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Hydride as a Leaving Group in the Reaction of Pinacolborane with Halides under Ambient Grignard and Barbier Conditions. One-Pot Synthesis of Alkyl, Aryl, Heteroaryl, Vinyl, and Allyl Pinacolboronic Esters

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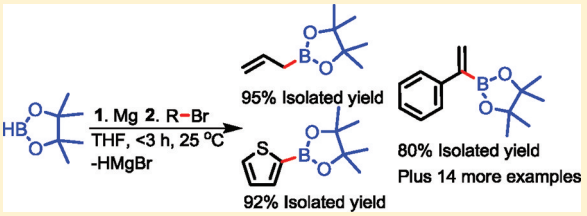
Supporting Information

ABSTRACT: Grignard reagents (aliphatic, aromatic, heteroaromatic, vinyl, or allylic) react with 1 equiv of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane, PinBH) at ambient temperature in tetrahydrofuran (THF) to afford the corresponding pinacolboronates. The initially formed dialkoxy alkylborohydride intermediate quickly eliminates hydridomagnesium bromide (HMgBr) and affords the product boronic ester in very good yield. Hydridomagnesium bromide (HMgBr) in turn disproportionates to a 1:1 mixture of magnesium hydride (MgH_2) and magnesium bromide ($MgBr_2$) on addition of pentane to the reaction mixture. DFT calculations (Gaussian09) at the B3LYP/6-31G(d) level of theory show that disproportionation of HMgBr to MgH_2 and $MgBr_2$ is viable in the coordinating ethereal solvents. This reaction also can be carried out under Barbier conditions, where the neat PinBH is added to the flask prior to the in situ formation of Grignard reagent from the corresponding organic halide and magnesium metal. Pinacolboronic ester synthesis under Barbier conditions does not give Wurtz coupling side products from reactive halides, such as benzylic and allylic halides. The reaction between PinBH and various Grignard reagents is an efficient, mild, and general method for the synthesis of pinacolboronates.



INTRODUCTION

Boronic acids and esters are extremely important and have found synthetic applications in medicinal and biological fields as cross-coupling reagents.[1,2] Boronic acid based cross-coupling reactions are also widely utilized in pharmaceuticals and agrochemical industries and are used in the synthesis of natural products.[3] More recent advances in cross coupling involving boronic acids include copper(II)-mediated oxygen and nitrogen arylation,[4] as well as coupling between alkenes,[5,6] alkynes,[7] carbonyl compounds,[8−11] and imines.[12,13] The syntheses of chiral homoallylic alcohols[14] and amines[15−17] have also been achieved through catalytic asymmetric allylboration using allylboronates.

A well-established method for producing arylboronic acids is the Brown−Cole transmetalation of aryllithium reagents with an excess of trialkylborate, such as trimethyl-, triethyl-, or triisopropylborate, followed by acid hydrolysis.[18] Due to the high reactivity of lithium reagents, the reaction must be carried out at −78 °C to avoid multiple additions. Several excellent catalytic methods have also been developed for synthesizing arylboronic acids using transition metals, such as palladium, rhodium, ruthenium, and iridium.[19−23] Most recently, arylboronic esters have been prepared through metal-catalyzed C−H activation.[24−27] These routes to boronic acids are attractive because of their functional group tolerance. The challenges associated with these methods are the high cost of the catalytic components, catalyst decomposition, regioselectivity, and nontrivial isolation of products free of heavy-metal impurities.

In comparison, Grignard reagents have found limited use in the synthesis of boronic acids.[28,29] Direct reaction of Grignard reagents with trialkylborates invariably gives a mixture of products arising from multiple additions. This problem could be circumvented by using excess amounts of trialkylborate. Cyclic dioxaborolanes such as isopropoxypinacolborane are also common boron sources used for the synthesis of boronic esters from Grignard reagents.[30,31] We were interested in investigating the reactions of Grignard reagents with other boron donors containing a B−H bond, such as 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane, PinBH).[32,33] Pinacolboronates are known to be oxidatively and hydrolytically very stable compared to boronic acids. Their added stability and compatibility as coupling partners in the Suzuki−Miyaura cross-coupling reaction makes pinacolboronates synthetically valuable targets.[34] Boronic acids have a lower molecular weight and therefore can be preferred on the basis of atom economy. However, allylpinacolboronates are preferred to allylboronic acids for catalytic asymmetric allylboration reactions, since allylpinacolboronates do not give background achiral allylboration. Moreover, pinacolborane is commercially available and it

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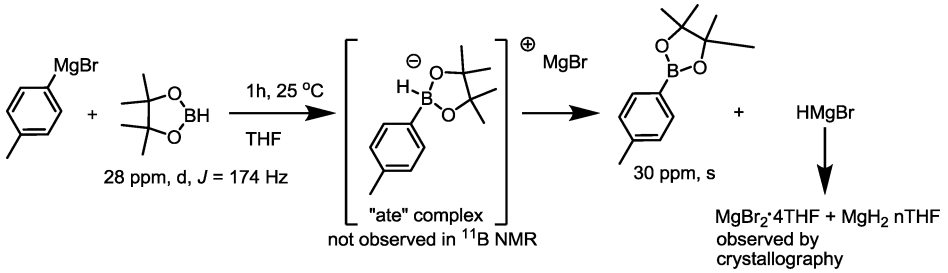
Scheme 1. Synthesis of *p*-Tolyl Pinacolboronate



can also be synthesized by the mixing of equimolar amounts of borane−THF, borane−methyl sulfide complex, or borane−amine complex and pinacol.[35,36]

Herein, we report the direct reaction between PinBH and various Grignard reagents, preformed and formed in situ, as an efficient and mild method for the synthesis of alkyl, aryl, heteroaryl, vinyl, benzylic, and allylic pinacolboronates.

