Borylation

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Selective Boryl-Anion Migration in a Vinyl sp^2–sp^3 Diborane Induced by Soft Borane Lewis Acids

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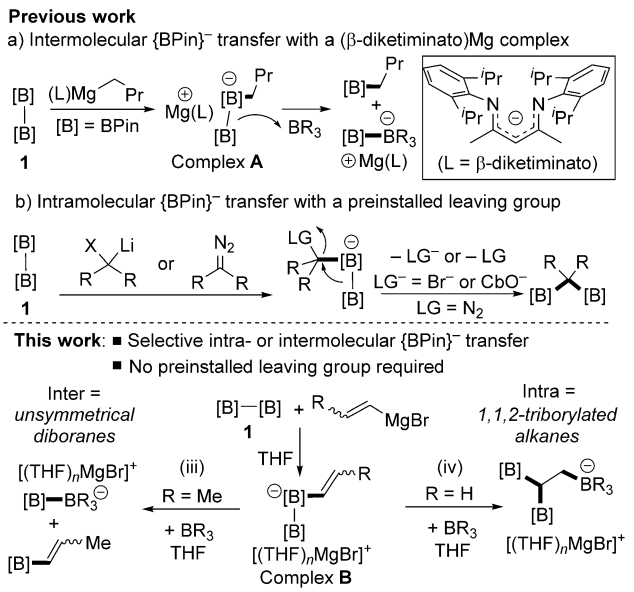
Abstract: *An intramolecular 1,2-boryl-anion migration from boron to carbon has been achieved by selective activation of the π system in [(vinyl)B_2Pin_2)]$^-$ using "soft" BR_3 electrophiles (BR_3 = BPh_3 or 9-aryl-BBN). The soft character is key to ensure 1,2-migration proceeds instead of oxygen coordination/B–O activation. The BR_3-induced 1,2-boryl-anion migration represents a triple borylation of a vinyl Grignard reagent using only B_2Pin_2 and BR_3 and forms differentially protected 1,1,2-triborylated alkanes. Notably, by increasing the steric bulk at the β position of the vinyl Grignard reagent used to activate B_2Pin_2, 1,2-boryl-anion migration can be suppressed in favor of intermolecular {BPin}$^-$ transfer to BPh_3, thus enabling simple access to unsymmetrical sp^2–sp^3 diboranes.*

The coordination of a Lewis base (LB) to diborane(4) compounds, such as B_2Pin_2 (**1**), generates an sp^2–sp^3 diborane in which the boron–boron bond is polarised,[1] which imparts nucleophilic character to the sp^2 boron atom, thereby enabling the mild generation of a functional equivalent of {BPin}$^-$.[1,2] This strategy has become a powerful transition-metal-free method to borylate organic substrates and generate desirable organoboronate esters. Alkoxides or N-heterocyclic carbenes (NHCs) are the typical LBs employed in the activation of **1**,[1–3] with the use of carbanions (R^-) having much less precedent,[4–9] despite the ability of carbanions to generate a more nucleophilic {BPin} moiety owing to their greater basicity relative to alkoxides and NHCs. Among the limited examples in this area, recent studies have shown that complex **A** synthesised from **1** and *n*Bu–MgL (L = β-diketiminato) transfers a boryl anion to boranes to form new unsymmetrical sp^2–sp^3 diboranes (Scheme 1 a).[10] Indeed, transfer of a boryl nucleophile to an external electrophile is the dominant reactivity pathway reported for B_2Pin_2 activated by simple carbanions.[10] It is important to extend the chemistry of [(R)B_2Pin_2)]$^-$ to enable new routes to highly functionalized organoboronates to be discovered. Such routes will be particularly desirable if readily accessible starting materials (e.g. RMgX/B_2pin_2) can be used.



Scheme 1. Top: Previous studies on intermolecular/intramolecular {BPin}$^-$ transfer in carbanion-activated B_2Pin_2. Bottom: Selective boryl-anion migration in vinyl sp^2–sp^3 diboranes as induced by soft borane Lewis acids.

