.3175.

3.4. Synthesis of *N*,*N*′,*N*″-trimethylborazine from $NaBH_4$ (Scheme 2)

To a 100 ml-flask equipped with a magnetic stirring bar and a distilling head, $NaBH_4$ (4.00 g, 105 mmol) and 2 M solution of methylamine in THF (70 ml, 140 mmol) were added. To this mixture was dropwise added $BF_3 \cdot Et_2O$ (12.7 ml, 100 mmol) at −78 °C. The temperature was allowed to reach 0 °C over 1 h. THF and excess $MeNH_2$ were removed in vacuo and the residual was then dissolved in tetraglyme (6 ml). The solution was gradually heated to 120 °C during 1 h. When the hydrogen evolution and forming were subsided, the temperature was slowly raised to 200 °C. *N*,*N*′,*N*″-Trimethylborazine (4.00 g, 98%) was distilled during heating at 200 °C.

3.5. Typical procedure for catalytic hydroboration of ethylene with *N*,*N*′,*N*″-trimethyl- and *N*,*N*′,*N*′-triethylborazine (Table 2)

A glass pressure bottle charged with *N*,*N*′,*N*″-trimethylborazine (10 mmol), $RhH(CO)(PPh_3)_3$ (0.001–0.3 mmol, 0.01–3 mol%), ligand (0–0.4 mmol, P/Rh = 2) in toluene (0.03–3 ml) was sealed under argon atmosphere. The flask was charged with ethylene and final ethylene pressure was adjusted to 8 kg/cm^2. The resulting mixture was stirred at 50 °C for a period shown in Table 2. The product was isolated by Kugelrohr distillation.

B,*B*′,*B*″-Triethyl-*N*,*N*′,*N*″-trimethylborazine (MeN-BEt)$_3$ (**6a**): ^{1}H NMR: $\delta = 0.96$–1.00 (m, 9H), 1.03–1.09 (m, 6H), 2.96 (s, 9H). ^{13}C NMR: $\delta = 7.1$, 8.0, 33.1 ^{11}B NMR: $\delta = 36.9$. MS (EI) *m*/*z* (%): 207 (M^+, 80), 178 (100), 150 (42), 122 (31). HRMS: calc for $C_9H_{24}N_3{}^{11}B_3$, $[M]^+ = 207.2249$; found: 207.2234.

B,*B*′,*B*″-Triethyl-*N*,*N*′,*N*″-triethylborazine (EtN-BEt)$_3$ (**6j**): ^{1}H NMR: $\delta = 0.92$–1.07 (m, 15H), 1.10 (t, $J = 7.0$ Hz, 9H), 3.28 (q, $J = 7.0$ Hz, 6H). ^{13}C NMR: $\delta = 6.4$, 9.9, 20.3, 39.9. ^{11}B NMR: $\delta = 37.3$. MS (EI) *m*/*z* (%): 249 (M^+, 20), 234 (100), 206 (50), 178 (16), 137 (15). HRMS: calc for $C_2H_{30}N_3{}^{11}B_3$, $[M]^+ = 249.2719$; found: 249.2726.

3.6. Typical procedure for catalyzed hydroboration of alkenes with *N*,*N*′,*N*″-trimethylborazines (Table 3)

A glass tube charged with *N*,*N*′,*N*″-trimethylborazine (0.5 mmol), alkene (3 mmol), $[RhCl(coe)_2]_2$ (0.0075 mmol), *t*-Bu_3P (0.033 mmol, P/Rh = 2.1) in toluene (0.5 ml) was sealed under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h. The product was isolated by Kugelrohr distillation.

B,*B*′,*B*″-Trihexyl-*N*,*N*′,*N*″-trimethylborazine, (MeN-B-(*n*-C_6H_{13}))$_3$ (**6b**): ^{1}H NMR: $\delta = 0.89$ (t, $J = 6.6$ Hz, 9H), 1.01–1.05 (m, 6H), 1.30–1.36 (m, 24H), 2.93 (s, 9H). ^{13}C NMR: $\delta = 14.1$, 15.6, 22.7, 24.4, 31.8, 33.2, 33.6. ^{11}B NMR: $\delta = 37.0$. MS (EI) *m*/*z* (%): 207 (M^+, 80), 178 (100), 150 (42), 122 (31). HRMS: calc for $C_{21}H_{48}N_3{}^{11}B_3$, $[M]^+ = 207.2249$; found: 207.2234.

N,*N*′,*N*″-Trimethyl-*B*,*B*′,*B*″-trioctyl-borazine, (MeN-B-(*n*-C_8H_{17}))$_3$ (**6c**): ^{1}H NMR: $\delta = 0.90$ (t, $J = 6.8$ Hz, 9H), 0.98–1.17 (m, 6H), 1.30–1.39 (m, 36H), 2.95 (s, 9H). ^{13}C NMR: $\delta = 14.1$, 15.7, 22.8, 24.5, 29.4, 29.6, 32.1, 33.59, 33.61. ^{11}B NMR: $\delta = 36.7$. MS (EI) *m*/*z* (%): 459 (M^+, 32), 361 (44), 263 (60), 165 (100), 122 (48). HRMS: calc for $C_{27}H_{60}N_3{}^{11}B_3$, $[M]^+ = 459.5066$; found: 459.5077.

