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Rearrangement

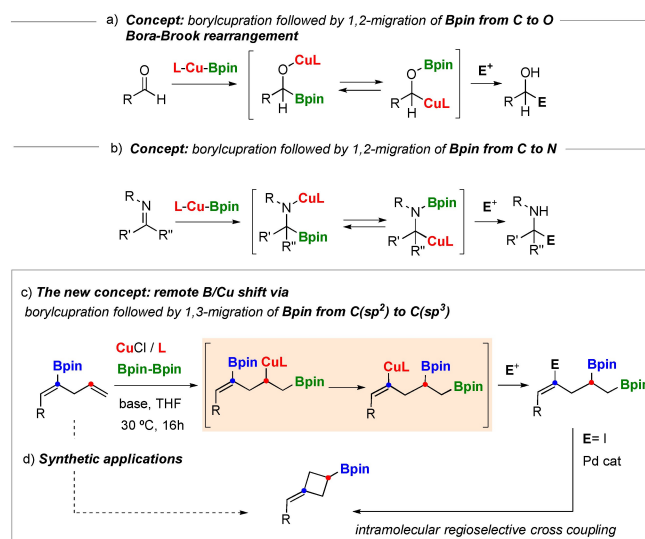
Boron-Copper 1,3-Rearrangement: the New Concept Behind the Boryl Migration from C(sp²) in Alkenyl Boranes to C(sp³)

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Dedicated to Professor Masahiro Murakami (Kyoto University) on the occasion of his retirement.

Abstract: Regioselective borylcupration of borylated skipped (*Z*)-dienes generates diborylated alkylcopper species that are involved in an intramolecular stereospecific B/Cu 1,3-rearrangement by migration of Bpin moiety from C(sp²) to C(sp³). DFT mechanistic studies showed that boryl migration occurs through the formation of 4-membered boracycle intermediate with a moderate free-energy barrier. Moreover, the use of KOMe forms stable Lewis base adducts with Bpin moieties that blocks the reaction. Subsequently to the 1,3-boron shift, the in situ electrophilic trapping allows selective C–H, C–C and C–X bonds, followed by intramolecular cross coupling giving access to cyclic functionalized alkylidencyclohexanes or alkylidencyclobutanes.

Migration of a boryl group from carbon to an adjacent oxygen atom (bora-Brook rearrangement) has been postulated to explain the observed nucleophilic reactivity of boryl-substituted alkoxide compounds towards electrophiles.^[1] This concept is exemplified when borylcupration of carbonyl compounds links the nucleophilic pinacolboryl unit (Bpin) to carbon and the Cu^I complex to oxygen,^[2] but intramolecular 1,2 migration of Bpin from C to O can take place and the new shifted intermediate might evolve towards the electrophilic trapping on the carbon atom (Scheme 1a).^[1,3] More recently, it has been identified a similar rearrangement from α -borylalkylamido copper intermediates to α -borylaminoalkyl copper species through 1,2-



Scheme 1. Borylcupration sequences followed by B/Cu shift.

migration of a pinacolboryl group from carbon to nitrogen, and consequently a copper migration from nitrogen to carbon with the concomitant electrophilic trapping on the carbon atom (Scheme 1b).^[4] The presence of neighboring heteroatoms (O, N) has been claimed to justify the enhanced migratory aptitude of Bpin moieties, as a balance between bond energy values and relative stability of the corresponding carbanions. The more stable boryl group Bmida (mida = N-methyliminodiacetic acid) has also experimented boryl migration sequences through 1,2-shifts with Cu or Au complexes,^[5] as well as in a transition metal free context, assisted by Lewis acids.^[6]

Conceptually, decisive electronic and steric factors can be controlled to guarantee the boron-copper 1,2-rearrangement, conditioning the exhibited reactivity of the electrophilic C, on C=O or C=N, with electrophiles, featuring an umpolung reactivity.^[1,4]

Inspired by the aforementioned borylcupration and consecutive B/Cu 1,2-rearrangement, we envisaged a conceptually new B/Cu shift from remote C(sp²)-Bpin and C(sp³)-Cu units generated through borylcupration of borylated skipped (*Z*)-dienes (Scheme 1c). The present discovery represents a novel carbon-to-carbon boryl migration, which is characterized by its high stereospecificity around the alkene, contributing to establish an in situ stereoselective

