A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201903721
Angew. Chem. 10.1002/ange.201903721

Link to VoR: http://dx.doi.org/10.1002/anie.201903721
http://dx.doi.org/10.1002/ange.201903721

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10.1002/anie.201903721

Photocatalysis

An Olefinic 1,2-Boryl-Migration Enabled by Radical Addition: Construction of *gem*-Bis(boryl)alkanes

*Binlin Zhao[+], Zexian Li[+], Yixiao Wu, Yandong Wang, Jiasheng Qian, Yu Yuan, and Zhuangzhi Shi**

Abstract: *A series of in situ-formed alkenyl diboronate complexes from alkenyl Grignard reagents (commercially available or prepared from alkenyl bromides and Mg) with B_2Pin_2 (bis(pinacolato)diboron) reacting with diverse alkyl halides by a Ru photocatalyst to give various gem-bis(boryl)alkanes is reported. Alkyl radicals add efficiently to the alkenyl diboronate complexes, and the adduct radical anions undergo radical-polar crossover, namely, a 1,2-boryl-anion shift from boron to the α-carbon sp^2 center. This transformation shows good functional group compatibility and can serve as a powerful synthetic tool for late-stage functionalization in complex compounds. Measurements of the quantum yield reveal that a radical chain mechanism is operative in which the alkenyl diboronates acts as reductive quencher for the excited state of the photocatalyst.*

Alkylboronic acids and their esters are of paramount importance to all facets of chemical science and have a broad spectrum of applications ranging from material science to drug discovery and organic synthesis.[1] Traditional methods for accessing these compounds by hydroboration of alkenes[2] or nucleophilic addition to Grignard or organolithium reagents with electrophilic boron species are well developed,[3] and recently emerging methods involving cross-couplings, radicals, and rearrangements promise to provide expanded access to these motifs.[4] Within this general context, 1,2-metalate rearrangement of boronate complexes has been developed[5] with several notable advances reported in the past few years.[6] In particular, the rearrangement of vinylboronate complexes for the generation of alkylboronates has attracted considerable attention from many research groups (Figure 1a). As early as 1967, Zweifel and coworkers for the first time demonstrated the 1,2-alkyl/aryl migration by electrophilic halogenation of vinylboronate complexes.[7] Half a century later, Morken et al. reported an important breakthrough for 1,2-alkyl/aryl migration[8] by carbopalladation of vinylboronate complexes with different coupling partners.[8a] In 2017, three groups independently extended this elegant chemistry to the radical-polar crossover process using vinyl boronate complexes and alkyl halides triggered by Et_3B/air,[9] visible-light[10] or nickel catalysts.[11]

Among various organoboron compounds, *gem*-bis(boryl)alkanes have drawn increasing attention in recent years due to their unique reactivity in both catalytic and noncatalytic processes to access value-added chemicals.[12] The 1,2-metalate rearrangement to such products has been demonstrated,[13] either with N_2 as the leaving group in the *gem*-diborylation of carbenoids[14] or with OBpin (Bpin = pinacolborane) as the leaving group in the *gem*-diborylation of aldehydes and ketones[15]. Very recently, Ingleson and coworkers demonstrated a 1,2-metalate rearrangement of a vinyl diboronate complex induced by soft boranes including BPh_3 and 9-Ph-BBN (Figure 1b).[16] This transformation is conceptually related to the Zweifel reaction, but the use of such boron "ate" complex can make Bpin act as a migrating group. Notably, this Lewis acid-induced reaction was sensitive to the steric hindrance, and the addition of BPh_3 to a complex derived from 1-propenylmagnesium bromide and B_2Pin_2 led in trace amount of the intramolecular rearrangement product. Inspired by radical-polar crossover and photochemistry[17-18], herein, we report a mild and operationally simple strategy for the rapid construction of *gem*-bis(boryl)alkanes through photocatalyzed, visible light-mediated addition of alkenyl diboronate complexes with alkyl halides and the subsequent cascade 1,2-boryl migration, greatly expanding the practicality of these boron complexes (Figure 1c). Salient features of our findings include a broad range of alkenyl diboronate complexes, diverse alkyl halides with good functional group compatibility, and late-stage diversification nature products.