B,*B*′,*B*″-Tri(3,3-dimetylbutyl)-*N*,*N*′,*N*″-trimethylborazine (MeN-B-($CH_2CH_2C(CH_3)_3$))$_3$ (**6d**): ^{1}H NMR: $\delta = 0.92$ (s, 27H), 0.95–0.99 (m, 6H), 1.17–1.22 (m, 6H), 2.91 (s, 9H). ^{13}C NMR: $\delta = 28.9$, 31.4, 33.2, 38.1. ^{11}B

NMR: $\delta = 37.2$. MS (EI) m/z (%): 375 (M^+, 18), 360 (30), 318 (75), 305 (100), 290 (37), 248 (20), 235 (17), 206 (17), 122 (28). HRMS: calc for $C_{21}H_{48}N_3{}^{11}B_3$, $[M]^+ = 375.4127$; found: 375.4122.

B,*B*′,*B*″-Tributyl-*N*,*N*′,*N*″-trimethylborazine (MeN-B-(*n*-Bu))$_3$ (**6e**): ^{1}H NMR: $\delta = 0.93$ (t, $J = 7.1$ Hz, 9H), 1.02–1.06 (m, 6H), 1.29–1.45 (m, 12H), 2.94 (s, 9H). ^{13}C NMR: $\delta = 14.0$, 15.3, 26.4, 26.7, 33.6. ^{11}B NMR: $\delta = 37.1$. MS (EI) m/z (%): 291 (M^+, 27), 249 (100), 207 (70), 165 (50), 122 (40), 81 (14). HRMS: calc for $C_{15}H_{36}N_3{}^{11}B_3$, $[M]^+ = 291.3188$; found: 291.3174.

Mixture of *B*,*B*′-di-*i*-butyl-*N*,*N*′,*N*″-trimethylborazine (**5f**) and *B*,*B*′,*B*″-tri-*i*-butyl-*N*,*N*′,*N*″-trimethylborazine (MeN-B-(*i*-Bu))$_3$ (**6f**): ^{1}H NMR: $\delta = 0.95$ (d, $J = 6.8$ Hz), 0.96 (d, $J = 6.3$ Hz), 1.01 (d, $J = 7.3$ Hz), 1.07 (d, $J = 7.3$ Hz), 1.80–1.96 (m, 5H), 2.96(s), 2.98 (s), 3.00 (s, 6H), 4.52 (bs). ^{13}C NMR: $\delta = 25.6$, 25.65, 25.71, 25.9, 29.1, 34.5, 34.8, 37.2. ^{11}B NMR: $\delta = 34.5$, 36.8. MS (EI) m/z (%), **5f**: 235 (M^+, 64), 193 (100), 178 (52), 164 (30), 151 (51), 136 (37), 122 (37), 81 (19), **6f**: 291 (M^+, 97), 276 (35), 249 (100), 234 (47), 207 (56), 192 (24), 178 (26), 165 (21), 122 (32), 81 (18), HRMS: calc for $C_{11}H_{28}N_3{}^{11}B_3$ (**5f**), $[M]^+ = 235.2562$; found: 235.2565, $C_{15}H_{36}N_3{}^{11}B_3$ (**6f**), $[M]^+ = 291.3188$; found: 291.3182.

Mixture of *B*,*B*′-bis(cyclohexylmethyl)-*N*,*N*′,*N*″-trimethylborazine (**5g**) and *B*,*B*′,*B*″-tris(cyclohexylmethyl)-*N*,*N*′,*N*″-trimethylborazine (**6g**): ^{1}H NMR: $\delta = 0.92$–1.30 (m), 1.52–1.85 (m), 2.99(s), 3.00 (s), 3.04 (s, 6H), 4.54 (bs). ^{13}C NMR: $\delta = 26.4$, 26.5, 27.0, 27.1, 34.6, 34.9, 35.6, 35.8, 36.45, 36.48, 37.2. ^{11}B NMR: $\delta = 35.6$. MS (EI) m/z (%), **5g**: 315 (M^+, 31), 233 (100), 151 (43), 136 (17), 122 (24), **6g**: 411 (M^+, 36), 329 (100), 247 (58), 165 (37), 122 (24), HRMS: calc for $C_{17}H_{36}N_3{}^{11}B_3$, $[M]^+ = 315.3188$; found: 315.3188, $C_{24}H_{48}N_3{}^{11}B_3$, $[M]^+ = 411.4127$; found: 411.4117.