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electrophilic trapping. The synthetic application of the novel homoallyl diborated product has pursued the palladium catalyzed regioselective intramolecular coupling to prepare functionalized alkylidenecyclobutanes considered highly strained yet stable molecules found in biologically active natural products (Scheme 1d).^[7]

To illustrate this concept, we worked on the borylcupration of borylated skipped (*Z*)-dienes, efficiently prepared from *gem*-diborylalkenes.^[8] We initially explored the influence of Cu salts, ligands and bases for the borylcupration of (*Z*)-2-pinacolboryl 1-(*p*-tolyl)penta-1,4-diene (**1a**), as model substrate. From the diverse array of potential copper(I) catalytic systems that perform borylcupration sequences,^[9] we selected the catalyst based on CuCl/Xantphos inspired by original Ito's work on regioselective borylcupration^[10] and our own experience.^[11] Conversion of **1a** into diborated alkene **2** was quantitative performed with 10 mol % of CuCl/Xantphos, in the presence of 1.2 equiv of B₂pin₂ and KO^tBu as base, at 30 °C, in THF (Table 1, entry 1). Alternatively, the use of [Cu(MeCN)₄]PF₆, instead of CuCl, also allowed the formation of **2** in similar quantitative yield (Table 1, entry 2). The nature of the base has a notable influence on the reaction outcome, since KO^tBu or LiO^tBu provides similar high transformation of **1a** into **2**, whereas KOMe seems to inhibit the borylcupration of **1a** (Table 1, entries 3, 4). It is worth mentioning that the site selective activation of *gem*-diborylalkenes with Cu^I, to synthesize the borylated (*Z*)-skipped dienes of type **1**, has also been reported to be inhibited by the presence of KOMe.^[8] Replacement of Xantphos by other diphosphines such as 1,3-bis(diphenylphosphino)propane (dppp) or monophosphines (PPh₃, PCy₃), resulted in a less efficient or even inhibited transformation (Table 1, entry 5).

Bearing in mind the optimized reaction conditions to sequentially conduct selective borylcupration—1,3-B/Cu shift—protonation, in a single operation, we explored the