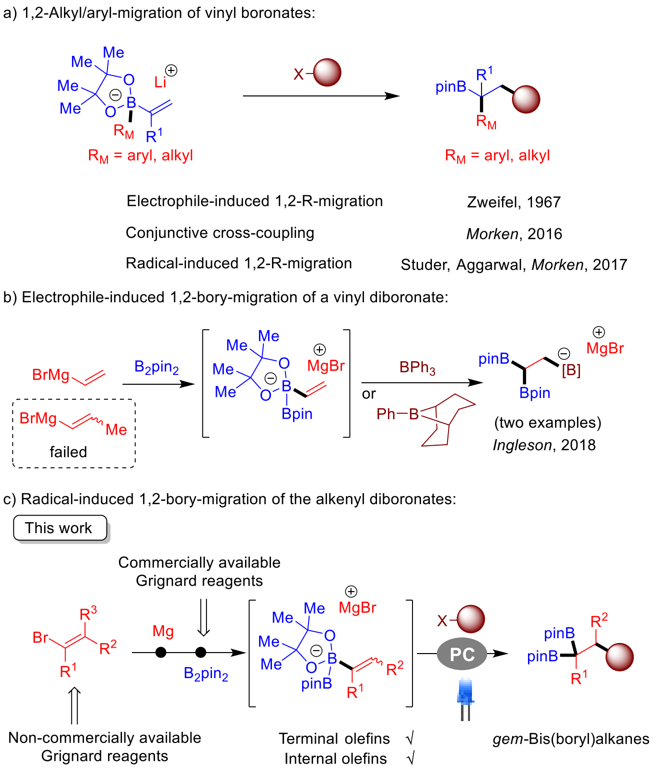

Figure 1. 1,2-Metalate rearrangement of alkenyl boronate complexes.

For an initial examination of the 1,2-boryl migration reaction, [(vinyl)B_2Pin_2)]MgBr (**3a**) was first generated in situ by treating the vinyl magnesium bromide (**1a**) and B_2pin_2 (**2a**) in THF (tetrahydrofuran) at -78 °C for two hours, as confirmed by ^{11}B NMR spectroscopy (broad signal at 37.4 ppm for the sp^2 boron and a sharp peak at 6.1 ppm for the sp^3 boron). After solvent removal without any further purification, a solution of commercially available substrate 2-bromoacetophenone (**4a**) and the photocatalyst were added to the vessel and the mixture was irradiated with visible-light irradiation (Table 1). The reaction was found to be facile, with 1.0 equiv of **4a**, 2.0 equiv of **3a**, 0.5 equiv of TBAB

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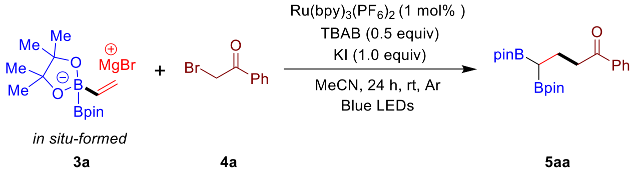
Table 1. Reaction development.[a]



Entry	Variation from the standard conditions	Yield of **5aa** (%)[b]
1	none	78 (75[c])
2	PC = $Ru(bpy)_3Cl_2$	65
3	PC = $Ir(ppy)_3$	8
4	PC = $Ir(ppy)_2(dtbbpy)PF_6$	48
5	-	0
6	in the dark	0
7	in THF	66
8	Without KI	68
9	Without TBAB	69
10	Without KI and TBAB	52
11	**1a**/**2a**/**4a** = 1:1.1:1	54
12	**1a**/**2a**/**4a** = 1:1.1:2	70

