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Selective boryl-anion migration in a vinyl sp^2-sp^3 diborane induced by soft borane Lewis acids

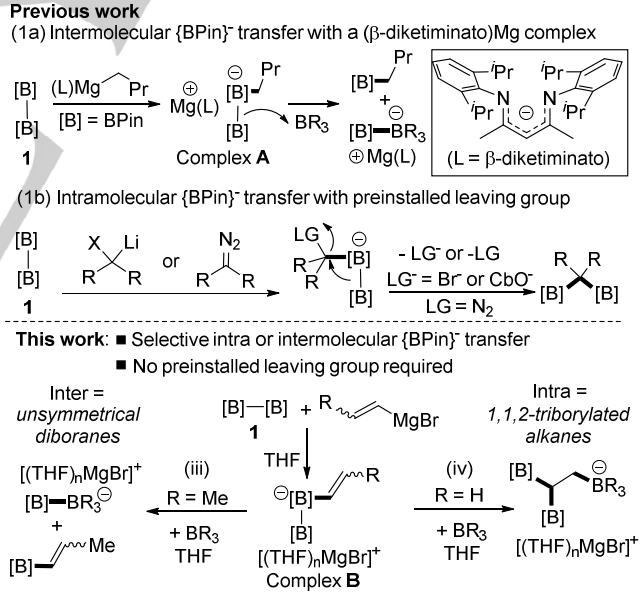
Valerio Fasano,[a] Jessica Cid,[a] Richard J. Procter,[a] Emily Ross,[a] and Michael J. Ingleson[a]*

Abstract: A novel 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 on the beta 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, which represents a simple way to access 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] This imparts nucleophilic character to the sp^2 boron, thereby enabling the mild generation of a functional equivalent of $\{BPin\}^-$.[1,2] This has become a powerful transition metal free methodology 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 precedence,[4-9] despite R^- being able to generate a more nucleophilic {BPin} moiety due to their greater basicity relative to alkoxides and NHCs. Among the limited examples in this area, recent work has showed that complex **A** synthesised from **1** and *n*Bu-MgL (L = β-diketiminato) transfers a boryl anion to boranes forming new unsymmetrical sp^2-sp^3 diboranes (Scheme 1, 1a).[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, as these will be desirable particularly if accessed using readily accessible starting materials (e.g. RMgX / B_2pin_2).

Prior to this work, 1,2-boryl-anion migration from boron to carbon in $[(R)B_2Pin_2]^-$ species had been limited to using functionalized "R^-" equivalents. For example, coordination of a carbanion containing a Br or OCb group (or a diazoalkane), to **1** led to loss of $[OCb]^-$, $[Br]^-$ (or N_2) and formation of 1,1-diborylalkanes (Scheme 1, 1b).[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 is attractive as it avoids prefunctionalization of the carbanion activator. This approach 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 via deprotonation / deborylation of the diborylated carbon.[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 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 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.



Scheme 1. Top, previous work on intermolecular / intramolecular $\{BPin\}^-$ transfer in carbanion activated B_2Pin_2. Bottom, selective boryl-anion migration in vinyl sp^2-sp^3 diboranes induced by soft borane Lewis acids.

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 β-methyl vinyl Grignard reagent changes the reaction outcome to intermolecular $\{BPin\}^-$ transfer to BR_3, generating an unsymmetrical diborane from simple starting materials.

