JOC Article

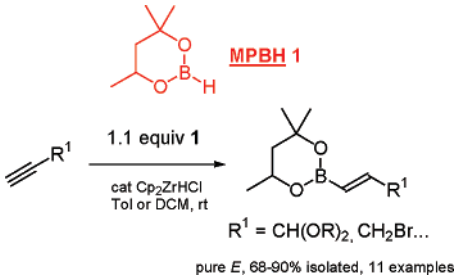
Methylpentanediolborane: Easy Access to New Air- and Chromatography-Stable, Highly Functionalized Vinylboronates

Nageswaran PraveenGanesh, Sylvain d'Hondt, and Pierre Yves Chavant*

Département de Chimie Moléculaire, CNRS, Université Joseph Fourier, BP-53, 38041 Grenoble Cedex 9, France

Pierre-Yves.Chavant@ujf-grenoble.fr

Received March 16, 2007



Methylpentanediolborane (MPBH) **1** can be prepared easily by reaction of hexyleneglycol with BH_3/DMS or B_2H_6 generated from $NaBH_4$ and I_2. MPBH hydroborates stereo- and regioselectively highly functionalized alkynes, including propargyl bromide and propionaldehyde acetal. MPBH compares favorably with pinacolborane in terms of reactivity. The obtained vinylboronic esters are air- and chromatography-stable.

Introduction

In the course of our study on the boron-to-zinc transmetalation of vinylboronic esters,[1] we found that the air-, water-, and chromatography-stable pinacol esters[2] could be used, but in rather harsh conditions that limited the scope. Preliminary experiments[3] with less hindered cyclic esters, for example with 2-(hexen-1-yl)-5,5-dimethyl-[1,3,2]dioxaborinane, were encouraging, but we had to prepare these reagents by esterification of the vinylboronic acid with the diol at the end of a multistep process.[4] Thus, we sought other vinylboronic esters that would be less hindered than pinacol esters, but that could also be prepared, purified, and stored very easily.

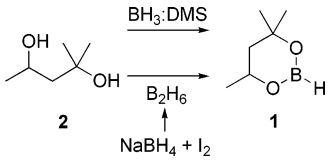
A straightforward access to vinylboronic esters is the direct hydroboration of alkynes, well known for catecholborane[5] or pinacolborane (PinBH).[6] Several catalysts[7,8] have considerably improved the efficiency and scope of this hydroboration. Nevertheless, analogous methods in the dioxaborinanes series received little attention.[7b,9] Although the preparation of 4,4,6-trimethyl-1,3,2-dioxaborinane **1** from cheap hexyleneglycol (2-methyl-2,4-pentanediol) **2**[10] and the ability of **1** to hydroborate alkynes to produce stable vinylboronic esters have been known since 1966, this reagent was scarcely used.[11]

We describe here easy and efficient preparations of 4,4,6-trimethyl-1,3,2-dioxaborinane **1** (methylpentanediolborane, MPBH; Scheme 1). We show that hydroboration with **1** catalyzed by Schwartz's reagent[8] allows a straightforward and

(1) Pandya, S. U.; Pinet, S.; Chavant, P. Y.; Vallée, Y. *Eur. J. Org. Chem.* **2003**, 3621.
(2) Vaultier, M.; Alcaraz, G. In *Science of Synthesis*; Kaufmann, D., Ed.; Thieme Chemistry: Stuttgart, 2004; Vol. 6, p 721.
(3) DeCandia, C.; Chavant, P. Y. (D.C.M., Université J. Fourier Grenoble, unpublished results, 2003).
(4) (a) Hoffmann, R. W.; Dresely, S. *Synthesis* **1988**, 103. See also: (b) Rasset-Deloge, C.; Vaultier, M. *Bull. Soc. Chim. Fr.* **1994**, *131*, 919. (c) Kamabuchi, A.; Moriya, T.; Miyaura, N.; Suzuki, A. *Synth. Commun.* **1993**, *23*, 2851. (d) Gravel, M.; Toure, B. B.; Hall, D. G. *Org. Prep. Proced. Int.* **2004**, *36*, 573. (e) Lombardo, M.; Morganti, S.; Tozzi, M.; Trombini, C. *Eur. J. Org. Chem.* **2002**, 2823.
(5) Lane, C. F.; Kabalka, G. W. *Tetrahedron* **1976**, *32*, 981.
(6) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.
(7) (a) Shirakawa, K.; Arase, A.; Hoshi, M. *Synthesis* **2004**, 1814 and references therein. (b) Vogels, C. M.; Westcott, S. A. *Curr. Org. Chem.* **2005**, *9*, 687. (c) Murata, M.; Kawakita, K.; Asana, T.; Watanabe, S.; Masuda, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 825. (d) Suseela, Y.; Prasad, A. S. B.; Periasamy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 446. (e) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synthesis* **2000**, 778. (f) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990. (g) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283.
(8) (a) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127. (b) Wang, Y. D.; Kimball, G.; Prashad, A. S.; Wang, Y. *Tetrahedron Lett.* **2005**, *46*, 8777.
(9) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.
(10) Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966**, *88*, 4667.