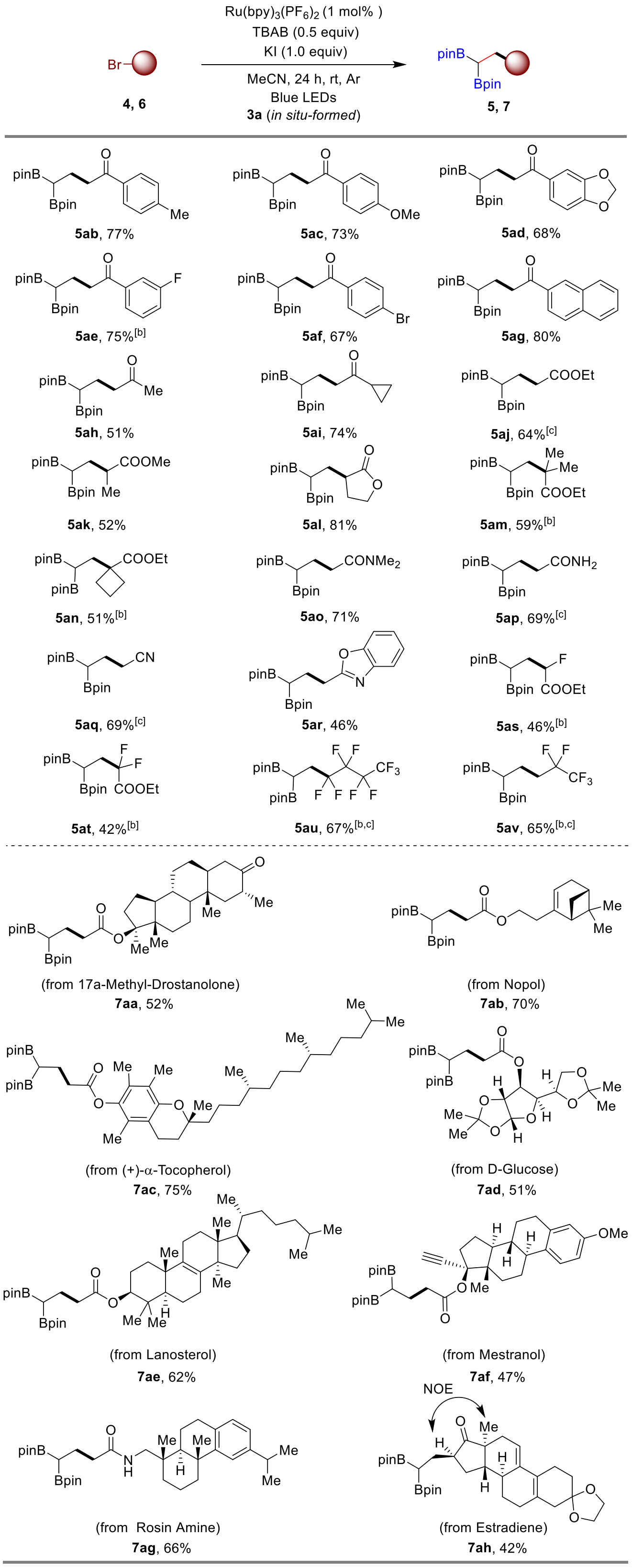
[a] Reaction conditions: **1a** (0.40 mmol, 2.0 equiv), **2a** (0.44 mmol, 2.2 equiv), in THF (0.5 mL), -78 °C, 2 h, under Ar; then 1 mol% of $Ru(bpy)_3(PF_6)_2$, **4a** (0.20 mmol, 1.0 equiv), rt , 24 h, in CH_3CN, blue LEDs. [b] Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c] Isolated yield.

(tetrabutylammonium bromide) and 1.0 equiv of KI in the presence of $Ru(bpy)_3(PF_6)_2$ (1 mol %), in MeCN after 24 h at room temperature affording the 1,2-boryl migration product **5aa** in 78% yield (entry 1). Other photocatalysts such as $Ru(bpy)_3Cl_2$, $Ir(ppy)_3$ and $Ir(ppy)_2(dtbbpy)PF_6$ were also effective for this transformation albeit with lower yields (entries 2-4). Control experiments showed that the reaction could not be conducted in the absence of the photocatalyst (entry 5) and only under irradiation with blue LEDs (entry 6). If the THF was not removed for the second step, only 66% yield of **5aa** could be formed (entry 7). Probably due to the in situ formed alkyl iodides from the corresponding bromides with KI using TBAB as a phase-transfer catalyst in this system, subjecting **4a** without KI or/and TBAB in reaction conditions would lower the yields of this transformation (entries 8-10), Finally changing the ratio of the three components **1a**, **2a** and **4a** to 1:1.1:1 (entry 11) or 1:1.1:2 (entry 12) decreased the yield as well.