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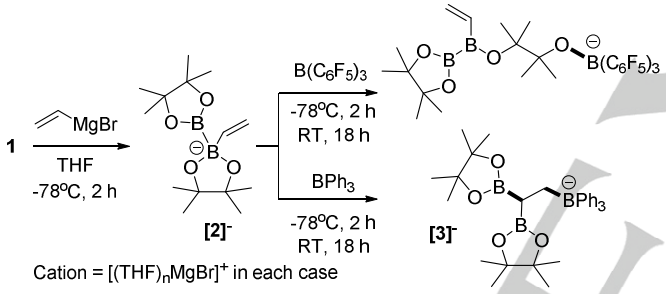
We started our investigation by probing the accessibility of the simplest vinyl adduct of **1**, $[(CH_2{=}CH)B_2Pin_2]^-$ (**[2]**$^-$). This could be generated as the major product by the addition of 1 equiv. of commercial vinyl magnesium bromide to **1** in THF at -78°C (Scheme 2, left). The successful formation of **[2]**$^-$ was indicated by ^{11}B NMR spectroscopy where two new resonances could be observed: one at 37.3 ppm (three coordinate boron) and the other at 4.8 ppm (four coordinate boron), analogous with that 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] Adding 1 equiv. of $B(C_6F_5)_3$ to **[2]**$^-$ (at -78°C) led after 2 hours to a single new ^{11}B resonance at -3.2 ppm, consistent with an $[RO\text{-}B(C_6F_5)_3]^-$ species (in contrast $[alkyl\text{-}B(C_6F_5)_3]^-$ anions have a ^{11}B resonance ca. -15 ppm). The ^{19}F NMR spectrum confirmed $[RO\text{-}B(C_6F_5)_3]^-$ formation, with ESI-MS analysis supporting the formation of an $[RO\text{-}B(C_6F_5)_3]^-$ 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 (Scheme 2, top). This is consistent with reports on BPin moieties in anionic borates undergoing B-O cleavage on addition of electrophiles.[24]



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

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 $[PinB\text{-}BPh_3]^-$ with no competitive reactivity at the oxo-sites reported (Scheme 1, 1a).[10] Adding 1 equiv. of BPh_3 in THF to the in-situ generated **[2][(THF)$_n$MgBr]** (at -78°C), resulted in the formation of the desired product **[3]**$^-$ formed from intramolecular {BPin}$^-$ transfer (Scheme 2, bottom). **[3]**$^-$ has diagnostic resonances in the ^{11}B NMR spectrum (34.7 ppm for the C-*B*Pin moieties, and -9.5 ppm for $[C\text{-}BPh_3]^-$) and in the ^{1}H NMR spectrum (broad signal at 0.55 ppm for the 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]**$^-$, yielding **[3]**$^-$ in 71% (in-situ conversion) as the major product. Repeating the reaction on larger scale allowed for the isolation of **[3][(THF)$_2$MgBr]** as a white solid by solvent removal and washing with Et_2O (70% isolated yield). Single crystals of **[3][(THF)$_2$MgBr]** were obtained by layering pentane onto a THF solution (Figure 1). In the solid state structure the cation is chelated by the two pinacolato moieties of **[3]**$^-$ via

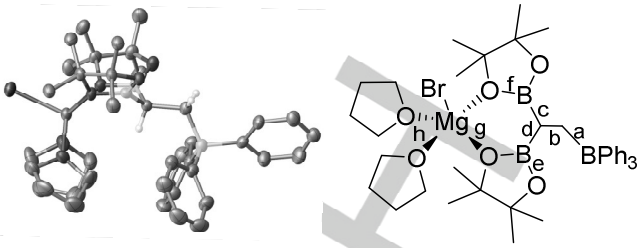


Figure 1. Left, solid-state structure of **[3][(THF)$_2$MgBr]** with ellipsoids at 50% probability (some hydrogens omitted for clarity). Right, schematic with select bonds labelled, distances (in Å) a = 1.663(9), b = 1.571(7), c = 1.545(8), d = 1.554(8), e = 1.358(8), f = 1.417(7), g = 2.118(3) and h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

oxygen coordination to magnesium. This results in a modest elongation of the B-O bonds involving oxygen coordinated to Mg (compare e and f Fig. 1). 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, d Vs. a Fig. 1). In d_8-THF solution, **[3][(THF)$_2$MgBr]** shows two singlets in the ^{1}H NMR spectrum at 298 K for the methyl groups of the pinacol groups, indicating the inequivalence of these protons on the NMR timescale due to chelation to Mg. Cation metathesis can be achieved using $[Me_4N][Cl]$ to form 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). It is noteworthy that the one-pot triborylation of a vinyl Grignard reagent has not been reported 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 would yield a 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 $B(C_6F_5)_3$, DFT calculations were performed at the M06-2X/6-311G(d,p), with a solvent polarisable continuum model (PCM, THF) level. Based on 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 (ΔG_{298K} = -9.8 Kcal mol^{-1}), despite the adverse entropic contribution (Scheme 3). Adduct **2′** showed a slightly elongated B-B bond relative to that of **1** (1.73 and 1.70 Å, respectively), as reported for other sp^2-sp^3 diboranes.[1,2] Addition of BPh_3 to **2′** to yield the product **[3][(THF)$_2$MgBr]** is energetically downhill (ΔG_{298K} = -42.0 Kcal mol^{-1}). To gain insight into the disparate borane reactivity (B-O activation *vs* π activation), the change in energy upon BR_3 coordination to the oxygen of **2′** was probed. For BPh_3 this process is energetically uphill (ΔG_{298K} = 5.2 Kcal mol^{-1}), in agreement with the reduced electrophilicity and oxophilicity of this borane relative to $B(C_6F_5)_3$. Replacing BPh_3 with $B(C_6F_5)_3$ (Scheme 3, bottom), *O*-coordination become significantly exergonic (ΔG_{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 to selectively trigger 1,2-boryl-migration. This is further emphasised by replacing $B(C_6F_5)_3$ with