10.1021/jo070504g CCC: $37.00
Published on Web 05/11/2007

SCHEME 1. Preparations of MPBH



stereoselective preparation of various highly functionalized *E* vinylboronic esters under mild conditions.

Results

Preparation of MPBH 1 and Hydroboration of 1-Alkynes. Our first preparation of MPBH **1** was directly inspired by the work of Tucker et al.[6] Reaction of neat borane/dimethylsulfide complex with 2-methyl-2,4-pentanediol **2** in dry dichloromethane at 0 °C led very efficiently to the formation of MPBH **1**. ^{11}B and ^{1}H NMR indicated that the sole impurity was excess BH_3/DMS.[12] Commercial solutions of BH_3 in THF led to impure samples.[13]

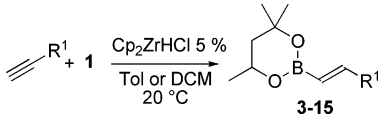
We also investigated a procedure inspired by the work of Suseela and Periasamy,[14] who showed that B_2H_6 can be conveniently generated from I_2 and $NaBH_4$ in ether solvents. Thus, we used a dropwise addition of a solution of I_2 in diglyme into a solution of $NaBH_4$ in the same solvent to generate a stream of B_2H_6 (and H_2). The gas was diluted with a stream of N_2 and bubbled in a separate flask through a solution of hexyleneglycol **2** in toluene or dichloromethane at 0 °C. A fast, slightly exothermic reaction took place.[15] To obtain complete conversion of diol **2**, it was sufficient to generate 1.5 mol equiv of B_2H_6 (from 1.5 equiv of I_2 and 3 equiv of $NaBH_4$). MPBH **1** was obtained in excellent purity, as confirmed by ^{1}H and ^{11}B NMR of the solution.

The standardized toluene or dichloromethane solutions of MPBH **1** could be kept for several months at 4 °C without any change in their NMR spectra.

Noticeably, the same protocol could be applied to the preparation of DMS-free solutions of pinacolborane in toluene, also in high purity. The uptake of borane by the pinacol solution was slower, and a larger excess of diborane was required (6 equiv of $NaBH_4$ involved instead of 3).[16]

Both preparations failed to produce pure samples of 5,5-dimethyl-1,3,2-dioxaborinane from 2,2-dimethyl-1,3-propanediol. In all attempts, fast disproportionation of the borinane led to contamination by a trialkoxyborane species (^{11}B NMR: 17 ppm). Worse, subsequent attempts to hydroborate alkynes with these solutions of impure dioxaborinane led to complex mixtures. One explanation is that concurrent hydroboration and disproportionation led to a mixture of boronic and borinic species.

TABLE 1. Hydroboration of Alkynes with MPBH



product	R^1 =	isolated yield
3	Ph	93[a](79[d])
4	*n*-Bu	90[a]
5	cyclohexen-1-yl	66[a]
6	$(CH_2)_3Cl$	66[a]
7	TMS	61[a]
8	CH_2OMe	70[b](49[a])
9	CH_2OAc	68[b](43[a])
10	CH_2OCOPh	0[c]
11	CH_2OtBu	82[a]
12	CH_2Cl	68[b]
13	CH_2Br	73[a]
14	$CH(OEt)_2$	80[a]
15	COOtBu	19[a,c]

[a] Obtained using MPBH in toluene. [b] Obtained using MPBH in DCM. [c] Remainder: starting material. [d] DCM, 40 °C, 4 h.