2. RESULTS AND DISCUSSION

We began our investigation by studying the reaction between dialkoxyboranes and *p*-tolylmagnesium bromide (*p*-tolylMgBr) and following the reaction by ^{11}B NMR spectroscopy. We found that Grignard reagents reacted with acyclic dialkoxyboranes, such as diisopropoxyborane, at 25 °C to yield a mixture of products due to multiple additions to the boron donor. We were delighted to find that (*p*-tolyl)MgBr reacted readily with the cyclic dialkoxyborane PinBH to give exclusively a monoaddition product. A literature search revealed a couple of analogous reactions between PinBH and (triorganylsilyl) lithium reagents[37] and alkynyllithium reagents.[38] However, these reactions are not general for alkyl- and aryllithium reagents and we found phenyllithium gives multiple addition products with PinBH, even at low temperature.

In comparison, aryl Grignard reagents give exclusively a monoaddition product with PinBH. Apparently, arylpinacolboronates are sterically demanding enough to prevent multiple additions. It should be pointed out that freshly prepared Grignard reagent and pure PinBH are needed to synthesize boronic esters in high purity. We observed that a PinBH solution in tetrahydrofuran (THF) degraded significantly at 25 °C over a few days. However, neat PinBH (97%) was stable at 25 °C for at least 7 months (see the Supporting Information). The main disproportionation product is 2,2′-(2,3-dimethyl-2,3-butanediyloxy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), B_2Pin_3, which gives multiple addition with Grignard reagents.[39,40] Consequently, we used neat PinBH in the reaction with Grignard reagents. When commercially available Grignard reagents were used, the molarity was confirmed by titration with iodine.

2.1. Reaction Characterization. *p*-Tolylmagnesium bromide was reacted with a PinBH/THF solution at 25 °C. After 1 h of stirring at 25 °C, an aliquot of the reaction mixture was analyzed by ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum showed essentially quantitative formation of the *p*-tolylpinacolboronate. Under these reaction conditions the initially formed dialkoxyarylborohydride adduct ("ate" complex) was not observed but rapidly disproportionated to the product pinacolboronate and HMgBr (Scheme 1).

Usually, dialkoxymonoalkylborohydride species display a broad singlet in the region of 0 to +10 ppm in the ^{11}B NMR spectrum.[41] They are also known to transfer their elements of metal hydride to more Lewis acidic di- and trialkylborates.[42] We observed by ^{11}B NMR analysis that, if the above reaction is carried out in an NMR tube or under nonstirring conditions, multiple additions occurred to afford byproducts, such as trialkylborohydride (d, −9.7 ppm) and tetraalkylborate (s, −15 ppm). This is most likely due to localized hot spots leading to disproportionation of PinBH and eventually to multiple addition of Grignard reagent. The dialkyl- and trialkylboranes formed under nonstirring conditions react with initially formed dialkoxyorganoborohydrides to give the corresponding borohydrides (see the Supporting Information).[41] Consequently, it is important to carry out the reaction of Grignard reagents with PinBH at ambient temperature (0−25 °C) with brisk magnetic stirring to ensure heat dissipation.

During our investigation on boronic ester synthesis from PinBH and Grignard reagents, Dunach and co-workers reported a synthesis of benzyl boronates by catalytic reductive coupling between benzyl bromides and PinBH.[43] They reported using 10 mol % of magnesium metal (Mg^0) and stoichiometric amounts of triethylamine (Et_3N) under reflux conditions in THF for 15 h. They also claimed that they observed the initial adduct, dialkoxymonoalkylborohydride, at δ −9.7 ppm (d, J = 86 Hz). However, this chemical shift is too close to the chemical shift range for trialkylborohydride species (δ −10 to −14 ppm).[42] Our experimental and spectroscopic results are substantially different from those reported by Dunach and co-workers and indicate a unique pathway for the reaction of Grignard reagents with PinBH in the absence of triethylamine. The reaction reported herein proceeds by a novel elimination of HMgBr, from the initially formed borate complex, which eventually disproportionates to $MgBr_2$ and MgH_2. On the basis of the spectroscopic observations, we suggest that the ^{11}B NMR data reported by Dunach and co-workers corresponds to tribenzylborohydride rather than to benzylpinacolborohydride.

The reaction of PinBH with alkylmagnesium bromide reagents produces a precipitate within minutes. In contrast, alkylmagnesium chloride reagents as well as arylmagnesium bromides and chlorides do not produce any precipitate until the addition of pentanes or hexanes to the reaction mixture. It should be pointed out that there was no gas evolution during this reaction. We speculated that our reaction proceeds through a distinctive pathway where hydridomagnesium bromide (HMgBr) is acting as the leaving group. By a slow pentane vapor diffusion technique crystals suitable for X-ray analysis were obtained from the reaction mixture. However, single-crystal X-ray diffraction showed it to be $MgBr_2(THF)_4$, a known compound (see the Supporting Information).[44] Earlier, Ashby et al. reported isolating $MgBr_2(THF)_4$ while attempting to crystallize HMgBr.[45] These results could be best explained by a facile disproportionation of HMgBr to MgH_2 and $MgBr_2$.

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The absence of any hydride-containing species in the isolated crystals suggested that the MgH_2 species is soluble in a THF/pentane mixture and did not precipitate upon pentane addition. This hypothesis was verified by measuring the number of moles of H_2 gas evolved after quenching aliquots of the reaction solution with water/methanol.[46] The experimentally measured molarity of MgH_2 (magnesium hydride) in THF/pentane was in 98% agreement with the theoretical value (see the Supporting Information). In addition, we qualitatively identified the MgH_2 byproduct by trapping it with addition of 1 equiv of BH_3·THF at 25 °C. ^{11}B NMR analysis of an aliquot showed the formation of a borohydride as a quintet at −40 ppm and the complete absence of the signal due to BH_3·THF at 0 ppm (Figure 1).