With the optimized reaction conditions in hand, we next examined the scope of this 1,2-boryl-migration reaction (Table 2). Cross-coupling reactions of in situ-formed complex **3a** with many alkyl halides **4** were first examined. In most cases, this rearrangement reaction proceeded efficiently to give the corresponding *gem*-bis(boryl)alkanes in moderate to good yields. 2-bromoacetophenone derivatives **4b-f** and 2-acetonaphthone **4g** proved to be good substrates, leading to the corresponding ketones **5ab-5ag** in 67-80% yields. Moreover, aliphatic ketones **4h-I** were also successfully employed. In particular, primary (**4j**), secondary (**4k-l**) and tertiary (**4m-n**) aliphatic esters could all be employed as the radical precursors, showing that the reaction tolerated the full spectrum of steric demand. Substrates bearing amide (**4o-p**) and cyano groups (**4q**) could also be utilized in this photoredox protocol. Besides that, the reaction of 2-(iodomethyl)benzo[*d*]oxazole (**4r**) with complex **3a** also gave the migration product **5ar** in modest yield. Fluorine-containing compounds have been widely used in biologically active compounds and functional materials. All mono-, di-, and multi-fluoroalkylation processes were compatible with this transformation (**5as-v**).

Having identified complex **3a** as an ideal reagent for the generation of *gem*-bis(boryl)alkanes under exceptionally mild of this

Table 2. Substrate scope of alkyl halides.[a]

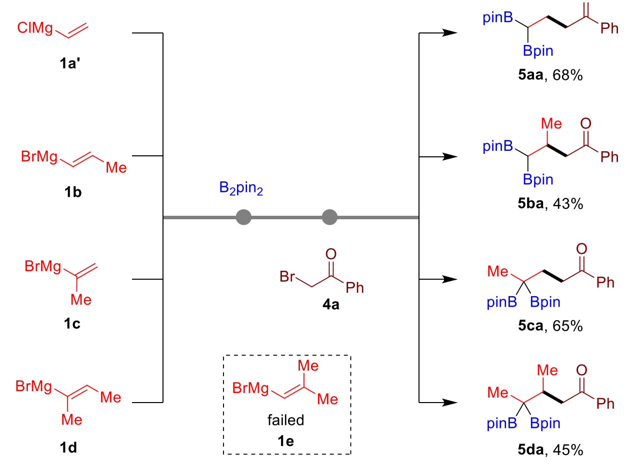


[a] **1** (0.40 mmol, 2.0 equiv), **2** (0.44 mmol, 2.2 equiv), in THF (0.5 mL), -78 °C, 2 h, under Ar; then 1 mol% of $Ru(bpy)_3(PF_6)_2$, **4** or **6** (0.20 mmol, 1.0 equiv), TBAB (0.10 mmol, 0.5 equiv), KI (0.2 mmol, 1.0 equiv), rt , 24 h, in CH_3CN, blue LEDs, isolated yield; [b] **1** (0.20 mmol, 1.0 equiv), **2** (0.22 mmol, 1.1 equiv), in THF (0.3 mL), -78 °C, 2 h, under Ar; then 1 mol% of $Ru(bpy)_3(PF_6)_2$, **4** (0.60 mmol, 3.0 equiv), TBAB (0.10 mmol, 0.5 equiv), KI (0.2 mmol, 1.0 equiv), rt , 24 h, in CH_3CN, blue LEDs, isolated yield; [c] Using iodoalkanes **4**, without TBAB and KI.