Hydroboration of 1-Alkynes with 1. We next used these toluene or dichloromethane (DCM) solutions of MPBH **1** for the hydroboration of various 1-alkynes, with a special interest for alkynes carrying heteroatoms on position 3. We chose the commercially available, easy-to-handle Schwartz's reagent[8a] as the catalyst, and the reactions were run in toluene or DCM at room temperature overnight. In these conditions, both preparations of MPBH led to the same results; DMS was not interfering. No reaction took place in the absence of catalyst. After completion, a simple filtration of the crude material on basic alumina yielded the vinylboronic ester in pure form.

As illustrated in Table 1, the MPBH/Cp_2ZrClH system hydroborated readily, in moderate to excellent yields and excellent purity, diversely functionalized alkynes, including propargyl chloride,[4d,e] bromide,[17] or protected propionaldehyde.[4b,c] Propargyl alcohol could be used, when protected as an acetate or *tert*-butyl ether (products **9** and **11**). Surprisingly, the corresponding benzoate (**10**) could not be hydroborated, despite repeated attempts. Toluene solutions of **1** are more easily stored than DCM solutions, but toluene removal can be problematic with volatile vinylboronic esters (**8** and **9**). The electron-poor *t*-butyl propiolate reacted very sluggishly at 20 °C (product **15**).

Comparison with Pinacolborane. The goal of the present work was to provide a convenient access to vinylboronic esters that would not be pinacol esters, and this is obviously the main difference between MPBH and PinBH. Nevertheless, it could be interesting to compare the intrinsic reactivity of MPBH and PinBH in the Zr-catalyzed hydroboration.

For this study, we used solutions of MPBH and PinBH in DCM, prepared by the $NaBH_4/I_2$ procedure. We chose to perform competition experiments (Scheme 2): a mixture of 1 equiv each of both boranes (MPBH **1** and PinBH) was reacted with the 1-alkyne (1-hexyne or phenylacetylene or propargyl bromide) in the presence of 10% Cp_2ZrClH, at 20 °C. We

(11) (a) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed.* **1985**, *24*, 87. (b) Kono, H.; Ito, K.; Nagai, Y. *Chem. Lett.* **1975**, 1095. (c) Fish, R. H. *J. Org. Chem.* **1973**, *38*, 158. (d) Fish, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 4435. Interesting applications of the parent 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane: (e) Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Org. Biomol. Chem.* **2005**, *3*, 3167. (f) Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Synlett* **2005**, 529. (g) Lightfoot, A. P.; Maw, G.; Thirsk, C.; Twiddle, S. J. R.; Whiting, A. *Tetrahedron Lett.* **2003**, *44*, 7645.

(12) 25.2 ppm (sharp, d, $J = 170$ Hz).

(13) Potyen, M.; Josyula, K. V. B.; Schuck, M.; Lu, S.; Gao, P.; Hewitt, C. *Org. Process Res. Dev.* **2007**, *11*, 210.

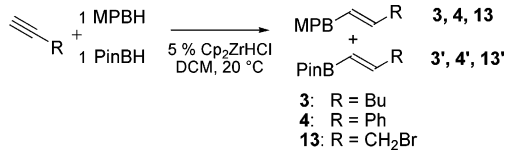
(14) Suseela, Y.; Periasamy, M. *J. Organomet. Chem.* **1993**, *450*, 47.

(15) We observed that only H_2 is evolving at the beginning of the addition, since the first step is the formation of NaB_2H_7: Brown, H. C.; Tierney, P. A. *J. Am. Chem. Soc.* **1958**, *80*, 1552.

(16) This difference showed that the uptake diborane by the pinacol is not quantitative. We checked by experiments involving sequential bubblers that it is the same with hexyleneglycol. Thus, the excess of diborane is actually swept through the solution by the H_2/N_2 mixture and must be carefully trapped.

(17) Gaddoni, L.; Lombardo, M.; Trombini, C. *Tetrahedron Lett.* **1998**, *39*, 7571.

SCHEME 2. Competition Experiments



monitored by GC (internal standard) the formation of the corresponding vinylboronate **3** (respectively **4** or **13**) and its pinacol-derived isomer **3′** (respectively **4′** or **13′**). This protocol ruled out any experimental bias that could evolve from contaminants in boranes or reagents (that could either poison the catalyst or act as catalysts[18]).