B-((4-*tert*-Butylcyclohexyl)methyl)-*N*,*N*′,*N*″-trimethylborazine (**4h**): ^{1}H NMR: $\delta = 0.86$ (s, 18H), 0.92–1.14 (m, 8H), 1.21–1.38 (m, 2H), 1.40–1.52 (m, 8H), 1.73 (m, 4H), 2.01 (m, 2H), 2.99 (s, 3H), 3.01 (s, 6H), 4.48 (s, broad, 1H). ^{13}C NMR: $\delta = 21.9$, 27.5, 27.8, 29.3, 33.3, 37.2, 48.6. ^{11}B NMR: $\delta = 34.1$. MS (EI) m/z (%): 207 (M^+, 80), 178 (100), 150 (42), 122 (31). HRMS: calc for $C_{14}H_{32}N_3{}^{11}B_3$, $[M]^+ = 275.2875$; found: 275.2877.

B,*B*′-Bis((4-*tert*-butylcyclohexyl)methyl)-*N*,*N*′,*N*″-trimethylborazine (**5h**): ^{1}H NMR: $\delta = 0.86$ (s, 9H), 0.92–1.11 (m, 4H), 1.24–1.53 (m, 5H), 1.72 (m, 2H), 2.04 (m, 1H), 3.02 (s, 6H), 3.04 (s, 3H), 4.49 (d, broad, 2H). ^{13}C NMR: $\delta = 21.9$, 27.6, 27.8, 32.4, 32.6, 33.3, 36.9, 48.6. ^{11}B NMR: $\delta = 37.1$. MS (EI) m/z (%): 275 (M^+, 22), 151 (21), 137 (100), 122 (55). HRMS: calc for $C_{25}H_{52}N_3{}^{11}B_3$, $[M]^+ = 427.4440$; found: 427.4438.

B,*B*′-Dicyclohexyl-*N*,*N*′,*N*″-trimethylborazine (**5i**): ^{1}H NMR: $\delta = 1.21$–1.40 (m, 6H), 1.47–1.78 (m, 16H), 3.04 (s, 9H). ^{13}C NMR: $\delta = 27.2$, 27.8, 28.5, 34.8, 37.5. ^{11}B NMR: $\delta = 36.1$. MS (EI) m/z (%): 287 (M^+, 75), 232 (57), 219 (100), 204 (31), 150 (25), 122 (81), 81(50). HRMS: calc for $C_{15}H_{32}N_3{}^{11}B_3$, $[M]^+ = 287.2875$; found: 287.2869.

B,*B*′,*B*″-Tri-*n*-hexyl-*N*,*N*′,*N*″-triethylborazine (EtN-B-(*n*-C_6H_{13}))$_3$ (**6k**): ^{1}H NMR: $\delta = 0.90$–1.08 (m, 42H), 1.76–1.94 (m, 6H), 2.96 (q, $J = 6.3$ Hz, 6H). ^{13}C NMR: $\delta = 24.9$, 25.6, 25.7, 25.9, 31.5, 34.4, 34.8, 37.2. ^{11}B NMR: $\delta = 36.5$. MS (EI) m/z (%): 417 (M^+, 70), 400 (100), 358 (33), 347 (74), 332 (48), 318 (57), 304 (31), 288 (44), 277 (50), 262 (24), 248 (54), 234 (41), 207 (24), 193 (33), 164 (61), 150 (20), 109 (22). HRMS: calc for $C_{24}H_{54}N_3{}^{11}B_3$, $[M]^+ = 417.4597$; found: 417.4601.

3.7. Mixed alkylborazine (7)

A glass tube charged with *B*,*B*′-dicyclohexyl-*N*,*N*′,*N*″-trimethylborazine (0.5 mmol), 1-hexene (3 mmol), $[RhCl(coe)_2]_2$ (0.0075 mmol), *t*-Bu_3P (0.033 mmol, P/Rh = 2.1) in toluene (0.5 ml) was sealed under argon atmosphere. The resulting mixture was stirred at 50 °C for 24 h. The product was isolated by Kugelrohr distillation.

B,*B*′-(Dicylohexyl)-*B*″-*n*-hexyl-*N*,*N*′,*N*″-trimethylborazine (**7**): ^{1}H NMR: $\delta = 0.90$–0.96 (m, 3H), 1.01–1.05 (m, 2H), 1.31–1.38 (m, 14H), 1.50–1.77 (m, 16H), 2.99 (s, 6H), 3.03 (s, 3H). ^{13}C NMR: $\delta = 14.2$, 22.7, 24.4, 27.3, 27.9, 28.6, 31.7, 33.3, 34.1, 34.7. ^{11}B NMR: $\delta = 36.9$. MS (EI) m/z (%): 371 (M^+, 56), 316 (32), 301 (73), 246 (19), 233 (58), 206 (27), 165 (27), 150 (16), 122 (100), 81 (85). HRMS: calc for $C_{21}H_{44}N_3{}^{11}B_3$, $[M]^+ = 371.3814$; found: 371.3823.

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