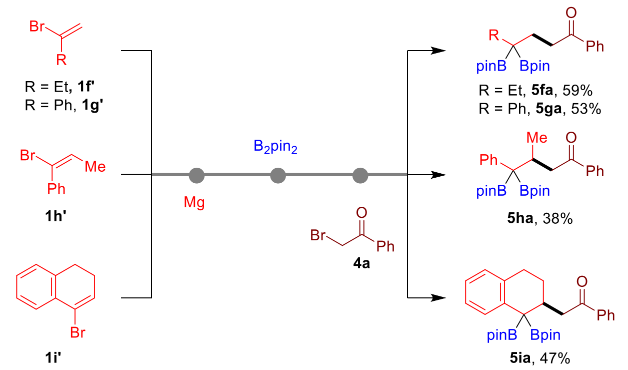
catalytic system. Toward this aim, the derivatives of pharmaceuticals and natural products that contain an alkyl bromide reaction conditions, we decided to demonstrate the synthetic utility were selected as the coupling partners for the olefinic 1,2-boryl-migration. For example, drostanolone derivative **6a** with a sensitive chiral α-carbonyl methyl group proceeded readily to produce **7aa** without any epimerization. Nopol derivative **6b** with a double bond could also be tolerated (67% yield). Derivatives of (+)-α-Tocopherol, D-glucose and lanosterol were shown to be compatible with our system (**7ac**-**ae**). Mestranol derivative **6f** with a terminal alkyne group could be transformed to provide *gem*-bis(boryl)alkane **7af** in 47% yield. Secondary amide **6g** derived from rosin amine proceeded smoothly to afford the desired product **7ag** in 66% yield. Finally, to further highlight the robustness of this strategy, stereospecific functionalization at α position of estradiene (**6h**) was achieved product **7ah** in modest yield.

To further explore the scope of this rearrangement, other alkenyl diboronate complexes were then investigated (Scheme 1a). The complex derived from alkenyl magnesium chlorides such as **1a'** could afford the desired product **5aa** in a slightly lower yield. The effect of increasing steric hindrance at the β-vinylic carbon atom by using the adduct **3b** in situ generated from Grignard reagent **1b** and B_2pin_2 (**2a**) was also explored. To our delight, the subsequent reaction of 2-bromoacetophenone (**4a**) with **3b** under this system could give the desired 1,2-boryl migration product **5ba** in 43% yield. Furthermore, α-substituted alkenyl Grignard reagents such as isopropenylmagnesium bromide (**1c**) could be employed to produce an internal geminal bis(boronate) **5ca** in 65% yield. Of note, the complex **3d** from di-substituted alkenyl Grignard reagents **1d** was tolerable as well. However, a bulky β, β'-dimethyl substituted Grignard reagent **1e** was failed in this reaction. Besides these commercially available Grignard reagents, our studies also investigated the subjecting "ate" complexes derived from alkenyl bromides and Mg (Scheme 1b). Alkenyl bromides bearing substituents like ethyl (**1f'**) and phenyl (**1g'**) at α-vinylic position could react with Mg and B_2pin_2 (**2a**), and further coupled with **4a** under the standard conditions, providing the corresponding product **5fa-ga** in 59% and 53% yield, respectively. The current method is noteworthy with regard to the bulky complexes **3h-i** from alkenyl bromide **1h'-i'**, and the products **5ha-ia** formed in modest yields.

a) From commercially available Grignard reagents:



b) From alkenyl bromides:



Scheme 1. Versatility of the alkenyl diboronate complexes.