We found that the curves of formation of all boronates were linear, up to about 40% conversion of **1**. Rates ratios were estimated from the slopes of the trend lines in this region. In the case of the reactive 1-hexyne (3 equiv), **3** formed 5 times faster than **3′**. With phenylacetylene (1 equiv), **4** formed 10 times faster than **4′**. In a separate experiment, we repeated Pereira and Srebnik's[8a] preparation of **4′** with our DMS-free solution of PinBH and obtained **4′** in 61% isolated yield (lit.[8a] 75%; corresponding yield in **4** from MPBH 93%; see Table 1).

The largest difference appeared with propargyl bromide. MPBH led to **13** in 73% isolated yield (5% cat.; Table 1). In the same conditions, no reaction took place between propargyl bromide and DMS-free PinBH (10% cat.).[19] We performed a competition experiment (2 equiv of propargyl bromide) and observed evolution of **13** and traces of **13′**; **13** was formed 14 times faster. After 20 h at 20 °C, the final GC yield was 67% for **13** and 5% for **13′**. In both phenylacetylene and propargyl bromide competition experiments, the reaction did not proceed further; ^{11}B NMR showed that both borinanes had disappeared.

Thus, we have shown that MPBH **1**, very easily prepared from hexyleneglycol and BH_3/DMS or $NaBH_4/I_2$, is an excellent reagent for the preparation of an unexploited[11] series of air- and chromatography-stable vinylboronic esters. A great variety of functional groups is tolerated, allowing an easy preparation of highly functionalized, valuable synthetic intermediates. We are currently investigating the hydroboration of alkenes with MPBH in the presence of Wilkinson's catalyst.[7g] For example, styrene provided exclusively the 2-borylated isomer 4,4,6-trimethyl-2-phenethyl-[1,3,2]dioxaborinane **16** (DCM, 1% RhCl-$(PPh_3)_3$, 0 °C, 16 h, quant.). An application of these vinylboronic esters to the vinylation of nitrones will be reported shortly.

Experimental Section

All reactions were performed under nitrogen using usual Schlenk techniques, in oven-dried glassware, with magnetic stirring. Solutions of BH_3 in THF (1 M) and BH_3/DMS (10 M) were purchased from Aldrich. DCM and 2-methyl-2,4-pentanediol were distilled from CaH_2. Toluene was distilled from sodium.

Preparation of MPBH 1 from BH_3/DMS. *Caution: Stench! H_2 evolution!* A solution of 2-methyl-2,4-pentanediol (10 mmol, 1.18 g) in dry dichloromethane or toluene (2.36 mL) was stirred and cooled to 0 °C. A solution of BH_3/DMS (11 mmol, 10 M in methyl sulfide, Aldrich) was added over 20−30 min to control the brisk evolution of gas. The reaction was stirred for 1 h at 0 °C and was then warmed to 25 °C and stirred for an additional 1 h until there was no further evolution of gas. The resulting solution was checked by ^{11}B and ^{1}H NMR; conversion of the diol was quantitative. This solution was used as such for hydroboration.

Preparation of MPBH 1 from $NaBH_4$ and I_2. *Caution: Diborane is a toxic and pyrophoric gas! H_2 evolution! Preparation should be carried out under an efficient fume hood!* In a 100-mL double-necked round-bottomed flask fitted with a pressure-equalizing dropping funnel, an efficient magnetic stirring, and a N_2 inlet, $NaBH_4$ (1.14 g, 30 mmol) was suspended in 6 mL of bis(2-methoxyethyl) ether (diglyme). This flask was connected through a double-ended needle to a second 25-mL cylindrical flask containing a solution of 2-methyl-2,4-pentanediol (1.18 g, 10 mmol) in 11.8 mL of dry dichloromethane or toluene, placed in an ice bath. The second flask was vented through a second double-ended needle bubbling into ethanol (to trap excess diborane). The dropping funnel was loaded with a solution of I_2 (15 mmol, 3.84 g) in diglyme (18 mL). The I_2 solution was added dropwise over 1 h; the temperature rose gently to 40 °C. The evolved gases[15] were bubbled through the solution of diol **2** in the second flask. All along the process, a small stream of N_2 (2−5 bubbles per second) was applied through the whole apparatus to ensure complete transfer of the diborane. At the end of the addition of I_2, the temperature of the second flask was brought to 20 °C, and the stream of N_2 was continued for 1 h; this step allowed the elimination of any excess diborane in the solution of MPBH **1**. The solution was transferred to a volumetric flask and diluted to 20 mL. ^{11}B and ^{1}H NMR indicated that the conversion of the diol was quantitative. Thus, the solution was considered 0.50 M in MPBH **1**. The solution could be kept at 4 °C for several months without change. Storage at room temperature was deleterious.