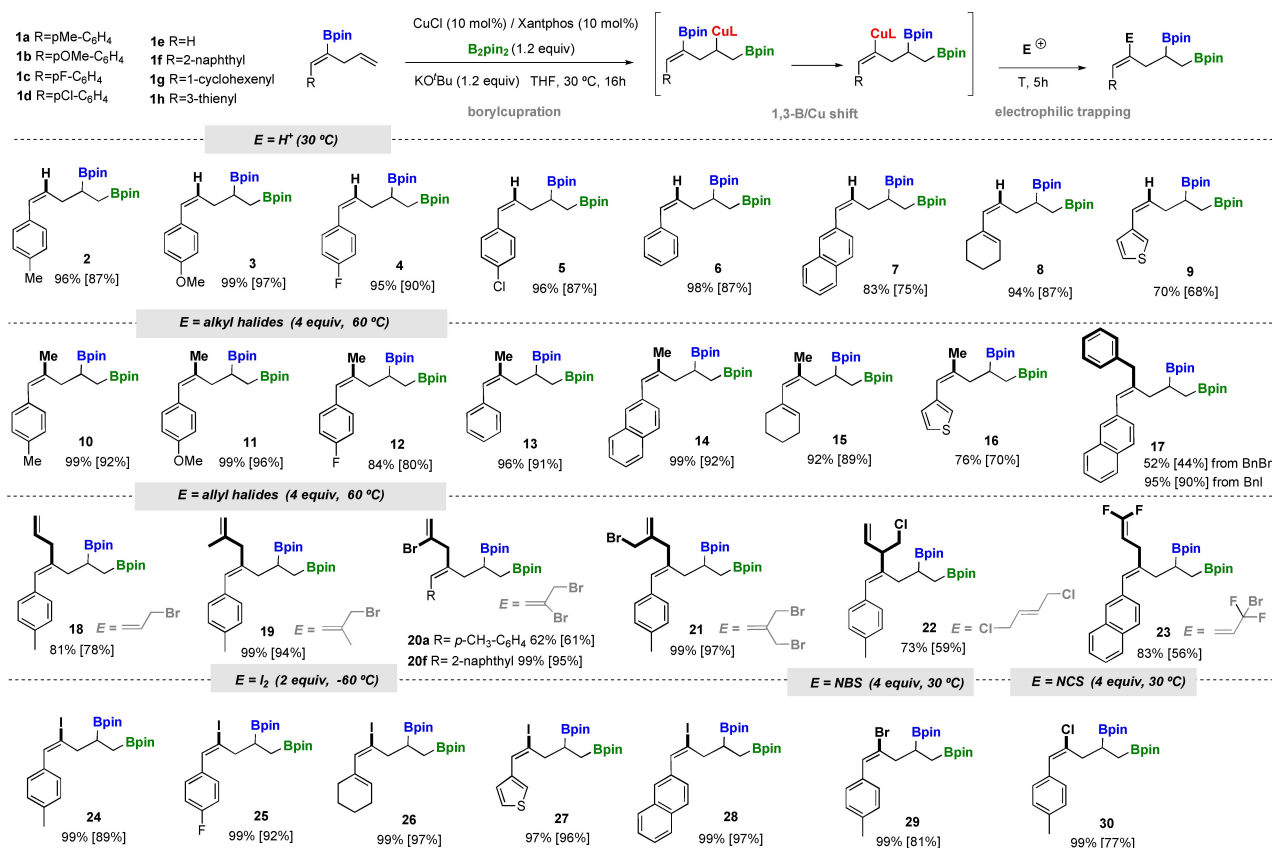
compatibility of aryl groups containing electron donating and electron withdrawing substituents (Scheme 2). In general, it was found that the substrates are transformed into the desired products **2–6**, independently of the electronic properties of the aryl group (Scheme 2). Additionally, the aryl group 2-naphthyl resulted compatible with the intramolecular 1,3-B/Cu shift, and the expected product **7** was isolated in high yield (Scheme 2). The borylated skipped (*Z*)-dienes **1g** and **1h**, containing the 1-cyclohexenyl or 3-thienyl group, respectively, undertook a chemoselective copper catalyzed borylcupration on the terminal double bond, followed by the stereospecific 1,3-B/Cu shift, generating the polyolefinic diborated compounds **8** and **9**, highlighting the compatibility of the reaction with other unsaturated functional groups (Scheme 2). Accordingly, we next explored the one pot borylcupration of **1a–1h**, with subsequent 1,3-B/Cu shift, followed by stereospecific C–C coupling with MeI (60 °C, during 5 h), and to our delight the methylated products were isolated in high yields and characterized as the stereoselective trisubstituted alkenes **10–16** (Scheme 2). The stereospecific coupling was extended to benzylhalides, transforming **1f** into compound **17** by reaction with BnBr or BnI, being the later the most reactive (Scheme 2). However, the electrophilic trapping resulted unproductive for secondary or tertiary alkyl halides, suggesting that the Cu–C(sp²) nucleophilic reaction might occur through a S_N2 type reaction.

When terminal and internal allyl halides were used as electrophilic partners, we observed an efficient transformation of **1a** or **1f** into products **18–22**, with moderate to high yields depending on the steric hindrance of the allyl bromide (Scheme 2). Reactivity with 3-bromo-3,3-difluoroprop-1-ene, converted **1a** into perfluorinated alkene system **23**, in high yield. In basis of the reaction outcome, the C–C coupling might proceed through a S_N2' mechanism. Complementarily, we also conducted the I₂-iodonolysis^[12] of the alkenyl copper (I) intermediates generated after borylcupration—1/3-B,Cu shift, providing the key vinylic iodide products **24–28** in high yields (Scheme 2). Alternatively the brominated and chlorinated trisubstituted alkenes **29** and **30** could also be efficiently generated by stereospecific electrophilic trapping through addition of NBS or NCS, respectively (Scheme 2). With regard to the nature of the boryl system, we have also pursued the formation of regioselective mixed diborated products, by means of two complementary strategies. Initially, when substrate **1f** reacted with bis(hexylene glycolato) diboron, (B₂hex₂) the borylcupration took place placing the Bhex moiety at the terminal position of the double bond with the concomitant 1,3-Bpin/Cu shift, followed by electrophilic coupling with MeI, generating the mixed product **14-BpinBhex**, (Scheme 3). In parallel, we transborylated **1f** into **1f-hex** via a convenient C(sp²)–Bpin / B₂hex₂ cross metathesis,^[13] with the aim to conduct the borylcupration of **1f-hex** with B₂pin₂, followed by 1,3-Bhex/Cu shift and eventual coupling with MeI, generating the mixed alkene **14-BhexBpin** in 95 % yield, containing the Bhex at the internal position (Scheme 3). Those experiments show that 1,3-B/Cu shift is compatible with boryl moieties