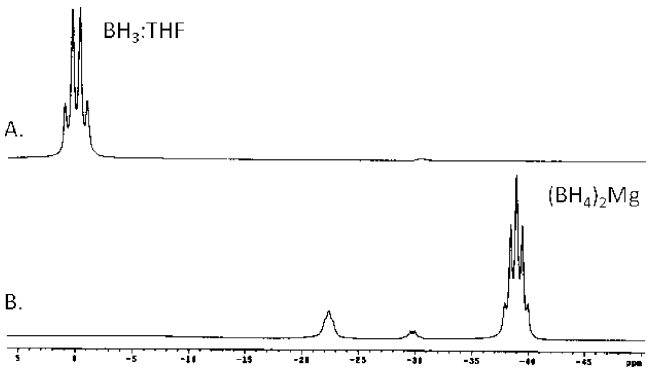

Figure 1. Reaction of BH_3·THF with magnesium hydride byproduct: (A) ^{11}B NMR of BH_3·THF; (B) ^{11}B NMR at 2 h of BH_3·THF + MgH_2 stirred at 25 °C.

We studied the disproportionation of 2 HMgBr to $MgBr_2$ and MgH_2 by DFT calculations (Gaussian09) at the B3LYP/6-31G(d) level of theory with the PCM polarized continuum solvent model (solvent THF) for geometry optimization and final energy. The reaction is endothermic by 0.56 kcal/mol. Formation of the bridged complex HMg(μ-HBr)MgH from 2 HMgBr (Figure 2) is exothermic by −21.0 kcal/mol. The μ-

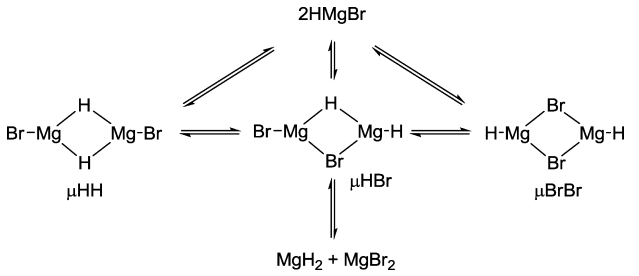

Figure 2. μ-HBr HMgBr dimer, the key intermediate in the Schlenk equilibrium.

HH dimer is more stable at −21.4 kcal/mol and the μ-BrBr dimer is less stable at −18.9 kcal/mol, but it is the μ-HBr dimer that enables the disproportionation by breaking opposite bonds of the bridge. As a model for THF, we chose dimethyl ether for explicit coordination together with PCM (solvent THF). The reaction in Scheme 1 was shown experimentally to occur also in pure diethyl ether, making dimethyl ether a good computational model. The disproportionation of two octahedral HMgBr−$(DME)_4$ to octahedral $MgBr_2$−$(DME)_4$ + MgH_2−$(DME)_4$ was found to be slightly exothermic by −0.51 kcal/mol. Formation of the bis-octahedral 3DME_3HMg(μ-HBr)-MgBrDME_3 intermediate from HMgBr−$(DME)_4$ is endothermic by +0.45 kcal/mol; thus, explicit solvation favors product formation. The transition states for interconversion of the bridged dimers, potential energy surfaces, and solvation studies are presented in the Supporting Information. This supports the observed disproportionation reaction in THF.

2.2. Syntheses of Alkyl and Aryl Pinacolboronates Using Preformed Grignard Reagents. The generality of this reaction was investigated by using commercially available Grignard reagents which have been titrated to ensure concentration.[47] The pinacolboronic ester free of magnesium hydrides was readily isolated by quenching the reaction mixture with hydrochloric acid (1 M) followed by diethyl ether extraction. Alternatively, saturated aqueous ammonium chloride can be added followed by extracting with diethyl ether. A wide variety of Grignard reagents could be accommodated in this reaction, affording the expected pure product in essentially quantitative yields (Table 1). Aryl Grignard reagents completely react with PinBH within 1 h at 25 °C (entries 1−6), whereas alkyl Grignard reagents only require about 30 min (entries 7−10) and do not require Et_3N or reflux conditions.[43] These products were characterized by ^{11}B NMR, ^1H NMR, and ^{13}C NMR spectral analyses.

It should be pointed out that functional groups cannot be incorporated in this boronic ester preparation due to an inherent limitation of any boronate synthesis involving Grignard reagents. We attempted to utilize Knochel's functionalized Grignard in this procedure. Unfortunately, the lithium salts present in Knochel's Grignard synthesis opens up the PinBH and cause multiple addition under the reaction conditions.

Interestingly, neopentylglycolborane (NptBH) can also be utilized in this reaction. Thus, the reaction of NptBH with *m*-tolylmagnesium bromide at 25 °C in THF afforded the corresponding boronate in good isolated yield (Scheme 2).[23,48]

2.3. Syntheses of Aryl and Alkyl Pinacolboronates Using Mg^0 under Barbier-Type Conditions. Under Barbier-type conditions and in the absence of Et_3N an array of aryl halides underwent smooth conversion to the corresponding boronates with excellent isolated yields. All the organic halides were added to a mixture of magnesium turnings and PinBH in THF at 25 °C with a 1/1/1 stoichiometry of reagents (Table 2). Entry 6 shows the compatibility of this methodology with masked carbonyl groups, such as acetal. Thus, *p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-benzaldehyde dimethyl acetal (entry 6) was isolated in 87% yield. This compound can be deprotected under acidic conditions to yield the *p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)benzaldehyde. 4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane was also synthesized under these conditions (entry 9). Entries 10 and 11 highlight the ability of this methodology to form heterocyclic boronates. We can also synthesize vinyl boronic esters from the corresponding halide under Barbier conditions (entry 12).