General Experimental Procedure for the Hydroboration of Alkynes by MPBH 1. A 5-mL round-bottom flask equipped with a side arm and magnetic stirring was charged with $HZrCp_2Cl$ (0.05 mmol, 13 mg) and dry dichloromethane or toluene (1 mL) under a N_2 atmosphere and cooled to 0 °C. Alkyne (1.0 mmol) was then added dropwise, the mixture then was stirred for 2 min, and MPBH **1** (1.1 mmol) was introduced dropwise via a syringe. Stirring was continued for 16 h at 20 °C, at which point GC analysis of a reaction aliquot showed completion of reaction. Isolation of the product was achieved by removing volatile matter under reduced pressure followed by flash column chromatography (3% ether in hexane) to provide the desired product as a clear oil.

All products were found to be >95% purity by gas chromatography (FID).

The above procedure was also applied for the hydroboration of styrene by changing the catalyst to $(PPh_3)_3RhCl$ (0.01 mmol, 9 mg).

Spectroscopic Data. *In the 75.5 MHz ^{13}C NMR spectra, C atoms that are directly bonded to boron, marked (br), were approximately 250 Hz wide and can easily remain undetected.*

1: MPBH (4,4,6-Trimethyl-1,3,2-dioxaborinane): ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.16 (dqd, J = 11.8, 6.2, 3.0 Hz, 1H), 1.76 (ddd, J = 13.9, 3.0, 1.7 Hz, 1H), 1.50 (dd, J = 13.9, 11.8 Hz, 1H), 1.27 (s, 3H), 1.26 (s, 3H), 1.23 (d, J = 6.21 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ ppm 70.8, 64.6, 46.1, 31.0, 28.1, 22.9. ^{11}B NMR (96 MHz, $CDCl_3$) δ ppm 25.2 (d, J = 170 Hz). IR (neat, cm^{-1}): 2551, 2498.

3: 4,4,6-Trimethyl-2-styryl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.5−7.4 (m, 2H), 7.35−7.2 (m, 4H), 6.11 (d, J = 18.2 Hz, 1H), 4.26 (dqd, J = 11.7, 6.2, 3.0 Hz, 1H), 1.80 (dd, J = 13.8, 3.0 Hz, 1H), 1.53 (dd, J = 13.8, 11.7 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ ppm 146.4, 137.9, 128.3, 128.2, 126.8, 121 (br), 70.7, 64.7, 45.9, 31.2, 28.1, 23.1. ^{11}B NMR (96 MHz, $CDCl_3$) δ 25.8 ppm. IR (cm^{-1}): 3023, 2974, 1624, 1577, 1213, 1162, 993,

(18) Pereira and Srebnik pointed out (ref 8a) that some hydroboration could take place without Cp_2ZrClH, depending on the preparation of PinBH. Hydroboration of 1-alkynes with PinBH is catalyzed by dicyclohexylborane (ref 7a); thus, the possibility of catalysis by products containing B−H bonds should be considered. Reference 7f showed that ether and amine ligands affect positively the Cp_2ZrClH catalysis.

(19) Hydroboration of propargyl bromide by Cy_2BH: Lombardo, M.; Morganti, S.; Trombini, C. *J. Org. Chem.* **2000**, *65*, 8767. Hydroboration of propargyl chloride with PinBH catalyzed by Cy_2BH was reported in ref 7a.

750. LRMS (EI) *m/z* (%) 230(100) [M^+], 130(71), 215(69), 229-(25), 231(17), 232(3). HRMS EI *m/z* calcd for $C_{14}H_{19}BO_2^+$ 230.1473; found 230.1478.

4: 2-Hex-1-enyl-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.52 (dt, J = 17.7, 6.4 Hz, 1H), 5.34 (dt, J = 17.7, 1.6 Hz, 1H), 4.20 (dqd, J = 11.8, 6.2, 2.9 Hz, 1H), 2.12 (m, 2H), 1.77 (dd, J = 13.9, 2.9 Hz, 1H), 1.49 (dd, J = 13.9, 11.8 Hz, 1H), 1.43−1.30 (m, 4H), 1.29 (s, 6H), 1.26 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 150.9, 123.7 (br), 70.3, 64.4, 45.9, 35.0, 31.2, 30.5, 28.0, 23.1, 22.2, 13.8. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.6 ppm. IR (cm^{-1}): 2973, 1639, 1388, 1164, 998, 768. LRMS (DCI NH_3/isobutane) *m/z* (%) 228(100) [$M + NH_4^+$]. HRMS (DCI NH_3) *m/z* calcd for $C_{12}H_{27}BNO_2^+$ 228.2129; found 228.2135.