Prior to this study, 1,2-boryl-anion migration from boron to carbon in [(R)B_2Pin_2]$^-$ species had been limited to the use of functionalized "R^-" equivalents. For example, coordination of a carbanion containing a Br or OCb group (or a diazoalkane) to **1** led to loss of [OCb]$^-$ or [Br]$^-$ (or N_2) and the formation of 1,1-diborylalkanes (Scheme 1 b).[11–17] We hypothesised that an alternative route to induce intramolecular 1,2-boryl-anion migration would be the activation of an unsaturated R^- group (e.g. $-CH{=}CH_2$) in [(R)B_2Pin_2]$^-$ by a borane Lewis acid. This approach is attractive as it avoids prefunctionalization of the carbanion activator. It is conceptually related to the Zweifel reaction,[18] but the use of borane Lewis acids and {BPin}$^-$ as the migrating group will lead to differentially functionalised 1,1,2-triborylated alkanes in one step. Related 1,1-diborylated alkanes have emerged as highly versatile reagents used in selective C–C bond formation by the Suzuki–Miyaura coupling reaction or by deprotonation/deborylation of the diborylated carbon atom.[19–22]

The selective (for intramolecular 1,2-boryl migration) activation of [(vinyl)B_2Pin_2]$^-$ (complex **B**, Scheme 1, bottom), requires judicious choice of the borane, BR_3, as a range of outcomes are feasible, including: i) vinyl-anion transfer from **B** to BR_3; ii) binding of BR_3 to an oxygen atom in **B** and subsequent C–O or B–O cleavage; iii) {BPin}$^-$ anion transfer from **B** to BR_3; iv) BR_3 activation of the vinyl π system and

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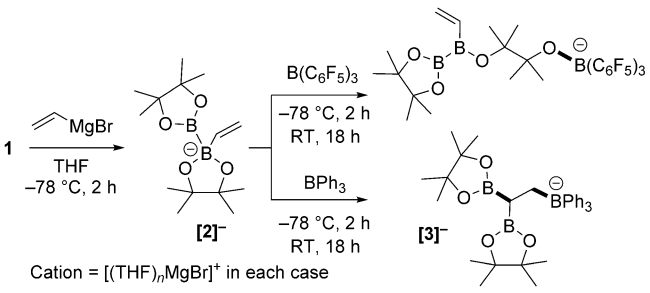
intramolecular {BPin}$^-$ transfer. While (i) and (ii) are undesirable, pathway (iii) would be an attractive route to unsymmetrical diboranes using commercial Grignard reagents as activators. Equally notable and our primary focus, intramolecular 1,2-boryl migration (pathway (iv)) would be a new and simple route to 1,1,2-triborylated alkanes.

Herein, we report that intramolecular 1,2-boryl migration in sp^2–sp^3 diboranes does not require preinstalled leaving groups in the carbanion. Instead, the formation of [(vinyl)-B_2Pin_2]$^-$, followed by selective activation of the π system by certain boranes, forms differentially functionalised (at boron) 1,1,2-triborylated alkanes. The use of a β-methyl vinyl Grignard reagent changes the reaction outcome to intermolecular {BPin}$^-$ transfer to BR_3, generating an unsymmetrical diborane from simple starting materials.

We started our investigation by probing the accessibility of the simplest vinyl adduct of **1**, [(CH_2=CH)B_2Pin_2]$^-$ (**[2]**$^-$), which could be generated as the major product by the addition of 1 equivalent of commercial vinyl magnesium bromide to **1** in THF at −78 °C (Scheme 2, left). The successful formation of **[2]**$^-$ was indicated by ^{11}B NMR



Scheme 2. Reaction of **1** with a vinyl Grignard reagent and $B(C_6F_5)_3$ or BPh_3.

spectroscopy, which showed two new resonances: one at 37.3 ppm (three-coordinate boron) and the other at 4.8 ppm (four-coordinate boron), analogous to the spectrum reported for [(Ph)B_2Pin_2]$^-$ (39.2 and 4.0 ppm, respectively).[6] Since $B(C_6F_5)_3$ can activate alkenes and alkynes even in the presence of certain oxo functionalities, the ability of $B(C_6F_5)_3$ to trigger the 1,2-boryl migration was explored.[23] The addition of $B(C_6F_5)_3$ (1 equiv) to **[2]**$^-$ (at −78 °C) led after 2 h to a single new ^{11}B resonance at −3.2 ppm, consistent with an [RO–$B(C_6F_5)_3$]$^-$ species (in contrast, [alkyl–$B(C_6F_5)_3$]$^-$ anions have a ^{11}B resonance at ca. −15 ppm). The ^{19}F NMR spectrum confirmed [RO–$B(C_6F_5)_3$]$^-$ formation, with ESIMS analysis supporting the formation of an [RO–$B(C_6F_5)_3$]$^-$ species derived from ring opening of one BPin moiety in **[2]**$^-$. With two additional ^{11}B resonances observed at 48.0 and 29.2 ppm, we tentatively assign the product as derived from $B(C_6F_5)_3$ activation of pinacol bound to the four-coordinate boron atom (Scheme 2, top). This assignment is consistent with reports on BPin moieties in anionic borates undergoing B–O cleavage on addition of electrophiles.[24]