When allyl bromide was used under the Barbier conditions described above, we observed by ^{11}B NMR analysis approximately a 1:1 mixture of the corresponding allylboronate and unreacted PinBH. Additionally, approximately 50% of the Mg^0 remained unreacted even after extended periods of reaction time. We suspected competitive Wurtz coupling due to the high reactivity of allyl bromide reagents toward homocoupling. However, ^1H NMR analysis of the product

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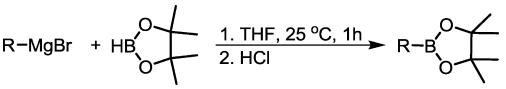
Table 1. Synthesis of Aryl and Alkyl Boronates From Grignard Reagents[a]



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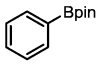
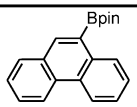
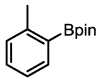
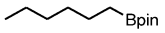
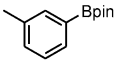
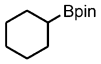
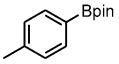
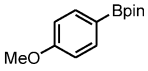
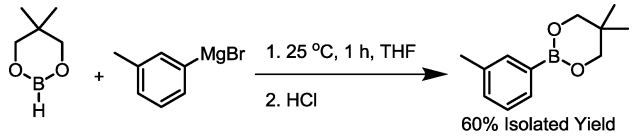
1		90	6		85[c]
2		80	7		90
3		90	8		82
4		89	9		65
5		70	10		99

[a]Reagents and conditions: PinBH (4.5 mmol), anhydrous THF (4.0 mL), Grignard reagent (4.5 mmol), argon, 25 °C, 1 h. The reaction mixture was acidified with 3 M HCl (3 mL) and extracted with diethyl ether. The organic layer was dried, and the solvent was evaporated under reduced pressure. [b]Yield of crude product. [c]Isolated yield after flash column chromatography (hexane/ethyl acetate, 30/1).

Scheme 2. Synthesis of 5,5-Dimethyl-2-*m*-tolyl-1,3,2-dioxaborinane



mixture showed no Wurtz coupling products or allyl bromide starting material. We then speculated the HMgBr byproduct was reducing the unreacted allyl bromide, which would account for the 1/1 mixture of allylboronate and PinBH observed in the ^{11}B NMR spectra. This problem was circumvented by the addition of another 1 equiv of allyl bromide. Thus, the synthesis of allylpinacolboronates (PinBAll) requires a stoichiometric amount of magnesium metal and portionwise addition of 2 equiv of allyl bromide for quantitative yield (Table 3). The method reported in this paper is one of the best ways to synthesize allyl, methallyl, and substituted allyl pinacolboronates from magnesium under Barbier conditions at room temperature.

To confirm the conversion of the allyl bromide reagents to the corresponding PinBAll reagent, 1 equiv of benzaldehyde was added to the reaction mixture (entry 1, Table 3). The corresponding homoallylic alcohol was isolated in 94% yield.

3. CONCLUSION

In summary, we have developed a mild, simple, and highly efficient method for synthesizing pinacolboronates utilizing PinBH and commercially available Grignard reagents in THF at 25 °C. We have also shown that under Barbier conditions aryl, vinyl, benzyl, and allylic halides are converted to the corresponding boronic esters essentially quantitatively. Additionally, performing the borylation reaction under Barbier conditions avoids Wurtz coupling byproducts as well as allowing use of a simple one-pot procedure for the synthesis of allylboronates from allyl bromides. Boronate ester synthesis by these methods avoids the use of low temperatures and expensive transition-metal catalysts. Neopentylglycolborane, another B−H-containing cyclic dialkoxyborane, was also compatible in this synthesis of boronate esters from Grignard reagents.

We suggest that this reaction proceeds through a unique pathway where hydridomagnesium bromide (HMgBr) is acting as the leaving group. X-ray analysis revealed that the precipitate formed by addition of hexanes was the known compound $MgBr_2(THF)_4$. DFT calculations indicated that disproportionation of HMgBr to MgH_2 and $MgBr_2$ is viable in the coordinating ethereal solvents. MgH_2 was qualitatively and quantitatively identified as a disproportionation byproduct by trapping it with 1 equiv of BH_3·THF and by hydride analysis, respectively.

The method reported herein is one of the best procedures available to quantitatively synthesize allyl, methallyl, and substituted allyl pinacolboronates without any Wurtz coupling under Barbier conditions at room temperature with a 1/1 stoichiometry between Mg^0 and PinBH.

4. EXPERIMENTAL SECTION

4.1. General Methods. All reactions were performed in oven-dried, argon-cooled glassware. The pinacolborane was used as received from Aldrich and stored under Ar in a refrigerator held at 15 °C. All Grignard reagents were used as received from Aldrich; they were stored in the bottle received and kept in the refrigerator at 15 °C. Magnesium metal was used as received from Aldrich. All air- and moisture-sensitive compounds were introduced via syringes or cannula through a rubber septum. Pinacolborane was added via syringe, with the dispensed amount measured by mass difference of the syringe before and after addition. Tetrahydrofuran (THF) was freshly obtained from a solvent purification system (Pure Solv MD, Innovative Technology Inc.). NMR spectra were recorded in $CDCl_3$. Chemical shifts are reported relative to TMS (δ 0) for ^{1}H NMR (500 MHz) and are referenced to the $CDCl_3$ resonance (δ 77) for ^{13}C

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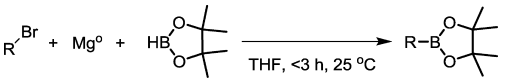
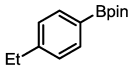
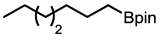
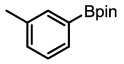
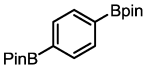
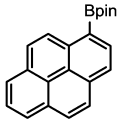
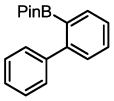
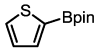
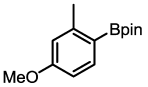
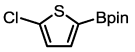
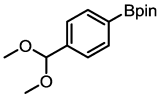
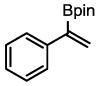
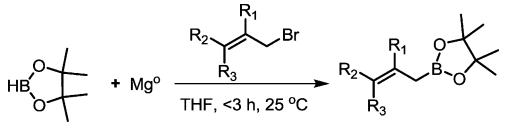
Table 2. Synthesis of Boronates under Barbier Conditions[a]