5: 2-Cyclohexen-1-enyl-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.91 (d, J = 17.6 Hz, 1H), 5.88 (br t, J = 3.2 Hz, 1H), 5.34 (d, J = 17.6 Hz, 1H), 4.20 (dqd, J = 11.8, 6.2, 3.0 Hz, 1H), 2.18−2.04 (m, 2H), 1.76 (dd, J = 13.9, 3.0 Hz, 1H), 1.68−1.53 (m, 4H), 1.47 (dd, J = 13.9, 11.8 Hz, 1H), 1.30−1.27 (m, 8H), 1.25 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 150.1, 137.1 (br), 132.4, 117.4, 70.4, 64.5, 45.9, 31.1, 28.0, 25.9, 23.9, 23.1, 22.4, 22.3. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 26.0 ppm. IR (cm^{-1}): 3018, 2974, 2929, 1634, 1607, 1300, 1162, 997, 795, 771. LRMS (DCI NH_3/isobutane) *m/z* (%) 235(100) [$M + H^+$], 247(40), 248(23), 250(34), 251(4). HRMS (DCI NH_3) *m/z* calcd for $C_{14}H_{24}BO_2$ 235.1864; found 235.1861.

6: 2-(5-Chloropent-1-enyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (200 MHz, *CDCl*$_3$) δ ppm 6.42 (dt, J = 17.7, 6.4 Hz, 1H), 5.33 (dt, J = 17.7, 1.5 Hz, 1H), 4.16 (dqd, J = 11.7, 6.2, 3.0 Hz, 1H), 3.48 (t, J = 6.7 Hz, 2H), 2.29−2.13 (tt, J = 8.1, 6.7 Hz, 2H), 1.85 (q, J = 8.1 Hz, 1H), 1.73 (dd, J = 13.9, 3.0 Hz, 1H), 1.44 (dd, J = 13.9, 11.7 Hz, 1H), 1.24 (s, 6H), 1.21 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 148.3, 125.2 (br), 70.5, 64.5, 45.9, 44.3, 32.3, 31.2(×2), 28.0, 23.0. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.5 ppm. IR (cm^{-1}): 2970, 2933, 1641, 1392, 1164, 995, 771. LRMS (DCI NH_3/isobutane) *m/z* (%) 248(100) [$M + NH_4^+$], 234(11), 236(7). HRMS (DCI NH_3) *m/z* calcd for $C_{11}H_{24}BClNO_2$ 248.1583; found 248.1586.

7: 4,4,6-Trimethyl-2-(2-trimethylsilanylvinyl)-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 7.01 (d, J = 21.6 Hz, 1H), 6.18 (d, J = 21.6 Hz, 1H), 4.24 (dqd, J = 11.7, 6.2, 3.0 Hz, 1H), 1.79 (dd, J = 13.8, 3.0 Hz, 1H), 1.51 (dd, J = 13.8, 11.7 Hz, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H), 0.07 (s, 9H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm: 153.3, 142 (br), 70.7, 64.7, 45.9, 31.1, 28.0, 26.8, 23.1, −1.6. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 24.6 ppm. IR (cm^{-1}): 2970, 1592, 1418, 1389, 1018, 862, 1166, 837, 744. LRMS (DCI NH_3/isobutane) *m/z* (%) 228(100) [$M + NH_4^+$], 209(9), 243(36), 245(12). HRMS (DCI NH_3) *m/z* calcd for $C_{11}H_{27}BNO_2Si$ 244.1899; found 244.1909.

8: 2-(3-Methoxypropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (200 MHz, *CDCl*$_3$) δ ppm 6.46 (dt, J = 17.9, 5.1, 1H), 5.52 (dt, J = 17.9, 1.3 Hz, 1H), 4.16 (dqd, J = 11.6, 6.3, 3.0 Hz, 1H), 3.91 (dd, J = 5.1, 1.3 Hz, 2H), 3.28 (s, 3H), 1.73 (dd, J = 13.8, 3.0 Hz, 1H), 1.43 (dd, J = 13.8, 11.6 Hz, 1H), 1.24 (s, 6H), 1.20 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 145.5, 126 (br), 74.4, 70.6, 64.6, 58.0, 45.9, 31.1, 28.0, 23.0. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.5 ppm. IR (cm^{-1}): 2974, 1644, 1392, 1120, 1001, 768, 620. LRMS (DCI NH_3/isobutane) *m/z* (%) 216(100) [$M + NH_4^+$], 184(26), 199(20), 215(36), 217(14). HRMS (DCI NH_3) *m/z* calcd for $C_{10}H_{23}BNO_3^+$ 216.1766; found 216.1708.