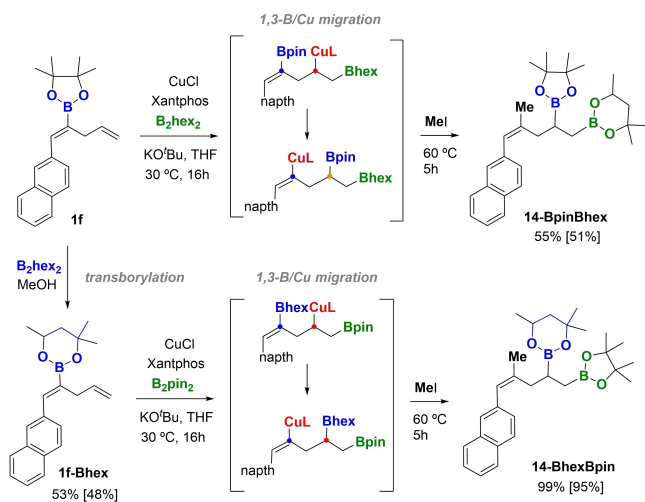
Table 1: Optimization conditions for borylcupration of (*Z*)-2-pinacolboryl 1-(*p*-tolyl)penta-1,4-diene (**1a**) with concomitant 1,3-B/Cu migration and protonation.

Entry ^[a]	Cu ^I	Ligand	Base	Conv % ^[b]	2 % ^[b] [%] ^[c]
1	CuCl	Xantphos	KO ^t Bu	96	96 [87]
2	[Cu(MeCN) ₄]PF ₆	Xantphos	KO ^t Bu	97	97
3	CuCl	Xantphos	LiO ^t Bu	98	98
4	CuCl	Xantphos	KOMe	0	–
5	CuCl	PPh ₃	KO ^t Bu	0	–

[a] General conditions: **1a** (0.2 mmol), B₂pin₂ (1.2 equiv), Cu^I source (10 mol%), Ligand = Xantphos (10 mol%), PPh₃ (20 mol%), base (1.2 equiv), THF (2 mL), 30 °C, 16 h. [b] Conversion and yield on **2** determined by ¹H NMR with naphthalene as internal standard. [c] Isolated Yield.



Scheme 2. Scope of borylcupration—1,3-B/Cu shift—electrophilic trapping. Yield determined by ¹H NMR with naphthalene as internal standard, and Isolated Yield in brackets.



Scheme 3. 1,3-B/Cu shift with mixed boryl systems and electrophilic trapping with MeI. Yields determined by ¹H NMR with naphthalene as internal standard, and isolated yields in brackets.

other than Bpin, and allows the synthesis of both regioisomers, **14-BpinBhex** and **14-BhexBpin**.

Next, we performed DFT calculations^[14] in order to elucidate the reaction mechanism of the stereospecific borylcupration—1,3-B/Cu shift—methylation of borylated

skipped (*Z*)-dienes, as well as to understand the role of the base on the catalytic activity. Firstly, we selected the substrate **1a**, B₂pin₂ as reactant, the Cu^I-Xantphos as catalyst, and KO^tBu as base. Figure 1 shows the corresponding potential, free-energy profile of the proposed mechanism. The active catalyst resulting from mixing CuCl, KO^tBu and Xantphos ligand is the Xantphos-Cu(O^tBu) complex **II**. As shown in previous computational studies,^[11] **II** undergoes σ-bond metathesis with B₂pin₂ to yield the Cu^I-boryl species (**12**), that is thermodynamically favorable by 17.7 kcal mol⁻¹ (Figure 1).

In the next step, substrate **1a** can coordinate to the Cu complex through the terminal double bond forming the **13** adduct (Figure 1). Subsequent regioselective insertion of the C=C double bond into the Cu–B bond yields the alkylcopper(I) complex **14** with the Bpin moiety bonded to the terminal carbon. This process (**12**→**14**) is exergonic (–22.2 kcal mol⁻¹) with a moderate free-energy barrier (14.3 kcal mol⁻¹, from **12** to **TS1**). Note that it has been experimentally proved that borylcupration is chemoselective over the terminal double bond in the presence of the internal or endocyclic alkene moieties (see for example the transformations of compound **1g** in Scheme 2).