Entry	Product	Isolated Yield (%)[b]	Entry	Product	Isolated Yield (%)[b]
1[a]		99	7		86
2		99	8		65[c]
3		78	9		75[d]
4		88	10		92
5		97	11		75
6		87	12		80

[a]Reagents and conditions: Mg^0 (2.4 mmol), PinBH (2.0 mmol), anhydrous THF (4.0 mL), organo halide (2.0 mmol), argon, 25 °C, 2−3 h. The reaction mixture was acidified with 3 M HCl (3 mL) and extracted with diethyl ether. The organic layer was dried, and the solvent was evaporated under reduced pressure. [b]Yield of crude product. [c]Mg^0 (2 equiv), PinBH (2 equiv). [d]2 equiv of (1-bromoethyl)benzene.

Table 3. Synthesis of Allylboronates under Barbier Conditions[a]



Entry	Product	Isolated Yield (%)[b]
1		90 (94)[c]
2		90[d]
3		90[e]
4		90
5		95

[a]Reagents and conditions: Mg^0 (2.4 mmol), PinBH (2.0 mmol) in anhydrous THF to make 0.5−1.0 M solution, allyl halide (4.0 mmol), argon, 25 °C, 3 h. The reaction mixture was acidified with 3 M HCl (3 mL) and extracted with diethyl ether. The organic layer was dried, and the solvent was evaporated under reduced pressure. [b]Yield of crude product. [c]Isolated yield of allylboration product with benzaldehyde (see the Experimental Section). [d]Used allyl chloride as starting halide. [e]Isomeric mixture of crotyl bromide was used (*E*/*Z* ratio 90/10).

NMR (125 MHz) spectra. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), coupling constant, and integration. Boron NMR samples were recorded at 160.4 MHz and are reported relative to external standard $BF_3{\cdot}Et_2O$ (δ 0).

4.2. Pinacolborane Stability Study by ^{11}B NMR Analysis. Four oven-dried NMR tubes (5 mm diameter) were capped with a rubber septum and flushed with argon. Tube 1 was filled with neat PinBH (0.70 mL). Tube 2 was charged with anhydrous THF (0.5 mL), tube 3 with anhydrous pentane (0.5 mL), and tube 4 with anhydrous dichloromethane (DCM) (0.5 mL). PinBH (0.2 mL, 1.77 mmol) was added to NMR tubes 2−4, to make a 2.5 M solution in the respective solvent. The NMR tube samples were stored at 25 °C and analyzed daily, for 35 days, by ^{11}B NMR spectroscopy. Integrating the PinBH and degradation product (B_2Pin_3) of the ^{11}B NMR spectrum yields an approximate quantization of reaction composition (Figure S1 and Table S2, Supporting Information). When refrigerated and stored in an argon-charged ampule, neat PinBH is stable for greater than 7 months, as confirmed by ^{11}B NMR analysis (see the Supporting Information).

4.3. Formation of Trialkylborohydride. An oven-dried NMR tube was charged with dry THF (0.27 mL) followed by PinBH (0.75 mmol, 0.108 mL) and cooled to −78 °C (acetone/dry ice). To this solution was added isopropylmagnesium chloride (0.75 mmol, 0.37 mL) without stirring. The reaction mixture was analyzed immediately by ^{11}B NMR spectroscopy (see the Supporting Information).

4.4. Vapor Diffusion Crystallization. A 20 mL scintillation flask fitted with a rubber septum was charged with pinacolborane (1.1 mL, 1 M/THF). *p*-Tolylmagnesium bromide (1.0 mL, 1M/THF) was added dropwise over 5 min at 25 °C. The scintillation flask was placed in a larger argon-charged flask containing a shallow layer of pentane (about 1 cm in height). The larger flask was covered with Parafilm and purged with argon. The Parafilm was quickly removed as well as the rubber septum in the scintillation flask. The flask was sealed with a screw top.

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Crystals form upon standing in the refrigerator held at 15 °C overnight. The resultant crystals were characterized by single-crystal X-ray diffraction (see the Supporting Information).

4.5. General Procedure for Gas Evolution Analysis: Measurement of MgH_2 Molarity. A 50 mL round-bottom flask equipped with a magnetic stir bar and fitted with a rubber septum was charged with anhydrous THF (3.45 mL) followed by pinacolborane (0.441 g, 0.5 mL, 3.45 mmol). *p*-Tolylmagnesium bromide (3.45 mmol, 1 M/THF) was added dropwise over 5 min at 25 °C with constant stirring. The reaction was complete after 1 h, as evidenced by ^{11}B NMR analysis. Hexanes (3 mL) were added to induce precipitation of $MgBr_2$. Aliquots from the supernatant (0.5 mL) were injected into the modified eudiometer with a 1/1/1 quenching solution of H_2O/MeOH/THF with constant stirring. The volume displaced by hydrogen gas was measured and converted to moles of hydrogen gas according to the ideal gas law ($PV = nRT$). The process was repeated eight times (Table S1, Supporting Information).

