1,\(n\)-Bisborylalkanes via Radical Boron Migration

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ABSTRACT: A systematic study of radical boron migration in diboronate complexes to form synthetically valuable 1,\(n\)-bisborylalkanes is reported. The boronate complexes are readily generated by reaction of commercial bis(pinacolato)diboron with alkyl Grignard compounds. C-radical generation at a defined position with respect to the diboron moiety is achieved either via intermolecular H-abstraction with a CF₃-radical or via alkene perfluoroalkyl radical addition. It is shown that radical 1,2- and 1,4-boron migrations to provide geminal and 1,3-bisborylalkanes are efficient transformations. The 1,5-boron migration in the homologous series leading to 1,4-bisborylalkanes is also occurring, albeit with lower efficiency. Experimental results are supported by DFT calculations which also reveal the corresponding 1,3-boron migration in such diboronate complexes to be feasible.

Bisborylalkanes are functionalized and versatile building blocks in organic synthesis. Such B-compounds can act as coupling partners in transition-metal-catalyzed cross-coupling reactions or as radical precursors, and both boryl moieties can, in principle, be selectively converted to different functionalities.⁷ Boronate complexes are reactive intermediates that are readily generated by the reaction of organoboronic esters with organometallic reagents. These B-ate complexes are reducing species that also undergo facile hydrolysis.² Recently, radical chemistry on boronate complexes has emerged.³ It was found that C-radicals of type I derived from boronate complexes are readily oxidized by single electron transfer (SET) to give zwitterions of type II in a radical/polar crossover step (Scheme 1A). Intermediates II in turn undergo a Matteson-type 1,2-alkyl/aryl shift to afford \(\alpha\)-functionalized boronic esters III.⁴ Although such transformations on boronate complexes generated from alkyl and aryl boronic esters are well investigated, the corresponding radical reactions on diboronate complexes derived from diborons (see IV) are underdeveloped. Along these lines, Shi recently reported the construction of 1,1-bisborylalkanes enabled by radical addition/1,2-boron migration.⁵ As mechanism of the boron migration, it was proposed that diboronate complexes IV (\(m = 0\)) are SET-oxidized to intermediates of type II (R′ = BPin), which rearrange to geminal bisborylalkanes via an ionic process.⁵ Herein, we disclose our results on the systematic study of radical boron migration in radical anions of type IV (\(m = 0–4\)) to give intermediates V, where the two B-atoms can interact. SET oxidation finally leads to 1,\(n\)-bisborylalkanes VI (Scheme 1B). Considering the 1,2-boron shift, the radicals VIII are generated from ate complexes VII via intermolecular hydrogen atom transfer (HAT)⁶ (Scheme 1C). Further, we will provide mechanistic insights into the reported⁵ 1,2-boron migration. In all other cases, site-selective C-radical generation (see XI) is achieved via radical addition to B-ate complexes of type X (Scheme 1D).

The 1,2-boron shift to access geminal bisborylalkanes was studied first. Notably, 1,1-bisborylalkanes are important building blocks to access multifunctionalized compounds.⁶,⁷ The current methods to prepare these compounds use gem-dihalides,⁸ diazo compounds,⁹ alkynes,¹⁰ alkenes, etc.¹¹ as substrates and mostly require a transition metal to catalyze or mediate the transformation.¹² It is of interest to develop a
convenient method to access 1,1-bisborylalkanes from simple starting materials under transition-metal-free conditions.

In 2019, our group achieved transition-metal-free cross-coupling of organometallic reagents and organoboron esters by intermolecular α-HAT on the corresponding boronate complexes with the trifluoromethyl radical followed by SET oxidation and ionic 1,2-alkyl/aryl migration. Encouraged by this study, we decided to apply this strategy to prepare 1,1-bisborylalkanes via diboronate complexes (see Scheme 1C). The reaction of bis(pinacolato)diboron (B\textsubscript{2}Pin\textsubscript{2}) with cyclopentylmagnesium bromide (1.2 equiv) targeting gem-bisborylalkane 2a was selected for optimization (Table 1).