From intermediate **14**, the intramolecular B/Cu 1,3-rearrangement by migration of Bpin moiety from C(sp²) to C(sp³) can occur in two steps (Figure 1). The geometry of the corresponding transition states, **TS2** and **TS3**, are shown

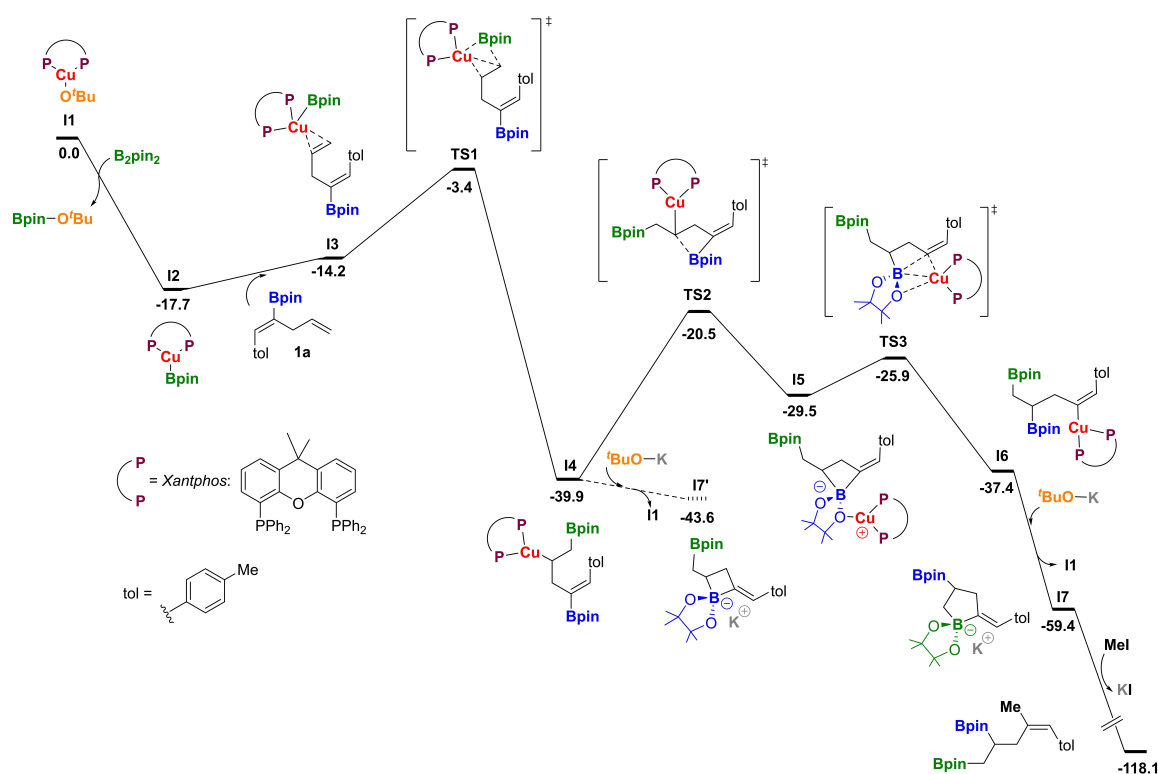


Figure 1. Free-energy profile [kcal mol^{-1}] for the borylcupration of (Z)-2-pinacolboryl 1-(p-tolyl)penta-1,4-diene (**1a**) with B_2pin_2 catalyzed by Cu^{I} -Xantphos complex in the presence of KO^tBu base.

in Figure 2. Firstly, the nucleophilic attack of copper-alkyl moiety to the boron atom bonded to the $\text{C}(\text{sp}^2)$ leads to a 4-membered boracycle structure, which remains bonded to the copper through an oxygen atom of pinacol group (intermediate **I5**). Secondly, the Cu migrates to the $\text{C}(\text{sp}^2)$ along with the ring opening of the $\text{B}-\text{C}(\text{sp}^2)$ bond that results in the alkenyl copper intermediate **I6**. Overall, the 1,3-B/Cu shift process needs to overcome a moderate free-energy barrier ($19.4 \text{ kcal mol}^{-1}$ from **I4** to **TS2**). Finally, the base KO^tBu can transmetallate with the Cu-alkenyl complex **I6**, forming the 5-membered boracycle compound **I7**, stabilized