The oxo-based reactivity of $B(C_6F_5)_3$ with **[2]**$^-$ was attributed to the high electrophilicity and oxophilicity of this borane. Therefore, softer boron electrophiles were explored, in particular BPh_3, since this borane reacts with complex **A** to generate [PinB–BPh_3]$^-$ with no competitive reactivity at the oxo sites reported (Scheme 1 a).[10] The addition of BPh_3 (1 equiv) in THF to **[2][(THF)$_n$MgBr]** generated in situ (at −78 °C) resulted in the formation of the desired product **[3]**$^-$ formed by intramolecular {BPin}$^-$ transfer (Scheme 2, bottom). Anion **[3]**$^-$ has diagnostic resonances in the ^{11}B NMR spectrum (34.7 ppm for the C–BPin moieties, and −9.5 ppm for [C–BPh_3]$^-$) and in the ^{1}H NMR spectrum (broad signal at 0.55 ppm for C*H*($BPin)_2$), with the formulation further confirmed by accurate mass spectrometry. Performing the reaction at −78 °C for 2 h and then room temperature for 18 h resulted in complete consumption of **[2]**$^-$ to yield **[3]**$^-$ (71 % in situ conversion) as the major product. When the reaction was repeated on a larger scale, **[3][(THF)$_2$MgBr]** was isolated as a white solid in 70 % yield by solvent removal and washing with Et_2O.

Single crystals of **[3][(THF)$_2$MgBr]** were obtained by slow diffusion of pentane into a THF solution (Figure 1). In the

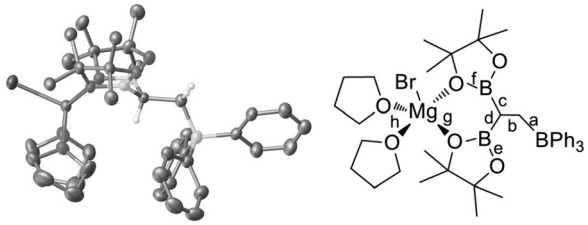
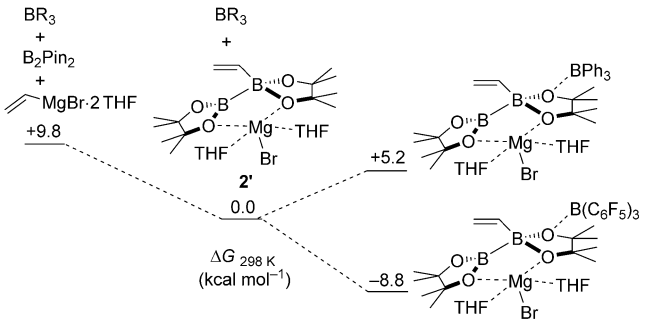


Figure 1. Left: Solid-state structure of **[3][(THF)$_2$MgBr]** with ellipsoids at 50 % probability (some hydrogen atoms omitted for clarity). Right: Molecular structure with selected bonds labelled, distances [Å]: a = 1.663(9), b = 1.571(7), c = 1.545(8), d = 1.554(8), e = 1.358(8), f = 1.417(7), g = 2.118(3), and h = 2.066(4).

solid-state structure, the cation is chelated by the two pinacolato moieties of **[3]**$^-$ through oxygen coordination to magnesium, which results in modest elongation of the B–O bonds involving oxygen atoms coordinated to Mg (compare bonds e and f in Figure 1).[25] Other distances and angles in **[3][(THF)$_2$MgBr]** are within the expected values, with C–BPin bond distances shorter than the C–BPh_3 distance (c and d vs. a in Figure 1). In solution in [D_8]THF, **[3][(THF)$_2$MgBr]** shows two singlets in the ^{1}H NMR spectrum at 298 K for the methyl groups of the pinacols, thus indicating the inequivalence of these hydrogen atoms on the NMR timescale owing to chelation to Mg. Cation metathesis using [Me_4N][Cl] formed the air-stable product **[3][Me$_4$N]**, in which the pinacol methyl groups now exhibit a single resonance in the ^{1}H NMR spectrum at 298 K (in THF). The one-pot triborylation of a vinyl Grignard reagent has not been reported previously to the best of our knowledge.