![Scheme 1C](https://i.imgur.com/123456.png)

**Table 1. Reaction Optimization for the 1,1-Diborylation of Cyclopentylmagnesium Bromide with B\textsubscript{2}Pin\textsubscript{2}**

| entry | PC | \(\text{conv} (%)\) |
|-------|----|------------------|
| 1     | Ir(ppy)\textsubscript{3} | 59 | 8 | 86 |
| 2     | Ir(ppy),(dibppy)PF\textsubscript{6} | 62 | 7 | 85 |
| 3     | Ru(bppy),(PF\textsubscript{6})\textsubscript{3} | 63 | 9 | 82 |
| 4     | Rose Bengal | 56 | 8 | 83 |
| 5     | Rhodamine B base | 35 | 20 | 82 |
| 6     | Eosin Y | 49 | 5 | 74 |
| 7\textsuperscript{\textdagger} | Ru(bppy),(PF\textsubscript{6})\textsubscript{3} | 52 | 7 | 82 |
| 8\textsuperscript{\textdagger} | Ru(bppy),(PF\textsubscript{6})\textsubscript{3} | 18 | 28 | 100 |
| 9     | – | 30 | 20 | 65 |
| 10\textsuperscript{\textdagger} | Ru(bppy),(PF\textsubscript{6})\textsubscript{3} | 68 | <1 | 82 |
| 11\textsuperscript{\textdagger} | – | 76 (74\% | <1 | 91 |
| 12\textsuperscript{\textdagger} | – | 16 | 17 | 61 |

\textsuperscript{\textdagger}Reactions were conducted on a 0.2 mmol scale in CH\textsubscript{3}CN (2 mL), conversion (\textit{conv}) was determined based on GC analysis with \(n\)-tetradecane as internal standard on the crude reaction mixture.

The diborane complex 1a was generated in 1,2-dimethoxyethane (DME) at 0 °C. The solvent was exchanged by acetonitrile, and CF\textsubscript{3}I was chosen as the terminal oxidant, with the CF\textsubscript{3}I-radical engaging in selective HAT abstraction at the α-position to the B-atom in B-ate complexes. Pleasingly, with tris[2-phenylpyridinato-C\textsubscript{2},N\textsubscript{2}]iridium(III) (Ir(ppy)\textsubscript{3}, 1 mol%) as a smart initiator at room temperature, 2a was formed in 59% yield (Table 1, entry 1). Besides 2a, we detected 8% cyclopentylboron compound pinacol ester (Cp-BPin) and 14% B\textsubscript{2}Pin\textsubscript{2}. Other metal-based and organic initiators gave similar results (entries 2–6). The complex derived from cyclopentylmagnesium chloride provided a slightly lower yield (52%, entry 7, compare with entry 3), but the yield significantly dropped to 18% with bis(neopentyl glycolato)diboron (B\textsubscript{2}(neop)\textsubscript{2}) in place of B\textsubscript{2}Pin\textsubscript{2} (entry 8). Without redox initiator, the reaction also proceeded, albeit with lower efficiency (entry 9). Upon lowering the temperature, formation of cyclopentylboronic acid pinacol ester was suppressed and the yield of 2a improved to 68% (entry 10). Initiation by simple UV (365 nm) irradiation at ~20 °C led to a further improvement, providing 2a in 76% yield (entry 11). The boronate complex derived from cyclopentylmagnesium bromide gave a poor yield under the optimized conditions (16%, entry 12).

With optimized conditions in hand, we prepared a series of 1,1-bisborylalkanes from different alkyl Grignard reagents (Table 2). Both primary (2c–d) and secondary (2a,b,e–o) alkylmagnesium bromides engaged in the transformation to afford 1,1-bisborylalkanes in moderate to good yields (28–80%). Some functionalities such as phenyl, trifluoromethyl, and alkoxycarbonyl moieties were tolerated. The reaction was found to be sensitive to steric. For example, ate complex 1b derived from 3-phenyl cyclopentylmagnesium bromide delivered the 1,1-bisoron compound 2b with a decreased yield (44%) as compared to its less bulky congener 1a (74%). Considering diborane complexes derived from primary alkylmagnesium bromides, the less bulky ethyl derivative (2c) gave a slightly better yield than the corresponding butyl-ate complex (2d). For complexes generated from secondary alkylmagnesium bromides, the least bulky isopropyl system provided the highest yield (80%, 2e). Due to the higher steric demand of an ethyl over a methyl group, the yield of 2o was lower than the yields obtained for 1,1-bisborylalkanes 2e–n. Of note, as Grignard reagents can be easily accessed from commercial alkyl bromides, the introduced method offers a cheap and convenient approach to 1,1-bisborylalkanes.