by K^+ counteraction, and recovering the $\text{Cu}-\text{O}^t\text{Bu}$ catalytic system **II** (Figure 1). This step (**I6** + KO^tBu \rightarrow **II** + **I7**) is quite exergonic ($-22 \text{ kcal mol}^{-1}$) and provides the thermodynamic driving force of the reaction. Similarly, we considered the transmetallation of **I4** with the base KO^tBu forming a 4-membered boracycle intermediate **I7'** and **II** (dashed lines in Figure 1). However, the computed free energy for this process is only slightly exergonic ($-3.7 \text{ kcal mol}^{-1}$). This suggests that even if the reaction takes place, **I7'** can be in equilibrium with intermediate **I4** that subsequently evolve to the formation of the highly stable intermediate **I7**. Finally, the 5-membered boracycle intermediate **I7**, stabilized by K^+ counteraction, can be trapped by an electrophile to complete the reaction. We evaluated the electrophilic trapping of **I7** with MeI , and it was computed to be highly favorable from the thermodynamic point of view (Figure 1).

The proposed mechanism can also explain the observed reaction inhibition upon replacing the KO^tBu by KOMe base. The corresponding alkoxides can coordinate to trivalent boron atom to form stable Lewis base adducts that are relevant for the catalytic activity. Alkoxy coordination on the boryl moiety within intermediate **I2** would have a significant impact in the reaction outcome by preventing the borylcupration on the terminal double bond through transition state **TS1** (Scheme 4). Ongoing from KO^tBu to KOMe , the $[\text{RO}^- \rightarrow \text{I2}]$ adduct (**I2**^{*t*Bu} and **I2**^{*Me*}) becomes energetically more stable due to lower steric repulsion between the small Me group and the Cu -Xantphos complex (Scheme 4). Thus, the methoxy adduct **I2**^{*Me*} represents a

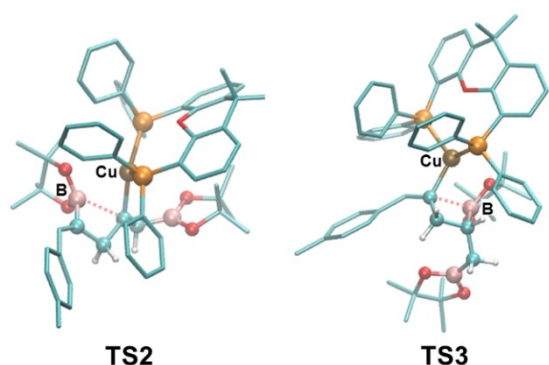
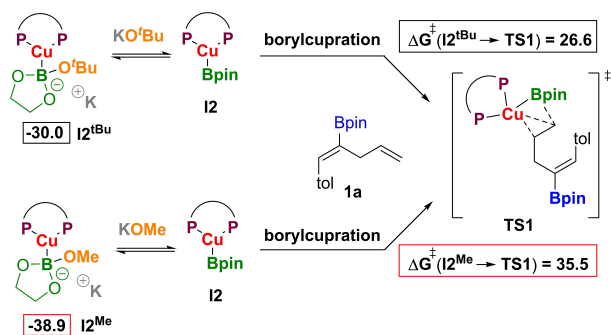


Figure 2. Molecular structures of the transition states, **TS2** and **TS3**, describing the intramolecular 1,3-B/Cu migration of Bpin moiety from $\text{C}(\text{sp}^2)$ to $\text{C}(\text{sp}^3)$.



Scheme 4. Free-energies (kcal mol^{-1}) for the coordination of two alkoxides (tBuO^- and MeO^-) to the Bpin moiety of intermediate **I2**, and overall free-energy barriers for the borylcupration in the presence of KO^tBu ($\text{I2}^{\text{tBu}} \rightarrow \text{TS1}$) and KOMe base ($\text{I2}^{\text{Me}} \rightarrow \text{TS1}$).

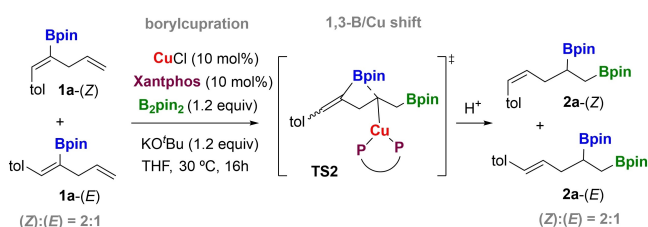
deep energy well in the reaction mechanism that results in a prohibitive free-energy barrier ($\text{I2}^{\text{Me}} \rightarrow \text{TS1}$) of $35.5 \text{ kcal mol}^{-1}$.