9: 2-(3-Acetoxypropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (200 MHz, *CDCl*$_3$) δ ppm 6.44 (td, J = 17.8, 4.9 Hz, 1H), 5.52 (td, J = 17.8, 1.7 Hz, 1H), 4.55 (dd, J = 4.9, 1.7 Hz, 2H), 4.15 (dqd, J = 11.6, 6.2, 3.1 Hz, 1H), 2.01 (s, 3H), 1.73 (dd, J = 13.9, 3.1 Hz, 1H), 1.42 (dd, J = 13.9, 11.6 Hz, 1H), 1.22 (s, 6H), 1.19 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 170.4, 142.3, 125 (br), 70.7, 65.6, 64.6, 45.8, 31.0, 27.9, 22.9, 20.7. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.6 ppm. IR (cm^{-1}): 3015, 2975, 2935, 1744, 1163, 993, 768. LRMS (DCI NH_3/isobutane) *m/z* (%) 227(100) [$M + H^+$], 244(52). HRMS (DCI NH_3) *m/z* calcd for $C_{11}H_{23}BNO_4^+$ 244.1715; found 244.1708.

11: 2-(3-*tert*-Butoxypropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.48 (dt, J = 17.8, 4.9 Hz, 1H), 5.52 (dt, J = 17.8, 1.2 Hz, 1H), 4.12 (dqd, J = 12.1, 6.2, 2.9 Hz, 1H), 3.88 (dd, J = 4.9, 1.2 Hz, 2H), 1.69 (dd, J = 13.9, 2.9 Hz, 1H), 1.39 (dd, J = 13.9,12.1 Hz, 1H), 1.20 (s, 6H), 1.17 (d, J = 6.2 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 147.3, 123.4 (br), 72.8, 70.4, 64.4, 63.9, 45.9, 31.1, 27.9, 27.4 (×3), 23.0. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.4 ppm. IR (cm^{-1}): 1644, 1391, 997, 768, 620. LRMS (DCI NH_3/isobutane) *m/z* (%) 258(100) [$M + NH_4^+$], 202(39), 256(11), 257(21), 259-(6). HRMS (ESI) calcd for $C_{13}H_{25}O_3BNa^+$ 263.17890(100), 262.18253(25), 264.18226(14); found 263.17891(100), 262.18258-(25), 264.18213(14).

12: 2-(3-Chloropropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (200 MHz, *CDCl*$_3$) δ ppm 6.52 (dt, J = 17.4, 6.3 Hz, 1H), 5.62 (dt, J = 17.4, 1.4 Hz, 1H), 4.22 (dqd, J = 11.5, 6.2, 3.0 Hz, 1H), 4.07 (dd, J = 6.3, 1.4 Hz, 2H), 1.80 (dd, J = 13.9, 3.0 Hz, 1H), 1.49 (dd, J = 13.9, 11.5 Hz, 1H), 1.29 (s, 6H), 1.26 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 143.3, 128.1 (br), 70.8, 64.7, 46.2, 45.8, 31.0, 27.9, 22.9. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.3 ppm. IR (cm^{-1}): 2974, 1641, 1421, 1162, 993, 767. We could not obtain any coherent mass spectrum for this compound.

13: 2-(3-Bromopropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.50 (td, J = 17.3, 7.2 Hz, 1H), 5.51 (td, J = 17.3, 1.1 Hz, 1H), 4.13 (dqd, J = 11.8, 6.2, 3.0 Hz, 1H), 3.88 (dd, J = 7.16, 1.1 Hz, 2H), 1.71 (dd, J = 13.9, 3.0 Hz, 1H), 1.41 (dd, J = 13.9, 11.8 Hz, 1H), 1.21 (s, 6H), 1.18 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 143.5, 128.6 (br), 70.9, 64.7, 45.8, 34.1, 31.1, 28.0, 23.0. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.2 ppm. IR (cm^{-1}): 2973, 2933, 1634, 1425, 1230, 1196, 1162, 993, 771. We could not obtain any coherent mass spectrum for this compound.