Regarding the mechanism of formation, the arrangement of boranes in **[3]**$^-$ excludes the possibility of vinyl transfer from **[2]**$^-$ to BPh_3, followed by diboration of the vinyl group in [(CH_2=CH)BPh_3]$^-$ with B_2Pin_2 (or base-activated B_2pin_2), since this reaction pathway would lead to 1,2-arrangement of the BPin groups and not 1,1.[1,2] To gain further insight into the reaction mechanism and the disparity between BPh_3 and

$B(C_6F_5)_3$, we performed DFT calculations at the M06-2X/6–311G(d,p) level with a solvent polarisable continuum model (PCM, THF). On the basis of the structure of **[3][(THF)$_2$MgBr]**, the cation $[(THF)_2MgBr]^+$ was included initially. The formation of the neutral adduct **2′** from **1** and the vinyl Grignard reagent is energetically favoured ($\Delta G_{298K} = -9.8$ kcal mol^{-1}), despite the adverse entropic contribution (Scheme 3). Adduct **2′** showed a slightly elongated B–B bond



Scheme 3. Free-energy profile for the formation of **2′** and O-coordination of the latter to the borane (the zero-energy reference is set as **2′** + BR_3 in each case).

relative to that of **1** (1.73 and 1.70 Å, respectively), as reported for other sp^2–sp^3 diboranes.[1,2] The addition of BPh_3 to **2′** to yield the product **[3][(THF)$_2$MgBr]** is energetically downhill ($\Delta G_{298K} = -42.0$ kcal mol^{-1}). To gain insight into the disparate borane reactivity (B–O activation vs. π activation), we probed the change in energy upon BR_3 coordination to the oxygen atom of **2′.** For BPh_3, this process is energetically uphill ($\Delta G_{298K} = 5.2$ kcal mol^{-1}), in agreement with the reduced electrophilicity and oxophilicity of this borane relative to $B(C_6F_5)_3$. Upon replacement of BPh_3 with $B(C_6F_5)_3$ (Scheme 3, bottom), O-coordination becomes significantly exergonic ($\Delta G_{298K} = -8.8$ kcal mol^{-1}), consistent with the observation of B–O cleavage on mixing **[2]**$^-$ and $B(C_6F_5)_3$. Thus, the correct tuning of the oxophilicity/electrophilicity of the borane employed is a key aspect in selectively triggering 1,2-boryl migration. This feature is further emphasised by replacing $B(C_6F_5)_3$ with the harder Lewis acid BF_3, with O-coordination now becoming much more exergonic ($\Delta G_{298K} = -26.4$ kcal mol^{-1} relative to **2′** and BF_3). Attempts to crystallise **[2][(THF)$_n$MgBr]** were unsuccessful in our hands; thus, owing to the unknown exact nature of the magnesium species coordinated to **[2]**$^-$, and to facilitate more detailed computational studies, additional DFT calculations were performed in the absence of the counterion. The calculated HOMO and HOMO-1 of **[2]**$^-$ are analogous to those of **2′**, thus indicating that while Mg coordination will effect energies to some extent it does not drastically effect the electronic distribution of the frontier orbitals. The HOMO of **[2]**$^-$ has polarised σ B–B character (consistent with the observed {BPin} nucleophilic character), as well as some σ B–C(vinyl) and lone-pair oxygen character (Figure 2, left). The π C=C orbital instead contributes to the HOMO-1, with the vinyl system almost completely aligned with the B–B bond (B-B-C=C 12.10°).