Our mechanistic proposal for the selective borylcupration—1,3-B/Cu shift—electrophilic trapping, conducted in a single operation, has associated computed moderated barriers which are in a favorable agreement with the mild reaction conditions used. To the best of our knowledge, this is the first example of an intramolecular B/Cu 1,3-shift, since only 1,3-boron shift-type reactions have been disclosed to occur intermolecularly on conjugated allylboronates or homoallynylboronates.^[15]

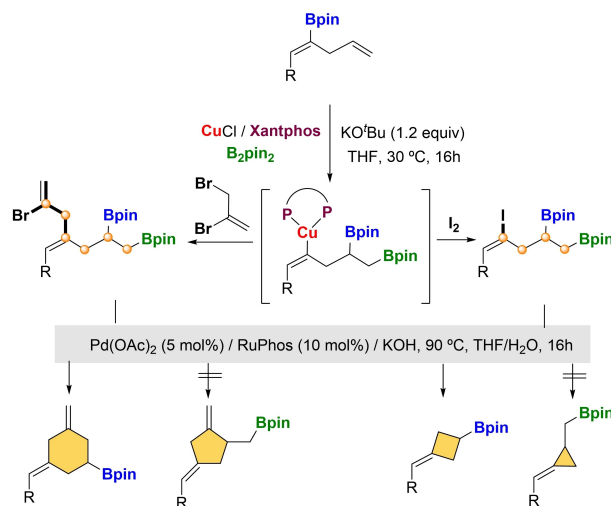
In order to have a complete picture of the mechanism, we conducted an experiment where both stereoisomers of borylated skipped diene **1a**, (*Z*):(*E*)=2:1 ratio, can be transformed via *one pot* borylcupration and subsequent 1,3-B/Cu shift—protonation towards **2-(Z)** and **2-(E)** within the same 2:1 ratio (Scheme 5). This reaction outcome suggests that both isomers proceed with similar energetic profile besides the relative position of the aryl group on the skipped diene substrate.

All the polyfunctionalized alkenes prepared in this work (**2–30**) are new, and some of them show potential synthetic application to be converted into functionalized alkylidenecycloalkanes, of six, five, four or three membered ring, throughout Pd catalyzed intramolecular cross coupling (Scheme 6).

To our delight, when the polyfunctionalized skipped compound **20a** reacted with $\text{Pd}(\text{OAc})_2/\text{Ruphos}$,^[16] a regiose-



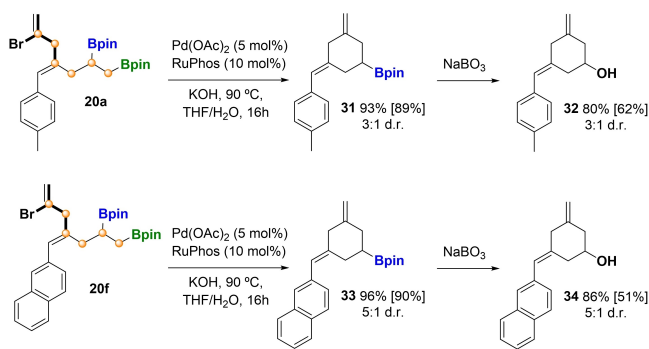
Scheme 5. Borylcupration of **1a-(Z)** : **1a-(E)** = 2:1 followed by 1,3-B/Cu migration—protonation.



Scheme 6. Potential synthetic application throughout Pd-catalyzed intramolecular cross coupling for alkylidenecycloalkanes synthesis.

lective cyclization with the terminal Bpin moiety took place generating exclusively the six-membered ring product **31**, containing two exocyclic alkene motifs and the original Bpin moiety from the starting material **1a** (Scheme 7). The alkylidenecyclohexane **31** was isolated as 3:1 stereoisomeric mixture and the oxidation provided the corresponding alkylidenecyclohexane **32** (Scheme 7). When the more sterically hindered polyfunctionalized skipped compound **20f** was submitted to the Pd catalyzed intramolecular cyclization, the alkylidenecyclohexane **33** was isolated in high yield and increased diastereomeric ratio (up to 5:1), that was also observed in the corresponding alcohol **34** (Scheme 7).