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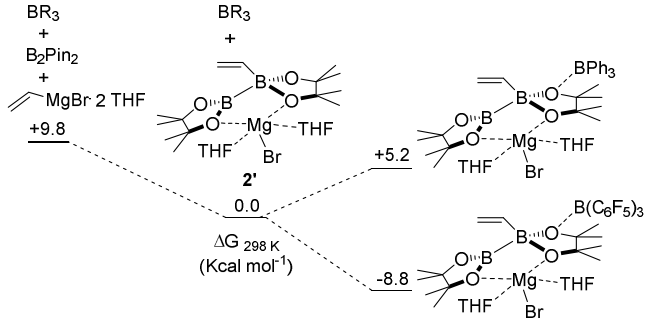


Scheme 3. Free energy profile for formation of **2'** and *O*-coordination of the latter to the borane (the zero energy reference is set as **2'** + BR_3 in each case).

the harder Lewis acid BF_3, with *O*-coordination now becoming much more exergonic (ΔG_{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 due 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 absence of the counterion. It should be noted that the calculated HOMO and HOMO-1 of **[2]**$^-$ are analogous to that of **2'** indicating that while Mg coordination will effect energies to some extent it does not drastically effect the electronic distribution. 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°).

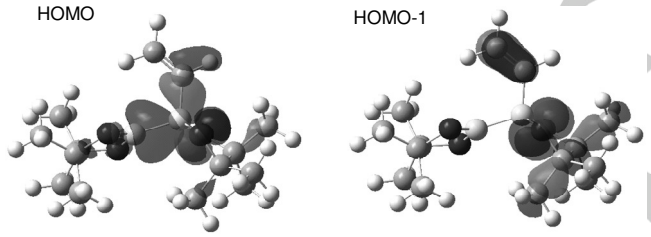
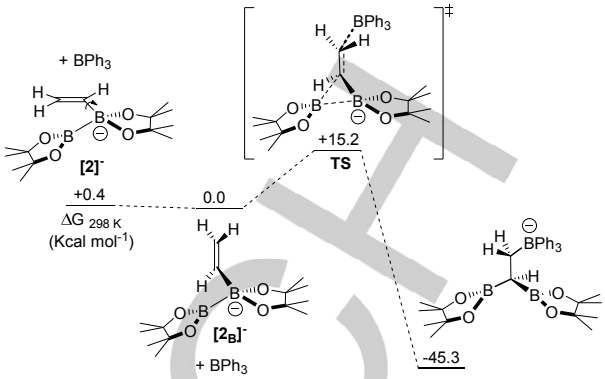


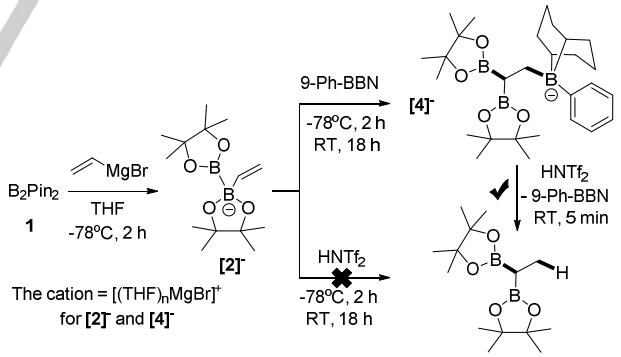
Figure 2. The calculated HOMO and HOMO-1 of **[2]**$^-$ (isovalue = 0.04). **[2]**$^-$ and **2'** showed similar geometry (particularly regarding the B-B-C=C dihedral angle) and HOMOs, thus the former geometry is provided and not that of **[2$_B$]**$^-$.