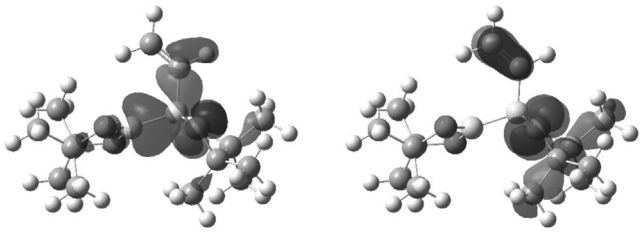
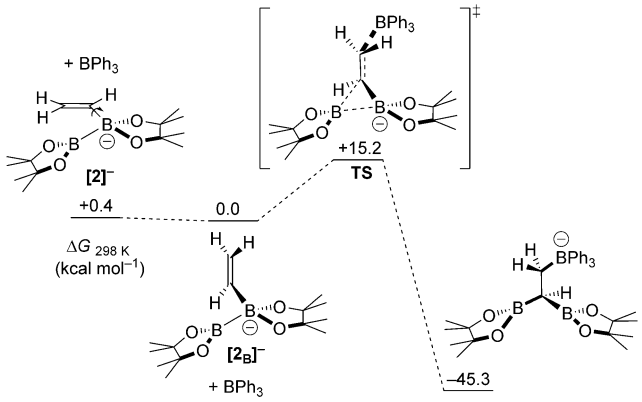


Figure 2. Calculated HOMO and HOMO-1 of **[2]**$^-$ (isovalue = 0.04). **[2]**$^-$ and **2′** showed similar geometry (particularly regarding the B-B-C=C dihedral angle) and HOMOs; thus, the former is provided and not **[2$_B$]**$^-$.

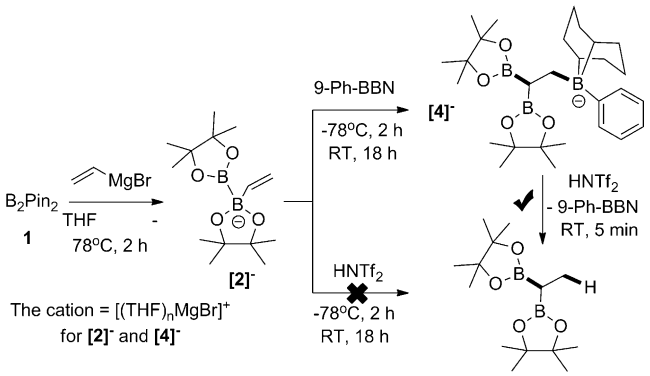
The potential-energy surface is flat where complex **[2]**$^-$ is located, with different local minima obtained by rotation of the vinyl group around the B–C(vinyl) bond. To trigger the intramolecular 1,2-boryl migration, a correct arrangement of the vinyl moiety relative to the B–B bond is required for the *trans* addition of BPh_3 and BPin to the C=C bond (Scheme 4).



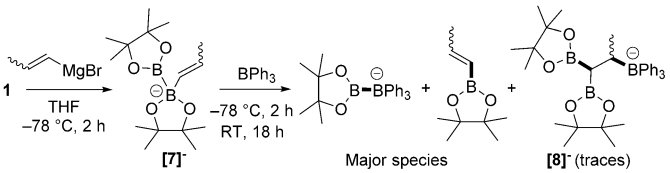
Scheme 4. Free-energy reaction profile for BPh_3-induced 1,2-boryl migration.

From this arrangement (**[2$_B$]**$^-$), the reaction proceeds via transition state **TS** with a low free-energy barrier of 15.2 kcal mol^{-1} at 298 K. In **TS**, the vinyl system is almost perpendicular to the B–B bond (torsional angle B-B-C=C 85.96°), with both the B–B and the C=C bonds slightly elongated as compared to **[2$_B$]**$^-$ (1.75 vs. 1.73 Å, and 1.36 vs. 1.33 Å, respectively). Bond-order analysis of **TS** revealed that the reaction proceeds through an asynchronous concerted mechanism, with the C–BPh_3 bond formed to a greater extent than the C–BPin bond (0.29 and 0.08, respectively).

Having gained this understanding of the reaction mechanism, we tested other soft boron-based Lewis acids. The addition of 9-Ph-BBN (1 equiv) to **[2]**$^-$ (at −78 °C) gave the desired product **[4]**$^-$, with diagnostic peaks observed in the ^{11}B NMR spectrum (34.0 ppm for the −BPin moieties, and −15.3 ppm for $[R(Ph)BBN]^-$) and in the ^{1}H NMR spectrum (upfield broad signal at 0.24 ppm for C*H*$(BPin)_2$), and mass spectrometry confirming the formulation for the anion **[4]**$^-$ (Scheme 5, top). **[4][(THF)$_2$MgBr]** was isolated in 52 % yield (^{1}H NMR spectroscopy indicated the coordination of two molecules of THF to $[MgBr]^+$). Interestingly, in this case the



Scheme 5. Top: Reaction of **1**, a vinyl Grignard reagent, and 9-phenyl-9-borabicyclo[3.3.1]nonane (9-Ph-BBN). Bottom: Synthesis of a 1,1-diborylethane through protodeboronation of **[4]**$^-$; the same product was formed in only low yield by the direct protonation of **[2]**$^-$.