4.6. General Procedure for the Preparation of B-aryl and B-alkyl Pinacolboronates from Preformed Grignard Reagents. The following procedure for the preparation of 4,4,5,5-tetramethyl-2-*m*-tolyl-1,3,2-dioxaborolane is representative. A 25 mL round-bottom flask equipped with a magnetic stir bar and fitted with a rubber septum was charged with anhydrous THF (4.0 mL) followed by pinacolborane (0.57 g, 4.5 mmol). *m*-Tolylmagnesium bromide (4.5 mmol, 1 M/THF) was added dropwise over 5 min at 25 °C with constant stirring. The reaction was complete after 1 h, as evidenced by the disappearance of pinacolborane starting material (δ +27.7, d, J = 173.9 Hz) and the appearance of a singlet at +30.5 ppm via ^{11}B NMR. The reaction mixture was then cooled to 0 °C (ice bath) and acidified with 3 M aqueous HCl (3 mL) (*Caution! hydrogen evolution*). After 10 min of stirring the reaction mixture was warmed to 25 °C and stirred for an additional 30 min. The reaction mixture was then transferred to a separatory funnel and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and dried in vacuo (25 °C, 1 Torr) to afford 4,4,5,5-tetramethyl-2-*m*-tolyl-1,3,2-dioxaborolane as a pale yellow oil. The results for the other pinacolborane esters prepared by this method are summarized in Table 1. For the ^{1}H, ^{13}C, and ^{11}B NMR spectra, see the Supporting Information.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (Table 1, Entry 1).[49] Colorless oil; 96% yield (0.598 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 12H), 7.38 (m, 2H), 7.47 (m, 1H), 7.83 (d, J = 7.2 Hz, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.0, 83.8, 127.9, 131.4, 134.9. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.8 (s).

4,4,5,5-Tetramethyl-2-o-tolyl-1,3,2-dioxaborolane (Table 1,Entry 2).[21] Colorless oil; 80% yield (0.865 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (s, 12H), 2.65 (s, 3H), 7.24−7.26 (m, 2H), 7.41 (t, J = 8, 1H), 7.89 (d, J = 7, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 22.5, 25.1, 83.6, 125.1, 130.1, 131.1, 136.4, 145.1. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +32.0 (s).

4,4,5,5-Tetramethyl-2-m-tolyl-1,3,2-dioxaborolane (Table 1, Entry 3).[26] Colorless oil; 78% yield (0.855 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 12H), 2.37 (s, 3H), 7.28−7.29 (m, 2H), 7.62−7.63 (m, 1H), 7.65 (s, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.3, 24.9, 83.8, 124.4, 127.8, 131.9, 132.2, 135.5, 137.3. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.3 (s).

4,4,5,5-Tetramethyl-2-p-tolyl-1,3,2-dioxaborolane (Table 1, entry 4).[21] Colorless/yellow oil; 89% yield (0.579 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (s, 12H), 2.48 (s, 3H), 7.32 (d, J = 2.4, 2H), 7.89 (d, J = 2.6 Hz, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.8, 25.0, 83.7, 128.7, 128.8, 135.1, 141.5. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +31.6 (s).

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 5).[21] Colorless oil; 70% yield (0.804 g). ^{1}H NMR (500 MHz, $CDCl_3$): 1.35 (s, 12H), 3.84 (s, 3H), 6.91 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.0, 55.2, 83.7, 113.5, 136.7, 160.2. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +29.6 (s).

4,4,5,5-Tetramethyl-2-(phenanthren-1-yl)-1,3,2-dioxaborolane (Table 1, Entry 6).[50] Colorless oil; 85% isolated yield after flash column chromatography (hexane/ethyl acetate, 30/1) (1.16 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47 (s, 12H), 7.60 (app dt, J = 1.5, 8 Hz, 1H), 7.64−7.66 (m, 2H), 7.68−7.72 (m, 1H), 7.95 (d, J = 8 Hz, 1H), 8.40 (s, 1H), 8.69 (d, J = 8 Hz, 1H), 8.71−8.73 (m, 1H), 8.84−8.86 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.1, 84.0, 122.6, 122.7, 126.3, 126.6, 126.8, 127.9, 128.7, 129.3, 129.5, 130.0, 131.2, 132.0, 134.5, 138.3. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +32.5 (s).

2-Hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 7).[41] Colorless oil; 90% yield (0.941 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.78 (t, J = 6.5 Hz, 2H), 0.89 (t, J = 5.0 Hz, 3H), 1.26 (s, 12H), 1.22−1.32 (m, 18H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.1, 22.6, 23.9, 24.8, 31.6, 32.1, 82.9. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +32.8 (s).

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 8).[51] Colorless oil; 82% yield (0.856 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.93−1.00(m, 1H), 1.23 (s, 12H), 1.26−1.40 (m, 4H), 1.54−1.70 (m, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.4, 26.5, 26.8, 27.7, 82.4. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.8 (s).

2-tert-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 1, Entry 9).[27] Colorless oil; 65% yield (0.598 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.23 (s, 12H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.6, 26.9, 82.8. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +34.6 (s).

4,4,5,5-Tetramethyl-2-(pentan-3-yl)-1,3,2-dioxaborolane (Table 1, Entry 10). Colorless oil; 98% yield (0.991 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, J = 7.8 Hz, 6H), 0.94 (t, J = 7.2, 1H), 1.24 (s, 12H), 1.41 (m, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.4, 23.8, 24.6, 82.6. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +34.2 (s).

4.7. Synthesis and Reaction of Neopentylglycolborane with *m*-Tolylmagnesium Bromide. A solution of neopentylglycol (17.8 mmol, 1.85 g, 1.2 equiv) in dry THF (10 mL) was stirred and cooled to 0 °C. A solution of BH_3·SMe_2 (15 mmol, 10 M in methyl sulfide) was added dropwise via syringe under argon. After 30 min of stirring at 0 °C, the reaction mixture was warmed to 25 °C and stirring was continued until no further evolution of hydrogen was observed (ca. 90 min). The solution was distilled under reduced pressure to isolate pure neopentylglycolborane as a clear oil.[23] *m*-Tolylmagnesium bromide (10 mmol, 1 M) was added dropwise at 25 °C with constant stirring. The reaction was complete after 1 h, as evidenced by the disappearance of neopentylglycolborane starting material (δ +26.9, d, J = 176.0 Hz) and the appearance of a singlet at +28.0 ppm via ^{11}B NMR analysis. The reaction mixture was then cooled to 0 °C (ice bath) and acidified with 3 M aqueous HCl (3 mL) (*Caution! hydrogen evolution*). After 10 min of stirring the reaction mixture was warmed to 25 °C and stirred for an additional 30 min. The reaction mixture was then transferred to a separatory funnel and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and dried in vacuo (25 °C, 1 Torr) to afford 5,5-dimethyl-2-*m*-tolyl-1,3,2-dioxaborinane as a pale yellow oil.