Similarly, the Pd intramolecular cyclization of (*E*)-iodo substituted alkene **24**, allowed the exclusive formation of the alkylidenecyclobutane **35**, that are considered a particular class of highly strained yet stable molecules. Since the later compounds have recently shown to be, not only useful structural motifs in a number of natural products^[7] but also versatile intermediates in organic synthesis,^[17] we plan to generalize the Pd-catalyzed intramolecular cyclization to



Scheme 7. Intramolecular regioselective Pd-cyclization towards alkylidenecyclohexane synthesis and oxidation to vinylidenecyclohexanols. Yields determined by $^1\text{H NMR}$ with naphthalene as internal standard, and isolated yields in brackets.

(*E*)-iodo substituted alkenes **24–28**. By conducting the designed reactions, we observed the general trend to synthesize the four-membered rings **35–39**, in high yield (Scheme 8). The transformations resulted to be tolerant with electron donating or electron withdrawing aryl or vinyl group present in the substrates, installing the exocyclic alkene motif and the genuine Bpin moiety from the starting material **1** in *trans* disposition. The oxidation of the C-Bpin bonds in the exobutanocyclic alkenes, allowed the formation of the aryl- or vinylidene cyclobutanols **40–44** in a quantitative manner, which to the best of our knowledge, have been synthesized for the first time in this work (Scheme 8).

We describe here a conceptually new 1,3-B/Cu shift based on a remote rearrangement between C(sp²)-Bpin and C(sp³)-Cu fragments generated through borylcupration of borylated skipped (*Z*)-dienes. This unprecedented carbon-to-carbon boryl migration takes place with stereospecificity around the alkene, contributing to the subsequent stereoselective electrophilic trapping by in situ addition of H⁺, alkyl halides, allyl halides, I₂, NBS or NCS. Mixed diborated products can be prepared via transborylated skipped (*Z*)-dienes. The reaction mechanism has been characterized by DFT calculations on the sequential borylcupration–1,3-B/Cu shift–methylation of borylated skipped (*Z*)-dienes, and with special emphasis on the role of the base along the catalytic activity. The computational study indicates that 1,3-B/Cu shift occurs via nucleophilic attack of the copper-alkyl moiety to the boron atom bonded to the C(sp²) leading to a 4-membered boracycle structure. Subsequently, copper migrates to the C(sp²) along with the ring opening of the B–C(sp²) bond that results in an alkenyl copper intermediate. The overall 1,3-B/Cu shift process has a moderate, computed free-energy barrier (19.4 kcal mol⁻¹). Calculations also show that the alkoxides from the bases (KO^tBu, LiO^tBu, or KOMe) can form Lewis base adducts with the Bpin motifs of the intermediates. While bulky *tert*-butoxide

prevents the formation of too stable adducts due to its steric hindrance with the Xantphos ligand, the methoxide group interacts strongly quenching the reaction activity. Eventually, the synthetic application of the novel homoallyl diborated products has pursued the palladium catalyzed regioselective intramolecular cross-coupling towards alkylidenecyclohexanes and alkylidenecyclobutanes, considered the later highly strained yet stable molecules found in biologically active natural products.

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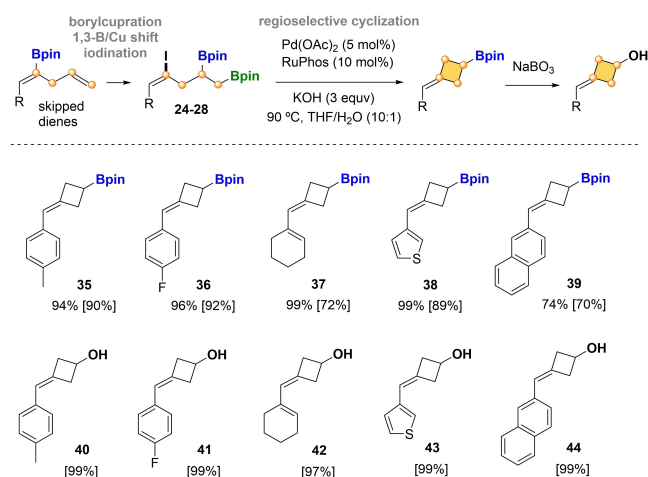
Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Alkylidenecyclobutanes • Boryl-Migration • Copper • DFT Calculations • Mechanism



Scheme 8. Intramolecular regioselective Pd-cyclization towards alkylidenecyclobutane synthesis and oxidation to vinylidene cyclobutanols. Yields determined by ¹H NMR with naphthalene as internal standard, and isolated yields in brackets.

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