14: 2-(3,3-Diethoxypropenyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.34 (dd, J = 18.0, 5.0 Hz, 1H), 5.60 (dd, J = 18.0, 1.2 Hz, 1H), 4.78 (dd, J = 5.0, 1.2 Hz, 1H), 4.13 (dqd, J = 11.7, 6.2, 3.0 Hz, 1H), 3.57 (m, 2H), 3.44 (dq, J = 9.5, 7.1 Hz, 2H), 1.71 (dd, J = 13.8, 3.0 Hz, 1H), 1.40 (dd, J = 13.8, 11.7 Hz, 1H), 1.21 (s, 6H), 1.18 (d, J = 6.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 145.2, 126.9 (br), 102.4, 70.7, 64.6, 61.0(×2), 45.9, 31.1, 28.0, 23.0, 15.1(×2). ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.5 ppm. IR (cm^{-1}): 2971, 2933, 1648, 1421, 1054, 1000, 896, 767. We could not obtain any coherent mass spectrum for this compound.

15: 3-(4,4,6-Trimethyl-[1,3,2]dioxaborinan-2-yl)-acrylic Acid *tert*-Butyl Ester: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 6.61 (d, J = 18.0 Hz, 1H), 6.46 (d, J = 18.0 Hz, 1H), 4.24 (dqd, J = 12.3, 6.2, 3.0 Hz, 1H), 1.82 (dd, J = 14.0, 3.0 Hz, 1H), 1.47 (s, 9H), 1.46 (m, 1H), 1.30 (s, 6H), 1.27 (d, J = 6.19 Hz, 3H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 165.5, 138 (br), 137.8, 79.8, 71.0, 64.9, 45.7, 30.9, 27.9(×3), 22.8. ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 25.4 ppm. IR (cm^{-1}): 3046, 2971, 2933, 1714, 1623, 1432, 1150, 1003, 765. LRMS (DCI NH_3/isobutane) *m/z* (%) 272(57) [$M + NH_4^+$], 215-(31), 216(100), 217(24), 271(35), 273(7). HRMS (ESI) calcd for $C_{26}H_{46}O_8B_2Na^+$ 531.32710(100), 530.33073(50), 532.33054(29); found 531.32705(100), 530.33071(41), 532.32991(42).

16: 4,4,6-Trimethyl-2-phenethyl-[1,3,2]dioxaborinane: ^{1}H NMR (300 MHz, *CDCl*$_3$) δ ppm 7.27−7.08 (m, 5H), 4.13 (dqd, J = 11.7, 6.2, 3.0 Hz, 1H), 1.71 (dd, J = 13.9, 3.0 Hz, 1H), 2.72−2.65 (m, 2H), 1.39 (dd, J = 13.9, 11.7 Hz, 1H), 1.24 (s, 3H), 1.23 (s, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.02 (m, 2H). ^{13}C NMR (75.5 MHz, *CDCl*$_3$) δ ppm 145.1, 128.0, 127.9, 125.1, 70.4, 64.4, 45.9, 31.1, 30.2, 28.0, 23.1, 17 (br). ^{11}B NMR (96 MHz, *CDCl*$_3$) δ 29.7 ppm. IR (cm^{-1}): 3024, 2974, 2933, 1389, 1182, 793, 771, 751. LRMS (DCI NH_3/isobutane) *m/z* (%) 250(100) [$M + NH_4^+$]. HRMS (DCI NH_3) *m/z* calcd for $C_{14}H_{25}BNO_2^+$ 250.1973; found 250.1966.

Acknowledgment. This article is dedicated to P. Knochel and C. Tucker. We gratefully thank Pr. G. Cahiez (CNRS) for fruitful discussion and Université J. Fourier (DCM-SERCO, ICMG FR-2607) and CNRS (UMR-5250) for financial support. N.P.G. thanks UJF (DCM) for a grant.

Note added in proof. During the edition of this article, the authors became aware of the recent paper by Murata et al., which reported the use of MPBH **1** in borylation reaction and Suzuki coupling: Murata, M.; Oda, T.; Watanabe, S.; Masuda, Y. *Synthesis* **2007**, 351.

Supporting Information Available: Detailed experimental procedures and copies of NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070504G