5,5-Dimethyl-2-m-tolyl-1,3,2-dioxaborinane.[52] Colorless oil; 60% yield based on *m*-tolylmagnesium bromide (0.612 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (s, 6H), 2.37 (s, 3H), 3.78 (s, 4H), 7.27−7.28 (m, 2H), 7.61−7.64 (m, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.9, 32.0 72.4, 127.7, 131.0, 131.6, 134.6, 137.3. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +28.0 (s).

4.8. General Procedure for the Preparation of B-aryl and B-alkyl Pinacolboronic Esters under Barbier-Type Conditions. The following procedure for the preparation *m*-tolyl pinacolborane is representative. A 25 mL round-bottom flask equipped with a magnetic stir bar was charged with magnesium turnings (0.058 g, 2.4 mmol) and was activated by addition of iodine crystals and warming until iodine sublimed. The flask was cooled to 25 °C and was purged with Ar. THF (3.5 mL) was added to the flask, followed by the addition of neat pinacolborane (0.29 mL, 2.0 mmol). *m*-Tolyl bromide (0.243 mL, 2.0 mmol) was then added dropwise over 5 min with constant stirring at 25 °C. The reaction was complete after 3 h, as evidenced by the disappearance of pinacolborane starting material (δ +27.7, d, J = 173.9 Hz) and the appearance of a singlet at +30.6 ppm via ^{11}B NMR. The reaction mixture was then cooled to 0 °C (ice bath) and acidified with 3 M aqueous HCl (3 mL) (*Caution! hydrogen evolution*). After 10 min of stirring the reaction mixture was warmed to 25 °C and stirred for an

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additional 30 min. The reaction mixtures given in Table 2, entries 4, 6, 7, and 8, were quenched with aqueous NH_4Cl (2.5 mL, 0.16 M). The reaction mixture was then transferred to a separatory funnel and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and dried in vacuo (25 °C, 1 Torr) to afford *m*-tolyl pinacolborane as a pale yellow oil. The results for the other pinacolborane esters prepared by this method are summarized in Table 2. For the ^1H, ^{13}C, and ^{11}B NMR spectra, see the Supporting Information.

2-(4-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 1).[53] Clear oil; 99% yield (0.483 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, J = 6 Hz, 3H), 1.34 (s, 12H), 2.67 (q, J = 7.5 Hz, 2H) 7.23 (d, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.4, 24.8, 29.1, 83.7, 127.4, 135.0. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.8 (s).

4,4,5,5-Tetramethyl-2-m-tolyl-1,3,2-dioxaborolane (Table 2, Entry 2).[26] Clear oil; 99% yield (0.436 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 12H), 2.37 (s, 3H), 7.26−7.29 (m, 2H), 7.63 (t, 1H), 7.65 (s, 1H), 7.54 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.3, 24.9, 83.7, 127.8, 131.9, 132.0, 132.2, 135.5, 137.2. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.6 (s).

4,4,5,5-Tetramethyl-2-(pyren-2-yl)-1,3,2-dioxaborolane (Table 2, Entry 3).[34] Deep red oil; 78% yield (0.511 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.51 (s, 12H), 8.12 (m, 7H), 8.57 (d, J = 7.5 Hz, 1H), 9.11 (d, J = 9.5 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 25.1, 84.0, 124.2, 125.0, 125.3, 125.4, 125.8, 125.9, 127.5, 127.6, 127.9, 128.2, 128.6, 130.9, 131.3, 133.6, 134.0, 136.6. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +22.50 (s), +31.9 (s).

2-(Biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 4).[54] Clear oil; 88% yield (0.351 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.24 (s, 12H), 7.35−7.49 (m, 8H); 7.76 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.6, 83.8, 126.4, 126.9, 127.9, 129.1, 129.3, 130.2, 134.6, 143.4, 147.7. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.7 (s).

2-(4-Methoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 5). Clear oil; 97% yield (0.483 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 12H), 2.56 (s, 3H), 3.82 (s, 3H), 6.74 (m, 2H), 7.77 (d, J = 7 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 22.4, 24.9, 54.9, 83.1, 110.1, 115.5, 137.8. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.7 (s).

2-(4-(Dimethoxymethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 6). Clear oil; 81% yield (0.450 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 12H), 3.35 (s, 6H), 5.38 (s, 1H), 7.41 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.7, 24.8, 52.4, 52.6, 83.8, 102.8, 10.1, 126.1, 134.7, 141.0. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.4 (s).

4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (Table 2, Entry 7).[55] Clear oil; 86% yield (0.411 g). ^1H NMR (500 MHz, $CDCl_3$): δ 0.76 (t, J = 7.5 Hz, 2H), 0.86 (t, J = 7 Hz, 3H), 1.23 (s, 12H), 1.25 (s, 8H), 1.38 (m, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.1, 22.7, 24.0, 24.8, 29.2, 29.4, 31.9, 32.4, 82.5. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.7 (s).

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (Table 2, Entry 8).[56] A 2.2 equiv amount of Mg^0 and 2.5 equiv of PinBH were used. Clear oil; 61% yield (0.404 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 24H), 7.81 (s, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.9, 134.0. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +30.7(s).

4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (Table 2, Entry 9).[57] Clear oil; 75% yield (0.351 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 6H), 1.275 (s, 6H), 1.40 (d, J = 7.5 Hz, 3H), 2.50 (q, J = 7.5 Hz, 1H), 7.30 (m, 5H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 17.1, 24.6, 47.5, 83.3, 125.1, 127.8, 128.3, 144.9. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.2 (s).