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). 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 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).



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

With an understanding of the reaction mechanism in hand, other soft boron based Lewis acids were tested. The addition of 1 equiv. of 9-Ph-BBN 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 the C*H*(BPin)$_2$), with mass spectrometry confirming the formulation for the anion **[4]**$^-$ (Scheme 5, top). **[4][(THF)$_2$MgBr]** was isolated in 52% yield (2 molecules of THF coordinated to [MgBr]$^+$ by ^{1}H NMR spectroscopy). It is interesting to note that in this case the tetra-coordinated 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 1.1 equiv. of $HNTf_2$, which yielded 9-Ph-BBN and $(PinB)_2CHMe$ as the major products, indicating cleavage of the C-(Ph)BBN bond dominates. In contrast, $(PinB)_2CHMe$ was formed in low amounts from the addition of $HNTf_2$ to the **[2]**$^-$, with formation of ethene and **1** dominating (Scheme 5, bottom).

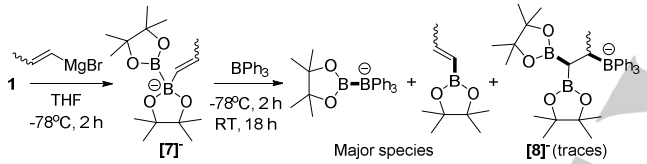


Scheme 5. Top, reaction with **1**, a vinyl Grignard reagent and 9-Ph-BBN. Bottom, synthesis of 1,1-diboryl-ethane via protodeboronation of **[4]**$^-$ with this product formed in low yield from direct protonation of **[2]**$^-$.

This highlights the importance of using a soft Lewis acid to selectively trigger the 1,2-boryl-migration over other potential pathways. To further support 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), 9-mesityl-BBN and 9-*o*-tolyl-BBN were evaluated. While the former gave no reaction with **[2]**$^-$ (presumably due 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 it is slower, a fact further emphasised by adding 9-*p*-anisyl-BBN to **[2]**$^-$, in which the 1,2-boryl anion migration proceeds to form **[6]**$^-$ but significantly slower due to the reduced borane Lewis acidity (see SI).

With the aim to disfavour borane Lewis acids interacting with the vinylic π system and thus switch selectivity from intra- to inter-molecular {BPin}$^-$ transfer, we explored the effect of increasing steric hindrance at the β-vinylic carbon. In particular, using the adduct **[7]**$^-$, which was generated in-situ by the addition of 1 equiv. of (E/Z)-1-propenylmagnesium bromide 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 $[PinB\text{-}BPh_3]^-$ (40% yield) and (E/Z)-1-propenyl-BPin were observed as the major new species after 18 h at room temperature, thus confirming switching of selectivity from intra- to inter-molecular {BPin}$^-$ transfer. This represents a simple route to access an unsymmetrical sp^2-sp^3 diborane using only commercial reagents.



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

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 intra- to inter-molecular 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: 1,2-migration • diboranes • Grignard reagents • borylation • boranes

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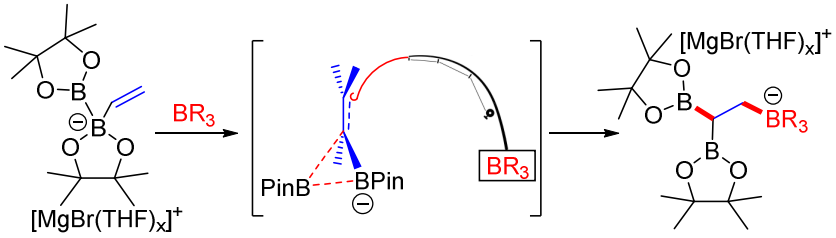

■ From commercial SMs ■ Selective π-activation ■ Triborylated product

Selective Pi fishing: an intramolecular 1,2-boryl anion migration has been achieved by selective activation of the π-system in vinyl sp^2-sp^3 diborane using "soft" borane Lewis acids.

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Selective boryl-anion migration in a vinyl sp^2-sp^3 diborane induced by soft borane Lewis acids