Scheme 6. Reaction of **1** with 1-propenyl Grignard reagent and then BPh_3. The cation is assigned as $[(THF)_nMgBr]^+$ throughout.

tetracoordinated boron centre in **[4]**$^-$ has restricted rotation causing desymmetrization of the bicyclo moiety. Notably, **[4][(THF)$_2$MgBr]** could be selectively deborylated by the addition of $HNTf_2$ (1.1 equiv), which yielded 9-Ph-BBN and $(PinB)_2CHMe$ as the major products, thus indicating that cleavage of the C–(Ph)BBN bond dominates. In contrast, $(PinB)_2CHMe$ was formed in low amounts from the addition of $HNTf_2$ to **[2]**$^-$, with the formation of ethene and **1** dominating (Scheme 5, bottom).

These results highlight the importance of using a soft Lewis acid to selectively trigger the 1,2-boryl migration over other potential pathways. To confirm that the reactivity difference between $B(C_6F_5)_3$ and BPh_3 (or 9-Ph-BBN) is not due to steric factors (as $B(C_6F_5)_3$ is significantly bulkier than BPh_3), we evaluated 9-mesityl-BBN and 9-*o*-tolyl-BBN. Whereas the former gave no reaction with **[2]**$^-$ (presumably owing to the large steric bulk around boron), the addition of *o*-tolyl-BBN to **[2]**$^-$ in THF led to the intramolecular 1,2-boryl-anion migration product **[5]**$^-$, albeit slower than when using 9-Ph-BBN. Importantly, no B–O cleavage products were observed, with the mass balance at this point being unreacted **[2]**$^-$ and *o*-tolyl-BBN. Thus, with bulkier, less Lewis acidic 9-aryl-BBN boranes, the 1,2-boryl migration still proceeds selectively but is slower. This reactivity was further emphasised by adding 9-*p*-anisyl-BBN to **[2]**$^-$, upon which the 1,2-boryl-anion migration proceeded to form **[6]**$^-$ but significantly slower owing to the reduced borane Lewis acidity (see the Supporting Information).

With the aim to disfavour the interaction of borane Lewis acids with the vinylic π system and thus switch the selectivity from intra- to intermolecular {BPin}$^-$ transfer, we explored the effect of increasing steric hindrance at the β-vinylic carbon atom by using the adduct **[7]**$^-$, which was generated in situ by the addition of (*E*/*Z*)-1-propenylmagnesium bromide (1 equiv) to **1** in THF at −78 °C. The subsequent addition of BPh_3 to **[7]**$^-$ resulted in suppression of 1,2-boryl migration, with **[8]**$^-$ detected only in trace amounts (Scheme 6). In this case, $[PinB–BPh_3]^-$ (40 % yield) and (*E*/*Z*)-1-propenyl-BPin were observed as the major new species after 18 h at room temperature, thus confirming the switching of selectivity from intra- to intermolecular {BPin}$^-$ transfer. This represents a simple route to an unsymmetrical sp^2–sp^3 diborane using only commercial reagents.

In summary, a novel intramolecular 1,2-boryl-anion migration has been induced by the addition of soft boranes to vinyl sp^2–sp^3 diboranes. Competitive strong oxygen coordination has to be prevented; thus, the softness of the borane is key in providing selective boryl transfer. With BPh_3 and 9-Ph-BBN, intramolecular 1,2-boryl migration enables the one-pot synthesis of differentially protected 1,1,2-triborylated alkanes from simple starting materials. Furthermore, the ability to switch {BPin}$^-$ transfer from an intra- to an intermolecular process by increasing the steric hindrance in the vinyl group allows access to unsymmetrical sp^2–sp^3 diboranes using commercial Grignard reagents and B_2Pin_2.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boranes · borylation · Grignard reagents · Lewis acids · 1,2-migration

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[25] CCDC 1856184 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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