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (Table 2, Entry 10).[21] White solid; 92% yield (0.193 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 12H), 7.21−7.19 (m, 1H), 7.27 (d, J = 4.5 Hz, 1H), 7.64−7.67 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.7, 84.1, 128.3, 132.5, 137.3. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +29.4 (s).

2-(5-Chlorothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 11).[58] Clear oil; 75% yield (0.360 g). IR (Nujol): 1019, 1056, 1146, 1211, 1302, 1377, 1463, 1522 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 12H), 6.98 (d, J = 3.5 Hz, 1H), 7.41 (d, J = 4 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.7, 84.3, 127.7, 136.9. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +28.1 (s).

4,4,5,5-Tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (Table 2, Entry 12).[59] Clear oil; 75% yield (0.352 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (s, 12H), 6.0 (d, J = 0.9 Hz, 1H), 6.11 (d, J = 0.8 Hz, 1H), 7.27 (dt, J = 1.5, 5.5 Hz, 1H), 7.34 (dt, J = 2, 5.5 Hz, 1H), 7.516 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.8, 83.9, 127.1, 127.3, 128.3, 131.0, 141.5. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +29.9(s).

4.9. General Procedure for the Preparation of *B*-Allylpinacolboronate and Subsequent Reaction with Benzaldehyde. The following procedure for the preparation of *B*-allylpinacolboronate is representative. A 25 mL round-bottom flask equipped with a magnetic stir bar was charged with magnesium turnings (0.04 g, 1.65 mmol) and fitted with a rubber septum. The flask was purged with Ar and charged with dry THF (2.3 mL) followed by PinBH (0.199 mL, 1.37 mmol). To the reaction mixture was added allyl bromide (0.116 mL, 1.37 mmol) dropwise with constant stirring over 5 min at 25 °C. After 30 min of stirring at 25 °C, another 1 equiv of allyl bromide (0.116 mL, 1.37 mmol) was added. After 90 min of stirring at 25 °C the magnesium turnings were fully consumed and ^{11}B NMR analysis confirmed the complete formation of allylpinacolboronate. The reaction was then diluted with hexanes (5 mL) and quenched with aqueous 0.1 M HCl (10 mL) (*Caution! hydrogen evolution*). After 10 min of stirring the reaction mixture was transferred to a separatory funnel and extracted with hexanes (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and dried in vacuo (25 °C, 1 Torr) to afford 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a clear oil. The results for the other substituted *B*-allylpinacolboronic esters prepared by this method are summarized in Table 3. For the ^1H, ^{13}C, and ^{11}B NMR spectra, see the Supporting Information.

2-Allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, Entry 1).[60] Clear oil; 90% yield (0.207 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 12H), 1.72 (d, J = 6.5 Hz, 2H), 4.93 (d, J = 10 Hz, 1H), 5.0 (d, J = 17 Hz, 1H), 5.83−5.89 (m, 1H); ^{11}B NMR (160.4 Hz, $CDCl_3$): δ +33.0 (s).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-but-1-ene (Table 3, Entry 3).[61,62] An isomeric mixture of crotyl bromide was used (E/Z ratio 90/10). Clear oil; 90% yield (0.224 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.09 (d, J = 7.5 Hz, 3H), 1.23 (s, 12H), 1.89 (quint, J = 7.5 Hz, 1H), 4.92 (app dt, J = 10 Hz, 2H), 4.97 (app dt, J = 17.5 Hz, 2H), 5.90−5.97 (m, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.1, 24.6, 25.5, 83.2, 112.0, 141.0. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.1 (s).

4,4,5,5-Tetramethyl-2-(2-methylallyl)-1,3,2-dioxaborolane (Table 3, Entry 4).[63] Clear/light yellow oil; 90% yield (0.222). ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 12H), 1.72 (s, 2H), 1.77 (s, 3H), 4.66−4.69 (m, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 24.4, 24.7, 83.3, 110.2, 142.9. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.1 (s).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-3-methylbut-1-ene (Table 3, Entry 5).[61] The starting halide was 1-bromo-3-methylbut-2-ene. Clear oil; 95% yield (0.242 g). ^1H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 6H), 1.22 (s, 12H), 4.90 (dd, J = 0.5, 0.5 Hz, 1H), 4.93 (dd, J = 0.3, 0.6 Hz, 1H), 5.96 (dd, J = 5.7, 3.3 Hz, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.4, 24.5, 83.2, 110.0, 146.7. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ +33.9 (s).

1-Phenyl-3-buten-1-ol (Table 3, Entry 1).[64] As an alternative to the aqueous quench, benzaldehyde (0.138 mL, 1.37 mmol) was then added and the reaction mixture was stirred for an additional 12 h at 25 °C. The reaction mixture was then diluted with hexane (5 mL), quenched with aqueous 1 M HCl (5 mL), and transferred to a separatory funnel. The organic layer was washed with aqueous 1 M NaOH (2 × 5 mL) and DI water (2 × 3 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and dried in vacuo (25 °C, 1 Torr) to afford 1-phenyl-3-buten-1-ol as a clear/light yellow oil; 94% yield (0.190 g). ^1H NMR (500 MHz, $CDCl_3$): δ 2.50−2.57 (m, 2H), 4.75 (dd, J = 5, 7.5 Hz, 1H), 5.15−5.20 (m, 2H), 5.79−5.87

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(m, 1H), 7.28−7.38 (m, 5H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 43.9, 73.3, 118.5, 125.9, 127.6, 128.5, 134.6, 144.0.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and a CIF file giving characterization data, ^{1}H, ^{13}C, and ^{11}B NMR spectra for all compounds prepared, DFT calculations of the transition states for interconversion of the μ-bridged dimers, potential energy surfaces, solvation studies, and atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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