Given the versatility and robustness features of this chemistry, we were intrigued to delineate its mode of action. Quantum yield measurements of the reaction between **3a** and iodoacetonitrile (**4q**) gave a value of $\Phi = 49.8$[19] (see Supporting Information), suggesting that a radical chain mechanism was operative.[20] A possible mechanism is proposed in Figure 2. The highly reducing Ru^+ is generated by single electron transfer (SET) from a sacrificial amount of the $[(vinyl)B_2Pin_2)]MgBr$ (**3a**, $E_{p/2}$ = +0.21 V *vs.* SCE) to the excited Ru^{2+} species ($E_{Ru^{II*}/Ru^{I}}$ = + 0.77 V *vs.* SCE), and the byproduct **3a′** was observed in the crude reaction mixtures.[21] Then, the Ru^+ ($E_{Ru^{I/II}}$ = -1.33 V *vs.* SCE) species undergoes single electron transfer with alkyl halides **4/6** (for **4q**, $E_{p/2}$ = -1.24 V *vs.* SCE) leading to the formation of the reactive electrophilic radical **A** and the regeneration of the Ru^{2+} catalyst. Radical **A** undergoes addition to the electron-rich complex **3a** to form boronate radical **B**. This electron-rich radical anion then undergoes facile single-electron oxidation with another molecule of alkyl halides **4/6**, thus triggering a rapid 1,2-boryl migration to afford the products **5/7**. The process also releases a new alkyl radical **A**, thereby feeding a radical chain propagation pathway.[22]

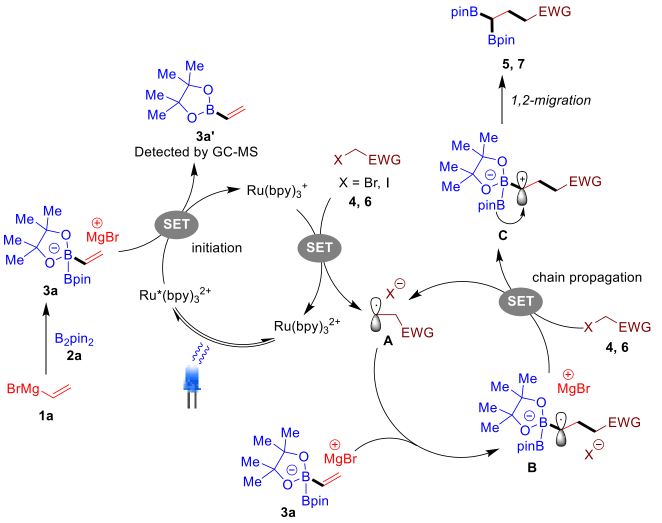


Figure 2. Plausible mechanism.

In summary, we show here that carbon radicals add efficiently to the alkenyl diboronate complexes leading to a 1,2-boryl migration from boron to the α-carbon sp^2 center. Together, these synthesis methods cover a vast substrate scope providing a novel and efficient multi-component coupling reaction based on ready accessible alkenyl magnesium bromides, B_2Pin_2 and alkyl halides. Owing to this impressive pool of *gem*-bis(boryl)alkanes that bear diverse functionalities, our efficient and cost-effective technique promises to be a powerful and reliable tool for total synthesis and development.

Acknowledgments

We thank the "1000-Youth Talents Plan" and the NSF of China (Grants 2167020084) for their financial support and the "Innovation & Entrepreneurship Talents Plan" of Jiangsu Province. This work was also supported by a program A for Outstanding PhD candidate of Nanjing University.

Keywords: Rearrangement ·*gem*-diborylation ·radical ·photocatalysis ·crossover

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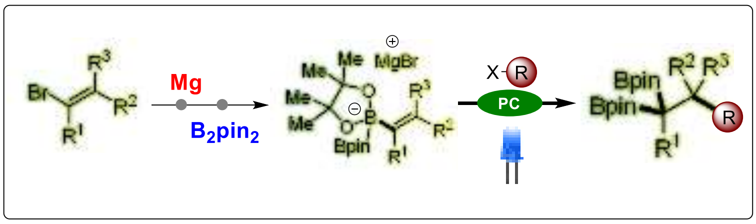
Photocatalysis

Binlin Zhao, Zexian Li, Yixiao Wu, Yandong Wang, Jiasheng Qian, Yu Yuan, and Zhuangzhi Shi*___ **Page – Page**

An Olefinic 1,2-Boryl-Migration Enabled by Radical Addition: Construction of *gem*-Bis(boryl)alkanes



B & Mg: A mild catalytic system was developed for the preparation of *gem*-bis(boryl)alkanes via an olefinic 1,2-boryl-migration. This method has good functional group compatibility and can serve as a powerful synthetic tool for late-stage functionalization in complex compounds.