We noted that there is currently no general method available for the synthesis of 1,\(n\)-bisborylalkanes (\(n > 1\)) and we assumed the unprecedented remote radical B-migration to offer a new approach to access such compounds. Along these lines, we first addressed the 1,4-boron migration and selected 3a, generated by reacting B\textsubscript{2}Pin\textsubscript{2} with bet-3-alkynylmagnesium bromide, as model substrate. To our delight, visible light irradiation (465 nm) of 3a in the presence of CF\textsubscript{3}I (1.5 equiv) afforded 4a in 80% yield.
and Ir(ppy)_3 (1 mol%) as an initiator in CH_3CN provided the 1,3-bisboronylalkane 4a in 79% yield besides the iodine atom transfer product 4a-I (4%) and recovered B_2Pin_2 (13%) (Table 3, entry 1). Solvent screening revealed that better yields were obtained in CH_3CN than in other polar solvents like DMSO, DMF, and DMA (entries 1-4). Ir(ppy)_3 could be replaced by Rose Bengal, and Rhodamine B (entries 1-4a). Ir(ppy)_3 could be replaced by Rose Bengal, and Rhodamine B base initiation protocol (Table 3, entry 9) that proved to be more general than the UV-initiation protocol. Without redox initiator, the reaction also worked, but with lower efficiency (44%, entry 8), and with the cheap organic dye Rhodamine B base as smart initiator, the yield further increased to 87% upon lowering the temperature to −20 °C (entry 10). Notably, simple UV irradiation (365 nm) at −20 °C increased to 87% upon lowering the temperature to −20 °C (entry 11). The boronate complex derived from but-3-enyllithium in the absence of any initiator provided a similar yield (entry 9). The yield further increased to 87% upon lowering the temperature to −20 °C (entry 10). 

Table 3. Reaction Optimization for 1,3,4-Trifunctionalization of Homoallylmagnesium Bromide—1,4-Boron Migration

| entry | PC             | solvent | yield (%) | 4a  | 4a-I | conv (%) |
|-------|----------------|---------|-----------|-----|------|---------|
| 1     | Ir(ppy)_3      | CH_3CN  | 79        | 4   | 87   |         |
| 2     | Ir(ppy)_3      | DMSO    | <1        | 33  | 85   |         |
| 3     | Ir(ppy)_3      | DMF     | 5         | 11  | 91   |         |
| 4     | Ir(ppy)_3      | DMA     | 2         | 2   | 93   |         |
| 5     | Eosin Y        | CH_3CN  | 76        | 3   | 77   |         |
| 6     | Rose Bengal    | CH_3CN  | 75        | 4   | 80   |         |
| 7     | Rhodamine B base| CH_3CN | 79        | 3   | 80   |         |
| 8     | –              | CH_3CN  | 44        | 16  | 94   |         |
| 9b    | Rhodamine B base| CH_3CN | 87       | 3   | 90   |         |
| 10f   | –              | CH_3CN  | 87        | 3   | 95   |         |
| 11e   | Rhodamine B base| CH_3CN | 5         | –   | 57   |         |

*aReactions were conducted on a 0.2 mmol scale in the specified solvent (2 mL), conversion (conv) was determined based on recovered bisboronyl reagent, and yields were determined by crude GC analysis with n-tetradecane as internal standard. bConducted at −20 °C. cIsolated yield. d365 nm (3 W) at −20 °C. eBut-3-etyl, in situ generated by lithium/iodine exchange reaction of t-BuLi and 4-iodo-1-butene, used instead of but-3-enylmagnesium bromide, and THF instead of DME as solvent.

obtained in CH_3CN than in other polar solvents like DMSO, DMF, and DMA (entries 1–4). Ir(ppy)_3 could be replaced by organic dyes such as Eosin Y, Rose Bengal, and Rhodamine B base without diminishing the yield (76–79%, entries 5–7). Without redox initiator, the reaction also worked, but with lower efficiency (44%, entry 8), and with the cheap organic Rhodamine B base as smart initiator, the yield further increased to 87% upon lowering the temperature to −20 °C (entry 9). Notably, simple UV irradiation (365 nm) at −20 °C increased to 87% upon lowering the temperature to −20 °C (entry 10). The boronate complex derived from but-3-enyl lithium gave a poor yield under the optimized conditions (5%, entry 11).

A scope study of the trifunctionalization of homoallylg Grignard reagents was conducted by applying the visible light/Rhodamine B base initiation protocol (Table 3, entry 9) that proved to be more general than the UV-initiation protocol. The perfluoroalkyl radical precursor was varied first, keeping complex 3a as the acceptor (Table 4). Linear n-perfluoroalkyl iodides provided the trifunctionalized 1,3-diboranes 4b-e in excellent yields (82–93%). The less reactive n-perfluoroalkyl bromide also worked as C-radical precursor, but as compared to the iodides, the yield dropped slightly (62%, 4f). Without perfluoroisopropyl iodide, a 64% yield of 4g was obtained. 1-Chloro-2-iodotetrafluoroethane reacted chemoselectively at the I-bearing C-atom to give 4h (61%). Iodoacetonitrile and ethyl iodoacetate gave only trace amounts of the targeted products (not shown). Unfortunately, diastereoselectivity for the 1,4-boron shift in open-chain systems was very low (see 4i,j). However, for the cyclic rigid diborate complex 3k, 1,4-syn-boron-migration selectivity was complete, and also the initial CF_3-radical addition occurred with excellent stereocontrol (trans-addition) to provide product 4k as a single diastereoisomer (64%).

With 4-pentenyldimagnesium bromide as starting material, we next addressed the 1,5-boron migration and noted that, with perfluoroalkyl iodides as C-radical precursors, the I-atom transfer compounds 5-I (not shown) were formed as major products and targets 5 were obtained in low yields. Therefore, we had to switch to the less reactive bromides. A moderate 31% yield of 5a was achieved with n-perfluorohexyl bromide under the conditions optimized for the 1,4-boron shift. The yield could be slightly improved to 44% (see 5b) by installing a 3,3-dimethyl substitution pattern, benefiting from the Thorpe–Ingold effect.

We also attempted the 1,6-boron migration on the homologous diborate complex derived from 5-hexenyl-magnesium bromide with CF_3-I as the radical precursor. However, the targeted 1,5 bisboronylalkane was not identified, and the reaction provided the corresponding I-atom transfer product as the major product. Switching to n-perfluorohexyl bromide, the 1,6-boron migration product 6 could not be identified, indicating that this migration cannot compete with other processes.

Finally, to complete the series, we tackled the 1,3-boron migration. The required diboronate complex was formed by the reaction of allylmagnesium bromide with B_2Pin_2. However, neither with perfluorobutyl iodide nor with its bromide was any 1,2-bisboronylalkane identified, and B_2Pin_2 was formed in a large amount (85%) as major product. Hence, SET oxidation of allyl-B_2Pin_2MgX under all tested conditions generating the stabilized allyl radical was too fast, and therefore this alkene could not act as a radical acceptor under the applied conditions. Since we did not find any suitable system to
experimentally investigate the 1,3-boron migration, we decided to approach that problem by using computational chemistry. DFT calculations were performed on a series of pent-(m+1)-yl-substituted radical anions 7a–d ($m = 0$–3, Scheme 2) to get a full picture on the boron migration aptitude in these diboronic radical anions.

**Scheme 2. DFT Model Calculations of Diboronate Radical Anion Rearrangements**

In the study of the reactions, we have found bisboronic radical anion intermediates 8 with the spin localized in a B–B single electron bond, similar to those found in the 1,2-carboboration of alkenes with B$_2$Cat$_2$. In the case of the 1,2-boron migration ($m = 0$), the initial radical 7a exhibits this structure already, which means that 1,2-boron radical migration is a spontaneous and barrierless process. In the case of the distonic ($m > 0$) radical anions 7b–d, a cyclization occurs with low free energy barriers (7–12 kcal/mol) to form the analogous intermediates 8b–d exergonically. These will readily transfer—likely assisted by the MgBr counterion—one electron to the iodo reagent and regenerate the trifluoromethyl radical, forming the 1,($m$+1)-bisborylalkanes 9a–d. Compared to the 1,4-boron migration, the barrier for the radical 1,3-boron migration increases (from 7.1 to 11.8 kcal/mol). The 1,5-boron migration (8.1 kcal/mol) showed a slightly higher barrier than the 1,4-shift. In the case of radical anion 7b (1,3-boron migration), in the computation we did not find any indication for facile $\beta$-fragmentation leading to B$_2$Pin$_2$-radical anion along with 1-pentene. This supports our suggestion that the observed formation of B$_2$Pin$_2$ in the reaction with allyl-B$_2$Pin$_2$MgX is likely caused by initial SET oxidation of allyl-B$_2$Pin$_2$MgX rather than $\beta$-fragmentation of the corresponding diatomic radical anion of type 7b.

In summary, radical 1,2- and 1,4-boron migration reactions in diboronic complexes derived from B$_2$Pin$_2$ are useful preparative processes to access synthetically valuable 1,1- and 1,3-bisborylalkanes. Considering the 1,3-functionalized compounds, high selectivity in the boron migration can be achieved in cyclic systems. The 1,5-boron migration leading to 1,4-bisborylalkanes also occurs, albeit with lower efficiency. The experimental findings on the B-shift were supported by DFT calculations, which further revealed the currently experimentally inaccessible 1,3-boron migration to be feasible. Since B$_2$Pin$_2$ is commercially available and the Grignard reagents are readily prepared from the corresponding alkyl bromides, the introduced methods offer a straightforward approach to 1,4-bisborylalkanes.
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